

Review

Hydrophobic Surface Modification of Microporous and Mesoporous Titanosilicates and Its Impact on Catalytic Performance in Epoxidation Reactions: A Review

Ana Belen Lozada ^{1,2} , Ayleen Villacrés ^{1,2} , Diana Endara ² , Ernesto de la Torre ² , Eric M. Gaigneaux ¹ 
and Lucia E. Manangon-Perugachi ^{2,*} 

- ¹ Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCLouvain), Place Louis Pasteur 1, P.O. Box L4.01.09, 1348 Louvain-la-Neuve, Belgium; ana.lozada@uclouvain.be (A.B.L.); ayleen.villacres@uclouvain.be (A.V.); eric.gaigneaux@uclouvain.be (E.M.G.)
² Department of Extractive Metallurgy, Escuela Politecnica Nacional, Quito 170517, Ecuador; diana.endara@epn.edu.ec (D.E.); ernesto.delatorre@epn.edu.ec (E.d.l.T.)
* Correspondence: lucia.manangon@epn.edu.ec

Abstract

Titanosilicates are Lewis acid catalysts widely applied in liquid-phase olefin epoxidation; however, in the presence of water, their performance is often limited by structural instability, active-site deactivation, and competing side reactions. This review critically examines hydrophobization strategies—based on controlled reduction in silanol groups or incorporation of organic functionalities—and discusses the experimental approaches used to evaluate surface hydrophobicity, including water adsorption measurements, infrared spectroscopy of silanols, contact angle analysis, and complementary spectroscopic methods. Although direct quantitative comparison among studies is hindered by differences in reaction systems and the lack of standardized catalytic metrics, consistent trends emerge. Lower silanol densities are generally associated with improved preservation of isolated tetrahedral Ti (IV) sites, higher H₂O₂ utilization efficiency, and reduced secondary epoxide ring-opening, leading to enhanced activity and selectivity under comparable conditions. These improvements are attributed to decreased local water activity, suppression of non-productive oxidant decomposition, and stabilization of Ti-peroxo intermediates responsible for direct epoxidation. Incorporation of organic groups produces a similar beneficial effect when introduced in moderate amounts, increasing surface hydrophobicity without significantly perturbing Ti coordination. However, beyond an optimal loading, catalytic performance declines due to pore blockage, diffusion limitations, and partial masking of active sites, revealing a threshold behavior. Fluoride also plays a dual role: when used during synthesis, it influences the insertion and distribution of framework Ti, whereas as a post-treatment, it primarily regulates silanol density and surface polarity while preserving active sites. Finally, hydrophobicity cannot be considered independently, as its impact depends on the solvent, oxidant, olefin nature, and active-site location, which collectively govern activity, selectivity, and catalyst stability.

Keywords: titanosilicates; hydrophobicity; silanol density; organic functionalization; epoxidation; one-pot; post-grafting



Academic Editor: Narendra Kumar

Received: 20 December 2025

Revised: 16 February 2026

Accepted: 9 March 2026

Published: 31 March 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\) license](https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Titanosilicates are important materials with fast development since the synthesis of the first TS-1 [1–5]. They are used in the selective oxidation of organic compounds,

displaying high catalytic activity [1,2,6–11]. The growing application of these heterogeneous catalysts for both the petrochemical and fine chemical industries has resulted in a substantial production of titanosilicates with improved catalytic performance, which could replace the traditional ones [12].

The active sites in titanosilicates are Ti atoms in tetrahedral coordination inserted into the silica framework (framework-Ti). Previous studies have shown that isomorphous substitution of Ti into the TS-1 framework is limited to a maximum atomic ratio of about 2.5% (Ti/(Si + Ti)) [13]. Beyond this composition, octahedral Ti species form outside the framework (extraframework Ti), which are catalytically inactive in selective oxidation reactions. In these reactions, Ti active sites interact with the oxidant, such as H₂O₂ or organic peroxides, to generate Ti-peroxo intermediate species (Ti-OOH or Ti-OOR), which are the active oxidation centers [14–16]. The tetrahedral Ti sites function as Lewis acid centers that activate the oxidant, enabling formation of the activated complex that subsequently reacts with substrates such as olefins during epoxidation [17–21].

Some alternatives have been used to improve the catalytic performance of titanosilicates, such as improving the textural properties [2,12], controlling the nature of the active sites [1,22], and modifying the hydrophobic/philic surface character. In recent years, the adjustment of hydrophobicity/philicity of materials such as metal-organic frameworks (MOFs) [23–25], aluminosilicates [26], and titanosilicates [27] has received more attention due to its great influence on their catalytic properties.

In the field of titanosilicates, the effect of hydrophobization has been particularly studied in the epoxidation of olefins in the liquid phase. Early studies proposed that the hydrophobicity of titanosilicates influences the competitive adsorption between non-polar substrates (olefin) and polar products (epoxide) [28,29], motivating efforts to increase the hydrophobic character of titanosilicates to improve the olefin adsorption. Later, studies showed that epoxidation proceeds via an Eley-Rideal [30] mechanism, where only the oxidant is adsorbed on the catalyst's surface. Under these conditions, a hydrophobic surface facilitates the rapid desorption of epoxide, preventing over-oxidation to diols.

Moreover, the hydrophobic environment reduces the adsorption of water, which is crucial because water promotes epoxide ring-opening and can deactivate the Ti active sites [31]. Water is added to the reaction together with the oxidant. For example, the commercially available H₂O₂ is normally a 30% (*w/w*) solution in water. Thus, the modification of the hydrophobicity of the surface of titanosilicates could regulate the interaction between the catalyst with both the reactants and products and prevent side reactions, resulting in high conversion and/or selectivity [32].

Several crystalline and amorphous titanosilicates have been hydrophobized by different methodologies. TS-1, which is already a hydrophobic titanosilicate, was further hydrophobized by controlling the silanol surface density to improve its catalytic activity. The improved hydrophobic character and Ti dispersion of TS-1 yielded a significant increment in the activity of the catalyst [33]. Also, hydrophobic TS-1 functionalized by post-grafting achieved higher epoxide selectivity than the non-modified one [34]. The microporous TS-1 zeolite enables the efficient oxidation of small substrates; however, its performance is limited for larger molecules due to diffusion constraints. To address this limitation, large-pore titanosilicate zeolites were developed. Ti-Beta, for example, provides improved molecular accessibility compared to TS-1, but is intrinsically more hydrophilic [35]. A common strategy to decrease the density of external silanol groups and increase hydrophobicity is to synthesize Ti-Beta in fluoride medium instead of alkaline conditions [36–38]. While hydrophobic Ti-Beta was traditionally considered more effective in epoxidation reactions, recent work by Bregante et al. [38] showed that hydrophilic Ti-Beta can exhibit turnover rates up to two orders of magnitude higher than hydrophobic

samples, indicating that the impact of hydrophobicity on catalytic performance requires further clarification.

Other large-pore titanosilicates, such as Ti-MCM-41 [39–43], Ti-MCM-48 [41], and Ti-SBA-15 [32], and amorphous Ti-SiO₂ [11,44–48] were functionalized by one-pot and post-grafting procedures and showed greater catalytic performance in the epoxidation of olefins.

It is notable that the hydrophobic properties of catalyst surfaces display an important role in the adsorption/desorption processes and consequently, in the catalytic performance of titanosilicates. In fact, several researchers have studied the hydrophobization of these materials, and the modification resulted in positive, negative, or non-significant effects on their catalytic activity. Even though the modification of hydrophobicity has been addressed in previous investigations, the variety of types of titanosilicates and the analytical techniques used to measure this property have not allowed for a consensus on the catalytic effects of hydrophobization. To the best of our knowledge, there is not yet a review article analyzing this effect. For this reason, a comparison and discussion about the effects of hydrophobization of titanosilicates will be addressed here, considering the type of titanosilicate, the hydrophobization strategy, the surface characterization, and the catalytic system.

2. Overview of the Topic

2.1. Types of Titanosilicates: Active Site, Acidity, and Textural Properties

Titanosilicates, both crystalline and amorphous, have attracted sustained interest since their initial discovery due to their high catalytic activity in selective oxidation reactions [1–5]. Crystalline titanosilicates have been widely applied in the liquid-phase oxidation of organic substrates such as alkanes, alkenes, alcohols, and aromatics, typically using hydrogen peroxide or organic peroxides as oxidants [1,2,6]. Amorphous titanosilicates have also been established as effective catalysts for olefin epoxidation [7–11,49]. Since the synthesis of the first titanosilicate zeolite, TS-1, in 1983, research efforts have continuously expanded the structural diversity and catalytic applications of these materials. This continuous interest is reflected in the steady growth in the number of publications on titanosilicates over the years (Figure 1).

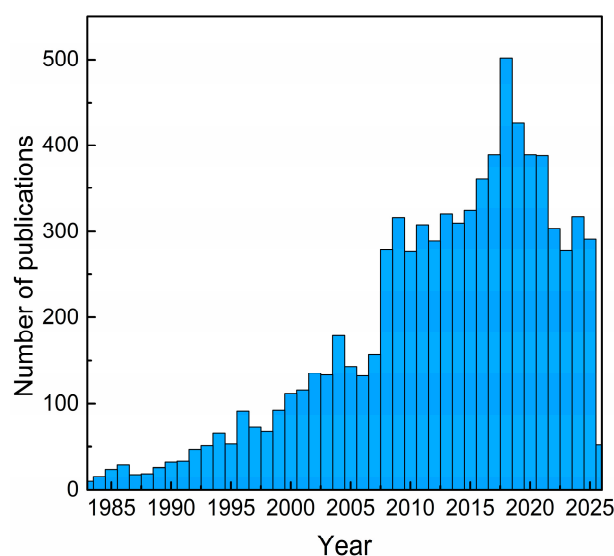


Figure 1. Number of publications per year related to titanosilicates. Source: Scopus, November 2025.

In this work, titanosilicates are considered materials in which titanium atoms are incorporated into a silica matrix. For analysis purposes, they are classified into two main

groups: (i) titanosilicates with a zeolite structure (Ti-zeolites), which have a well-defined crystal framework, and (ii) titanosilicates without a zeolite structure (Ti-SiO₂), characterized by an amorphous organization of the silica network. Their active site, associated acidity, and the main structural differences between the two types of materials are described below.

2.1.1. Active Sites of Titanosilicates

Titanosilicate catalysts contain isolated Ti(IV) centers embedded within a silica matrix, where they function as redox-active sites capable of activating H₂O₂ or organic peroxides to form Ti-OOH and Ti-OOR intermediates—the key oxidizing species in olefin epoxidation [1,50]. These Ti(IV) atoms are introduced primarily through isomorphous substitution of Si⁴⁺ by Ti⁴⁺ during synthesis, producing framework-bound, molecularly dispersed sites. Although Pauling's radius-ratio rules suggest that Ti⁴⁺ is too large to fit in a perfect tetrahedral environment, the Ti-O radius ratio (0.515) exceeds the 0.225–0.414 range characteristic of tetrahedral geometry [51], flexible structures such as MFI can accommodate distorted (“pseudotetrahedral”) TiO₄ environments [52], which gives rise to the canonical reactivity of TS-1 and related materials.

In TS-1 and related Ti-zeolites, the incorporation of framework Ti (FW-Ti, Figure 2a,b) is limited to approximately 2.5 mol% Ti/(Ti + Si). The lattice can no longer compensate for the strain imposed by Ti-O bond lengths, leading to the formation of extraframework Ti species (EFW-Ti, Figure 2c) such as octahedral TiO₆ units, anatase-like TiO₂ domains, or small TiO_x clusters [53]. These species differ markedly from framework Ti in electronic structure and catalytic behavior; they often promote unselective oxidation or accelerate H₂O₂ decomposition rather than epoxide formation [54,55]. Similar substitution limits and defect-dependent behaviors have been reported for other titanosilicates, including Ti-Beta [56], Ti-MCM-41 [57], and amorphous Ti-SiO₂, though the precise limit depends on framework topology, defect density, and preparation method.

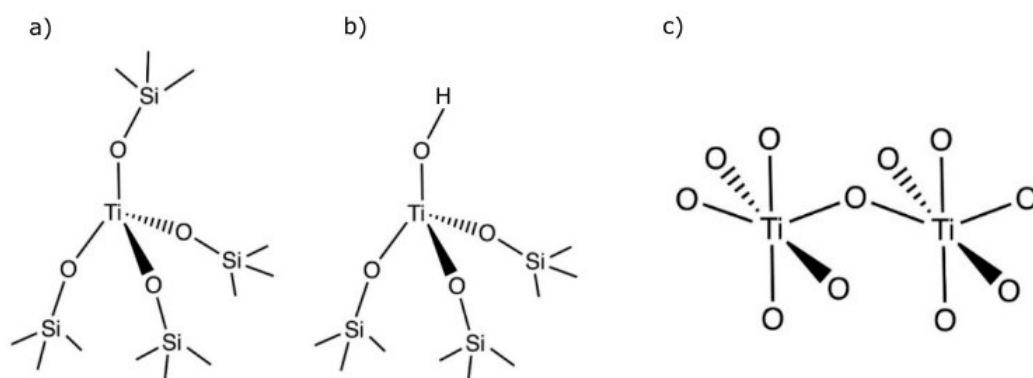


Figure 2. Titanium species in titanosilicates: framework titanium (FW-Ti): (a) open site, (b) close site and (c) extraframework titanium (EFW-Ti).

The catalytic relevance of each Ti species is therefore closely tied to its coordination environment and the local microstructure. Early interpretations assumed that the only active sites were isolated, closed tetrahedral Ti(OSi)₄ units. More recent work, however, demonstrates a much broader family of catalytically competent Ti(IV) environments. Yu et al. [58], identified at least four microenvironments in MWW-type titanosilicates—Ti(OSi)₄(OTiO₅)₂, Ti(OSi)₄, Ti(OSi)₃OH, and Ti(OSi)₃OH(HO-Si)_n—and established a clear activity hierarchy for H₂O₂ epoxidation, in which closed or partially blocked sites are far less active than open Ti(OSi)₃OH environments. In particular, open Ti(OSi)₃OH sites exhibit stronger Lewis acidity and form Ti-OOH intermediates more efficiently, while Ti(OSi)₃OH(HO-Si)_n

environments containing additional silanol nests further stabilize peroxo intermediates by hydrogen bonding and suppress unproductive H_2O_2 decomposition.

This framework is consistent with findings by Bregante et al. [38] for Ti-BEA, where highly hydrophilic environments rich in $(\text{SiOH})_4$ nests produce epoxidation turnover rates up to two orders of magnitude higher than nearly hydrophobic, defect-poor analogs. Importantly, these enhancements do not arise from changes in the intrinsic electronic structure of Ti(IV) but from cooperative hydrogen-bond networks involving Ti-OOH species, vicinal silanols, and confined water that stabilize key transition states. Broader group IV/V substitution studies corroborate that the kinetically relevant oxidizing species are Ti-OOH and $\text{Ti}(\text{O}_2)^{2-}$ peroxo complexes reacting with olefins via an Eley–Rideal mechanism, in which only the oxidant—not the olefin—is adsorbed [30].

More recent spectroscopic and computational work, summarized by Wang et al. [59] expands the palette of relevant Ti species even further. Beyond classical tetrahedral TiO_4 , titanosilicates may contain framework-associated penta- and hexa-coordinated Ti species—including mononuclear TiO_6 , $\text{Ti}(\text{OH})_4(\text{OSi})_2$ units, and binuclear Ti-O-Ti motifs, that can exhibit comparable or even superior activity for certain oxidation reactions. These species often arise from local flexibility, defect rearrangement, or interaction with water and silanol groups, emphasizing that catalysis in titanosilicates cannot be fully described by a single coordination environment.

The microenvironment surrounding Ti, especially its degree of hydrophobicity/philicity, plays a decisive role in determining which Ti species form and how they function. Hydrophilic surfaces rich in silanol groups tend to stabilize higher-coordination Ti species, promote water adsorption, and facilitate epoxide ring-opening, reducing selectivity and in some cases deactivating Ti sites [22–24]. Conversely, hydrophobic surfaces promote rapid epoxide desorption, suppress competitive water adsorption, and help maintain Ti in its active tetrahedral or pseudotetrahedral configuration. Thus, understanding Ti-active sites requires integrating not only Ti coordination but also the interplay between framework flexibility, defect chemistry, and surface hydrophobicity, all of which collectively dictate the formation, stability, and catalytic behavior of Ti species.

The identification of these species relies on a suite of spectroscopic and structural techniques, including FTIR and Raman vibrational spectroscopy, EPR, XPS, DR UV-Vis, and EXAFS/XANES. In MFI materials, FW-Ti is typically associated with IR/Raman features near 960 cm^{-1} and UV-Vis bands at 200–210 nm, whereas absorptions at 260–280 nm indicate octahedral TiO_6 species and those at 310–330 nm reflect anatase-like TiO_2 . Resonant UV-Raman and advanced XANES/EXAFS methods now enable discrimination among TiO_4 , framework-associated TiO_6 , and highly dispersed TiO_2 clusters even at low concentrations. The comprehensive correlation of these signatures with local coordination provided by Vayssilov [1] and more recently by Wang et al. [59] remains a key reference for interpreting Ti speciation across titanosilicate families.

2.1.2. Acidity of Titanosilicates

Because this review covers both amorphous and zeolitic titanosilicates, it is first necessary to outline how acidity arises in zeolite frameworks, since the presence or absence of framework charge directly determines the type and strength of acid sites that can coexist with Ti active centers.

The acidity of zeolitic materials depends strongly on the nature of the heteroatoms incorporated into the silica framework. In aluminosilicate zeolites, isomorphous substitution of Si^{4+} by Al^{3+} generates a negatively charged lattice that must be balanced by extra-framework cations [50,60]. When the compensating cation is H^+ , Brønsted acid sites (BAS) form as bridging hydroxyls ($\equiv\text{Si}-\text{OH}-\text{Al}\equiv$), while partially coordinated Al species

or extra-framework Al contribute Lewis acid sites (LAS) [61]. These hydroxylated centers increase the hydrophilicity of the material because they strongly interact with water [62,63]. These acid groups significantly increase hydrophilicity because hydroxyls readily adsorb water [64]. In contrast, defect-free siliceous frameworks dominated by Si-O-Si linkages are inherently hydrophobic and resist water adsorption, whereas surfaces rich in silanol groups readily retain water molecules and water clusters [65]. Hydrophilicity thus increases with rising silanol density, and indeed the hydrophobicity index (HI) has been shown to decrease with increasing concentration of Brønsted acid sites [63].

In titanosilicates such as TS-1, substitution of Si^{4+} by Ti^{4+} does not introduce a formal framework charge, and therefore does not create Brønsted acidity analogous to aluminosilicates [50,51].

Early studies demonstrated that dehydrated, well-defined TS-1 lacks detectable BAS associated with Ti, as evidenced by pyridine adsorption followed by FT-IR spectroscopy and ^1H MAS NMR [51]. Although some authors have proposed the existence of titanol (Ti-OH) groups that might act as proton donors [66], direct spectroscopic evidence remains limited and often ambiguous. In hydrated or defect-rich samples, OH groups can be observed; however, the consensus is that these signals arise predominantly from silanol nests (Si-OH) generated at framework defects rather than from Brønsted-acidic Ti-OH groups [67]. Thus, any measurable BAS in titanosilicates typically originates from defect-derived silanols, not from the Ti centers themselves.

The dominant acidity in well-defined titanosilicates is Lewis acidity, arising from tetrahedral Ti(IV) centers capable of coordinating and activating molecules such as H_2O_2 [54]. These Ti sites act as strong Lewis acids due to their vacant d-orbitals and distorted coordination, enabling the formation of Ti-OOH and Ti-OOR peroxo intermediates crucial for selective oxidation. Recent studies show that Lewis acidity varies depending on the local microenvironment of Ti: closed $\text{Ti}(\text{OSi})_4$ units exhibit weaker acidity, whereas open $\text{Ti}(\text{OSi})_3\text{OH}$ and defect-associated $\text{Ti}(\text{OSi})_3\text{OH}(\text{HO-Si})_n$ species display significantly stronger Lewis character and higher H_2O_2 activation efficiency [58,68]. Moreover, penta- and hexa-coordinated Ti species, previously considered inactive, can also act as Lewis acid sites under certain conditions, particularly in defective or partially hydrated environments [59].

Hydrophilic materials enriched in silanol nests or trace Al retain more water, which can solvate Ti-OOH intermediates and assist proton-transfer steps, but also promote epoxide ring-opening and undesired side reactions [38]. Conversely, hydrophobic surfaces limit water adsorption, preserve Ti in its active tetrahedral/pseudotetrahedral form, and accelerate epoxide desorption, thereby improving selectivity [37]. In Ti-Beta, for example, reducing Al content lowers silanol density and increases hydrophobicity, modifying both acid character and catalytic behavior [64]. Hydrophobic modification, therefore, tunes the effective Lewis acidity of Ti not by altering the Ti center itself but by controlling the degree of solvation, hydrogen-bonding interactions, and hydroxyl coverage within its microenvironment.

Advanced spectroscopic techniques (including FTIR with pyridine or nitrile probes, UV-Vis, Raman, photoluminescence, XPS, and XANES/EXAFS) remain essential to distinguishing Brønsted vs. Lewis acid sites and identifying the coordination state of Ti [1,64]. Vibrational features around 1450 and 1610 cm^{-1} indicate Lewis-bound pyridine, while Ti-perturbed Si-O stretches near 960 cm^{-1} and UV-Vis bands at 200–210 nm are characteristic of framework Ti^{4+} [69].

2.1.3. Titanosilicates Based on Zeolite Frameworks (Ti-Zeolite)

Ti-zeolites have a crystalline structure composed of SiO_4 tetrahedral units in which one or more Si atoms can be replaced by Ti atoms without introducing negative charges [70]. Ti-zeolites have been used as catalysts of selective oxidation reactions (e.g., epoxidation of olefins, hydroxylation of phenol, ammoximation of ketone, oxidative desulfurization and oxidation of pyridine derivatives) [71]. The differences in shape, size and channel topology of zeolites enable their use in a wide range of industrial applications. Ti-zeolites are important not only for the technical performance but also because they are environmentally friendly, since the optimization of these catalysts has turned certain processes more efficient and less waste is generated, following the principles of green chemistry [2].

Research on Ti-zeolites has advanced rapidly over the last four decades, and their development has been closely tied to advances in synthesis, structure elucidation, and catalytic applications. In this line, several comprehensive reviews have shaped our current understanding. Ratnasamy and colleagues [22] in 2004, provided an influential state-of-the-art discussion on the nature of Ti active sites and intermediate species in crystalline titanosilicates provided an influential state-of-the-art discussion on the nature of Ti active sites and intermediate species in crystalline titanosilicates. Later in 2014, Moliner and Corma [70] highlighted progress in the preparation of ordered titanosilicates, with particular emphasis on how textural engineering influences catalytic behavior. Xu and Wu in 2017 [12] further expanded this perspective by summarizing advances in topology control, crystal morphology, and the evolution of the local chemical environment in Ti-containing zeolites. The catalytic implications of these structural features were then synthesized by Přeč [2] in 2018, who reviewed the performance of titanosilicates in selective oxidation reactions.

Přeč has also proposed a valuable and systematic classification of Ti-zeolites based on their textural properties, pore architecture, and distribution of Ti active sites, an organizational framework that remains widely used. In this scheme, Ti-zeolites are categorized into four groups: (i) conventional Ti-zeolites (Table 1) which display uniform microporous structures without significant mesoporosity or structural defects; (ii) hierarchical Ti-zeolites combining intrinsic zeolitic micropores with secondary mesopores (20–430 Å) that enhance diffusion; (iii) lamellar Ti-zeolites consisting of layered crystalline units separated by mesoporous regions; and (iv) mesoporous titanosilicates which lack long-range crystalline order but possess an ordered system of mesopores (~20 Å) [2]. This classification is especially valuable for correlating framework architecture with catalytic performance, diffusion behavior, and the accessibility of Ti sites.

Table 1. Pore size of conventional Ti-zeolites [2].

Group	Sub-Group	Ring Pores	Diameter (Å)
Conventional Ti-zeolites	Medium-pore	10	4.5–5.5
	Large-pore	12	5.5–7.0
	Extra-large-pore	14	>7.0

Since the synthesis of TS-1 in 1983, more than 30 Ti-zeolites have been developed. However, only a few of them, including Ti-Beta, Ti-MWW, and Ti-MOR, have been used on an industrial scale [12,71]. TS-1 has been efficiently used as a catalyst for the oxidation of small molecules using aqueous H_2O_2 as oxidant. However, TS-1 and other medium-pore Ti-zeolites such as Ti-YNU-2 [72] presented limitations in the diffusion of reactants and products due to its intrinsic microporosity. Large substrates such as linear olefins or phenol cannot access the internal active sites, causing the reaction to occur only on the

outer surface [73,74]. In order to solve this limitation, new Ti-zeolites have been synthesized, including large-pore Ti-zeolites as Ti-MCM-41 [57], Ti-MCM-48 [75], Ti-Beta [76] and Ti-MOR [77], and extra-large Ti-UTL [78]. Another alternative to improve the porosity and exposure of the active sites is the introduction of mesoporous systems in the intrinsic microporosity to obtain hierarchical zeolites [13,71,74,79] or lamellar zeolites such as Ti-MFI [80], Ti-MWW [81] and Ti-FER [82,83]. The synthesis of nanocrystals of Ti-zeolites has also appeared as an interesting strategy to increase the specific surface area of these materials [84]. The improvement of the textural properties allows the diffusion of bulky substrates. However, these materials display more hydrophilicity, which affects their catalytic performance, compared to TS-1 [54,85,86]. For this reason, modifying the hydrophobicity of the catalyst surface could enhance the catalytic performance, as it has been proposed by some researchers [40,87,88].

To bring this overview in line with current developments, it is essential to highlight several more recent and impactful reviews. Bai and Yu [71], in 2021, discussed strategies for generating hierarchical TS-1 zeolites and their impact on mass transport and catalytic efficiency. Luan et al. (2022) [79] summarized advances in TS-1 synthesis, including low-cost precursors, solvent-free methods, and nano- and hierarchical architectures. Wang and co-workers [89], in 2024, provided an extensive overview of the synthesis and emerging applications of TS-1 in green oxidation processes, whereas Yang and Li [90] examined the mechanistic and technological evolution of TS-1-catalyzed propylene epoxidation. Most recently, Xue and Li [91] and Wang and Zhang [59] revisited the nature of active species in TS-1 at the atomic scale, highlighting new insights into framework and extra-framework Ti, defect-associated Ti environments, and the role of water and solvent in shaping activity.

Beyond diffusion considerations, pore architecture in Ti-zeolites plays a decisive role in shaping the physicochemical environment of the Ti active sites. In conventional microporous systems such as TS-1, the highly siliceous and defect-poor framework creates a relatively hydrophobic and spatially confined environment, which has been associated with enhanced stabilization of Ti-hydroperoxo intermediates formed upon interaction with H_2O_2 [22,59,91]. This confinement limits competitive adsorption of water and suppresses non-productive oxidant decomposition, thereby improving catalytic efficiency in selective oxidation reactions. Consequently, activity and selectivity are governed not only by pore size, but also by the polarity and local coordination environment surrounding the isolated framework Ti species.

When hierarchical, lamellar or mesoporous architectures are introduced, the increase in external surface area and mesoporosity enhances accessibility of bulky reactants. However, these modifications are frequently accompanied by a higher density of silanol groups and structural defects, leading to increased surface hydrophilicity. Such changes alter the local electronic environment of Ti sites and may influence the stability and reactivity of Ti-peroxo species in aqueous media. Although improved mass transport can enhance conversion for large substrates, the more polar environment may promote water adsorption and affect selectivity in epoxidation reactions. Therefore, the catalytic performance of Ti-zeolites reflects a delicate balance between diffusional accessibility, framework confinement, and hydrophobic character.

2.1.4. Titanosilicates Without Zeolite Frameworks (Ti-SiO₂)

The discovery of TS-1 represents a breakthrough in the oxidation of organic compounds with solid catalysts under mild conditions. However, due to the mass-transfer limitations in microporous TS-1, several large and ultra-large Ti-zeolites have been synthesized. There is an increasing interest in the fabrication of titanosilicates with even larger pore sizes and a higher number of Ti active sites that can be used with bulkier substrates.

In this way, amorphous titanasilicates with no zeolitic framework (Ti-SiO_2), also called titania-silica ($\text{TiO}_2\text{-SiO}_2$) mixed oxides, have been prepared for oxidation reactions [3,8].

The first Ti-SiO_2 was synthesized by Shell researchers in 1971 [92] and they were used as a catalyst for propylene epoxidation with alkylhydroperoxides as oxidants. The active sites of this type of catalyst are tetrahedral Ti isolated by O-Si fragments. The formation of Ti-O-Si bonds renders chemical stability to the Ti-SiO_2 catalysts and prevents leaching problems [93]. Also, the dispersion of titanium into the silica matrix generates Lewis acid sites. The catalyst acidity increases with the higher dispersion of titanium in the silica matrix [94].

Ti-SiO_2 catalysts can be prepared by the sol-gel method. The first attempts to use sol-gel to synthesize Ti-SiO_2 for cyclohexene and cyclooctene epoxidation with H_2O_2 were reported by Neumann et al. in 1993 [95]. Ti-SiO_2 was efficient in the olefin's epoxidation after 20 h [95]. The influence of the sol-gel preparation method and drying conditions on the structural and chemical properties of Ti-SiO_2 was studied by Hutter et al. in the 1990s [3]. It has been demonstrated that with appropriate preparation and drying conditions, an amorphous material with high surface area and outstanding titania dispersion (20%wt TiO_2) in silica matrix can be achieved. In a second part of their investigation, Hutter et al. reported on the catalytic properties of Ti-SiO_2 for epoxidation of olefins [96]. High catalytic activity and selectivity can be expected for Ti-SiO_2 with mesoporous structure regarding the epoxidation of linear or cyclic olefins and electron-deficient olefins such as α -isophorone, which are difficult to epoxidize [93].

The remarkable catalytic activity of Ti-SiO_2 is related to its textural and structural properties (mesoporosity and high dispersion of Ti). Therefore, the Ti content has an influence on the structural and catalytic properties of Ti-SiO_2 catalysts and consequently in the accessibility of the reactants on the Ti active sites in tetrahedral coordination [3]. Initially, it was determined that an increase in the content of Ti from 2 to 20 wt% TiO_2 increased the Si-O-Ti heteroconnectivity, so a maximum of 20 wt% TiO_2 was appropriate for epoxidation catalysts. An increase to 30 wt% TiO_2 leads to agglomerates of TiO_2 , bad dispersion of Ti and lower catalytic activity. Another relevant factor that regulates the textural properties is the aging of the wet sol-gel which strengthens the gel network and thereby preserves the porous network of the dried gel [97].

Ti-SiO_2 catalysts are commonly used for olefin isomerization [98–100], aromatics amination [98], alcohols dehydration [101], aromatics dealkylation [101] and selective oxidation [45,46,102–113]. Since the first synthesis of Ti-SiO_2 , several researchers have focused on the study of this group of materials. A review, published by Davis and Liu in 1997, summarizes valuable information about the microstructural characteristics and catalytic activity of Ti-SiO_2 catalysts [114]. Other applications of Ti-SiO_2 in the catalytic field can be found in the literature [106,108,115–120].

However, unlike crystalline Ti-zeolites, amorphous titanium silicalites have a high density of surface silanol groups and structural defects, which gives them a markedly hydrophilic character [111,112,121]. The absence of a hydrophobic crystalline framework and confinement effects means that Ti sites in tetrahedral coordination are more exposed to the reaction medium. In systems that use H_2O_2 as an oxidant, this surface polarity favors the competitive adsorption of water molecules on the Ti-O-Si centers, which can alter the stability of the active Ti-hydroperoxo species and promote the unproductive decomposition of the oxidant [111,121,122]. Consequently, catalytic activity depends not only on titanium dispersion and mesoporosity, but also on the degree of condensation of the Si-O-Si network and the density of silanols, parameters that determine the local polarity around the active site.

Hydrophobic modification of the surface, through silylation treatments or adjustment of the synthesis and drying conditions, has been shown to reduce water affinity and improve oxidative efficiency in epoxidation reactions [44,111,112]. Thus, in amorphous Ti-SiO₂, catalytic performance results from a delicate balance between textural accessibility, dispersion of Ti in tetrahedral coordination, and control of surface polarity.

2.2. Description of the Hydrophobization Methodologies and Techniques for Measuring the Hydrophobicity of Titanosilicates

2.2.1. Hydrophobicity Basics

The term hydrophobicity/phobicity refers to the affinity that exists between a solid surface and water. A hydrophobic surface can be defined similarly to a hydrophobic substance. Nonpolar substances are hydrophobic and have low solubility in water at room temperature. The accumulation of the nonpolar molecules in aqueous media produces a high cohesive energy density of water that decreases the interface between the nonpolar substance and water, explaining the hydrophobic effect. Therefore, to transfer nonpolar molecules into an aqueous medium, the enormously stable hydrogen bond among water molecules must be disrupted (Figure 3) [123,124].

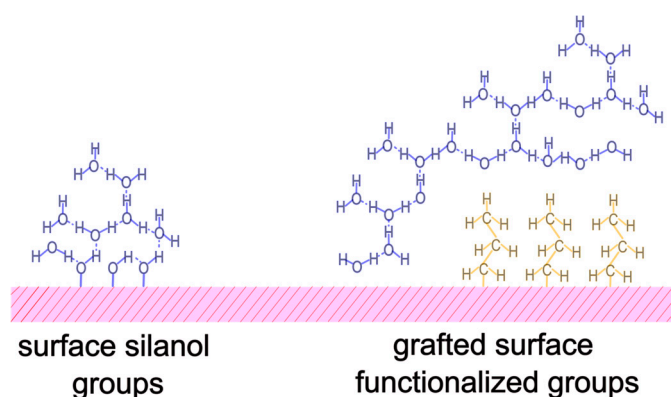


Figure 3. Schematic illustration of hydrophobic/hydrophilic interactions at titanosilicate surfaces governed by surface groups. Surface silanol groups and hydrogen-bonded water molecules are shown in blue, grafted hydrophobic organic groups in yellow, and the silica surface as the pink hatched region.

Although there are some analytical techniques that provide information about the hydrophobicity of flat surfaces, there is no specific technique for porous solid surfaces. The hydrophobic effect in solids is related to the absence of interfacial interactions with water or similar dipolar and protic molecules. And more exactly, a better definition can be achieved by contemplating the possible forces between a solid surface and an adsorbate molecule. The interactions of water with a solid surface are commonly generated from specific surface sites such as functional groups that can act as Brønsted or Lewis acids or bases (Table 2) [123].

Table 2. Functional groups that affect the hydrophilic character of solid porous surfaces. Adapted from Ref. [123]. Copyright © 2008 John Wiley and Sons.

Functional Group		Occurrence
Hydroxyl	-OH	Oxides, hydroxides
Carboxyl	-COOH	Carbons
Carbonyl	-C=O	Carbons
Ether	-O-	Oxides, carbons
	Ionic species (i.e., H ⁺ , Na ⁺ , Mg ⁺² , Cl ⁻)	Ion exchanger

The mutual molecular interactions that affect the wettability of a solid surface are reflected in a macroscopic parameter known as contact angle (CA) formed between the solid phase boundary and the liquid phase [125]. It is possible to quantify the hydrophobicity of the solid surface as a function of the CA. However, there are some limitations to measuring the CA of rough solid surfaces or surfaces with defects such as functional groups (i.e., silanol groups) [123].

It should be noted that hydrophobicity/hydrophilicity is a relevant property that must be considered for the synthesis of porous solid catalysts. The catalytic performance of a solid catalyst is not only associated with the active sites but is also influenced by the catalyst's wettability, which affects the adsorption and desorption processes and mass transfer on the surface. Adjustment of the surface hydrophobicity could enhance the activity, selectivity and lifetime of catalysts [126]. Thus, it is necessary to inquire into the concepts of hydrophobicity to apply the measuring techniques in the correct form.

2.2.2. Methodologies for Hydrophobization of Titanosilicates

Two main strategies to increase the surface hydrophobicity of titanosilicates can be distinguished in the literature. The first strategy is controlling the surface density of silanol groups. It is well established that defect-free siliceous surfaces dominated by Si-O-Si bonds exhibit hydrophobic behavior [65], whereas surfaces containing hydroxyl groups (Si-OH) and bridging hydroxyl groups (i.e., Si-OH-Ti, Si-OH-Al) are intrinsically hydrophilic [62]. Consequently, an increase in the surface density of silanol groups enhances the hydrophilic character of titanosilicates, leading to greater water adsorption [64]. The silanol surface density can be controlled by improving the crystallinity of titanosilicates (which at the same time may improve the incorporation of Ti) and by synthesizing them in fluoride (F^-) medium instead of OH^- medium.

The second strategy relies on surface functionalization with organic groups targeting both the external surface and the internal porosity, where the active sites are located. This can be achieved either by “one-pot functionalization” [127,128] or “post-grafting” of organic groups [88]. Both approaches effectively increase surface hydrophobicity, thereby generating environments that can markedly influence the reactivity of microporous and mesoporous titanosilicates.

Control of Silanol Surface Density

The density of silanol defects in titanosilicates is governed by the crystallization conditions, which can be adjusted through the synthesis parameters, such as the silica source, templates, and structure-directing agents (SDAs). Crystallization of titanosilicates is more complex than that of aluminosilicates as Ti(IV) displays a weaker structure-directing role compared to Al(III). Moreover, the Ti-O bond (1.80 Å) is longer than the Si-O bond (1.61 Å), which distorts the structure around Ti and results in a slow isomorphous substitution of Si by Ti(IV) and the formation of undesired phases. Fan et al. [33] demonstrated that $(NH_4)_2CO_3$ acts as an effective crystallization-mediating agent, improving the isomorphous incorporation of Ti(IV) into the silica framework of TS-1 while significantly reducing the density of silanol defects. Highly crystallized TS-1 has fewer Si-OH terminal groups and is more hydrophobic.

Structure-directing agents (SDAs), such as tetraethylammonium hydroxide (TEAOH) and TPAOH, have also been shown to improve Ti insertion in silicalite-1, leading to a progressive decrease in the population of silanol protons H-bonded to siloxy oxygens at defect sites [129].

An alternative methodology to control the density of silanol groups in titanosilicates involves starting from an aluminosilicate framework, followed by dealumination and

subsequent titanium insertion. In microporous and mesoporous silica-based materials, extended Si-O-Si and Si-O-M networks enhance heteroatom coordination, limit hydrolysis and leaching, and promote a hydrophobic environment that prevents the formation of water phases near them, thereby preventing the deactivation of active sites in aqueous media. Silica and metal oxide networks (Si-O-Si, Si-O-M) are present in Brønsted and Lewis acid oxides [64].

In aluminosilicates, framework composition plays a key role in water affinity. The low silicious zeolites (Si/Al = 1–2) possess high amounts of AlO_4 units and Si-O-Al bridges, so they are more hydrophilic than high silicious zeolites (Si/Al = 10– ∞) [130]. The Al-O bond is more polar (40% covalent and 60% ionic bond) than the Si-O bond (100% covalent bond), and thus, strong interactions with water are produced [131]. Moreover, silanol groups and bridging hydroxyl groups form hydrophilic domains in the silica framework [62], and these polar hydroxyl groups adsorb water. Thus, water uptake decreases with increasing Si/Al ratio, as reported for ZSM-5 [132,133], Beta [62], MCM-41 [134], and Ti-Beta [37].

In this context, the combination of dealumination and post-insertion of heteroatoms can produce materials with higher hydrophobicity [38]. According to the IR characterization of dealuminated Ti-Beta, a higher content of Si-OH groups was detected with the decrease in Al content [135]. In contrast, when titanium heteroatoms were incorporated into dealuminated Beta zeolite, the density of isolated silanol groups decreased, whereas silanol nests (SiOH_4) decreased in Beta zeolites with less amount of Al compared with those with high Al content [38]. As shown in Figure 4, dealumination generates framework vacancy defects that promote the formation of silanol nests, resulting in increased hydrophilicity. Subsequent incorporation of Ti atoms into these vacancies decreases the silanol nest density.

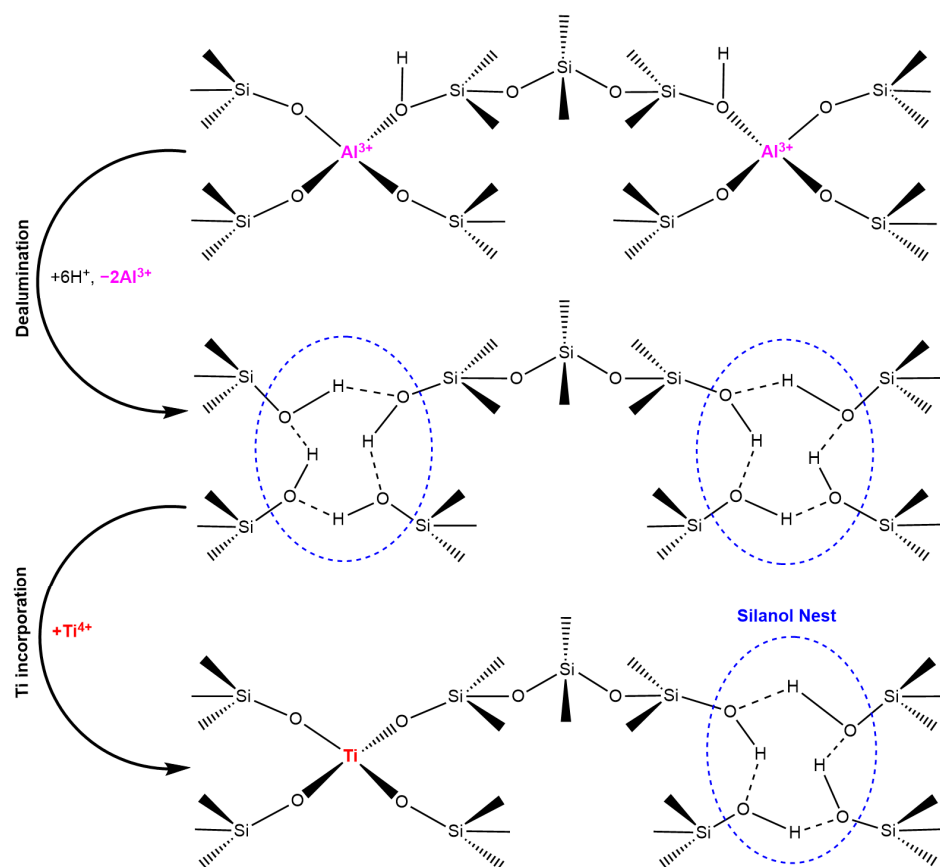


Figure 4. Dealumination and post-incorporation of Ti to prepare Ti-Beta.

Other alternative methodologies to obtain Al-free Ti-Beta by indirect ways are the synthesis of Ti-Beta using dealuminated seeds of Beta zeolite, and the post-synthetic modification of commercial Beta zeolite [36,136].

Furthermore, there is a direct way to synthesize hydrophobic Al-free Ti-Beta, which uses fluoride (F^-) medium instead of aqueous (OH^-) medium. The F^- medium prevents the formation of anionic framework vacancy defects since the cationic charges of SDAs employed in the synthesis are counterbalanced by F^- forming strong ion-pairs [136,137]. As shown in Figure 5, when OH^- anions are used in the synthesis, anionic framework vacancy defects are produced, and after removal of SDA cations, silanol nests are formed in the zeolite framework, increasing the hydrophilicity of the material.

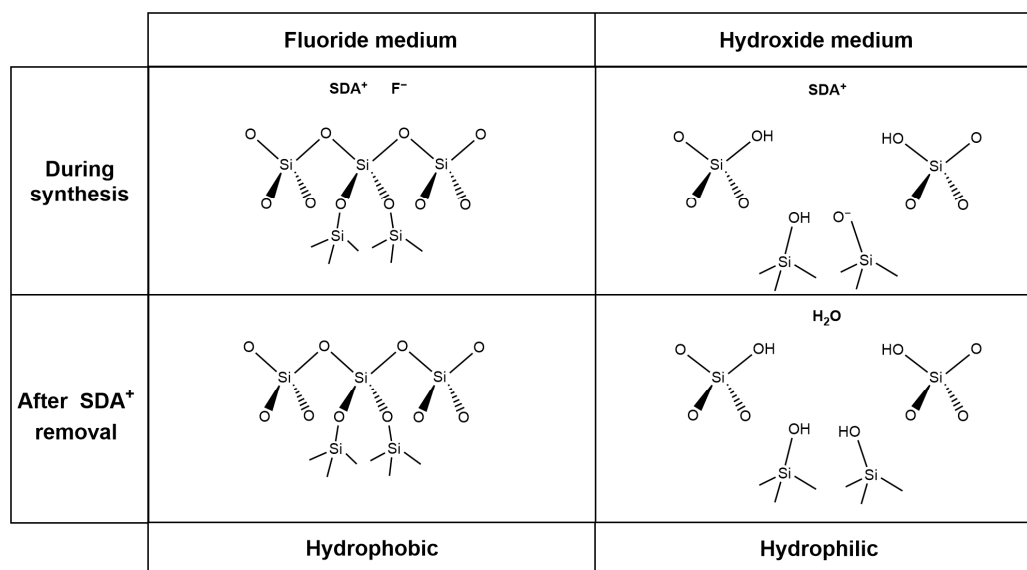


Figure 5. Preparation of zeolites in fluoride medium and aqueous medium. Adapted from Ref. [137]. Copyright © 2013 American Institute of Chemical Engineers.

It should be noted, however, that the strong Si-F interaction may also influence crystallization kinetics and local structural environments during synthesis [138]. Although the overall BEA topology is generally preserved under comparable structure-directing conditions, fluoride-mediated synthesis does not merely act as a surface modifier but as a framework-condensation route that affects defect distribution and structural organization. In this context, the reduced silanol density and improved framework connectivity are the features most directly related to the enhanced intrinsic hydrophobicity relevant for catalytic applications [36,37].

As already mentioned, the silanol surface density of titanosilicates can be modified through the presence of F^- ions during synthesis. However, the presence of F^- ions reduces the incorporation of Ti atoms into the final material. Therefore, determining the optimal concentration of F^- ions able to decrease the silanol surface density while maintaining an effective incorporation of heteroatoms in the titanosilicates is essential. Indeed, the ratio between HF/SDA (SDA corresponds to tetrapropylammonium hydroxide (TPAOH)) was optimized by Bregante et al. for zeolitic materials with MFI structure (Silicalite-1), where heteroatoms Nb, Ta, and Ti were inserted. The relative silanol density was quantified using IR spectroscopy. The authors normalized the area of $\nu(\text{Si-OH})$ relative to that of the $\nu(\text{Si-O-Si})$, observing a linearly decrement as the HF/TPAOH ratio (x) increases. With $x < 1$, the relative silanol density decreased by 4–8-fold, whereas for $x = 1.5$, the relative silanol density decreased 30–100 times compared to materials synthesized in OH^- medium. For $x > 1.5$, the relative silanol density was undetectable. The formation of the strong ion-pairs

between TPAOH cation (TPA^+) and F^- is reversible, and the concentrations of species are defined by the equilibrium. Finally, water adsorption experiments of TS-1 showed that TS-1 synthesized in F^- medium stabilized ~ 5 water molecules at vapor pressure at 293 K and adsorbed 7–100 times less water than TS-1 synthesized in OH^- medium. The number of water molecules stabilized by Ti was calculated from the difference between the H_2O uptake of TS-1 and silicalite-1, which is then normalized by the number of Ti atoms [139].

Additional approaches currently explored include the conventional synthesis of TS-1 followed by a defect-healing post-treatment using a combination of ammonium fluoride (NH_4F) and TEAOH. In contrast to fluoride-mediated synthesis, this post-synthetic approach effectively heals framework defects, yielding defect-free TS-1 with enhanced hydrophobicity [140].

Organic Surface Functionalization

The insertion of organic groups into titanosilicate catalysts has been mainly achieved through two distinct methodologies: one-pot synthesis and post-grafting functionalization (Figure 6).

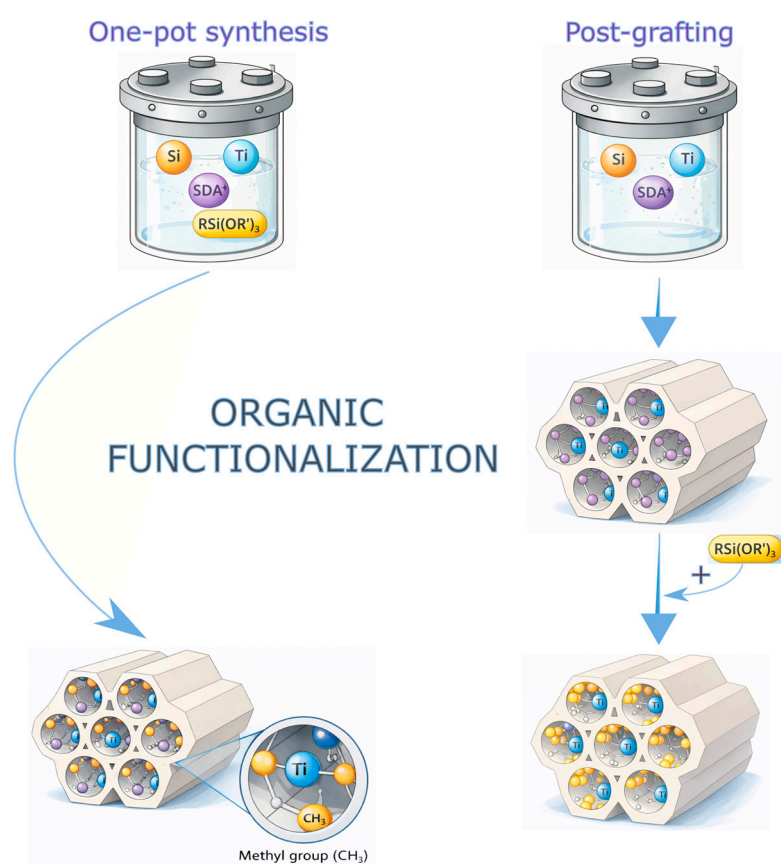


Figure 6. Schematic comparison of organic functionalization strategies in Ti-MCM-41 catalysts. In the one-pot approach, organic silanes are co-introduced with Si and Ti precursors during hydrothermal synthesis, leading to a relatively homogeneous distribution of organic groups along the pore walls. In contrast, post-grafting involves the anchoring of organic moieties onto pre-formed Ti-MCM-41, typically resulting in a higher concentration of organic groups near pore entrances and external surfaces. These differences in spatial distribution may influence pore accessibility, local polarity, and the interaction between reactants, solvent, and Ti active sites.

In the one-pot synthesis, organic silane precursors (e.g., $\text{R-Si}(\text{OR}')_3$) are co-condensed with silicon and titanium sources in the presence of an SDA during the hydrothermal synthesis. This approach allows the organic groups to be incorporated directly into the

inorganic framework or pore walls as the material forms, leading to a relatively homogeneous distribution of hydrophobic functionalities throughout the mesoporous structure. As a result, the organic groups are intimately integrated with the silica network, often yielding catalysts with uniformly modified internal surfaces and tunable hydrophobicity.

In contrast, post-grafting involves the chemical modification of a pre-synthesized titanosilicate. In this method, organosilanes react selectively with surface silanol groups (Si-OH) after the material has been formed, typically under mild conditions. Consequently, the organic groups are preferentially anchored near the external surface and pore mouths, and their distribution is more heterogeneous and spatially constrained. While post-grafting enables precise control over surface chemistry without altering the bulk structure, excessive grafting may reduce pore accessibility or partially block active sites.

Organic functionalization of titanosilicates through one-pot and post-grafting methods was applied to obtain more hydrophobic catalysts. The silanol density in functionalized materials was lower than in the non-functionalized ones [11,27,39,40,47,48,141]. This low density was mainly attributed to the substitution of Si-OH groups by organic moieties, and it was confirmed by IR spectroscopy and ^{29}Si NMR analysis [11,39,40,48].

The effect of the organic functionalization on the catalytic activity was, in some cases, either positive for Ti-SiO₂ [47] and Ti/SiO₂ [48], or negative for Ti-Beta [6] or non-significant for TS-1 [6] and Ti/SiO₂ [142]. A possible explanation for the different catalytic effects was that the post-grafting can also modify the structure and textural properties of catalysts, and the nature of active sites [44]. For example, Ti/SiO₂ functionalized with poly(methylhydrosiloxane) (PMHS) by post-grafting was more hydrophobic than conventional Ti/SiO₂ [48]. In the same way, Ti-MCM-41 functionalized by the one-pot procedure with organosilanes exhibited lower silanol surface density and a strong hydrophobic character [39]. Hydrophobic environments, both on the external and internal surface have important consequences on the reactivity of porous catalysts [64].

The principal difference between post-grafting and one-pot methods lies in the Ti dispersion. According to XPS and DRUV-Vis analysis, titanosilicates functionalized by the one-pot method exhibited lower Ti dispersion. One-pot functionalization method is faster, and it can be controlled by the chemistry of precursors [44]. Ti speciation was not affected by post-grafting in most of the cases. Regarding the textural properties, both functionalization procedures diminished the specific surface area and pore size. This difference in textural properties can affect the catalytic performance of functionalized catalysts [47].

Ti dispersion on one-pot synthesis was enhanced using aerosol-assisted sol-gel. With this method, not only the Ti dispersion but also the organic functionalization and textural properties were controlled [11]. The effective dispersion of Ti with this method was attributed to the fast drying of the atomized mixture of precursors, which produces the quenching of kinetic condensation and leads to the formation of stable solid phases with homogeneous compositions [143]. A summary of hydrophobization methodologies applied to titanosilicates is presented in Table 3.

2.2.3. Determination of Hydrophobicity of Titanosilicates

Some analytical techniques applied for the characterization of the hydrophobic character of porous solids will be discussed in this section. Due to the absence of a precise definition of the term hydrophobicity and its origin, the analytical techniques applied to characterize this property in solids differ particularly regarding the experimental method and the physical/chemical properties considered for the evaluation of the porous solid surface. In fact, analytical techniques have ranked a given set of porous solids according to their hydrophobic character, but a quantitative assessment, considering the theory, remains a challenge. Also, it is important to keep in mind that the conditions under which

the experimental analysis is carried out do not always correspond to the conditions in the application, especially in the case of catalysts. In addition, the applicability of the characterization techniques will depend on each type of porous solids [123].

Table 3. Hydrophobization methodologies applied to titanosilicates.

Material	Hydrophobization Technique			
	Improvement of Crystallization/Ti Insertion	Synthesis in Fluoride (F [−]) Medium	One-Pot Synthesis	Post-Grafting
TS-1	[33] *	[139,140]		[6]
Ti-Beta		[36–38]		
Ti-MCM-41			[39,128,141]	[40,41,144,145]
Ti-MCM-48				[40,41]
Ti-SBA-15				[27,32]
Ti-SiO ₂			[11,44–47]	[47,48]

* as post-treatment.

Contact Angle Measurement

The contact angle (CA) is a known technique that allows the characterization of surface wettability. The CA is related to the lowest state of energy that characterizes a three-phase system (solid-liquid-gas). This experimental thermodynamic property corresponds to the observed angle at the contact line among these three phases. This angle is bounded by the tangent to the liquid-fluid interface and the tangent to the solid surface [146]. The CA is computed using the Young equation [147]. The Young's equation associates several terms as the solid surface energy γ_{sv} , the solid-liquid surface tension γ_{ls} , the liquid surface tension γ_{lv} and the cosine of the contact angle θ . As soon as a resting drop reaches the mechanical equilibrium on a plane solid surface, these three forces are balanced and can be described as expressed in Equation (1) [148].

$$\gamma_{sv} = \gamma_{ls} + \gamma_{lv} \cos \theta \quad (1)$$

For a drop with a certain radius of curvature, the CA equals the Young contact angle as long as this radius is larger than the nanometric scale. The Young contact angle is related to the equilibrium state reached by a drop on an ideal solid. However, a correction term needs to be applied for drops with smaller radii of curvature [146,149–151]. The ideal determination of the CA may encounter some difficulties, starting even before the measurements with the correct preparation of the solid surface and then during the measurements with the control of the equilibrium conditions. These challenges render the experimental determination not always feasible [146].

Contact angles are principally reported as static and dynamic. On the one hand, if the three-phase boundary is not moving and the droplet is sitting on the surface, measurements of static contact angles are obtained. On the other hand, if the three-phase boundary moves, measurements of dynamic contact angles are registered. These angles are defined as advancing (when the droplet front is advancing) and receding (when the droplet front is receding). The term hysteresis refers to the contact angles is then established as the comparison between these two angles (advancing and receding). Experimental approaches like the sessile drop and/or captive bubble [152–156] are preferred methods for the measurement of contact angles at ambient conditions on flat surfaces under different pressure and temperature conditions [157].

Several factors affect contact angles, including deformation, roughness, contamination, and surface geometry. Thus, it is not uncommon to find more than one contact angle

value reported for a certain system, taking into account all the variables that affect the experimental determination of the CA [146]. Furthermore, in most natural materials, the effective contact angle observed at larger scales is influenced by the surface roughness detected at the nanometer scale. Regarding the porous media as the closest approach to understanding the wettability of porous solids, such as titanosilicates, some challenges are identified. In general, contact angles in porous media can be not only variable throughout the pore space, but also scale-dependent and hysteretic owing to the presence of local surface roughness enhanced by variations in mineralogy and coating. However, it has been possible to determine geometrical contact angle values in the pore space. Some of the more common measurements include automated algorithms [158,159] or visual observation [160,161]. Other methods analyze the solid and fluid interfaces through the deficit curvature between them [162]. Recently, 3D images of fluids in the pore space generated by mCT (micro-computed X-ray tomography) were used for geometrical analysis of contact angles [163,164]. Nevertheless, the interpretation of these measurements is still difficult, regarding the broad range of variation found in the contact angle values obtained by this technique [165,166]. In fact, the scale of the pore size distribution of titanosilicates, which can vary from 5 Å to ~100 nm, is even smaller compared to the roughness scale range (~200 µm) reached through the most sophisticated techniques for determining the contact angle in porous media. Thus, the information that could be eventually obtained from the contact angle of titanosilicates does not adequately describe the whole hydrophilic-hydrophobic nature of the studied material.

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measures the mass variation in a sample while it is heated, cooled, or isothermally maintained under a defined atmosphere, inert or oxidizing. The analysis can be carried out at constant temperature or constant heating rate. A typical TGA curve shows the mass loss steps generally associated with the loss of volatile components, carbon black combustion, polymer decomposition, and final residues due to the temperature changes. This method permits the study of materials decomposition and their products, drawing conclusions about their individual components [167].

TGA is used to determine the water capacity that is the quotient between the mass loss due to the water desorption and the mass of dry solid [168]. In the hydrophobicity studies, TGA is a common analytical technique used for the determination of water affinity of solids or for the quantification of hydroxyl groups on the surface, which is an indirect way to quantify the water affinity of solid surfaces [169]. However, the sample preparation and storage could have an impact on the measurement of physisorbed water and lead to imprecise conclusions about the hydrophobicity/phobicity of a material. Thus, comparison of the hydrophobicity of materials must be performed carefully since the measurement of physisorbed water is expressed per gram of sample, so materials with higher surface areas will display a higher amount of physisorbed water per gram of sample. The comparison is clearer when physisorbed water is normalized by the specific surface area.

One way to quantify the hydrophobicity of the surface of microporous solids is the “hydrophobicity index” (HI), which was first introduced by Anderson and Klinowski [170]. This model is based on water adsorption and is not useful for the characterization of zeolitic sorbents. The mass losses at each temperature range are measured by TGA, and the HI is determined according to Equation (2).

$$HI = \frac{\text{Mass loss up to } 150\text{ }^{\circ}\text{C}}{\text{Mass loss up to } 400\text{ }^{\circ}\text{C}} \quad (2)$$

If $HI = 1$, the material is considered hydrophobic, and when $HI = 0$, it is a hydrophilic material. Another definition of HI was given by Giaya et al. [171] as shown in Equation (3):

$$HI = \frac{V_t - V_{>150\text{ }^{\circ}\text{C}}}{V_t} \quad (3)$$

where V_t is the total pore volume of the sorbent and $V_{>150\text{ }^{\circ}\text{C}}$ is the volume of water desorbed at a temperature above $150\text{ }^{\circ}\text{C}$. If $HI = 1$, the material is presented as very hydrophobic, and when $HI = 0$, the material is presented as very hydrophilic [171].

TGA measurements provide information about the water adsorbed physically, but not necessarily about the affinity. As Mueller et al. stated in 2003 [172], the water mass loss at temperatures below $120\text{ }^{\circ}\text{C}$ was attributed to the loss of water adsorbed physically, but this value is not related to the water affinity of the material surface. In fact, Mueller found that the presence of OH groups on the SiO_2 surface can be measured in the temperature range of $120\text{--}800\text{ }^{\circ}\text{C}$, and the OH content was normalized to the specific surface area to be able to compare the OH/m^2 of each material [172].

It is actually a challenge to distinguish between adsorbed water and actual hydroxyl surface density, that is, distinguishing between dehydration and dihydroxylation [173]. For this, an alternative to measure the actual amount of water that a sample contains was proposed by Lin et al. In this study, TG analysis was carried out starting from samples of Ti-MCM-41 Ti-zeolite saturated with NH_4Cl solution to guarantee the maximum level of water adsorption. The total number of molecules of water adsorbed on the surface was determined from the mass loss between 25 and $150\text{ }^{\circ}\text{C}$ [128]. In this procedure, the authors controlled the ambient conditions of the sample before TGA experiments, which allowed them to compare the samples independently of the synthesis and storage conditions.

Infrared Spectroscopy (IR)

Infrared Spectroscopy (IR) is a common technique applied to characterize solid catalysts. It can be used as a direct way to study the composition of solid surfaces or as an indirect way, providing information about the interactions between the surface and the adsorbate [169].

IR is a popular technique to measure the affinity of water for solids. With IR spectroscopy, the polar (e.g., OH) or non-polar groups of the solid surface can be directly quantified, providing an idea of the polarity of the surface. Infrared spectra offer information about the types of sorbed water molecules that are identified through the measurement of the frequency of the corresponding IR peaks. The intensity of the absorption band is used to measure the amount of water sorbed [168].

In comparison with TGA, IR spectroscopy provides more information about the distinction between physically adsorbed and chemically bound water. In fact, when IR spectra are analyzed, the water deformation band and the hydroxyl stretching vibration do not overlap; nevertheless, water -OHs contribute to the intensity of the -OH stretching vibration, which entangles the separation between inner and surface hydroxyls [174]. One of the characteristic bands of the IR spectrum of silica is related to the presence of -OH groups at 3750 cm^{-1} , which is assigned to isolated -OH groups. A close-lying band (a tail) formed by the weakly H-bonded -OH groups, appears in the $3600\text{--}3750\text{ cm}^{-1}$ region. The band of strongly H-bonded -OH groups and/or desorbed water appears in the $3400\text{--}3500\text{ cm}^{-1}$ range. The water -OH groups band appears at 1630 cm^{-1} (water deformation) and contributes to the bands in this region [175–177]. In order to quantify the hydrophobicity of metal-substituted zeolites, the silanol IR signals are usually normalized by the band of $\nu(\text{Si-O-Si})$ at 1990 and 1865 cm^{-1} (assuming this band is constant in the compared materials) [38].

In the specific case of titanosilicates, the IR spectra in the OH region display two intense bands at about 3740 and 4550 cm^{-1} corresponding to terminal Si-OH and hydrogen-bonded silanol groups at defect sites, respectively [52]. For titanosilicates that have been functionalized by post-grafting, the silanol band intensity decreases since the silane binds to surface -OH groups producing Si-O bonds. The C-H vibrational frequency appears after functionalization with organosilane groups [178,179]. C-H stretching and bending vibration bands that reflect the incorporation of alkyl groups appear at 2850–2985 and around 1460 cm^{-1} [178]. Thus, the lower intensity of the silanol band can be used as an indicator of an increase in hydrophobicity due to the functionalization success [180]. Additionally, the presence of Si-CH₃ at 1279 cm^{-1} [44], Si-CH₂ at 1410 cm^{-1} [181], as well as Si-C, Si-CH₂-CH₃, is also indicative of functionalization. Furthermore, the IR analysis of titanosilicates shows the characteristic bands at 1082 and 802 cm^{-1} attributed to the asymmetric and symmetric stretching vibration of Si-O-Si [179] and the Si-OH band that appears at 950 cm^{-1} in titanosilicates.

Adsorption Isotherms

Information about the affinity of the surface for a specific compound or, in general, properties related to the surface can be analyzed with the application of adsorption techniques. The adsorption from the gas phase on materials has been employed as a tool to evaluate the affinity for water [169].

Water affinity can be understood by recording the water adsorption isotherms. A hydrophobic material displays low affinity for water and low water adsorption capacity. In contrast, a hydrophilic material displays high affinity for water, but does not necessarily exhibit a high water adsorption capacity since the latter depends on the pore volume [168]. Therefore, to know if a material is more hydrophobic or hydrophilic, it is necessary to determine the amount of adsorbed water per unit area or mass in the range of low relative pressures [182]. In fact, the measurement of water adsorption capacity at higher relative pressures does not provide information about water affinity since the adsorbate-adsorbate interactions result in a multilayer adsorption and/or pore condensation. To solve this drawback, the water adsorption capacity must be analyzed at low loading (low amount of water adsorbed), without surpassing the monolayer adsorption, to minimize the influence of adsorbate-adsorbate interactions. Also, it is important to consider that using water as an adsorbent, a defined monolayer is not easy to obtain, and the presence of highly polar sites or acidic sites could increase the local water concentration due to hydrogen bonding. Consequently, it is better to compare materials of the same nature under similar conditions [123].

The hydrophobicity of sorbents has been classified according to the International Union of Pure and Applied Chemistry (IUPAC). This assignment is based on the type of adsorption isotherm. There are some characteristic curves of hydrophilic and hydrophobic materials. For instance, the type I isotherm is assigned to a highly hydrophilic material, the type II isotherm corresponds to a hydrophilic material, the type III isotherm represents a hydrophobic/low hydrophilic material with weak sorbent-water interactions, the type IV isotherm represents a hydrophilic material, the type V isotherm is associated with a hydrophobic/low hydrophilic material with weak sorbent-water interactions, the type VI isotherm corresponds to a hydrophilic material with multiple sorbent-water interactions and stepwise sorption, and the type VII isotherm is characteristic of a very hydrophobic material [168].

Figure 7 illustrates three water adsorption isotherms of zeolitic materials with different degrees of hydrophobicity and with the same pore volume [183]. Curve (a) is a type I isotherm in which the sorption equilibrium in the material is reached after the adsorption

of high amount of water at very low relative pressures (P/P_0), curve (b) is also a type I isotherm in which the sorption equilibrium is reached at higher P/P_0 , the curve (c) corresponds to a type V isotherm where just a small amount of water is adsorbed at low P/P_0 until the sorption capacity is reached, this is a hydrophobic or weakly hydrophilic solid, and curve (d) represents a type VII isotherm where a very small amount of water is adsorbed in all range of relative pressures, this material is considered highly hydrophobic. According to the adsorption isotherms of materials (a) and (b) at low loading, the material with the steeper slope is defined as more hydrophilic [168,183].

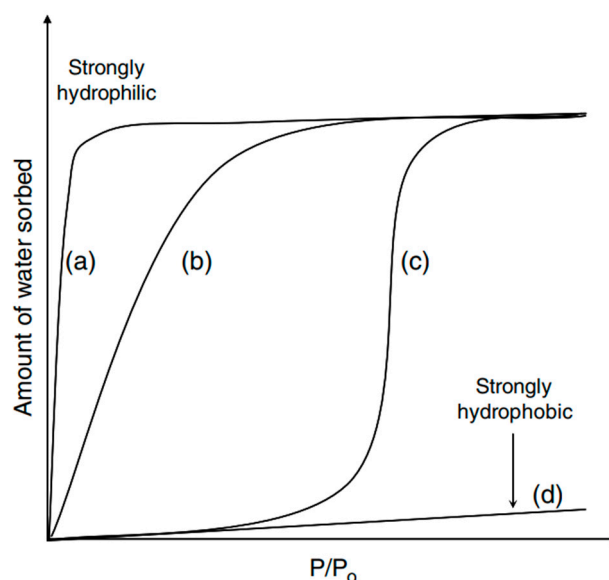


Figure 7. Water adsorption isotherms for ideally hydrophobic and hydrophilic zeolitic materials normalized to pore volume. Curve (a) corresponds to a highly hydrophilic material (type I isotherms) with steep adsorption at very low relative pressures (P/P_0). Curve (b) represents a less hydrophilic material (type I isotherm), where adsorption equilibrium is reached at higher P/P_0 . Curve (c) corresponds to a hydrophobic or weakly hydrophilic material (type V isotherm), while curve (d) represents a highly hydrophobic material (type VII isotherm). Reproduced with permission from Ref. [168]. Copyright © 2008 Elsevier.

Weitkamp et al. used the HI of zeolites for multicomponent sorption based on a competitive sorption between hydrocarbon and water to quantify the hydrophobicity. The HI is calculated by the (4).

$$HI = \frac{X_{\text{Hydrocarbon}}}{X_{\text{Water}}} \quad (4)$$

where X is the content of molecules adsorbed. A higher HI means a higher adsorption of hydrocarbon compared to water; thus, it is a more hydrophobic material [184]. In addition, the water adsorption capacity can be obtained by the standard contact porometry and sorptometry, which employ the mass change measures of the sorbents under constant water vapor pressure/humidity [185].

Calorimetric Techniques

Calorimetry has been widely employed to investigate solid-liquid interfacial properties. In this section, we review one of the most commonly used calorimetric techniques to assess the affinity of solid surfaces for water. This approach is based on the measurement of the heat of immersion, also referred to as the heat of wetting or immersion enthalpy, which corresponds to the enthalpy change at constant temperature and pressure upon immersion of a solid in a liquid. The magnitude of the heat of immersion reflects both the chemical

interactions between the liquid and the solid surface and the textural characteristics of the solid [123,145,168]. Therefore, characterization of microporous solids by calorimetry is not so simple due to the contributions of interactions of different nature [186]. This technique has been widely used to study microporous materials such as activated carbon and zeolites [187]. Silvestre-Alberó and co-authors employed immersion calorimetry to compare the hydrophobic character of Ti-MCM-41 and silylated Ti-MCM-41. A series of probe liquids with different polarities, ranging from non-polar hydrocarbons to polar molecules such as water and alcohols, was used. Their results showed that silylated Ti-MCM-41 exhibits an enhanced hydrophobic character, as evidenced by a progressive decrease in the heat of immersion in water with increasing degrees of silylation. In contrast, silylation had a much weaker effect on the heat of immersion in cyclohexane, indicating that interactions between hydrophobic surfaces and non-polar liquids are limited and likely dominated by textural properties rather than surface chemistry [145].

Solid State Nuclear Magnetic Resonance (Solid-State NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is based on the interaction of atomic nuclei with an external magnetic field and radiofrequency radiation. When a sample is placed in a magnetic field and irradiated at an appropriate frequency, its nuclei can absorb energy. The radiation frequency required to produce this absorption depends on the type of nucleus, its position within the magnetic field, and its chemical environment [188,189].

Solid-state NMR is a powerful tool to assess the hydrophobic character of solid materials, as it allows the identification and quantification of hydrophilic sites (-OH groups) as well as organic moieties bonded to Si atoms. For instance, the relative intensities of hydroxyl groups and molecularly adsorbed water can be evaluated from low-temperature ^1H NMR spectra [129]. In addition, several studies have employed solid-state NMR to assess the degree of condensation in (titano-)silicates through deconvolution of the ^{29}Si NMR spectrum into Q^4 , Q^3 , and Q^2 (See Figure 8) [38,46,140]. Besides the condensation degree, this analysis is strongly related to the hydrophobicity/philicity of the material since silanols (Si-OH) are hydrophilic sites, so the higher the fraction of Q^3 and Q^2 relative to Q^4 , would indicate a hydrophilic the character. If the origin of hydrophobicity lies in surface functionalization with organic moieties, solid-state NMR spectroscopy can also be employed. For instance, the fraction of Si atoms bonded to methyl groups has been quantified to assess the extent and effectiveness of methyl functionalization in amorphous titanosilicates (Ti-SiO₂) [46].

There are two modes for the experimental approaches of solid-state NMR. The cross-polarization mode allows to excite the contributions of T^2 and T^3 , so they are better appreciated even at low organic content. Nevertheless, this method cannot be used for the quantification of each resonance. The direct excitation mode is applied for quantification, and once the spectra are recorded, contributions are quantified by deconvolution of peaks using Gaussian functions. Indeed, some previous studies have used cross-polarization to verify the surface functionalization [46].

Solid-state NMR cannot be used to study the Ti nucleus at very low Ti molar ratios [22,129]. Another nucleus that can be followed by solid-state NMR is ^{13}C . In this case, the analysis provides information about organic functionalization or the degree of removal of the templating agents [190].

A summary of the analytic techniques employed for the evaluation of the hydrophobicity of titanosilicates is presented in Table 4.

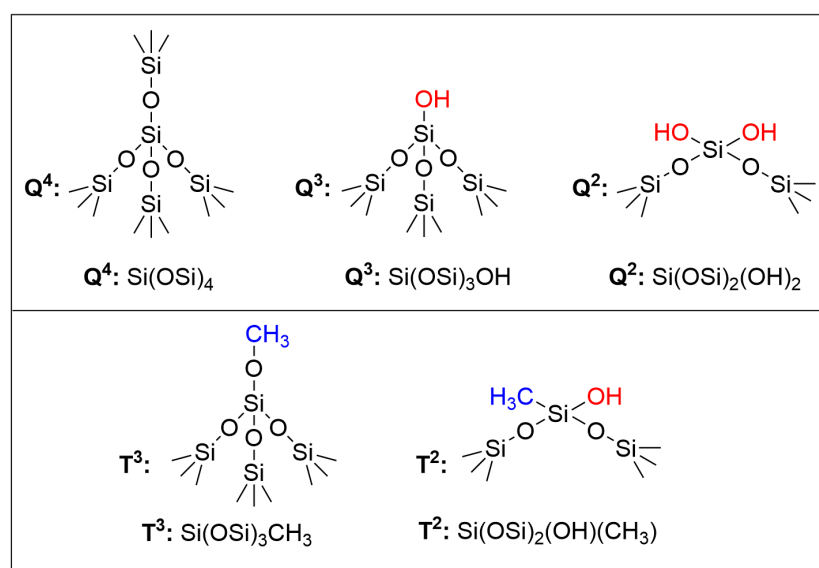


Figure 8. Typical types of resonance contributions of a solid-state ^{29}Si NMR spectrum. Hydroxyl groups (-OH) are highlighted in red, while methyl groups (-CH₃) are shown in blue.

Table 4. Analytic techniques used for the characterization of the hydrophobicity of titanosilicates.

Characterization Technique	Measurement	References
Thermogravimetric Analysis (TGA)	Mass losses of catalysts under controlled temperature	[11,32,33,41,44–47,128,141]
Infrared Spectroscopy (IR)	OH [−] adsorption band (isolated and hydrogen bonding), and Si-CH _x vibration band in the IR spectrum	[11,32,33,37,38,40,44,46,47,111,139–141,144]
Adsorption Isotherms	Water adsorption capacity	[11,32,37–40,44,47,128,139,186]
Calorimetric Techniques	Heat of immersion (heat of wetting or immersion enthalpy)	[145]
Solid State Nuclear Magnetic Resonance (Solid-State NMR)	Hydrophilic sites (-OH) and organic moieties bonded to Si atoms of ^{29}Si NMR and ^1H NMR spectra ^1H and ^{29}Si NMR for TS-1	[11,33,37–40,44,46,111,128,139,144] [129]

Rather than providing only a general overview of available characterization methods, it is useful to offer practical guidance for researchers entering the field. If a recommendation can be made, we consider that water vapor sorption constitutes the most appropriate primary technique to assess hydrophobicity in both microporous and mesoporous titanosilicates, as it directly probes the interaction of water with the internal pore system under catalytically relevant conditions. In microporous materials, adsorption isotherms at low relative pressures are particularly sensitive to silanol defect density and framework polarity. In mesoporous systems, water sorption further captures the combined influence of surface chemistry and pore size distribution [168]. To establish a structural correlation, ^{29}Si MAS NMR spectroscopy should be employed as a complementary method, since it enables quantification of Q³ and Q⁴ species and provides direct insight into the defect population governing hydrophobic behavior. Although contact angle measurements offer a rapid and straightforward evaluation of wettability, their application to porous powders presents inherent limitations, as they predominantly reflect external surface properties and are strongly affected by sample preparation, compaction, and roughness, which may hinder rigorous quantitative comparison.

3. Discussion

3.1. General Considerations on Hydrophobicity in Titanosilicates-Catalyzed Epoxidation

The hydrophobic modification of titanosilicates has been widely proposed as a strategy to improve their catalytic performance in oxidation reactions, particularly in processes involving peroxides as oxidizing agents [2,39,44]. However, the effects reported in the literature are not unanimous: while numerous studies describe significant increases in activity, selectivity, and stability after hydrophobic modification [32,33,36,39–41,128,135,141,144], others report marginal [37,47] or even negative effects [38,44,46,48,73,191–193]. This apparent contradiction does not necessarily reflect experimental inconsistencies, but rather the inherent complexity of the catalytic system, where multiple structural and chemical variables operate simultaneously.

The catalytic performance of a hydrophobic titanosilicate depends on an interrelated set of factors, including (i) the structural and textural nature of the material (amorphous or crystalline and microporous or mesoporous), (ii) the type and distribution of Ti sites, (iii) the methodology used to induce hydrophobicity, and (iv) the specific catalytic system, including reactants, solvent, and water concentration. In this context, hydrophobicity should not be understood as an isolated property, but rather as a parameter that modulates the microenvironment of the active site, affecting interactions with reactants, products, intermediate species, and polar molecules in the reaction medium.

Additionally, quantitative comparison of the hydrophobicity of different titanosilicates remains challenging due to the diversity of techniques used for their evaluation (water vapor sorption, IR spectroscopy of silanols, contact angles, solid-state NMR, among others). This lack of standardization makes it difficult to establish direct correlations between hydrophobicity and catalytic performance, reinforcing the need for critical analyses that integrate multiple types of experimental evidence.

The influence of hydrophobicity can be explored in several oxidation reactions, such as phenol hydroxylation and olefin epoxidation, although a comprehensive comparison falls beyond the scope of this review. Here, the focus is placed on olefin epoxidation, a reaction of major industrial relevance in which epoxides serve as key intermediates [32,107,194]. Mechanistically, it provides a suitable model to assess surface hydrophobicity because it involves hydrophobic olefins and more polar products, meaning that the catalyst's affinity for polar or nonpolar species directly affects adsorption-desorption equilibria and active-site stability under reaction conditions.

Building on the role of hydrophobicity in modulating titanium speciation and oxygen-transfer pathways in the olefin epoxidation, the following section integrates mechanistic and durability aspects by examining the nature of Ti-peroxo species, their competitive reaction pathways, and the influence of solvent and water on peroxide activation and selectivity, while simultaneously addressing stability metrics, regeneration strategies, and structure-stability relationships to connect active-site chemistry with long-term catalyst performance.

3.1.1. Nature of Ti-Peroxo Species, Competitive Pathways, Solvent and Water Effects

As shown in Figure 9, the epoxidation of olefins catalyzed by titanium silicalites using H_2O_2 as an oxidizing agent can proceed by two competitive routes: the direct epoxidation, and the allylic oxidation through the formation of Ti-peroxo species, widely recognized as key intermediates in the process. However, various experimental and spectroscopic studies have shown that these species are neither unique nor structurally equivalent, but can exist as hydroperoxo (Ti-OOH) or lateral/bidentate peroxo (Ti-O₂) species, whose relative stability critically depends on the chemical environment of the Ti site, including solvent polarity and the presence of adsorbed water [54,195–197].

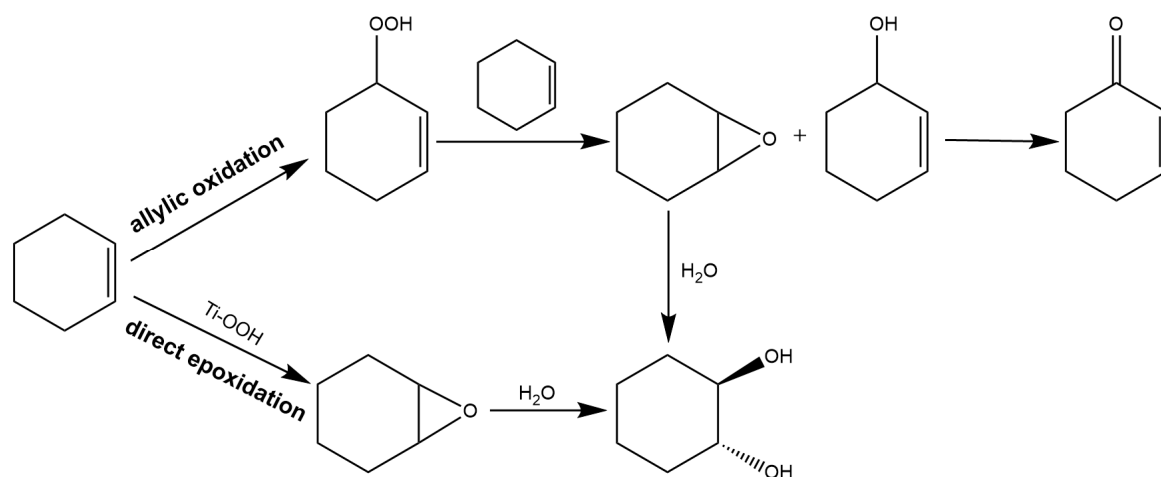


Figure 9. Direct epoxidation and allylic route for cyclohexene oxidation. Adapted from Ref. [47]. Copyright © 2018 Elsevier.

In mechanistic terms, the direct epoxidation pathway is mainly associated with Ti-OOH species, which favor selective oxygen transfer to the olefinic double bond (direct epoxidation) via an Eley–Rideal-type mechanism. In this mechanism, the oxidant initially coordinates to the Ti site, forming active Ti-OOH species, which subsequently react with the olefin from the liquid phase to generate the epoxide, which desorbs from the catalyst. In this mechanistic framework, the hydrophobicity of the Ti environment emerges as a determining factor in controlling the stability and reactivity of these intermediate species [47]. In contrast, allylic oxidation involves radical species ($\text{Ti-O}\cdot$ and $\cdot\text{OH}$) generated by the homolysis of Ti-OOH or by the stabilization of side peroxy species, leading to a broader distribution of oxygenated products, including alcohols and ketones [198]. In this context, it has been established that lateral peroxy species tend to promote less selective pathways and the unproductive decomposition of H_2O_2 , reducing both epoxide selectivity and the overall efficiency of the oxidant.

The presence of water plays a particularly relevant role in the balance between the active species. High water concentrations favor excessive coordination of Ti and the stabilization of highly hydrated species, promoting competitive pathways that decrease selectivity toward the desired epoxide. In addition, water can induce oxirane ring opening, leading to diol formation, and accelerate catalytic deactivation processes associated with the hydrolysis of Ti-OOH species and the cleavage of Ti-O-Si bonds, resulting in the formation of catalytically inactive or poorly selective Ti-(OH)_x centers. Consequently, the accumulation of water in the vicinity of the active site affects not only reaction selectivity but also material stability and H_2O_2 utilization efficiency, highlighting that the reactivity of the system is governed by both the intrinsic nature of the Ti site and its local chemical microenvironment [198].

The selectivity between direct epoxidation and allylic oxidation does not depend exclusively on the intrinsic activation mechanism of the peroxide, but also on the microenvironment in which the active species is generated. The hydrophobicity of the catalyst and the nature of the solvent act in tandem, modulating Ti speciation, oxidant activation, and the stability of the product formed. In relatively hydrophobic frameworks with low silanol density, isolated tetrahedral Ti(IV) sites are preserved, and the local concentration of water around the active center is minimized; this favors the formation of well-defined Ti-OOH or Ti-OOR species and promotes predominantly heterolytic activation of the peroxide, consistent with a highly selective direct epoxidation pathway. In contrast, more hydrophilic environments—associated with defects, silanol nests, or partially open Ti—stabilize higher

coordination species through interaction with water and H_2O_2 , altering the equilibrium of surface intermediates and increasing both the non-productive decomposition of the oxidant and the probability of homolytic O-O bond cleavage, which can divert the reaction toward radical-type allylic oxidations.

The solvent reinforces or counteracts these structural tendencies. Aprotic polar solvents such as acetonitrile tend to favor epoxide selectivity by stabilizing peroxo intermediates without contributing significant nucleophilicity or increasing the effective microacidity of the medium, thus limiting secondary epoxide opening and isomerization. However, their coordination ability can slow down the reaction by competing with the hydroperoxide for the Ti site. In contrast, protic solvents such as methanol establish extensive hydrogen bonding networks with the oxidant and water generated in situ, stabilize higher coordination Ti species, and can increase the initial rate; however, they also increase the local activity of nucleophiles and facilitate epoxide opening and solvolysis, reducing overall selectivity. Furthermore, the spatial distribution of active Ti—in hydrophobic internal domains or on more hydrophilic external surfaces—introduces an additional dependence on the substrate and medium, such that the same solvent can favor epoxidation in a confined environment and simultaneously promote consecutive reactions in more exposed regions [6,141,194].

Consequently, the selectivity observed arises from the dynamic equilibrium between the hydrophobicity of the solid, the polarity and proticity of the solvent, competition for coordination in the Ti, and local water concentration. These factors determine which Ti-peroxo species dominates, whether peroxide activation proceeds mainly via heterolytic or homolytic pathways, and how stable the epoxide is within the porous microenvironment, thus integrating structure, reaction medium, and mechanism into a single interpretative framework.

3.1.2. Stability Metrics, Regeneration Strategies, and Structure-Stability Relationships

The stability of titanosilicates in olefin epoxidation should be evaluated not merely in terms of catalyst recyclability, but in relation to their ability to preserve the active Ti speciation responsible for selective heterolytic peroxide activation. Because the catalytic performance arises from a delicate balance between isolated framework Ti(IV), local hydrophobicity, and controlled water activity, stability metrics must capture both catalytic persistence and structural integrity under oxidative conditions.

It is important to distinguish between reversible deactivation processes, such as surface blocking by oxygenated by-products, and irreversible deactivation associated with structural degradation of the Ti environment. Hydrophobic modification has proven to be particularly effective in mitigating this second type of deactivation by reducing water accessibility and stabilizing Ti-O-Si bonds under oxidizing conditions. In some cases, this stabilization even allows for partial regeneration of the catalyst through mild treatments, such as thermal drying or solvent exchange [48,197,199].

From a catalytic standpoint, long-term time-on-stream experiments and cumulative turnover numbers (TON) provide more meaningful indicators than batch reuse tests. Monitoring oxidant efficiency—defined as the fraction of H_2O_2 or TBHP converted into desired oxygenated products—offers additional insight into the evolution of non-productive peroxide decomposition pathways. A progressive decrease in oxidant utilization efficiency often precedes observable losses in epoxide selectivity and may signal the emergence of extra-framework Ti species or radical-mediated pathways.

Regarding turnover numbers (TON), comparisons between pristine and hydrophobized titanosilicates in most of the cases reveal a positive effect on the stability of the catalyst. Hydrophobization appears to create a protective microenvironment that preserves the integrity of Ti active centers. A quantitative comparison of TON values for pristine and

hydrophobized TS-1, Ti-Beta, Ti-MCM-41, Ti-MWW, Ti-SBA-15, and Ti-SiO₂ is presented in Figure 10. All reported data correspond to materials modified via organic functionalization, either by post-grafting or one-pot synthesis. Figure 10 is divided into two sections: the upper one compiles data for 1-hexene epoxidation, and the bottom one for cyclohexene epoxidation. The selected studies report TON values measured at 333–338 K. Additionally, Fraile et al. [142] reported that in cyclohexene epoxidation at 353 K, hydrophobized Ti-SiO₂ exhibited a tenfold increase in TON relative to the pristine material.

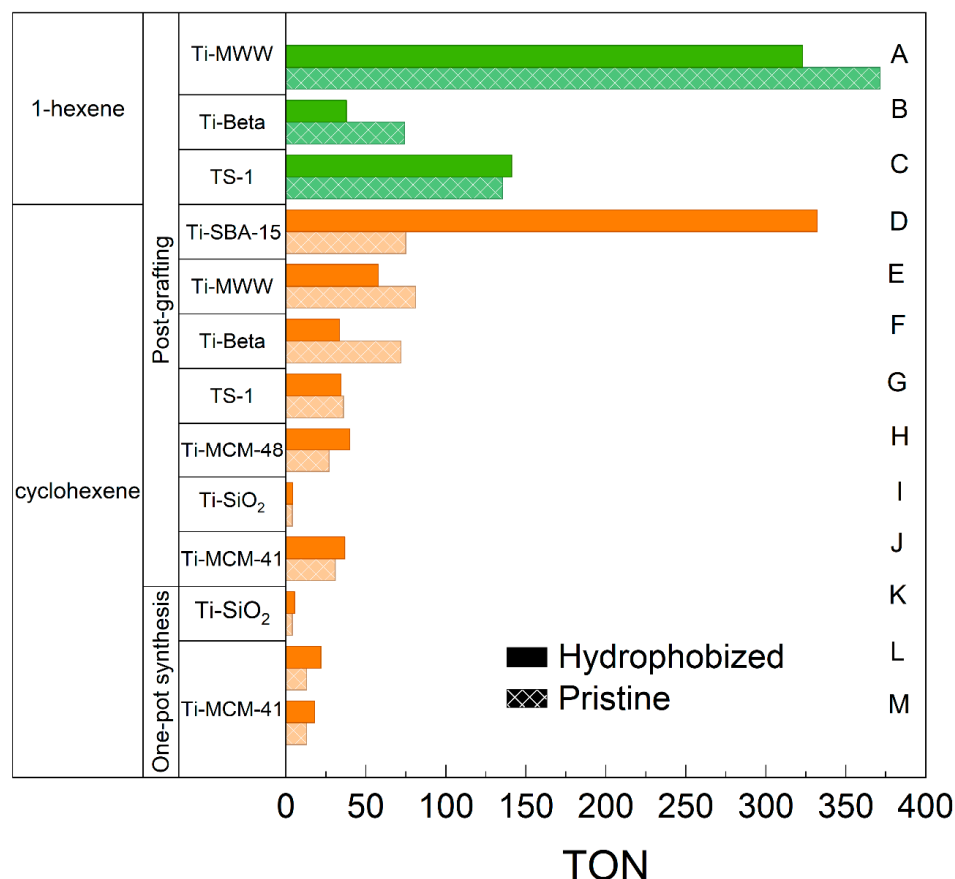


Figure 10. Turnover number (TON, mol/mol) as a function of the mol of substrate converted per mole of Ti in the catalyst for hydrophobically modified titanate catalysts, compiled from representative literature reports. The data predominantly correspond to the epoxidation of 1-hexene (A, B, C [6]) and cyclohexene (D [27]; E, F, G [6]; H, J, L [40]; M, I, K [47]) using H₂O₂ as oxidant at 333–338 K. Pristine catalysts are shown with cross-hatching symbols while functionalized materials are shown with filled symbols.

Moreover, some studies evaluated catalyst stability through hot filtration tests [39,105] to examine the integrity of the Ti site and the heterogeneity of the catalytic system. Ti sites in hydrophobized (by one-pot functionalization) titanates exhibited negligible leaching [105]. Organic functionalization of Ti-MCM-41 effectively suppressed Ti leaching during the oxidation reaction, whereas the inorganic Ti-MCM-41 displayed significant framework-Ti loss under similar reaction conditions [39].

Complementary recyclability tests further support these findings. Hydrophobized catalysts maintained their activity over multiple cycles, showing no significant loss after four runs [128]. Similarly, Fraile et al. [142], reported that hydrophobized Ti-SiO₂ retained its activity after three cycles, while the hydrophilic analog experienced a ~50% decrease in TOF. Collectively, these results demonstrate that hydrophobic modification generally enhances the stability of Ti-based catalysts.

Structural stability must be assessed in parallel. Changes in the Ti coordination environment can reveal framework-to-extra-framework migration or the formation of TiO_x clusters. Variations in silanol density, hydrophobicity, and microporosity provide complementary information on hydrolytic degradation or defect formation. In liquid systems, particularly when protic solvents or aqueous H_2O_2 are employed, the risk of partial Ti leaching should be evaluated through hot filtration tests and elemental analysis of the reaction medium.

Importantly, stability should be interpreted as a structure-function relationship rather than a purely operational parameter. Conditions that favor selective epoxidation—isolated tetrahedral Ti sites within a hydrophobic microenvironment—are typically those that confer greater resistance to hydrolytic attack, uncontrolled peroxide decomposition, and structural reorganization. Conversely, defect-rich or hydrophilic materials may exhibit higher initial activity but undergo faster deactivation due to site restructuring, Ti migration, or accumulation of strongly adsorbed by-products. Thus, stability metrics must be designed to track not only catalytic longevity but the preservation of the active Ti-peroxo ensemble that governs the mechanistic pathway.

The differences between amorphous and crystalline materials are particularly relevant in this context. In titanosilicates with amorphous silica walls, such as Ti-MCM-41, as or in fully amorphous Ti-SiO₂, the Ti sites, although isolated, are found in structurally flexible and frequently stressed environments, located in defect-rich silica walls. This lack of structural rigidity favors excessive coordination of polar molecules, increases susceptibility to hydrolysis, and leads to lower H_2O_2 efficiency. In these systems, hydrophobic modification acts primarily as a compensatory strategy, necessary to counteract intrinsic structural limitations.

In contrast, in crystalline zeolites such as TS-1 or Ti-BETA, Ti sites are incorporated into a rigid and well-defined crystal lattice, which confers greater geometric and electronic stability. This structural robustness naturally limits overhydration of the active site and favors selective epoxidation pathways. In these materials, hydrophobicity is not strictly necessary to prevent deactivation, but it does function as an optimization strategy, improving selectivity, oxidant efficiency, and stability under demanding operating conditions.

On this basis, the following subsections critically analyze how different hydrophobization strategies—including the control of silanol group density and the incorporation of organic groups—affect the nature of the active species, reaction selectivity, and catalytic stability in microporous and mesoporous materials, encompassing both amorphous and crystalline titanosilicates.

3.2. Discernment of the Results of the Effect of the Hydrophobic Modification on the Catalytic Activity of Titanosilicates

Modification of crystallinity in titanosilicates was used to regulate the amount of hydroxyl groups on the surface of TS-1. A YNU (Yokohama National University) method that consists of the use of $(\text{NH}_4)_2\text{CO}_3$ as a crystallization-mediating agent was applied to increase the crystallinity of TS-1 [33]. In this study, the increase in catalytic activity observed after improving the crystallinity of TS-1 should not be interpreted only as a structural effect, but as a direct consequence of the decrease in silanol defects and the resulting hydrophobicity of the Ti environment. This reduction in Si-OH groups is evidenced by the decrease in the IR band at 3738 cm^{-1} and the increase in the Q^4/Q^3 ratio in the ^{29}Si MAS NMR spectra, and is accompanied by a predominant incorporation of Ti in framework positions, confirmed by the band at $\sim 210\text{ nm}$ in UV-Vis DR and the Ti-O-Si signal at 960 cm^{-1} in IR. The lower density of silanol groups limits water adsorption in the vicinity of the active site, favoring the stability of selective Ti-OOH species and suppressing non-productive decomposition pathways of H_2O_2 . Consequently, this result suggests

that, in crystalline systems, hydrophobicity acts mainly by reinforcing an already intrinsic selectivity of the Ti site, rather than correcting structural deficiencies, in contrast to what is typically observed in amorphous materials.

Ti-Beta is one of the most extensively studied titanosilicates in relation to hydrophobization strategies, particularly through the regulation of the density of surface silanol groups [6,36,37]. In this material, the presence of Al^{3+} heteroatoms in the crystal lattice introduces Si-OH or Si-OH-Al structural defects when synthesis is carried out in an alkaline medium (OH^-), which confers a more hydrophilic character to the material, in addition to generating additional acidic sites (see Section Control of Silanol Surface Density) [64]. Consequently, it was proposed that the removal of Al through the use of de-aluminated Beta seeds during crystallization would allow for the production of more selective and stable Ti-Beta catalysts in epoxidation reactions.

In fact, Al-free Ti-Beta catalysts showed a significant improvement in selectivity toward epoxide in the epoxidation of 1-hexene with H_2O_2 , with a progressive increase in selectivity (~40% to 60% conversion) as the Al content decreased. However, even in samples that were practically Al-free ($\text{Si}/\text{Al} > 5000$), epoxide ring opening was detected. This behavior was attributed to the presence of residual silanol groups or Ti species with different acidity. This hypothesis was supported by comparing the oxidation of the epoxide on Ti-Beta without Al, where ring opening was observed, with the reaction on de-aluminated Beta without Ti, where this phenomenon did not occur [135]. These results indicate that, although the removal of Al reduces strong acidity and improves selectivity, the influence of the hydrophilic environment of Ti cannot be ruled out.

Beyond controlling the Al content, a particularly effective strategy for reducing silanol density and increasing the hydrophobicity of Ti-Beta consists of synthesis in a fluoride (F^-) medium instead of an alkaline medium. In the pioneering studies by Blasco et al. [36,37], F^- -assisted crystallization led to Al-free Ti-Beta materials with higher crystallinity and significantly superior thermal and hydrothermal stability. In particular, Ti-Beta synthesized in F^- medium retained its crystalline structure after calcination at 1223 K and after severe hydrothermal treatments (100% humidity at 1023 K), while Ti-Beta synthesized in OH^- medium suffered structural collapse and loss of Ti under the same conditions.

From a catalytic point of view, the hydrophobization of Ti-Beta through synthesis in F^- medium had a positive effect on the epoxidation of substrates such as methyl oleate [36] with greater activity, epoxide selectivity, and efficiency in the use of H_2O_2 observed compared to Ti-Beta synthesized in OH^- medium. This behavior was attributed to more efficient desorption of the epoxide from the hydrophobic surface of Ti-Beta(F^-), which reduces its permanence near the active site and, therefore, the probability of oxirane ring opening.

The more hydrophobic nature of Ti-Beta(F^-) was corroborated by X-ray absorption spectroscopy, where the XANES spectra at the Ti K-edge showed a pre-peak of similar intensity in calcined and rehydrated samples. In contrast, in Ti-Beta(OH^-), this pre-peak decreased significantly and broadened after rehydration, indicating greater coordination of Ti with water molecules. These results suggest that in Ti-Beta synthesized in OH^- medium, there is a larger fraction of Ti sites susceptible to overhydration, compared to Ti-Beta(F^-) [36].

Subsequent studies directly comparing Ti-Beta(F^-) and Ti-Beta(OH^-) in the epoxidation of 1-hexene and oleate/oleic acid in different solvents (acetonitrile and methanol) reinforced this interpretation [37]. Although only about 50% of the Ti was incorporated into the network in the case of Ti-Beta(F^-), due to the formation of soluble Ti-F complexes at low pH, the catalytic activity was comparable to that of Ti-Beta(OH^-). However, differences in selectivity became apparent in more polar media: while in acetonitrile both catalysts

achieved selectivities close to 100%, in methanol Ti-Beta(F[−]) showed a significantly higher epoxide selectivity (76.6%) than Ti-Beta(OH[−]) (54.9%). This behavior confirms that the hydrophobicity of the Ti environment is particularly relevant when the catalytic system favors interaction with polar species.

These results demonstrate that synthesis in fluoride media not only reduces the density of silanol groups and increases the hydrophobicity of Ti-Beta, but also contributes to the stabilization of active sites against water-induced deactivation. However, the amount of F[−] must be carefully controlled, as an excess can limit the incorporation of Ti into the crystal lattice through the formation of Ti(OH)_xF_y complexes, negatively affecting catalytic performance (see Section Control of Silanol Surface Density) [139].

According to previous reports, hydrophobic catalysts performed better than hydrophilic ones. For instance, TS-1, which is intrinsically more hydrophobic, has shown superior activity in the epoxidation of olefins compared to more hydrophilic titanosilicates such as Ti-Beta [86]. These results stimulated a major effort to increase the hydrophobicity of titanosilicates by systematically reducing surface silanol groups.

However, more recent studies have shown that excessive hydrophobicity does not always lead to improved catalytic activity. In particular, it has been observed that a controlled increase in silanol density can favor epoxide formation in reactions such as the epoxidation of cyclohexene and 1-hexene [38,73,191–193]. A paradigmatic example is the work of Bregante et al. [38], who conducted an exhaustive study on the epoxidation of alkenes with H₂O₂ using Ti-Beta with different silanol defect contents.

In this study, Ti-Beta catalysts with varying densities of silanol (SiOH)₄ nests were prepared by controlled dealuminization of commercial Beta zeolites, followed by partial incorporation of Ti. This strategy made it possible to obtain materials with different degrees of surface hydrophilicity while maintaining the structural nature of the active site. Additionally, a Ti-Beta practically free of silanols was synthesized by crystallization in a fluoride medium. Catalytic comparison in the epoxidation of 1-octene revealed that reaction rates increased significantly with (SiOH)₄ density, reaching values up to two orders of magnitude higher for materials with approximately five silanol sites per unit cell compared to virtually defect-free Ti-Beta.

Based on spectroscopic, thermodynamic, and kinetic analyses, the authors demonstrated that these differences in activity were not due to changes in the nature of the active Ti-OOH species or in the epoxidation mechanism, but rather to the stabilization of these species by water clusters anchored to the silanol nests. In this case, the presence of localized hydrophilic domains favors molecular interactions that stabilize the active intermediate and reduce the energy barrier of the reaction, highlighting that certain degrees of hydrophilicity can be beneficial for epoxidation kinetics.

These conclusions are particularly useful for interpreting the results reported by Li et al. [140]. Although these authors synthesized TS-1 in fluoride medium (TS-1-HF), using a methodology conceptually similar to that used by Bregante et al. [139], their study focused mainly on TS-1 materials obtained by conventional alkaline synthesis with different Si/Ti ratios, subsequently subjected to a liquid-phase defect curing treatment. This post-treatment selectively removes excessive silanol defects without compromising the active tetrahedral coordination of Ti.

Interestingly, the treated TS-1 catalysts showed superior catalytic performance to TS-1-HF in the epoxidation of olefins, despite being less hydrophobic according to water adsorption measurements. This result indicates that, while fluoride synthesis is effective in suppressing silanol defects, it can also limit the incorporation and accessibility of active Ti, as previously noted [127]. In contrast, the defect-curing strategy developed by Li et al.

decouples the control of hydrophobicity from Ti incorporation, allowing efficient active sites to be preserved while finely adjusting the polarity of the porous environment.

These studies demonstrate that catalytic performance does not necessarily increase with absolute hydrophobicity, but rather depends on achieving an optimal balance between silanol density, local polarity, and the stability of the Ti active site. In this context, hydrophobicity should be regarded as a tunable parameter, whose impact can be either kinetic or stabilizing depending on the spatial distribution of silanol groups and the structural environment of the titanosilicate.

While the control of silanol density modulates hydrophobicity through structural defects and framework condensation, organic functionalization introduces hydrophobicity via covalently anchored organic moieties. This strategy enables a more direct tuning of surface polarity but also introduces steric and coordination effects that critically influence catalytic behavior.

Organic functionalization through one-pot synthesis introduces hydrophobicity homogeneously during material formation, generating organic domains distributed throughout the silica matrix. However, unlike silanol control, this strategy does not necessarily eliminate the structural hydrophilicity of the support, especially in titanosilicates with amorphous silica walls, such as Ti-MCM-41, as well as in fully amorphous Ti-SiO₂ systems. In these systems, the induced hydrophobicity is predominantly superficial, and its catalytic impact depends on a delicate balance between local polarity, active site accessibility, and steric effects.

Studies on one-pot functionalized Ti-MCM-41 consistently show that not all organic groups produce the same catalytic effect, despite increasing overall hydrophobicity. In particular, only functionalization with small groups such as methyl leads to significant improvements in olefin epoxidation activity, while more bulky groups (phenyl, pentyl) have marginal or even negative effects [39,128,141]. This behavior indicates that hydrophobicity alone is not a sufficient descriptor of catalytic performance in one-pot systems, and that the size and chemistry of the organic group determine whether the modification favors or disrupts the Ti environment.

From a structural point of view, one-pot functionalization can compromise the dispersion and nature of active Ti when the degree of functionalization is high. In Ti-SiO₂ functionalized with methyl groups, for example, the Si-O-Ti/Si-O-Si ratio decreased from 0.75 in the pristine material to values between 0.49 and 0.57 after functionalization, indicating a lower incorporation of Ti in tetrahedral coordination [46]. This structural disturbance resulted in decreased activity in the epoxidation of 1-hexene and cyclohexene, attributed to a combination of reduced surface area, pore blockage, and decreased Ti dispersion [46].

Consistently, several studies showed that catalytic activity increases with the degree of organic functionalization only up to a critical threshold. In methyl-functionalized Ti-SiO₂ with increasing degrees of methylation (1, 5, and 14%), the initial epoxidation rate of cyclooctene increased up to an intermediate degree of functionalization but decreased markedly at 14%, even below that of the non-functionalized material [44]. This behavior was attributed to partial inhibition of oxidant adsorption, reinforcing the idea that one-pot functionalization generates beneficial hydrophobicity only when it does not interfere with the formation and reactivity of Ti-OOH species.

A direct comparison between one-pot functionalization and post-grafting reveals a fundamental conceptual difference: while the one-pot strategy inevitably couples hydrophobicity with framework formation and Ti dispersion, post-grafting allows the adjustment of hydrophobicity to be decoupled from the generation of the active site [47].

In Ti-SiO₂ catalysts prepared by non-hydrolytic sol-gel, one-pot functionalization with methyl groups further reduced activity in acetonitrile/water mixtures, resulting in

epoxide yields lower than those of the pristine material (2.1% vs. 18.3% under conditions comparable to TS-1) [47]. This effect was attributed to the capping of active Ti sites, which prevents the formation of effective oxidizing species in the presence of water. In contrast, post-grafting functionalization led to a clear improvement in epoxide yield (5.1% vs. 2.1%) without affecting overall conversion, demonstrating greater resistance to water-induced deactivation [47].

These results demonstrate that, in systems where the stability of Ti against hydrolysis is critical, hydrophobicity must be introduced after the formation of the active site to avoid inhibitory effects. In this context, post-grafting acts primarily as a strategy for stabilizing Ti, rather than as a simple modifier of surface affinity.

Post-grafting studies on Ti-MCM-41, Ti-MCM-48, and Ti-SBA-15 show that partial silylation of silanol groups is sufficient to drastically reduce water adsorption and improve oxidant efficiency. For example, although only ~21% of Si-OH groups were silylated by trimethylsilylation, the amount of adsorbed water decreased from ~55% by mass to ~0.29% after functionalization. This modification resulted in up to 20-fold increases in conversion and TON in the epoxidation of cyclohexene [41].

More importantly, several studies show that post-grafting can directly modify the nature of the active site. In silylated Ti-MCM-41, the appearance of ^{29}Si NMR signals assigned to $(\text{CH}_3)_3\text{Si-O-Ti}(\text{OSi})_3$ species increased with silylation time and Ti content, correlating with an increase in catalytic activity [144]. This result suggests that the formation of functionalized Si-O-Ti bonds favors direct epoxidation over allylic pathways.

An even more detailed analysis was obtained in Ti-SBA-15 functionalized with silyl amides of different chain lengths. Epoxide selectivity increased significantly when both Si-OH and Ti-OH groups were silylated, reaching values of 66% compared to only 11.6% in the non-functionalized material [32]. These results confirm that the improvement in selectivity is not solely due to an increase in surface hydrophobicity, but to a chemical redefinition of the active Ti environment.

Finally, post-grafting functionalization with hydrophobic polymers such as PMHS highlights the role of hydrophobicity as a long-term stabilization strategy. Although this modification reduced the initial activity in the epoxidation of 1-octene with TBHP, PMHS-modified catalysts showed much lower deactivation rates in the presence of water (-0.03 to $-0.09\% \text{ h}^{-1}$) compared to pristine Ti/SiO₂ ($-0.32\% \text{ h}^{-1}$). After Soxhlet extraction in hot water, the pristine Ti/SiO₂ catalyst lost up to 62% of its TON, while the PMHS-1-modified material showed no appreciable loss of TON [48]. The transformation from active tetrahedral Ti to inactive octahedral species observed by UV-Vis DR in the unprotected material confirms that the hydrophobicity introduced by post-grafting acts as a barrier to hydrolysis of the active site.

The studies discussed in this section demonstrate that the impact of hydrophobic modification affects olefin epoxidation in fundamentally different ways depending on whether it is achieved through silanol density control, one-pot organic functionalization, or post-synthetic grafting, with catalytic performance emerging from a balance between local polarity, steric accessibility, and preservation of the Ti coordination environment rather than from maximal surface hydrophobicity.

Figure 11 reveals a consistent, non-monotonic dependence of epoxide yield on the degree of organic functionalization for titanasilicates, predominantly Ti-MCM-41 and Ti-SiO₂.

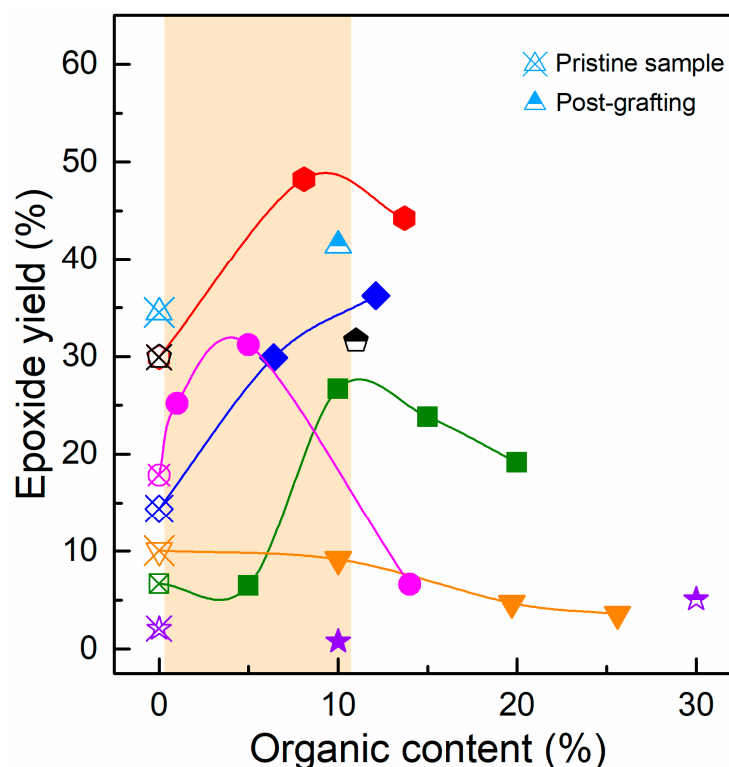


Figure 11. Epoxide yield as a function of organic group content for hydrophobically modified titanasilicate catalysts, compiled from representative literature reports. The data predominantly correspond to the epoxidation of cyclohexene (Ti-MCM-41 ■ [141], ▼ [46], ◆ [128], ◐ [40], ● [39]; Ti-MCM-48 ▲ [40]) and cyclooctene (Ti-SiO₂ ● [44], ★, ☆ [47]) at 333 K using methyl-functionalized catalysts. Pristine catalysts are shown with open symbols, while functionalized materials are shown with filled symbols. The shaded region is a guide to the eye, highlighting the positive organic functionalization rather than strict statistical boundaries.

It should be noted that the catalytic data compiled in this analysis originate from independent studies performed under non-identical reaction conditions. Parameters such as solvent nature, oxidant type and concentration, substrate-to-oxidant ratio, catalyst loading, titanium content, and reaction time vary from one report to another. Although a strict quantitative comparison is therefore not possible, the data have been selected and grouped to minimize these differences, focusing primarily on similar substrates (cyclohexene and cyclooctene), comparable temperatures (typically around 333 K), and closely related titanium silicalite frameworks. Consequently, the trends discussed herein should be interpreted with caution and regarded as qualitative rather than absolute. Nonetheless, when analyzed collectively, these datasets provide meaningful insight into the general influence of hydrophobic modification strategies, silanol density, and framework structure on the epoxidation performance of titanium-based silicalite catalysts.

Despite these limitations, joint analysis of the data reveals a recurring behavior for both one-pot and post-grafting strategies: epoxide yield initially increases with increasing organic content, reaches a maximum at intermediate loads (typically below 15% organic groups), and decreases markedly with further increases in the degree of functionalization.

This conduct suggests that moderate hydrophobization optimizes the local environment of the Ti active site by balancing water management and reactant accessibility, while excessive functionalization introduces steric restrictions, partial pore blockage, or excessive dilution of the polar character of the framework necessary for efficient H₂O₂ activation.

The behavior observed for Ti-SiO₂ catalysts (purple symbols) highlights the importance of active site integrity. Despite exhibiting a more hydrophobic character after function-

alization, these materials show consistently low epoxide yields, which has been attributed to the partial or total deactivation of Ti sites in the presence of water, even when organic modification strategies are employed [47]. This result reinforces the idea that surface hydrophobicity alone does not guarantee high catalytic performance if the coordination environment of Ti is not adequately preserved.

The trends observed in Figure 11 closely match the conclusions of Bregante et al. [38], who demonstrated that localized hydrophilicity—in particular the presence of silanol (Si-OH)₄—can favor epoxidation rates by stabilizing peroxo intermediate species through hydrogen bridge interactions, rather than through direct modification of the nature of the Ti active site. In this context, excessive hydrophobicity suppresses beneficial water-framework interactions and can compromise catalytic efficiency.

Complementarily, this analysis also rationalizes the results of Li et al. [140], who showed that post-synthetic defect-healing treatments can improve catalytic performance by selectively removing excessive silanol defects while preserving isolated Ti sites in tetrahedral coordination. This strategy avoids the limitations associated with fluoride-mediated synthesis—which, as previously evidenced, effectively removes silanols but can hinder Ti incorporation—and allows for an optimal compromise between hydrophobicity, local polarity, and active site accessibility.

This analysis supports a unified view in which maximum epoxidation activity is not achieved through extreme hydrophobicity, but rather through fine-tuning of the surface environment to preserve isolated Ti sites while maintaining sufficient hydrophilicity to stabilize reactive intermediates. This conceptual framework reconciles the apparent disparity in results reported for hydrophobic and hydrophilic titanasilicates and explains why controlled modification strategies can outperform fully hydrophobic materials, even when the latter have a lower residual silanol density.

Figure 12 reveals a clear structure-dependent separation when turnover frequency (TOF) is plotted against epoxide yield. To see more details about the reaction conditions, see Figure S1 in the Supplementary Information. Figure S2 shows the comparison of TOF (h^{-1}) as a function of Epoxide selectivity (%).

Catalysts based on crystalline TS-1 systematically populate the high-TOF region, whereas mesoporous Ti-MCM-41/48 remain confined to lower TOFs, even when comparable epoxide yields are achieved through hydrophobic modification. This distinction indicates that catalytic performance cannot be rationalized solely in terms of surface hydrophobicity, but instead reflects how silanol groups are controlled within a given framework and how this control impacts the nature and accessibility of isolated Ti sites.

The superior TOFs (h^{-1}) reported by Li et al. [140] arise from a strategy fundamentally different from conventional hydrophobization. As mentioned earlier, their catalysts were synthesized in alkaline medium, ensuring high incorporation of framework-isolated Ti species, followed by a liquid-mediated defect healing treatment that selectively condenses vicinal silanol defects without disrupting Ti speciation. As a result, these materials retain catalytically competent Ti-OOH intermediates while minimizing non-coordinated silanol nests that promote unproductive hydrogen-bonding networks or water over-stabilization. In contrast, TS-1, which is synthesized directly in fluoride medium, following the methodology developed by Bregante et al. [139], effectively suppresses silanol defects but simultaneously reduces Ti incorporation.

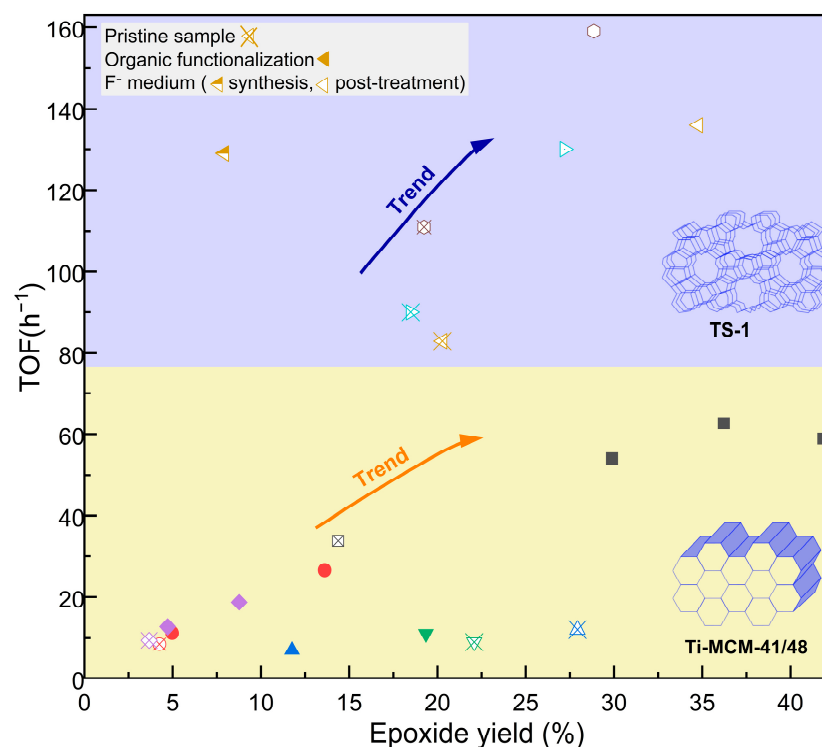


Figure 12. Turnover frequency (TOF, h^{-1}) as a function of the epoxide yield ratio for hydrophobically modified titanosilicate catalysts, compiled from representative literature reports. The data predominantly correspond to the epoxidation of cyclohexene (■ [128]), 1-octene (●, ◆ [144]) and terpineol (▲ [40]) using Ti-MCM-41 and Ti-MCM-48 (▼ [40]), and 1-hexene (◀, ▶, △, ○ [140]) using amorphous TS-1, at 333 K. Pristine catalysts are shown with open symbols, while functionalized materials are shown with filled symbols. The arrows indicate the general trend showing how TOF increases relative to epoxide yield under the corresponding conditions.

By contrast, hydrophobic modification via organic group insertion (one-pot or post-grafting) in mesoporous Ti-MCM-41/48 increases epoxide yields by mitigating diffusional limitations and water adsorption, but does not recover the high TOFs characteristic of crystalline TS-1. This limitation reflects the broader distribution of Ti environments, weaker confinement effects, and the absence of the cooperative hydrophilic domains identified by Bregante as kinetically beneficial.

On the other hand, the lower TOF values observed for the modified samples (via organic group insertion) in the oxidation of α -terpineol, in contrast to the positive effect seen for 1-hexene and 1-octene, highlight the substrate-dependent nature of hydrophobization. Unlike linear, apolar olefins, α -terpineol is bulkier and contains a hydroxyl group, which increases its polarity and enables competitive interactions with the Ti center. In hydrophobized materials, the reduced silanol density and increased surface hydrophobicity may limit favorable interactions between the polar substrate and the active site, while steric effects arising from organic modification can further hinder diffusion within mesoporous channels. Additionally, when H_2O_2 is used as an oxidant, the more hydrophobic microenvironment may alter the balance between aqueous oxidant accessibility and substrate adsorption, particularly for polar molecules. These combined factors can decrease the effective formation rate of reactive Ti-peroxo species or their interaction with α -terpineol, leading to lower apparent TOF [6,54,58]. This behavior underscores that the catalytic consequences of hydrophobization are not universal but strongly dependent on substrate structure, oxidant nature, and the interplay between diffusion, adsorption, and active-site speciation.

4. Current Needs in the Research Area

4.1. Discussion of Current Challenges in Understanding the Effect of the Hydrophobization of Titanosilicates on Their Catalytic Activity

Various titanosilicates were hydrophobized in an attempt to enhance their catalytic performance on the basis that the olefin adsorption and epoxide desorption would be improved by a hydrophobic catalyst surface. With the advances in catalyst synthesis, characterization and hydrophobization methodologies, the nature of the active sites was identified as an important role-player in the selectivity to epoxide. Thus, the fabrication of titanosilicates with high hydrophobicity and well distribution of Ti active sites became crucial to promote the direct epoxidation over the allylic route. Several works have been published about this topic, but these results have not yet been compiled in a review. In this context, we discuss the challenges in understanding the effect of hydrophobization of titanosilicates on the catalytic performance in the epoxidation of olefins according to the hydrophobization methodology.

Despite significant advances in the synthesis and characterization of titanosilicates, understanding the effect of hydrophobicity on their catalytic performance in the epoxidation of olefins continues to face conceptual and methodological challenges. One of the main obstacles lies in the fact that hydrophobicity is not a one-dimensional property, but rather a set of interrelated structural and chemical characteristics. The density and nature of silanol groups (isolated or forming nests), the degree of organic functionalization, the local polarity of the pore, and the accessibility to the active site all contribute simultaneously to defining the microenvironment of Ti. Consequently, it is not possible to interpret hydrophobicity as an isolated descriptor of catalytic behavior.

A second challenge consists of separating the purely hydrophobic effect from the structural changes induced by the modification methodologies. Many hydrophobization strategies alter not only surface polarity but also Ti dispersion, coordination (tetrahedral vs. octahedral), pore accessibility, and material acidity. Therefore, improvements observed in activity or selectivity cannot be attributed exclusively to a lower affinity for water or better epoxide desorption, but are often associated with a concomitant modification of the electronic and structural environment of the active site. This overlap of effects makes it difficult to establish direct and universal relationships between hydrophobicity and catalytic performance.

Furthermore, most hydrophobicity characterizations are performed under dry or static conditions, whereas epoxidation occurs in the liquid phase and in the simultaneous presence of olefin, oxidant, solvent, and water. Under these conditions, the Ti environment is dynamic and governed by competitive solvation processes, hydrogen bond network formation, and local reorganization of the medium. In this context, the effective “hydrophobicity” of the catalyst is not solely an intrinsic property of the solid, but rather the result of the interaction between the surface and the entire reactive system. The stabilization or destabilization of Ti-OOH species, the formation of lateral peroxo species, and the probability of oxirane ring opening depend on this dynamic microenvironment rather than on a surface parameter measured *ex situ*.

Another critical aspect is the strong dependence of catalytic performance on the reaction system used. The type of oxidant (H_2O_2 versus organic hydroperoxides), the nature and polarity of the solvent, the water concentration, and the size or polarity of the olefin have a decisive influence on the balance between direct epoxidation and allylic oxidation pathways. In fact, the direct epoxidation route depends on the electrophilicity (strength of the Lewis acidity) of the Ti active species. Moreover, the choice of the oxidant also plays an important role, since the reaction route depends on the electrophilicity of the active intermediate species. It is known that Ti-OOR ($\text{R} = \text{alkyl}$), formed from the activation

of an organic hydroperoxide with the Ti active sites, displays lower electrophilicity than Ti-OOH, formed from the activation of hydrogen peroxide with the Ti active sites. The alkyl group is an electron-donor group that decreases the electrophilicity of the oxygen-donating species for epoxidation [22]. Therefore, a hydrophobization strategy that is beneficial in one specific system may not reproduce the same effect under different conditions.

From a methodological point of view, it remains difficult to quantify and compare the hydrophobicity of materials from different studies (see the techniques for measuring the hydrophobicity/philicity of a catalyst in Section 2.2.3). There is no universal descriptor that comprehensively captures the density of hydrophilic sites, the degree of organic functionalization, and actual accessibility under reaction conditions. Although combinations of techniques (water adsorption, solid-state NMR, FTIR, TGA, XPS) have made it possible to establish trends within individual studies, cross-sectional comparisons between different systems remain limited. The development of standardized metrics—for example, expressed per unit of specific area or in relation to the density of accessible active sites—could contribute to a more robust interpretation.

To conclude, the accumulated evidence indicates that maximum activity and selectivity in epoxidation are not achieved through extreme hydrophobicity, but through fine-tuning of the chemical microenvironment that preserves isolated Ti sites, maintains adequate local polarity, and controls interaction with water and the oxidant. Future research integrating operating spectroscopic studies, detailed kinetic analysis, and computational modeling will be essential to unravel the interactions between surface and reactive medium and advance toward the rational design of titanosilicates with optimized properties.

4.2. Broader Catalytic Relevance of Hydrophobicity Beyond Epoxidation

This review focused on the catalytic performance of hydrophobized titanosilicates in olefin epoxidation. However, titanosilicates have also been evaluated in other reactions in which surface hydrophobicity plays a critical role, including saccharide isomerization, phenol oxidation, and propionic acid ketonization. For instance, Cordon et al. [200] reported higher glucose isomerization rates over hydrophobic Ti-Beta compared to its hydrophilic counterpart. In the same line, lower saccharide isomerization rate constants were observed for hydrophilic Ti-Beta, which were partially attributed to enhanced coordination of polar solvent molecules to the hydroxyl groups neighboring the Ti sites [201]. Similarly, enhanced phenol oxidation efficiency has been associated with increased hydrophobicity of titanosilicate catalysts [202]. In the ketonization of propionic acid, the superior catalytic performance of TS-1 was attributed to its higher intrinsic hydrophobicity compared to Ti-Beta [203].

Complementary computational studies on Ti-FAU have further demonstrated that solvation thermodynamics within zeolitic pores are dictated by both pore hydrophobicity and adsorbate polarity, explaining the complexity of confined solvation phenomena and rationalizing the conflicting results reported across different reaction systems, zeolite frameworks, and solvent environments [24].

Beyond titanosilicates, the influence of surface hydrophobicity extends to other catalytic systems in which solvent-surface interactions critically determine activity and stability. This is particularly evident in biomass valorization processes, where the balance between hydrophobic and hydrophilic domains governs water tolerance and substrate adsorption. For example, hydrophilic Sn-Beta exhibited gradual deactivation during hydroxymethylfurfural etherification with ethanol, which was attributed to proton exchange between ethanol and surface hydroxyl groups. Similarly, in Meerwein-Ponndorf-Verley-Oppenauer oxidation (MPV-O) reactions, higher reaction rates were reported for hydrophobic Sn-Beta relative to more hydrophilic analogs [204]. Dehydration of sugars to furans over

hydrophobized SBA-15 (by organic functionalization) reached higher fructose conversions and selectivity to 5-hydroxymethylfurfural (HMF) [205]. Vivian et al. [190], demonstrated that organic functionalization of Sn-silicates led to improved catalytic activity and selectivity in the conversion of dihydroxyacetone to ethyl lactate. Modification of surface hydrophobicity has also been successfully implemented in metal-organic frameworks (MOFs) in photocatalytic oxidation of tetrahydrofuran (THF) [206] and hydrogenation of nitrobenzene [24].

More recently, analogous considerations have emerged in electrochemical systems, where the local microenvironment at the catalyst-electrolyte interface critically determines reaction pathways and product selectivity. In electrocatalysis, tuning surface hydrophobicity can modulate mass transport, interfacial solvation, and local reactant, providing an additional lever to control catalytic performance [207].

In electrocatalytic hydrogen evolution reaction (HER), one of the most intensively studied research areas due to global efforts toward sustainable energy development, the efficiency is significantly hindered by mass transport limitations, related to reactant delivery to the electrode surface and product removal from the electrode-electrolyte interface. In recent years, engineering balanced hydrophobic/hydrophilic interfaces has therefore emerged as an effective strategy to facilitate interfacial transport and bubble detachment, thereby enhancing HER [207,208]. This approach is particularly relevant for gas-involving reactions such as CO₂ reduction (CO₂RR). Incorporating hydrophobic additives, e.g., polytetrafluoroethylene (PTFE) nanoparticles, into the catalyst layer enhances CO₂ availability at active sites and promotes selectivity to multicarbon products [207]. Although copper (Cu) electrocatalysts can convert CO₂ into value-added multicarbon products, their selectivity is strongly dictated by the local microenvironment at the catalyst surface [209].

Overall, the collected evidence demonstrates that surface hydrophobicity is a decisive parameter governing catalytic activity, selectivity, and stability across heterogeneous and electrochemical systems. From titanosilicates in oxidation, isomerization, and ketonization reactions to biomass valorization catalysts, MOFs, and electrocatalytic processes such as HER and CO₂RR, modulation of the interfacial microenvironment consistently influences solvation, reactant accessibility, mass transport, and product removal. These findings highlight hydrophobicity modulation as a versatile strategy for catalyst design across diverse reaction platforms.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16040299/s1>.

Author Contributions: Conceptualization, A.B.L., L.E.M.-P. and E.M.G.; methodology, A.B.L. and L.E.M.-P.; formal analysis, A.B.L., L.E.M.-P. and A.V.; investigation, A.B.L. and L.E.M.-P.; writing—original draft preparation, A.B.L., L.E.M.-P. and E.M.G.; writing—review and editing, L.E.M.-P., D.E. and E.M.G.; visualization, A.B.L., L.E.M.-P. and A.V.; supervision, L.E.M.-P. and E.M.G.; project administration, L.E.M.-P., E.d.I.T. and E.M.G.; funding acquisition, L.E.M.-P., E.d.I.T. and E.M.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Escuela Politécnica Nacional through the research project PIGR-22-08. The authors also acknowledge financial support from the Communauté française de Belgique through the ARC programme (Polarcat 15/20-069). A.B.L. and A.V. acknowledge the Conseil de l'Action Internationale (CAI) of UCLouvain for their Partenariat Sud scholarships. A.V. also acknowledges support from the Erasmus+ programme during her Master's studies.

Data Availability Statement: No new data were generated or analyzed in this review. All data discussed are available in the cited literature.

Acknowledgments: A.B.L. and A.V. acknowledge UCLouvain for the Partenariat Sud scholarships for their doctoral studies. The authors thank Escuela Politecnica Nacional for the financial support

through the research project PIGR-22-08. The artificial intelligence tool ChatGPT-5.3 (developed by OpenAI) was used occasionally as writing assistant. It was used to reformulate certain passages to improve clarity, flow and structure, but not to modify the scientific content or the data presented. All ideas, analyses and interpretations are the author's own.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Vayssilov, G.N. Structural and Physicochemical Features of Titanium Silicalites. *Catal. Rev.* **1997**, *39*, 209–251. [\[CrossRef\]](#)
2. Přech, J. Catalytic Performance of Advanced Titanosilicate Selective Oxidation Catalysts—A Review. *Catal. Rev.-Sci. Eng.* **2018**, *60*, 71–131. [\[CrossRef\]](#)
3. Hutter, R.; Dutoit, D.C.M.; Mallat, T.; Schneider, M.; Baiker, A. Novel Mesoporous Titania-Silica Aerogels Highly Active for the Selective Epoxidation of Cyclic Olefins. *J. Chem. Soc. Chem. Commun.* **1995**, 163–164. [\[CrossRef\]](#)
4. Ward, D.A.; Ko, E.I. Preparing Catalytic Materials by the Sol-Gel Method. *Ind. Eng. Chem. Res.* **1995**, *34*, 421–433. [\[CrossRef\]](#)
5. Keshavaraja, A.; Ramaswamy, V.; Soni, H.S.; Ramaswamy, A.V.; Ratnasamy, P. Synthesis, Characterization, and Catalytic Properties of Micro-Mesoporous, Amorphous Titanosilicate Catalysts. *J. Catal.* **1995**, *157*, 501–511. [\[CrossRef\]](#)
6. Fan, W.; Wu, P.; Tatsumi, T. Unique Solvent Effect of Microporous Crystalline Titanosilicates in the Oxidation of 1-Hexene and Cyclohexene. *J. Catal.* **2008**, *256*, 62–73. [\[CrossRef\]](#)
7. Liu, Z.F.; Tabora, J.; Davis, R.J. Relationships between Microstructure and Surface Acidity of Ti-Si Mixed Oxide Catalysts. *J. Catal.* **1994**, *149*, 117–126. [\[CrossRef\]](#)
8. Liu, Z.; Crumbaugh, G.M.; Davis, R.J. Effect of Structure and Composition on Epoxidation of Hexene Catalyzed by Microporous and Mesoporous Ti-Si Mixed Oxides. *J. Catal.* **1996**, *159*, 83–89. [\[CrossRef\]](#)
9. Kochkar, H.; Figueras, F. Synthesis of Hydrophobic TiO₂-SiO₂ Mixed Oxides for the Epoxidation of Cyclohexene. *J. Catal.* **1997**, *171*, 420–430. [\[CrossRef\]](#)
10. Smeets, V.; Boissière, C.; Sanchez, C.; Gaigneaux, E.M.; Peeters, E.; Sels, B.F.; Dusselier, M.; Debecker, D.P. Aerosol Route to TiO₂-SiO₂ Catalysts with Tailored Pore Architecture and High Epoxidation Activity. *Chem. Mater.* **2019**, *31*, 1610–1619. [\[CrossRef\]](#)
11. Manangon-Perugachi, L.E.; Smeets, V.; Vivian, A.; Kainthla, I.; Eloy, P.; Aprile, C.; Debecker, D.P.; Gaigneaux, E.M. Mesoporous Methyl-Functionalized Titanosilicate Produced by Aerosol Process for the Catalytic Epoxidation of Olefins. *Catalysts* **2021**, *11*, 196. [\[CrossRef\]](#)
12. Xu, H.; Wu, P. Recent Progresses in Titanosilicates. *Chin. J. Chem.* **2017**, *35*, 836–844. [\[CrossRef\]](#)
13. Kong, Z.; Yue, B.; Deng, W.; Zhu, K.; Yan, M.; Peng, Y.; He, H. Direct Synthesis of Hierarchically Porous TS-1 through a Solvent-Evaporation Route and Its Application as an Oxidation Catalyst. *Appl. Organomet. Chem.* **2014**, *28*, 239–243. [\[CrossRef\]](#)
14. Drago, R.S.; Dias, S.C.; McGilvray, J.M.; Mateus, A.L.M.L. Acidity and Hydrophobicity of TS-1. *J. Phys. Chem. B* **1998**, *102*, 1508–1514. [\[CrossRef\]](#)
15. Bellussi, G.; Carati, A.; Clerici, M.G.; Maddinelli, G.; Millini, R. Reactions of Titanium Silicalite with Protic Molecules and Hydrogen Peroxide. *J. Catal.* **1992**, *133*, 220–230. [\[CrossRef\]](#)
16. Xia, Q.-H.; Chen, X.; Tatsumi, T. Epoxidation of Cyclic Alkenes with Hydrogen Peroxide and Tert-Butyl Hydroperoxide on Na-Containing Ti β Zeolites. *J. Mol. Catal. A Chem.* **2001**, *176*, 179–193. [\[CrossRef\]](#)
17. Ouyang, X.; Hwang, S.-J.; Xie, D.; Rea, T.; Zones, S.I.; Katz, A. Heteroatom-Substituted Delaminated Zeolites as Solid Lewis Acid Catalysts. *ACS Catal.* **2015**, *5*, 3108–3119. [\[CrossRef\]](#)
18. Boronat, M.; Corma, A.; Renz, M.; Viruela, P.M. Predicting the Activity of Single Isolated Lewis Acid Sites in Solid Catalysts. *Chem.-A Eur. J.* **2006**, *12*, 7067–7077. [\[CrossRef\]](#)
19. Boronat, M.; Concepción, P.; Corma, A.; Renz, M.; Valencia, S. Determination of the Catalytically Active Oxidation Lewis Acid Sites in Sn-Beta Zeolites, and Their Optimisation by the Combination of Theoretical and Experimental Studies. *J. Catal.* **2005**, *234*, 111–118. [\[CrossRef\]](#)
20. Boronat, M.; Concepción, P.; Corma, A.; Navarro, M.T.; Renz, M.; Valencia, S. Reactivity in the Confined Spaces of Zeolites: The Interplay between Spectroscopy and Theory to Develop Structure–Activity Relationships for Catalysis. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2876–2884. [\[CrossRef\]](#)
21. Jenzer, G.; Mallat, T.; Maciejewski, M.; Eigenmann, F.; Baiker, A. Continuous Epoxidation of Propylene with Oxygen and Hydrogen on a Pd–Pt/TS-1 Catalyst. *Appl. Catal. A Gen.* **2001**, *208*, 125–133. [\[CrossRef\]](#)
22. Ratnasamy, P.; Srinivas, D.; Knözinger, H. Active Sites and Reactive Intermediates in Titanium Silicate Molecular Sieves. *Adv. Catal.* **2004**, *48*, 196702692.

23. Burtch, N.C.; Jasuja, H.; Walton, K.S. Water Stability and Adsorption in Metal-Organic Frameworks. *Chem. Rev.* **2014**, *114*, 10575–10612. [\[CrossRef\]](#)
24. Chen, X.; Qian, P.; Zhang, T.; Xu, Z.; Fang, C.; Xu, X.; Chen, W.; Wu, P.; Shen, Y.; Li, S.; et al. Catalyst Surfaces with Tunable Hydrophilicity and Hydrophobicity: Metal–Organic Frameworks toward Controllable Catalytic Selectivity. *Chem. Commun.* **2018**, *54*, 3936–3939. [\[CrossRef\]](#)
25. Jayaramulu, K.; Geyer, F.; Schneemann, A.; Kment, Š.; Otyepka, M.; Zboril, R.; Vollmer, D.; Fischer, R.A. Hydrophobic Metal–Organic Frameworks. *Adv. Mater.* **2019**, *31*, 1900820. [\[CrossRef\]](#)
26. Wang, C.; Guo, H.; Leng, S.; Yu, J.; Feng, K.; Cao, L.; Huang, J. Regulation of Hydrophilicity/Hydrophobicity of Aluminosilicate Zeolites: A Review. *Crit. Rev. Solid State Mater. Sci.* **2020**, *46*, 330–348. [\[CrossRef\]](#)
27. Ruddy, D.A.; Brutchey, R.L.; Tilley, T.D. The Influence of Surface Modification on the Epoxidation Selectivity and Mechanism of TiSBA15 and TaSBA15 Catalysts with Aqueous Hydrogen Peroxide. *Top. Catal.* **2008**, *48*, 99–106. [\[CrossRef\]](#)
28. Figueras, F.; Kochkar, H.; Caldarelli, S. Crystallization of Hydrophobic Mesoporous Titano-Silicates Useful as Epoxidation Catalysts. *Microporous Mesoporous Mater.* **2000**, *39*, 249–256. [\[CrossRef\]](#)
29. Sheldon, R.A.; Dakka, J. Heterogeneous Catalytic Oxidations in the Manufacture of Fine Chemicals. *Catal. Today* **1994**, *19*, 215–245. [\[CrossRef\]](#)
30. Bregante, D.T.; Flaherty, D.W. Periodic Trends in Olefin Epoxidation over Group IV and V Framework-Substituted Zeolite Catalysts: A Kinetic and Spectroscopic Study. *J. Am. Chem. Soc.* **2017**, *139*, 6888–6898. [\[CrossRef\]](#)
31. Corma, A.; Domine, M.; Gaona, J.A.; Jordá, J.L.; Navarro, M.T.; Rey, F.; Pérez-Pariente, J.; Tsuji, J.; McCulloch, B.; Nemeth, L.T. Strategies to Improve the Epoxidation Activity and Selectivity of Ti-MCM-41. *Chem. Commun.* **1998**, 2211–2212. [\[CrossRef\]](#)
32. Brutchey, R.L.; Ruddy, D.A.; Andersen, L.K.; Tilley, T.D. Influence of Surface Modification of Ti–SBA15 Catalysts on the Epoxidation Mechanism for Cyclohexene with Aqueous Hydrogen Peroxide. *Langmuir* **2005**, *21*, 9576–9583. [\[CrossRef\]](#)
33. Fan, W.; Duan, R.-G.; Yokoi, T.; Wu, P.; Kubota, Y.; Tatsumi, T. Synthesis, Crystallization Mechanism, and Catalytic Properties of Titanium-Rich TS-1 Free of Extraframework Titanium Species. *J. Am. Chem. Soc.* **2008**, *130*, 10150–10164. [\[CrossRef\]](#) [\[PubMed\]](#)
34. D’Amore, M.B.; Schwarz, S. Trimethylsilylation of Ordered and Disordered Titanosilicates: Improvements in Epoxidation with Aqueous H₂O₂ from Micro- to Meso-Pores and Beyond. *Chem. Commun.* **1999**, 121–122. [\[CrossRef\]](#)
35. Corma, A.; Esteve, P.; Martinez, A.; Valencia, S. Oxidation of Olefins with Hydrogen Peroxide and Tert-Butyl Hydroperoxide on Ti-Beta Catalyst. *J. Catal.* **1995**, *152*, 18–24. [\[CrossRef\]](#)
36. Blasco, T.; Cambor, M.A.; Corma, A.; Esteve, P.; Martínez, A.; Prieto, C.; Valencia, S. Unseeded Synthesis of Al-Free Ti-β Zeolite in Fluoride Medium: A Hydrophobic Selective Oxidation Catalyst. *Chem. Commun.* **1996**, 2367–2368. [\[CrossRef\]](#)
37. Blasco, T.; Cambor, M.A.; Corma, A.; Esteve, P.; Guil, J.M.; Martínez, A.; Perdigón-Melón, J.A.; Valencia, S. Direct Synthesis and Characterization of Hydrophobic Aluminum-Free Ti–Beta Zeolite. *J. Phys. Chem. B* **1998**, *102*, 75–88. [\[CrossRef\]](#)
38. Bregante, D.T.; Johnson, A.M.; Patel, A.Y.; Ayla, E.Z.; Cordon, M.J.; Bukowski, B.C.; Greeley, J.; Gounder, R.; Flaherty, D.W. Cooperative Effects between Hydrophilic Pores and Solvents: Catalytic Consequences of Hydrogen Bonding on Alkene Epoxidation in Zeolites. *J. Am. Chem. Soc.* **2019**, *141*, 7302–7319. [\[CrossRef\]](#)
39. Igarashi, N.; Kidani, S.; Ahemaito, R.; Hashimoto, K.; Tatsumi, T. Direct Organic Functionalization of Ti–MCM-41: Synthesis Condition, Organic Content, and Catalytic Activity. *Microporous Mesoporous Mater.* **2005**, *81*, 97–105. [\[CrossRef\]](#)
40. Igarashi, N.; Hashimoto, K.; Tatsumi, T. Catalytic Studies on Trimethylsilylated Ti-MCM-41 and Ti-MCM-48 Materials. *Microporous Mesoporous Mater.* **2007**, *104*, 269–280. [\[CrossRef\]](#)
41. Tatsumi, T.; Koyano, K.A.; Igarashi, N. Remarkable Activity Enhancement by Trimethylsilylation in Oxidation of Alkenes and Alkanes with H₂O₂ Catalyzed by Titanium-Containing Mesoporous Molecular Sieves. *Chem. Commun.* **1998**, 325–326. [\[CrossRef\]](#)
42. Bu, J.; Rhee, H.-K. Improvement in Hydrophobicity of Ti-MCM-41 Using a New Silylation Agent MSTFA. *Catal. Lett.* **2000**, *65*, 141–145. [\[CrossRef\]](#)
43. Bu, J.; Rhee, H.-K. Silylation of Ti-MCM-41 by Trimethylsilyl-Imidazole and Its Effect on the Olefin Epoxidation with Aqueous H₂O₂. *Catal. Lett.* **2000**, *66*, 245–249. [\[CrossRef\]](#)
44. Manangon-Perugachi, L.E.; Vivian, A.; Eloy, P.; Debecker, D.P.; Aprile, C.; Gaigneaux, E.M. Hydrophobic Titania-Silica Mixed Oxides for the Catalytic Epoxidation of Cyclooctene. *Catal. Today* **2019**, *363*, 128–136. [\[CrossRef\]](#)
45. Müller, C.A.; Deck, R.; Mallat, T.; Baiker, A. Hydrophobic Titania-Silica Aerogels: Epoxidation of Cyclic Compounds. *Top. Catal.* **2000**, *11*, 369–378.
46. Müller, C.A.; Maciejewski, M.; Mallat, T.; Baiker, A. Organically Modified Titania-Silica Aerogels for the Epoxidation of Olefins and Allylic Alcohols. *J. Catal.* **1999**, *184*, 280–293. [\[CrossRef\]](#)
47. Smeets, V.; Ben Mustapha, L.; Schnee, J.; Gaigneaux, E.M.; Debecker, D.P. Mesoporous SiO₂-TiO₂ Epoxidation Catalysts: Tuning Surface Polarity to Improve Performance in the Presence of Water. *Mol. Catal.* **2018**, *452*, 123–128. [\[CrossRef\]](#)
48. Guo, Y.; Hwang, S.-J.; Katz, A. Hydrothermally Robust Ti/SiO₂ Epoxidation Catalysts via Surface Modification with Oligomeric PMHS. *Mol. Catal.* **2019**, *477*, 110509. [\[CrossRef\]](#)

49. Lozada, A.B.; Sango, A.; Sangurima-Cedillo, A.; Debut, A.; Endara, D.; de la Torre, E.; Gaigneaux, E.M.; Manangon-Perugachi, L.E. Mesoporous Titanosilicate-Silica-Coated Cobalt Ferrite Core-Shell Catalysts for the Oxidation of Styrene. *Catal. Today* **2024**, *430*, 114513. [\[CrossRef\]](#)
50. Notari, B. *Microporous Crystalline Titanium Silicates*; Eley, D.D., Haag, W.O., Gates, B.B.T., Eds.; Advances in Catalysis; Academic Press: Cambridge, MA, USA, 1996; Volume 41, pp. 253–334, ISBN 0360-0564.
51. Taramasso, M.; Perego, G.; Notari, B. Preparation of Porous Crystalline Synthetic Material Comprised of Silicon and Titanium Oxides US 4410501, 18 October 1983.
52. Lamberti, C.; Bordiga, S.; Zecchina, A.; Artioli, G.; Marra, G.; Spanò, G. Ti Location in the MFI Framework of Ti–Silicalite-1: A Neutron Powder Diffraction Study. *J. Am. Chem. Soc.* **2001**, *123*, 2204–2212. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Millini, R.; Previde Massara, E.; Perego, G.; Bellussi, G. Framework Composition of Titanium Silicalite-1. *J. Catal.* **1992**, *137*, 497–503. [\[CrossRef\]](#)
54. Clerici, M.G.; Ingallina, P. Epoxidation of Lower Olefins with Hydrogen Peroxide and Titanium Silicalite. *J. Catal.* **1993**, *140*, 71–83. [\[CrossRef\]](#)
55. Notari, B. Titanium Silicalite: A New Selective Oxidation Catalyst. In *Chemistry of Microporous Crystals*; Inui, T., Namba, S., Tatsumi, T., Eds.; Studies in Surface Science and Catalysis; Elsevier: Amsterdam, The Netherlands, 1991; Volume 60, pp. 343–352, ISBN 0167-2991.
56. Corma, A.; Cambor, M.A.; Esteve, P.; Martinez, A.; Perezpariente, J. Activity of Ti-Beta Catalyst for the Selective Oxidation of Alkenes and Alkanes. *J. Catal.* **1994**, *145*, 151–158. [\[CrossRef\]](#)
57. Blasco, T.; Corma, A.; Navarro, M.T.; Pariente, J.P. Synthesis, Characterization, and Catalytic Activity of Ti-MCM-41 Structures. *J. Catal.* **1995**, *156*, 65–74. [\[CrossRef\]](#)
58. Yu, Y.; Wang, R.; Liu, W.; Chen, Z.; Liu, H.; Huang, X.; Tang, Z.; Liu, Y.; He, M. Control of Ti Active-Site Microenvironment in Titanosilicate Catalysts and Its Effect on Oxidation Pathways. *Appl. Catal. A Gen.* **2021**, *610*, 117953. [\[CrossRef\]](#)
59. Wang, Y.; Wang, K.; Wang, F.; Zhai, Y.; Bing, C.; Fan, X.; Shen, Q.; Zhang, X. A Review on the Active Sites for Titanium Species in Zeolites: Coordination Structure, Synthetic Strategies and Activity. *Mater. Chem. Front.* **2025**, *9*, 8–29. [\[CrossRef\]](#)
60. Davis, M.E.; Lobo, R.F. Zeolite and Molecular Sieve Synthesis. *Chem. Mater.* **1992**, *4*, 756–768. [\[CrossRef\]](#)
61. Li, Y.; Li, L.; Yu, J. Applications of Zeolites in Sustainable Chemistry. *Chem* **2017**, *3*, 928–949. [\[CrossRef\]](#)
62. Chen, N.Y. Hydrophobic Properties of Zeolites. *J. Phys. Chem.* **1976**, *80*, 60–64. [\[CrossRef\]](#)
63. Cundy, C.S.; Cox, P.A. The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *Chem. Rev.* **2003**, *103*, 663–702. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Gounder, R. Hydrophobic Microporous and Mesoporous Oxides as Brønsted and Lewis Acid Catalysts for Biomass Conversion in Liquid Water. *Catal. Sci. Technol.* **2014**, *4*, 2877–2886. [\[CrossRef\]](#)
65. Young, G.J. Interaction of Water Vapor with Silica Surfaces. *J. Colloid Sci.* **1958**, *13*, 67–85. [\[CrossRef\]](#)
66. Arca, V.; Boscolo Boscoletto, A.; Fracasso, N.; Meda, L.; Ranghino, G. Epoxidation of Propylene on Zn-Treated TS-1 Catalyst. *J. Mol. Catal. A Chem.* **2006**, *243*, 264–277. [\[CrossRef\]](#)
67. Lin, W.; Frei, H. Photochemical and FT-IR Probing of the Active Site of Hydrogen Peroxide in Ti Silicalite Sieve. *J. Am. Chem. Soc.* **2002**, *124*, 9292–9298. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Klinyod, S.; Yomthong, K.; Suttipat, D.; Pornsetmetakul, P.; Kidkhunthod, P.; Choojun, K.; Namuangruk, S.; Sooknoi, T.; Wattanakit, C. Tailoring the First Coordination Shell of Isolated Ti(IV) Active Sites in Zeolite Frameworks Boosting Catalytic Activity in Epoxidation. *ChemCatChem* **2025**, *17*, e202401862. [\[CrossRef\]](#)
69. Leofanti, G.; Tozzola, G.; Padovan, M.; Petrini, G.; Bordiga, S.; Zecchina, A. Catalyst Characterization: Characterization Techniques. *Catal. Today* **1997**, *34*, 307–327. [\[CrossRef\]](#)
70. Moliner, M.; Corma, A. Advances in the Synthesis of Titanosilicates: From the Medium Pore TS-1 Zeolite to Highly-Accessible Ordered Materials. *Microporous Mesoporous Mater.* **2014**, *189*, 31–40. [\[CrossRef\]](#)
71. Bai, R.; Song, Y.; Bai, R.; Yu, J. Creation of Hierarchical Titanosilicate TS-1 Zeolites. *Adv. Mater. Interfaces* **2020**, *8*, 2001095. [\[CrossRef\]](#)
72. Sasaki, M.; Sato, Y.; Tsuboi, Y.; Inagaki, S.; Kubota, Y. Ti-YNU-2: A Microporous Titanosilicate with Enhanced Catalytic Performance for Phenol Oxidation. *ACS Catal.* **2014**, *4*, 2653–2657. [\[CrossRef\]](#)
73. Ge, T.; Hua, Z.; Lv, J.; Zhou, J.; Guo, H.; Zhou, J.; Shi, J. Hydrophilicity/Hydrophobicity Modulated Synthesis of Nano-Crystalline and Hierarchically Structured TS-1 Zeolites. *CrystEngComm* **2017**, *19*, 1370–1376. [\[CrossRef\]](#)
74. Wang, B.; Lu, L.; Ge, B.; Chen, S.; Zhu, J.; Wei, D. Hydrophobic and Hierarchical Modification of TS-1 and Application for Propylene Epoxidation. *J. Porous Mater.* **2019**, *26*, 227–237. [\[CrossRef\]](#)
75. Koyano, K.A.; Tatsumi, T. Synthesis of Titanium-Containing Mesoporous Molecular Sieves with a Cubic Structure. In *Studies in Surface Science and Catalysis*; Chon, H., Ihm, S.-K., Uh, Y.S., Eds.; Elsevier: Amsterdam, The Netherlands, 1996; Volume 105, pp. 93–100, ISSN 0167-2991, ISBN 9780444823441. [\[CrossRef\]](#)

76. Cambor, M.A.; Corma, A.; Pérez-Pariente, J. Synthesis of Titanosilicates Isomorphous to Zeolite Beta, Active as Oxidation Catalysts. *Zeolites* **1993**, *13*, 82–87. [\[CrossRef\]](#)
77. Wu, P.; Komatsu, T.; Yashima, T. Characterization of Titanium Species Incorporated into Dealuminated Mordenites by Means of IR Spectroscopy and 18O-Exchange Technique. *J. Phys. Chem.* **1996**, *100*, 10316–10322. [\[CrossRef\]](#)
78. Přech, J.; Čejka, J. UTL Titanosilicate: An Extra-Large Pore Epoxidation Catalyst with Tunable Textural Properties. *Catal. Today* **2016**, *277*, 2–8. [\[CrossRef\]](#)
79. Luan, H.; Xu, C.; Wu, Q.; Xiao, F.-S. Recent Advances in the Synthesis of TS-1 Zeolite. *Front. Chem.* **2022**, *10*, 1080554. [\[CrossRef\]](#)
80. Na, K.; Jo, C.; Kim, J.; Ahn, W.-S.; Ryoo, R. MFI Titanosilicate Nanosheets with Single-Unit-Cell Thickness as an Oxidation Catalyst Using Peroxides. *ACS Catal.* **2011**, *1*, 901–907. [\[CrossRef\]](#)
81. Wu, P.; Nuntasri, D.; Ruan, J.; Liu, Y.; He, M.; Fan, W.; Terasaki, O.; Tatsumi, T. Delamination of Ti-MWW and High Efficiency in Epoxidation of Alkenes with Various Molecular Sizes. *J. Phys. Chem. B* **2004**, *108*, 19126–19131. [\[CrossRef\]](#)
82. Chen, H.L.; Li, S.W.; Wang, Y.M. Synthesis and Catalytic Properties of Multilayered MEL-Type Titanosilicate Nanosheets. *J. Mater. Chem. A* **2015**, *3*, 5889–5900. [\[CrossRef\]](#)
83. Corma, A.; Diaz, U.; Domine, M.E.; Fornés, V. New Aluminosilicate and Titanosilicate Delaminated Materials Active for Acid Catalysis, and Oxidation Reactions Using H₂O₂. *J. Am. Chem. Soc.* **2000**, *122*, 2804–2809. [\[CrossRef\]](#)
84. Wang, J.; Zhao, Y.; Yokoi, T.; Kondo, J.N.; Tatsumi, T. High-Performance Titanosilicate Catalyst Obtained through Combination of Liquid-Phase and Solid-Phase Transformation Mechanisms. *ChemCatChem* **2014**, *6*, 2719–2726. [\[CrossRef\]](#)
85. Chen, L.Y.; Chuah, G.K.; Jaenicke, S. Propylene Epoxidation with Hydrogen Peroxide Catalyzed by Molecular Sieves Containing Framework Titanium. *J. Mol. Catal. A Chem.* **1998**, *132*, 281–292. [\[CrossRef\]](#)
86. Corma, A.; Esteve, P.; Martínez, A. Solvent Effects during the Oxidation of Olefins and Alcohols with Hydrogen Peroxide on Ti-Beta Catalyst: The Influence of the Hydrophilicity–Hydrophobicity of the Zeolite. *J. Catal.* **1996**, *161*, 11–19. [\[CrossRef\]](#)
87. Wang, J.; Yokoi, T.; Kondo, J.N.; Tatsumi, T.; Zhao, Y. Titanium(IV) in the Organic-Structure-Directing-Agent-Free Synthesis of Hydrophobic and Large-Pore Molecular Sieves as Redox Catalysts. *ChemSusChem* **2015**, *8*, 2476–2480. [\[CrossRef\]](#)
88. Fan, W.; Wu, P.; Namba, S.; Tatsumi, T. Synthesis and Catalytic Properties of a New Titanosilicate Molecular Sieve with the Structure Analogous to MWW-Type Lamellar Precursor. *J. Catal.* **2006**, *243*, 183–191. [\[CrossRef\]](#)
89. Wang, J.; Duan, N.; Li, P.; Liu, Y.; Wu, X.; Li, B. Recent Advances in the Synthesis and Application of TS-1 Zeolite for Green Catalytic Oxidation. *Adv. Sustain. Syst.* **2025**, *9*, 2400719. [\[CrossRef\]](#)
90. Yang, J.; Liu, S.; Liu, Y.; Zhou, L.; Wen, H.; Wei, H.; Shen, R.; Wu, X.; Jiang, J.; Li, B. Review and Perspectives on TS-1 Catalyzed Propylene Epoxidation. *iScience* **2024**, *27*, 109064. [\[CrossRef\]](#) [\[PubMed\]](#)
91. Xue, Y.; Liu, S.; Wang, J.; Zhang, H.; Wei, H.; Liu, Y.; Wang, X.; Tian, J.; Jiang, J.; Li, B. A Review on Understanding and Strengthening of Active Species in Titanium Silicalite-1 (TS-1) Catalysts. *Adv. Sci.* **2025**, *12*, e12531. [\[CrossRef\]](#) [\[PubMed\]](#)
92. Wulff, H.P. Process for the Oxidation of Olefins to Olefin Oxides. UK Patent 1 249 079, 6 October 1971.
93. Hutter, R.; Mallat, T.; Baiker, A. Titania-Silica Mixed Oxides: III. Epoxidation of α -Isophorone with Hydroperoxides. *J. Catal.* **1995**, *157*, 665–675. [\[CrossRef\]](#)
94. Calvino, J.J.; Cauqui, M.A.; Gatica, J.M.; Perez, J.A.; Rodriguez-Izquierdo, J.M. Development of Acidity on Sol-Gel Prepared TiO₂-SiO₂ Catalysts. In *Proceedings of the Materials Research Society Symposium Proceedings*; PN: Pittsburgh, PA, USA, 1994; Volume 346, pp. 685–690.
95. Neumann, R.; Chava, M.; Levin, M. Hydrogen Peroxide Oxidations Catalysed by Metallosilicalite Xerogels. *J. Chem. Soc. Chem. Commun.* **1993**, 1685–1687. [\[CrossRef\]](#)
96. Hutter, R.; Mallat, T.; Baiker, A. Titania Silica Mixed Oxides: II. Catalytic Behavior in Olefin Epoxidation. *J. Catal.* **1995**, *153*, 177–189. [\[CrossRef\]](#)
97. Dutoit, D.C.M.; Schneider, M.; Hutter, R.; Baiker, A. Titania-Silica Mixed Oxides: IV. Influence of Ti Content and Aging on Structural and Catalytic Properties of Aerogels. *J. Catal.* **1996**, *161*, 651–658. [\[CrossRef\]](#)
98. Itoh, M.; Hattori, H.; Tanabe, K. The Acidic Properties of TiO₂-SiO₂ and Its Catalytic Activities for the Amination of Phenol, the Hydration of Ethylene and the Isomerization of Butene. *J. Catal.* **1974**, *35*, 225–231. [\[CrossRef\]](#)
99. Ko, E.I.; Chen, J.-P.; Weissman, J.G. A Study of Acidic Titania/Silica Mixed Oxides and Their Use as Supports for Nickel Catalysts. *J. Catal.* **1987**, *105*, 511–520. [\[CrossRef\]](#)
100. Nakabayashi, H. Properties of Acid Sites on TiO₂-SiO₂ and TiO₂-Al₂O₃ Mixed Oxides Measured by Infrared Spectroscopy. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 914–916. [\[CrossRef\]](#)
101. Sohn, J.R.; Jang, H.J. Correlation between the Infrared Band Frequency of the Silanol Bending Vibration in TiO₂-SiO₂ Catalysts and Activity for Acid Catalysis. *J. Catal.* **1991**, *132*, 563–565. [\[CrossRef\]](#)
102. Radu, D.C.; Pârvolescu, V.I.; Câmpăanu, V.; Bartha, E.; Jonas, A.; Grange, P. Chemoselective Oxidation of 2-Thiomethyl-4,6-Dimethyl-Pyrimidine and 2-Thiobenzyl-4,6-Dimethyl-Pyrimidine over Titania-Silica Catalysts. *Appl. Catal. A Gen.* **2003**, *242*, 77–84. [\[CrossRef\]](#)

103. Gisler, A.; Bürgi, T.; Baiker, A. Epoxidation on Titania-Silica Aerogel Catalysts Studied by Attenuated Total Reflection Fourier Transform Infrared and Modulation Spectroscopy. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3539–3548. [\[CrossRef\]](#)
104. Beck, C.; Mallat, T.; Baiker, A. Epoxidation of Allylic Alcohols with $\text{TiO}_2\text{-SiO}_2$: Hydroxy-Assisted Mechanism and Dynamic Structural Changes during Reaction. *Catal. Lett.* **2003**, *88*, 203–209. [\[CrossRef\]](#)
105. Lorret, O.; Lafond, V.; Mutin, P.H.; Vioux, A. One-Step Synthesis of Mesoporous Hybrid Titania–Silica Xerogels for the Epoxidation of Alkenes. *Chem. Mater.* **2006**, *18*, 4707–4709. [\[CrossRef\]](#)
106. Gao, X.; Wachs, I.E. Titania-Silica as Catalysts: Molecular Structural Characteristics and Physico-Chemical Properties. *Catal. Today* **1999**, *51*, 233–254. [\[CrossRef\]](#)
107. Clerici, M.G.; Kholdeeva, O.A. *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Wiley: Hoboken, NJ, USA, 2013; ISBN 9781118356753.
108. Dusi, M.; Mallat, T.; Baiker, A. Titania-Silica Mixed Oxides: Influence of Reaction Additives on the Epoxidation of (E)-2-Hexen-1-ol. *J. Catal.* **1998**, *173*, 423–432. [\[CrossRef\]](#)
109. Gisler, A.; Müller, C.A.; Schneider, M.; Mallat, T.; Baiker, A. Synthesis of Organically Modified Titania-Silica Aerogels: Application for Epoxidation of Cyclohexenol. *Stud. Surf. Sci. Catal.* **2000**, *130*, 1637–1642. [\[CrossRef\]](#)
110. Murata, C.; Yoshida, H.; Hattori, T. Titania-Silica Catalysts Prepared by Sol-Gel Method for Photoepoxidation of Propene with Molecular Oxygen. *Stud. Surf. Sci. Catal.* **2000**, *143*, 845–853.
111. Müller, C.A.; Schneider, M.; Gisler, A.; Mallat, T.; Baiker, A. Titania-Silica Epoxidation Catalysts Modified by Acetoxypentyl Groups. *Catal. Lett.* **2000**, *64*, 9–14. [\[CrossRef\]](#)
112. Müller, C.A.; Schneider, M.; Mallat, T.; Baiker, A. Titania-Silica Epoxidation Catalysts Modified by Polar Organic Functional Groups. *J. Catal.* **2000**, *189*, 221–232. [\[CrossRef\]](#)
113. Berli, C.; Ferraris, G.; Guidotti, M.; Moretti, G.; Psaro, R.; Ravasio, N. A Comparison between [Ti]-MCM-41 and Amorphous Mesoporous Silica-Titania as Catalysts for the Epoxidation of Bulky Unsaturated Alcohols. *Microporous Mesoporous Mater.* **2001**, *44–45*, 595–602. [\[CrossRef\]](#)
114. Davis, R.J.; Liu, Z. Titania-Silica: A Model Binary Oxide Catalyst System. *Chem. Mater.* **1997**, *9*, 2311–2324. [\[CrossRef\]](#)
115. Mariscal, R.; López-Granados, M.; Fierro, J.L.G.; Sotelo, J.L.; Martos, C.; Van Grieken, R. Morphology and Surface Properties of Titania-Silica Hydrophobic Xerogels. *Langmuir* **2000**, *16*, 9460–9467. [\[CrossRef\]](#)
116. Beck, C.; Mallat, T.; Bürgi, T.; Baiker, A. Nature of Active Sites in Sol-Gel $\text{TiO}_2\text{-SiO}_2$ Epoxidation Catalysts. *J. Catal.* **2001**, *204*, 428–439. [\[CrossRef\]](#)
117. Beck, C.; Mallat, T.; Baiker, A. On the Limited Selectivity of Silica-Based Epoxidation Catalysts. *Catal. Lett.* **2001**, *75*, 131–136. [\[CrossRef\]](#)
118. Mohamed, M.M.; Salama, T.M.; Yamaguchi, T. Synthesis, Characterization and Catalytic Properties of Titania-Silica Catalysts. *Colloids Surfaces A Physicochem. Eng. Asp.* **2002**, *207*, 25–32. [\[CrossRef\]](#)
119. Pabón, E.; Retuert, J.; Quijada, R.; Zarate, A. $\text{TiO}_2\text{-SiO}_2$ Mixed Oxides Prepared by a Combined Sol-Gel and Polymer Inclusion Method. *Microporous Mesoporous Mater.* **2004**, *67*, 195–203. [\[CrossRef\]](#)
120. Cao, S.; Yao, N.; Yeung, K.L. Synthesis of Freestanding Silica and Titania-Silica Aerogels with Ordered and Disordered Mesopores. *J. Sol-Gel Sci. Technol.* **2008**, *46*, 323–333. [\[CrossRef\]](#)
121. Gisler, A.; Müller, C.A.; Schneider, M.; Mallat, T.; Baiker, A. Titania-Silica Epoxidation Catalysts Modified by Mono- and Bidentate Organic Functional Groups. *Top. Catal.* **2001**, *15*, 247–255. [\[CrossRef\]](#)
122. Hu, S.; Willey, R.J.; Notari, B. An Investigation on the Catalytic Properties of Titania-Silica Materials. *J. Catal.* **2003**, *220*, 240–248. [\[CrossRef\]](#)
123. Gläser, R.; Weitkamp, J. Surface Hydrophobicity or Hydrophilicity of Porous Solids. *Handb. Porous Solids* **2002**, 395–431.
124. Blokzijl, W.; Engberts, J.B.F.N. Hydrophobic Effects. Opinions and Facts. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1545–1579. [\[CrossRef\]](#)
125. Kinloch, A.J. The Science of Adhesion. *J. Mater. Sci.* **1980**, *15*, 2141–2166. [\[CrossRef\]](#)
126. Wang, L.; Xiao, F.-S. The Importance of Catalyst Wettability. *ChemCatChem* **2014**, *6*, 3048–3052. [\[CrossRef\]](#)
127. Iglesias, J.; Melero, J.A.; Sainz-Pardo, J. Direct Synthesis of Organically Modified Ti-SBA-15 Materials. *J. Mol. Catal. A Chem.* **2008**, *291*, 75–84. [\[CrossRef\]](#)
128. Lin, K.; Pescarmona, P.P.; Houthoofd, K.; Liang, D.; Van Tendeloo, G.; Jacobs, P.A. Direct Room-Temperature Synthesis of Methyl-Functionalized Ti-MCM-41 Nanoparticles and Their Catalytic Performance in Epoxidation. *J. Catal.* **2009**, *263*, 75–82. [\[CrossRef\]](#)
129. Parker, W.O.; Millini, R. Ti Coordination in Titanium Silicalite-1. *J. Am. Chem. Soc.* **2006**, *128*, 1450–1451. [\[CrossRef\]](#)
130. Csicsery, S.M. Catalysis by Shape Selective Zeolites-Science and Technology. *Pure Appl. Chem.* **1986**, *58*, 841–856. [\[CrossRef\]](#)
131. Takeuchi, M.; Kimura, T.; Hidaka, M.; Rakhmawaty, D.; Anpo, M. Photocatalytic Oxidation of Acetaldehyde with Oxygen on $\text{TiO}_2/\text{ZSM-5}$ Photocatalysts: Effect of Hydrophobicity of Zeolites. *J. Catal.* **2007**, *246*, 235–240. [\[CrossRef\]](#)

132. Sano, T.; Yamashita, N.; Iwami, Y.; Takeda, K.; Kawakami, Y. Estimation of Dealumination Rate of ZSM-5 Zeolite by Adsorption of Water Vapor. *Zeolites* **1996**, *16*, 258–264. [\[CrossRef\]](#)
133. Zhang, K.; Lively, R.P.; Noel, J.D.; Dose, M.E.; McCool, B.A.; Chance, R.R.; Koros, W.J. Adsorption of Water and Ethanol in MFI-Type Zeolites. *Langmuir* **2012**, *28*, 8664–8673. [\[CrossRef\]](#) [\[PubMed\]](#)
134. Zhao, X.S.; Lu, G.Q.; Whittaker, A.K.; Millar, G.J.; Zhu, H.Y. Comprehensive Study of Surface Chemistry of MCM-41 Using ²⁹Si CP/MAS NMR, FTIR, Pyridine-TPD, and TGA. *J. Phys. Chem. B* **1997**, *101*, 6525–6531. [\[CrossRef\]](#)
135. Cambor, M.A.; Costantini, M.; Corma, A.; Gilbert, L.; Esteve, P.; Martínez, A.; Valencia, S. Synthesis and Catalytic Activity of Aluminium-Free Zeolite Ti-β Oxidation Catalysts. *Chem. Commun.* **1996**, 1339–1340. [\[CrossRef\]](#)
136. Cambor, M.A.; Corma, A.; Valencia, S. Spontaneous Nucleation and Growth of Pure Silica Zeolite-β Free of Connectivity Defects. *Chem. Commun.* **1996**, 2365–2366. [\[CrossRef\]](#)
137. Gounder, R.; Davis, M.E. Beyond Shape Selective Catalysis with Zeolites: Hydrophobic Void Spaces in Zeolites Enable Catalysis in Liquid Water. *AIChE J.* **2013**, *59*, 3349–3358. [\[CrossRef\]](#)
138. Cambor, M.A.; Corma, A.; Valencia, S. Synthesis in Fluoride Media and Characterisation of Aluminosilicate Zeolite Beta. *J. Mater. Chem.* **1998**, *8*, 2137–2145. [\[CrossRef\]](#)
139. Bregante, D.T.; Potts, D.S.; Kwon, O.; Ayla, E.Z.; Tan, J.Z.; Flaherty, D.W. Effects of Hydrofluoric Acid Concentration on the Density of Silanol Groups and Water Adsorption in Hydrothermally Synthesized Transition-Metal-Substituted Silicalite-1. *Chem. Mater.* **2020**, *32*, 7425–7437. [\[CrossRef\]](#)
140. Li, B.; Iyoki, K.; Techasarintr, P.; Elangovan, S.P.; Simancas, R.; Okubo, T.; Yokoi, T.; Wakihara, T. Hydrophobicity Manipulation of Titanium Silicalite-1 with Enhanced Catalytic Performance via Liquid-Mediated Defect Healing Treatment. *ACS Catal.* **2023**, *13*, 15155–15163. [\[CrossRef\]](#)
141. Roy, S.K.; Dutta, D.; Talukdar, A.K. Highly Effective Methylated Ti MCM-41 Catalyst for Cyclohexene Oxidation. *Mater. Res. Bull.* **2018**, *103*, 38–46. [\[CrossRef\]](#)
142. Fraile, J.M.; García, J.I.; Mayoral, J.A.; Vispe, E. Effect of the Reaction Conditions on the Epoxidation of Alkenes with Hydrogen Peroxide Catalyzed by Silica-Supported Titanium Derivatives. *J. Catal.* **2001**, *204*, 146–156. [\[CrossRef\]](#)
143. Debecker, D.P. Innovative Sol-Gel Routes for the Bottom-Up Preparation of Heterogeneous Catalysts. *Chem. Rec.* **2018**, *18*, 662–675. [\[CrossRef\]](#) [\[PubMed\]](#)
144. Lin, K.; Wang, L.; Meng, F.; Sun, Z.; Yang, Q.; Cui, Y.; Jiang, D.; Xiao, F.-S. Formation of Better Catalytically Active Titanium Species in Ti-MCM-41 by Vapor-Phase Silylation. *J. Catal.* **2005**, *235*, 423–427. [\[CrossRef\]](#)
145. Silvestre-Alberó, J.; Domine, M.E.; Jordá, J.L.; Navarro, M.T.; Rey, F.; Rodríguez-Reinoso, F.; Corma, A. Spectroscopic, Calorimetric, and Catalytic Evidences of Hydrophobicity on Ti-MCM-41 Silylated Materials for Olefin Epoxidations. *Appl. Catal. A Gen.* **2015**, *507*, 14–25. [\[CrossRef\]](#)
146. Marmur, A.; Della Volpe, C.; Siboni, S.; Amirfazli, A.; Drelich, J.W. Contact Angles and Wettability: Towards Common and Accurate Terminology. *Surf. Innov.* **2017**, *5*, 3–8. [\[CrossRef\]](#)
147. Young, T., III. An Essay on the Cohesion of Fluids. *Philos. Trans. R. Soc. Lond.* **1805**, *95*, 65–87. [\[CrossRef\]](#)
148. Subedi, D. Contact Angle Measurement for the Surface Characterization of Solids. *Himal. Phys.* **2011**, *2*, 1–4. [\[CrossRef\]](#)
149. Amirfazli, A.; Neumann, A.W. Status of the Three-Phase Line Tension: A Review. *Adv. Colloid Interface Sci.* **2004**, *110*, 121–141. [\[CrossRef\]](#)
150. Drelich, J. The Significance and Magnitude of the Line Tension in Three-Phase (Solid-Liquid-Fluid) Systems. *Colloids Surf. A Physicochem. Eng. Asp.* **1996**, *116*, 43–54. [\[CrossRef\]](#)
151. Schimmele, L.; Napiórkowski, M.; Dietrich, S. Conceptual Aspects of Line Tensions. *J. Chem. Phys.* **2007**, *127*, 164715. [\[CrossRef\]](#)
152. Dingle, N.M.; Harris, M.T. A Robust Algorithm for the Simultaneous Parameter Estimation of Interfacial Tension and Contact Angle from Sessile Drop Profiles. *J. Colloid Interface Sci.* **2005**, *286*, 670–680. [\[CrossRef\]](#)
153. Espinoza, D.N.; Santamarina, J.C. Water-CO₂-Mineral Systems: Interfacial Tension, Contact Angle, and Diffusion—Implications to CO₂ Geological Storage. *Water Resour. Res.* **2010**, *46*, W07537. [\[CrossRef\]](#)
154. Promraksa, A.; Chen, L.-J. Modeling Contact Angle Hysteresis of a Liquid Droplet Sitting on a Cosine Wave-like Pattern Surface. *J. Colloid Interface Sci.* **2012**, *384*, 172–181. [\[CrossRef\]](#)
155. Iglaier, S.; Pentland, C.H.; Busch, A. CO₂ Wettability of Seal and Reservoir Rocks and the Implications for Carbon Geo-Sequestration. *Water Resour. Res.* **2015**, *51*, 729–774. [\[CrossRef\]](#)
156. Schmitt, M.; Groß, K.; Grub, J.; Heib, F. Detailed Statistical Contact Angle Analyses; “Slow Moving” Drops on Inclining Silicon-Oxide Surfaces. *J. Colloid Interface Sci.* **2015**, *447*, 229–239. [\[CrossRef\]](#)
157. Arif, M.; Al-Yaseri, A.Z.; Barifcani, A.; Lebedev, M.; Iglaier, S. Impact of Pressure and Temperature on CO₂-Brine-Mica Contact Angles and CO₂-Brine Interfacial Tension: Implications for Carbon Geo-Sequestration. *J. Colloid Interface Sci.* **2016**, *462*, 208–215. [\[CrossRef\]](#)
158. AlRatrou, A.; Raeini, A.Q.; Bijeljic, B.; Blunt, M.J. Automatic Measurement of Contact Angle in Pore-Space Images. *Adv. Water Resour.* **2017**, *109*, 158–169. [\[CrossRef\]](#)

159. Scanziani, A.; Singh, K.; Blunt, M.J.; Guadagnini, A. Automatic Method for Estimation of in Situ Effective Contact Angle from X-Ray Micro Tomography Images of Two-Phase Flow in Porous Media. *J. Colloid Interface Sci.* **2017**, *496*, 51–59. [\[CrossRef\]](#)
160. Andrew, M.; Menke, H.; Blunt, M.J.; Bijeljic, B. The Imaging of Dynamic Multiphase Fluid Flow Using Synchrotron-Based X-Ray Microtomography at Reservoir Conditions. *Transp. Porous Media* **2015**, *110*, 1–24. [\[CrossRef\]](#)
161. Khishvand, M.; Alizadeh, A.H.; Oraki Kohshour, I.; Piri, M.; Prasad, R.S. In Situ Characterization of Wettability Alteration and Displacement Mechanisms Governing Recovery Enhancement Due to Low-Salinity Waterflooding. *Water Resour. Res.* **2017**, *53*, 4427–4443. [\[CrossRef\]](#)
162. Sun, C.; McClure, J.E.; Mostaghimi, P.; Herring, A.L.; Berg, S.; Armstrong, R.T. Probing Effective Wetting in Subsurface Systems. *Geophys. Res. Lett.* **2020**, *47*, e2019GL086151. [\[CrossRef\]](#)
163. Santini, M.; Guilizzoni, M.; Fest-Santini, S. X-Ray Computed Microtomography for Drop Shape Analysis and Contact Angle Measurement. *J. Colloid Interface Sci.* **2013**, *409*, 204–210. [\[CrossRef\]](#)
164. Mascini, A.; Cnudde, V.; Bultreys, T. Event-Based Contact Angle Measurements inside Porous Media Using Time-Resolved Micro-Computed Tomography. *J. Colloid Interface Sci.* **2020**, *572*, 354–363. [\[CrossRef\]](#)
165. Blunt, M.J.; Lin, Q.; Akai, T.; Bijeljic, B. A Thermodynamically Consistent Characterization of Wettability in Porous Media Using High-Resolution Imaging. *J. Colloid Interface Sci.* **2019**, *552*, 59–65. [\[CrossRef\]](#)
166. Akai, T.; Alhammedi, A.M.; Blunt, M.J.; Bijeljic, B. Modeling Oil Recovery in Mixed-Wet Rocks: Pore-Scale Comparison Between Experiment and Simulation. *Transp. Porous Media* **2019**, *127*, 393–414. [\[CrossRef\]](#)
167. Gabbott, P. *Principles and Applications of Thermal Analysis*; Wiley: Hoboken, NJ, USA, 2008; ISBN 9780470698129.
168. Ng, E.-P.; Mintova, S. Nanoporous Materials with Enhanced Hydrophilicity and High Water Sorption Capacity. *Microporous Mesoporous Mater.* **2008**, *114*, 1–26. [\[CrossRef\]](#)
169. Cavuoto, D.; Zaccheria, F.; Ravasio, N. Some Critical Insights into the Synthesis and Applications of Hydrophobic Solid Catalysts. *Catalysts* **2020**, *10*, 1337. [\[CrossRef\]](#)
170. Anderson, M.W.; Klinowski, J. Zeolites Treated with Silicon Tetrachloride Vapour. Part 1.—Preparation and Characterisation. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1986**, *82*, 1449–1469. [\[CrossRef\]](#)
171. Giaya, A.; Thompson, R.W.; Denkwicz, R., Jr. Liquid and Vapor Phase Adsorption of Chlorinated Volatile Organic Compounds on Hydrophobic Molecular Sieves. *Microporous Mesoporous Mater.* **2000**, *40*, 205–218. [\[CrossRef\]](#)
172. Mueller, R.; Kammler, H.K.; Wegner, K.; Pratsinis, S.E. OH Surface Density of SiO₂ and TiO₂ by Thermogravimetric Analysis. *Langmuir* **2003**, *19*, 160–165. [\[CrossRef\]](#)
173. Vansant, E.F.; Van Der Voort, P.; Vrancken, K.C. *Characterization and Chemical Modification of the Silica Surface*; Elsevier Science: Amsterdam, The Netherlands, 1995; ISBN 9780080528953.
174. Fripiat, J.J.; Uytterhoeven, J. Hydroxyl Content in Silica Gel “Aerosil”. *J. Phys. Chem.* **1962**, *66*, 800–805. [\[CrossRef\]](#)
175. Peri, J.B. Infrared Study of OH and NH₂ Groups on the Surface of a Dry Silica Aerogel. *J. Phys. Chem.* **1966**, *70*, 2937–2945. [\[CrossRef\]](#)
176. Hambleton, F.H.; Hockey, J.A.; Taylor, J.A.G. Investigation by Infra-Red Spectroscopic Methods of Deuterium Exchange Properties of Aerosil Silicas. *Trans. Faraday Soc.* **1966**, *62*, 801–807. [\[CrossRef\]](#)
177. Hockey, J.A.; Pethica, B.A. Surface Hydration of Silicas. *Trans. Faraday Soc.* **1961**, *57*, 2247–2262. [\[CrossRef\]](#)
178. Wei, Y.; Li, G.; Liu, J.; Yi, Y.; Guo, H. Organic Groups-Regulated High-Efficiency Catalysis of Hybrid Ti-Containing Mesoporous Silicates for Bi-Phase Interfacial Epoxidation. *Microporous Mesoporous Mater.* **2021**, *310*, 110668. [\[CrossRef\]](#)
179. Li, X.; Shi, B.; Li, M.; Mao, L. Synthesis of Highly Ordered Alkyl-Functionalized Mesoporous Silica by Co-Condensation Method and Applications in Surface Coating with Superhydrophilic/Antifogging Properties. *J. Porous Mater.* **2015**, *22*, 201–210. [\[CrossRef\]](#)
180. Bui, T.V.; Umbarila, S.J.; Wang, B.; Sooknoi, T.; Li, G.; Chen, B.; Resasco, D.E. High-Temperature Grafting Silylation for Minimizing Leaching of Acid Functionality from Hydrophobic Mesoporous Silicas Used as Catalysts in the Liquid Phase. *Langmuir* **2019**, *35*, 6838–6852. [\[CrossRef\]](#)
181. Barczak, M.; Dąbrowski, A.; Iwan, M.; Rzączyńska, Z. Mesoporous Organosilicas Functionalized by Alkyl Groups: Synthesis, Structure and Adsorption Properties. *J. Phys. Conf. Ser.* **2009**, *146*, 12002. [\[CrossRef\]](#)
182. Pires, J.; Pinto, M.; Estella, J.; Echeverría, J.C. Characterization of the Hydrophobicity of Mesoporous Silicas and Clays with Silica Pillars by Water Adsorption and DRIFT. *J. Colloid Interface Sci.* **2008**, *317*, 206–213. [\[CrossRef\]](#)
183. Olson, D.H.; Haag, W.O.; Borghard, W.S. Use of Water as a Probe of Zeolitic Properties: Interaction of Water with HZSM-5. *Microporous Mesoporous Mater.* **2000**, *35–36*, 435–446. [\[CrossRef\]](#)
184. Weitkamp, J.; Kleinschmit, P.; Kiss, A.; Berke, C.H. *The Hydrophobicity Index—A Valuable Test for Probing the Surface Properties of Zeolitic Adsorbents or Catalysts*; von Ballmoos, R., Higgins, J.B., Treacy, M.M.J.B.T., Eds.; Proceedings from the Ninth International Zeolite Conference; Butterworth-Heinemann: Oxford, UK, 1993; pp. 79–87, ISBN 978-1-4832-8383-8.
185. Rübner, K.; Balköse, D.; Robens, E. Methods of Humidity Determination Part I: Hygrometry. *J. Therm. Anal. Calorim.* **2008**, *94*, 669. [\[CrossRef\]](#)

186. Silvestre-Albero, J.; Gómez de Salazar, C.; Sepúlveda-Escribano, A.; Rodríguez-Reinoso, F. Characterization of Microporous Solids by Immersion Calorimetry. *Colloids Surf. A Physicochem. Eng. Asp.* **2001**, *187*–188, 151–165. [\[CrossRef\]](#)
187. Piraján, J.C.M. *Calorimetry: Design, Theory and Applications in Porous Solids*; IntechOpen: London, UK, 2018; ISBN 9781789234381.
188. Rule, G.S.; Hitchens, T.K. *Fundamentals of Protein NMR Spectroscopy; Focus on Structural Biology*; Springer: Dordrecht, The Netherlands, 2006; ISBN 9781402035005.
189. Koutcher, J.A.; Burt, C.T. Principles of Nuclear Magnetic Resonance. *J. Nucl. Med.* **1984**, *25*, 101–111. [\[CrossRef\]](#)
190. Vivian, A.; Fusaro, L.; Debecker, D.P.; Aprile, C. Mesoporous Methyl-Functionalized Sn-Silicates Generated by the Aerosol Process for the Sustainable Production of Ethyl Lactate. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14095–14103. [\[CrossRef\]](#)
191. Grosso-Giordano, N.A.; Schroeder, C.; Okrut, A.; Solovyov, A.; Schöttle, C.; Chassé, W.; Marinković, N.; Koller, H.; Zones, S.I.; Katz, A. Outer-Sphere Control of Catalysis on Surfaces: A Comparative Study of Ti(IV) Single-Sites Grafted on Amorphous versus Crystalline Silicates for Alkene Epoxidation. *J. Am. Chem. Soc.* **2018**, *140*, 4956–4960. [\[CrossRef\]](#)
192. Wang, L.; Sun, J.; Meng, X.; Zhang, W.; Zhang, J.; Pan, S.; Shen, Z.; Xiao, F.-S. A Significant Enhancement of Catalytic Activities in Oxidation with H₂O₂ over the TS-1 Zeolite by Adjusting the Catalyst Wettability. *Chem. Commun.* **2014**, *50*, 2012–2014. [\[CrossRef\]](#)
193. Wu, L.; Tang, Z.; Yu, Y.; Yao, X.; Liu, W.; Li, L.; Yan, B.; Liu, Y.; He, M. Facile Synthesis of a High-Performance Titanosilicate Catalyst with Controllable Defective Ti(OSi)₃OH Sites. *Chem. Commun.* **2018**, *54*, 6384–6387. [\[CrossRef\]](#)
194. Laha, S.C.; Kumar, R. Selective Epoxidation of Styrene to Styrene Oxide over TS-1 Using Urea–Hydrogen Peroxide as Oxidizing Agent. *J. Catal.* **2001**, *204*, 64–70. [\[CrossRef\]](#)
195. Wu, H.; Lin, H.; Jin, Y.; Liu, D.; Yu, Y.; Liu, Y. Efficient Allylic Oxidation of Cyclohexene Catalyzed by Ti-MCM-41 Using H₂O₂ as Oxidant. *Microporous Mesoporous Mater.* **2024**, *378*, 113263. [\[CrossRef\]](#)
196. Bonino, F.; Damin, A.; Ricchiardi, G.; Ricci, M.; Spanò, G.; D'Aloisio, R.; Zecchina, A.; Lamberti, C.; Prestipino, C.; Bordiga, S. Ti-Peroxo Species in the TS-1/H₂O₂/H₂O System. *J. Phys. Chem. B* **2004**, *108*, 3573–3583. [\[CrossRef\]](#)
197. Deng, X.; Xu, Y.; Liu, J.; Lin, D.; Zong, Z.; Yuan, J.; Li, Z.; Zhao, G.; Zhang, Y.; Liu, Y.; et al. Regulating the Coordination Mode of Ti Atoms in the Beta Zeolite Framework to Enhance the 1-Hexene Epoxidation. *Ind. Eng. Chem. Res.* **2024**, *63*, 3817–3826. [\[CrossRef\]](#)
198. Jorda, E.; Tuel, A.; Teissier, R.; Kervennal, J. Synthesis, Characterization, and Activity in the Epoxidation of Cyclohexene with Aqueous H₂O₂ of Catalysts Prepared by Reaction of TiF₄ with Silica. *J. Catal.* **1998**, *175*, 93–107. [\[CrossRef\]](#)
199. Yao, Y.; Yang, Z.; Zheng, P.; Diao, Z. Enhancing the Accessible TiO₆ Concentration and the Hydrophobicity of Hierarchical TS-1 Zeolites for Alkene Epoxidation and Oxidative Desulfurization. *Chem. Eng. J.* **2023**, *475*, 146053. [\[CrossRef\]](#)
200. Cordon, M.J.; Harris, J.W.; Vega-Vila, J.C.; Bates, J.S.; Kaur, S.; Gupta, M.; Witzke, M.E.; Wegener, E.C.; Miller, J.T.; Flaherty, D.W.; et al. Dominant Role of Entropy in Stabilizing Sugar Isomerization Transition States within Hydrophobic Zeolite Pores. *J. Am. Chem. Soc.* **2018**, *140*, 14244–14266. [\[CrossRef\]](#)
201. Gounder, R.; Davis, M.E. Monosaccharide and Disaccharide Isomerization over Lewis Acid Sites in Hydrophobic and Hydrophilic Molecular Sieves. *J. Catal.* **2013**, *308*, 176–188. [\[CrossRef\]](#)
202. Inagaki, S.; Takeyama, M.; Asanuma, K.; Yokose, Y.; Zhang, S.; Okuda, T.; Nakamura, K.; Nishi, Y.; Kubota, Y. Preparation of Hydrophobic Ti-Beta Catalyst Derived from Al-Rich Zeolite Beta Synthesized without Using Organic Structure-Directing Agent and Its Enhanced Catalytic Performance for Phenol Oxidation. *Microporous Mesoporous Mater.* **2022**, *346*, 112323. [\[CrossRef\]](#)
203. Yang, Z.; Yu, Q.; Wang, H.; Ge, Q.; Zhu, X. Ketoneization of Propionic Acid over TS-1 and Ti-Beta Zeolites: Mechanism and Effects of Topology and Hydrophobicity. *J. Catal.* **2024**, *429*, 115247. [\[CrossRef\]](#)
204. Di Iorio, J.R.; Johnson, B.A.; Román-Leshkov, Y. Ordered Hydrogen-Bonded Alcohol Networks Confined in Lewis Acid Zeolites Accelerate Transfer Hydrogenation Turnover Rates. *J. Am. Chem. Soc.* **2020**, *142*, 19379–19392. [\[CrossRef\]](#)
205. Crisci, A.J.; Tucker, M.H.; Lee, M.-Y.; Jang, S.G.; Dumesic, J.A.; Scott, S.L. Acid-Functionalized SBA-15-Type Silica Catalysts for Carbohydrate Dehydration. *ACS Catal.* **2011**, *1*, 719–728. [\[CrossRef\]](#)
206. Shi, W.; Cao, L.; Zhang, H.; Zhou, X.; An, B.; Lin, Z.; Dai, R.; Li, J.; Wang, C.; Lin, W. Surface Modification of Two-Dimensional Metal–Organic Layers Creates Biomimetic Catalytic Microenvironments for Selective Oxidation. *Angew. Chemie Int. Ed.* **2017**, *56*, 9704–9709. [\[CrossRef\]](#)
207. Shi, K.; Ren, Z.; Meng, Z.; Feng, X. Hydrophilic or Hydrophobic? Optimizing the Catalyst Microenvironment for Gas-Involving Electrocatalysis. *ChemCatChem* **2024**, *16*, e202301308. [\[CrossRef\]](#)
208. Zhang, C.; Xu, Z.; Han, N.; Tian, Y.; Kallio, T.; Yu, C.; Jiang, L. Superaerophilic/Superaerophobic Cooperative Electrode for Efficient Hydrogen Evolution Reaction via Enhanced Mass Transfer. *Sci. Adv.* **2026**, *9*, eadd6978. [\[CrossRef\]](#)
209. Kim, C.; Bui, J.C.; Luo, X.; Cooper, J.K.; Kusoglu, A.; Weber, A.Z.; Bell, A.T. Tailored Catalyst Microenvironments for CO₂ Electroreduction to Multicarbon Products on Copper Using Bilayer Ionomer Coatings. *Nat. Energy* **2021**, *6*, 1026–1034. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.