

PAPER

Role of Lewis and Brønsted acid sites in resorcinol *tert*-butylation over heteropolyacid-based catalysts†

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The role of Brønsted and Lewis acid sites at the surface of heteropolyacid-based catalysts was studied in resorcinol alkylation with methyl-*tert*-butylether. Three sets of catalysts, SiO₂/HPW, TiO₂/HPW and ZrO₂/HPW (where HPW stands for phosphotungstic acid hydrate), synthesized by the hydrolytic sol-gel method were investigated. The surface total acidity was characterized by ammonia chemisorption and thermo-programmed desorption. In addition, infrared analysis of adsorbed pyridine was performed to distinguish between Brønsted and Lewis sites. The resorcinol conversion was correlated to the fraction of Brønsted sites present at the catalyst surface based on the total acidity. The results pointed out the importance of considering both Brønsted and Lewis sites as active players in the mechanism of resorcinol alkylation: Lewis sites have the role of adsorbing the substrate close to the *tert*-butyl cation, which is formed on Brønsted sites. Resorcinol conversion can be increased to a maximum if the right Brønsted/Lewis ratio is attained at the catalyst surface.

1. Introduction

Alkylation of aromatics is an essential reaction in organic chemistry due to its extensive application in the fine chemical, petrochemical, perfume, dye, pesticide and pharmaceutical industries.¹ Friedel–Crafts butylation of resorcinol with methyl-*tert*-butyl ether (MTBE) to mono-*tert*-butylated products is most significant due to its involvement in the synthesis of antioxidants, polymer stabilizers, therapeutics, and organic synthetic applications.² Alkylation of resorcinol with MTBE gives a mixture of alkylated benzene diols.³ Being thermodynamically favoured (monoalkylated readily undergoes a consecutive alkylation), dialkylated 4,6-di-*tert*-butyl resorcinol (4,6-DTBR) is usually the major product. However, 4-*tert*-butylresorcinol (4-TBR) is of particular interest as an antioxidant in food preservatives and in treatment of skin diseases. Therefore, selective synthesis of 4-TBR at a high conversion of resorcinol is a difficult and challenging task.⁴

Traditionally, homogeneous catalysts (AlCl₃, FeCl₃, H₂SO₄, H₃PO₄) catalysed the reaction. The limitations and

unsafe nature of these conventional acid catalysts recommend the use of heterogeneous catalysts.⁵ There are a few solid acid catalysts that have been studied for the reaction such as montmorillonite clay,⁶ zeolites,^{7,8} ZrO₂ supported phosphotungstic acid,⁹ dodecatungstophosphoric acid supported on K-10,³ sulphated zirconia,² and heteropolyacid and H₂SO₄ supported mesoporous materials.^{4,10} With these emerging heterogeneous catalysts in Friedel–Crafts alkylation of resorcinol, a subject of study concerns the role of Brønsted and Lewis acid sites present at the solid catalyst surface in the alkylation mechanism. In this framework, the role of catalyst acidic sites appears to be crucial for the complete understanding of the reaction mechanism. Several authors elucidated the role of Brønsted (B) and Lewis (L) sites in resorcinol butylation.^{3,7} Great attention was directed toward the characterization of catalyst surface acidity and a synergistic effect between Lewis and Brønsted sites on resorcinol conversion and selectivity for 4-TBR and 4,6-DTBR. Yet, B sites were identified to be responsible for the MTBE conversion to the *tert*-butyl cation, some aspects concerning the role of Lewis sites in the resorcinol conversion are still unclear; precisely it is still difficult to determine whether the Lewis sites have an active role in the resorcinol conversion mechanism.

In this context, direct incorporation of phosphotungstic acid hydrate (HPW) in oxide matrices by the hydrolytic sol-gel method was the strategy we selected as it allows:

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• Introducing strong B acid sites (provided by HPW) in an oxide matrix – having L acid sites.

• Tuning the acido-basic properties of the support to evaluate its impact on the catalytic activity.

• Homogeneously dispersing the HPW inside the support matrix. This is crucial to assess the presence of a synergistic effect between L and B sites.

• Immobilizing the HPW in the oxide matrix to prevent its leaching in the liquid phase.

• Removing the catalyst from the medium by simple filtration at the end of the reaction and thus promote catalyst recycling.

To do so, three sets of catalysts, SiO₂/HPW, TiO₂/HPW and ZrO₂/HPW were synthesized at different HPW loadings to reach different ratios of B/L sites on the surface. The supports were chosen for their different acidic, structural and textural properties. These oxides exhibit different acidic and textural properties: SiO₂ possesses strong acid sites, but these are so few that globally the material can be considered neutral, while TiO₂ and ZrO₂ have an amphoteric character and present more Lewis sites.

The aim was to evaluate the impact of the physico-chemical properties of the support on HPW immobilization and on the final catalyst reactivity. The catalysts were characterized using inductively coupled plasma (ICP-AES), infrared (FT-IR) and Raman spectroscopies, thermogravimetric analysis (TGA), X-ray diffraction (XRD), and nitrogen physisorption. Attention was particularly devoted to the characterization of surface acidity, which was carried out by infrared analysis of adsorbed pyridine and by ammonia chemisorption and thermo-programmed desorption. The catalytic activity in terms of resorcinol conversion was linked to the catalyst surface acidity and the impact of the B/L ratio on resorcinol conversion was investigated.

2. Experimental

Chemicals

Ethanol (Normapur, absolute), ethylene glycol (Fluka, ≥99.5%), hydrochloric acid (Sigma Aldrich, 37% hereafter denoted as HCl), tetraethyl orthosilicate (Janssen Chimica, 98%, hereafter denoted as TEOS), titanium tetraisopropoxide (Janssen Chimica, 98%, hereafter denoted as TTIP), zirconium(IV) propoxide solution, 70 wt% in 1-propanol (Sigma Aldrich, hereafter denoted as ZP), resorcinol (Sigma Aldrich, 99%), methyl-*tert*-butylether (Sigma Aldrich, ≥99%, hereafter denoted as MTBE), 1,3-di-nitrobenzene (Sigma Aldrich, 97%), phosphotungstic acid hydrate (Sigma Aldrich, reagent grade, H₃PW₁₂O₄₀, hereafter denoted as HPW), 4,6-di-*tert*-butylresorcinol (Sigma Aldrich, HPLC grade, hereafter denoted as 46DTBR), zirconium(IV) oxide, <5 micron, 99% monoclinic (Sigma Aldrich, hereafter denoted as *m*-ZrO₂), tungsten(IV) oxide, powder, 99.995% trace metal basis (Sigma Aldrich, hereafter denoted as WO₃) were purchased and used as received.

Catalysts synthesis

Synthesis of SiO₂/HPW catalysts. A mixture composed of 10 mL of ethanol, 7.5 mL of ethylene glycol and 6 mL of distilled water was poured into a 100 mL round bottom flask and purged with a continuous nitrogen flux under magnetic stirring. 10 mL of TEOS was then added dropwise under continuous agitation. A quantity of solid heteropolyacid HPW, varied between 0.505 g and 5.530 g, was dissolved in the mixture, which was heated up to 80 °C and kept under continuous stirring and under a nitrogen atmosphere for 1 hour. Then, 5 mL of 37% w/w of HCl solution was added to catalyse the gelation (the gelation does not occur if HCl is not added). The gelation was completed, and the gel was recovered in a crystallizer and dried overnight under the hood. The gel was dried in an oven, under vacuum (20 000 Pa), for 3 hours at 140 °C. After that, the gel was calcined for 6 hours at 500 °C at a heating rate of 10 °C min⁻¹. The catalyst was recovered, slightly ground (particles >100 µm) and washed in ethanol for approximately 12 h in a Soxhlet extractor. The powder was finally dried in a vacuum at 20 000 Pa and 50 °C for 1 hour, ground again and sieved until particles with a size lower than 100 µm were obtained.

Synthesis of TiO₂/HPW catalysts. A mixture composed of 20.4 mL of ethanol and 20.8 mL of TTIP was poured into a 100 mL round bottom flask and purged with a continuous flux of nitrogen under magnetic stirring at room temperature. A quantity of HPW, varied between 0.588 and 4.239 g, was then dissolved in a second mixture composed of 20.4 mL of ethanol, 1.3 mL of distilled water and 0.6 mL of HCl, which was then added dropwise under continuous agitation. The sol was poured into a crystallizer and dried under the hood overnight. During the night, the sol turned into a gel. Then, the gel was dried in an oven under vacuum (20 000 Pa) for 3 hours at 140 °C. After that, the gel was calcined for 6 hours at 500 °C at a heating rate of 10 °C min⁻¹. The catalyst was recovered, slightly ground (particles >100 µm) and washed in ethanol for approximately 12 h in a Soxhlet extractor. The powder was finally dried in a vacuum at 20 000 Pa and 50 °C for 1 hour, ground again and sieved to recover the fraction <100 µm diameter.

Synthesis of ZrO₂/HPW catalysts. A mixture composed of 50 mL of ethanol and 25 mL zirconium propoxide was poured into a 500 mL round bottom flask and kept under magnetic stirring at room temperature for 30 minutes. A quantity of HPW, varied between 0.575 and 2.303 g, was added and the mixture was left under continuous agitation for 1 h prior to dropwise addition of 50 mL of water. The resulting white mixture was kept under agitation for 30 minutes prior to pouring into a crystallizer and dried under the hood overnight. After that, the gel was calcined for 6 hours at 500 °C at a heating rate of 2 °C min⁻¹. The catalyst was recovered, slightly ground (particles >100 µm) and washed in ethanol for approximately 12 h in a Soxhlet extractor. The powder was finally dried in a vacuum at 20 000 Pa and 50 °C for 1 hour, ground again and sieved to recover the fraction <100 µm diameter.

Catalyst characterization

HPW content assessment. The content of Si, Ti, P and W was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation. The amount (wt%) of immobilized HPW was calculated by using the formula $\text{H}_3\text{PW}_{12}\text{O}_{40}$. For the ZrO_2/HPW catalysts, the UV-vis spectra of ethanol after Soxhlet extraction were collected on a Beckman Coulter DU800 spectrometer in absorption mode between 200 nm and 800 nm at a speed of 1200 nm min^{-1} . A blank was collected analysing fresh ethanol in a quartz cuvette. Calibration was performed by analysing solutions of HPW in ethanol at known concentrations. The mass of heteropolyacid in the catalysts was calculated subtracting the amount of HPW recovered after Soxhlet extraction from the mass of HPW employed during the synthesis.

Catalyst bulk. FT-IR spectra were recorded in transmission mode using a spectrometer IFS55 Equinox (Bruker) equipped with a DTGS detector. The spectra were recorded with 100 scans between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} . The samples were analysed after dilution in potassium bromide (KBr) by a weight factor of 10. Raman spectra were collected using a RAMAN Microscope DRX, Thermo-Scientific, equipped with a 780 nm laser focused on the samples using an optical microscope ($10\times$ magnification lens). The analysis parameters were set as follows: exposure time 30 s, laser power 10 mW, aperture $50 \mu\text{m}$ in pinhole mode. The Raman shifts were scanned in the range $400\text{--}1800 \text{ cm}^{-1}$ with a resolution range of $3.0\text{--}4.1 \text{ cm}^{-1}$.

Catalyst surface acidity. Acidity measurements of the catalyst surface were conducted by pyridine adsorption and temperature programmed desorption as follows. The catalysts were pressed to obtain a wafer. The wafer was weighed and then placed in a sample holder inside a Pyrex cell specially designed for the controlled heating of the sample under vacuum and equipped with an optical NaCl window. The sample holder was movable, and it allowed the sample placement in the infrared beam for the recording of spectra or in the furnace for thermal treatment. In a typical measurement, the sample was heated at 300°C under vacuum (between 10^{-4} and 10^{-5} Pa) for 3 h to desorb physisorbed molecules from the surface. After cooling under vacuum, 1000 Pa of pyridine was introduced at room temperature into the cell and adsorption was allowed for 30 minutes. The sample was then outgassed at 10^{-5} Pa in five steps: at room temperature and at 100°C , 150°C , 200°C , and 250°C . For each desorption step, once the value of 10^{-5} Pa was reached, the sample was kept under vacuum for 1 h. FT-IR spectra were taken in transmission mode before and after pyridine adsorption and after each desorption step using a spectrometer IFS55 Equinox (Bruker) equipped with a DTGS detector. The spectra were recorded with 100 scans between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} . For the analysis of TiO_2/HPW catalysts the protocol was slightly modified: the wafers were outgassed at 100°C for 1 hour and

pyridine was desorbed in two steps at 50 and 100°C . The difference in the protocol with respect to SiO_2/HPW catalysts was due to the darkening and embrittlement of the catalyst wafer upon exposure to higher temperatures, which made the analysis impossible. Percentages of Brønsted and Lewis sites were calculated using the intensity of B and L signals (Table S1†) obtained from the spectra after pyridine desorption at 100°C . This choice was made to take only chemisorbed pyridine into account. The details of the calculation are reported in section 1 of the ESI.†

The total surface acidity was characterized by ammonia chemisorption and temperature programmed desorption ($\text{NH}_3\text{-TPD}$). A bed of about 1 cm of solid was placed between two glass wool layers in a quartz tubular reactor. The sample underwent thermal pre-treatment at 300°C for 1 hour under an argon flow ($50 \text{ cm}^3 \text{ min}^{-1}$). After cooling at 100°C a flow of helium containing 5% ammonia ($20 \text{ cm}^3 \text{ min}^{-1}$) and mixed with a flow of argon ($30 \text{ cm}^3 \text{ min}^{-1}$) was introduced into the reactor for 35 minutes. The temperature was then raised at a rate of 5°C min^{-1} until attaining 600°C under a flow of argon ($50 \text{ cm}^3 \text{ min}^{-1}$). The effluent gas was analysed using a Hiden Analytical QGA mass spectrometer equipped with a quadrupole detector. The amount of acid sites in terms of $\mu\text{mol m}^{-2}$ was obtained integrating the area under the curve of ammonia chemisorption *versus* time and normalized by the catalyst surface area (obtained using the Brunauer–Emmett–Teller method (BET) measurements) and by the catalyst weight. The calculation is reported in section 1 of the ESI.†

Catalyst structure and texture. The catalyst structure was investigated from the X-ray diffractograms (XRD) collected using a Siemens D5000 diffractometer equipped with a 1.6 kW Cu source working at 40 kV–40 mA and a scintillation detector. The 2theta range scanned was between 5 and 80° with at a rate of $0.01^\circ \text{ s}^{-1}$.

Specific surface area, pore volume and pore size distributions were obtained through nitrogen adsorption-desorption experiments performed using a Micromeritics Tristar 3000. Before the analysis, the samples were degassed overnight under vacuum (6 Pa) at 150°C . The measurements were performed at -196°C and relative pressures in the range of $0.01\text{--}1.00$ (p/p_0). The specific surface area was calculated from the adsorption isotherm in the p/p_0 range of $0.05\text{--}0.30$ using the Brunauer–Emmett–Teller method (BET) and denoted afterwards as S_{BET} . The pore size distribution, mean pore diameter and pore volume were calculated by the Barrett–Joyner–Halenda method (BJH) using the data from the desorption isotherm.

Catalytic test

Reaction standard test. Friedel–Crafts alkylation of resorcinol with methyl-*tert*-butylether (MTBE) was performed using 7 g of resorcinol dissolved in 45 mL of MTBE in a 100 mL three neck round bottom flask surmounted by a refrigerator. The reactor was placed in an oil bath under

magnetic stirring (1500 rpm) and heated at 60 °C under autogenic pressure. Then 0.7 g of catalyst was added. 1,3-Dinitrobenzene was used as an internal standard. All catalytic studies were compared to a blank test where the reaction was carried out under the same conditions described above but without a catalyst. All the supports (0.7 g SiO₂, 0.7 g TiO₂ or 0.7 g of ZrO₂) were tested as well.

Product identification. The change in the composition of the reaction medium was followed using a gas chromatograph VARIAN 3800 equipped with a capillary column SGE HT5 (12 m × 0.53 mm, i.d. 0.15 µm).[‡] The temperature program was composed of two steps: a first segment from 70 °C to 85 °C, 2 °C min⁻¹ and a second segment from 85 °C to 180 °C 2 °C min⁻¹. The injector and detector temperatures were 320 and 360 °C, respectively. Helium was used as carrier gas at a flow rate of 20 mL min⁻¹. 1 µL of sample was injected into the GC system, with the injector in split mode 50. The resorcinol conversion was calculated integrating the chromatographic peaks and using the formula:

$$X_{\text{resorcinol}} = \frac{A_{\text{resorcinol}_{t_0}} - A_{\text{resorcinol}_{t_1}}}{A_{\text{resorcinol}_{t_0}}}$$

The reaction selectivity for the product *i* was calculated for each product using the formula:

$$S_i = \frac{C_i}{\sum_1^n C_i}$$

where *C_i* is the concentration of the product *i* and the denominator is the sum of the concentration of all the products present in the reaction mixture. For the unidentified products (hereafter denoted as “other products”) the calculations were made assuming a response factor equal to one.

After the catalytic test, the catalyst was removed by filtration and the filtrate was evaporated to remove the solvent and deposited onto Celite® 545 (VWR) and placed at the top of a column of preparative flash chromatography. Flash chromatography was performed using a petroleum ether/ethyl acetate solvent system and on normal phase silica gel (ROCC 60F, 40 63 Dm). The eluent was analysed by thin layer chromatography (TLC) analysis performed on commercial aluminium plates bearing a 0.25 mm layer of Merck silica gel 60F 254. The eluent was then eliminated by evaporation in a rotary evaporator and the compounds in the solid state were recovered to be further analysed by NMR and HR-MS.

The alkylated products recovered by flash chromatography in the solid state were diluted in deuterated chloroform (CDCl₃) and then identified and characterized by ¹H and ¹³C

[‡] The experimental error was limited at 10% of the value when the experiments were performed with a VARIAN 3800 gas chromatograph, while it was limited at 3% when the experiments were performed with a Shimadzu GC-2010.

NMR. Spectra were recorded on a Bruker 300 spectrometer at 300 MHz. ¹H and ¹³C NMR chemical shifts are reported relative to tetramethylsilane (TMS), (0 ppm) or CDCl₃ (7.26 ppm for ¹H, 77.0 ppm for ¹³C).

For further confirmation of the structure of the alkylated products, high-resolution mass spectra were obtained using a Thermo Scientific Q Exactive Reactive Electron spray. The analysis was run in negative polarity. The component identification was conducted using the Xcalibur software, with accurate mass reported for the molecular ion or suitable fragment ions. The mass balance is reported in section 1 of the ESI.[†]

3. Results

Heteropolyacid content assessment

The catalysts SiO₂/HPW, TiO₂/HPW and ZrO₂/HPW were analysed by ICP-AES to determine the effective heteropolyacid content (Table S2[†]). The catalysts were named SiO₂/HPW_{xx} (or TiO₂/HPW_{xx}), with *xx* being the effective HPW weight percentage measured in the samples. The HPW wt% in the silica samples was measured to be 8, 17, 25, 31 and 51%, while the HPW wt% in the titania samples was 7, 20, 24 and 29%. The HPW content in the catalysts ZrO₂/HPW was calculated indirectly using UV-vis data (Table S2[†]). The catalysts were named ZrO₂/HPW_{xx}, with *xx* being the effective HPW content measured in the samples. The HPW wt% in the zirconia samples was found to be 7, 20, 24 and 29%. As a general trend, the HPW wt% increased with the increasing HPW mass used during the synthesis.

Spectroscopic analysis of the solids

Infrared spectra were collected to investigate the HPW interaction with the oxide matrices. In the infrared spectra of SiO₂/HPW the band associated with the tungsten-terminal oxygen bond vibration (W=O_d) was visible and its position was found to shift toward lower wavenumbers (between 955 and 960 cm⁻¹) with respect to the bulk HPW in the solid state which is usually found at 981 cm⁻¹ (Fig. S1a[†]).

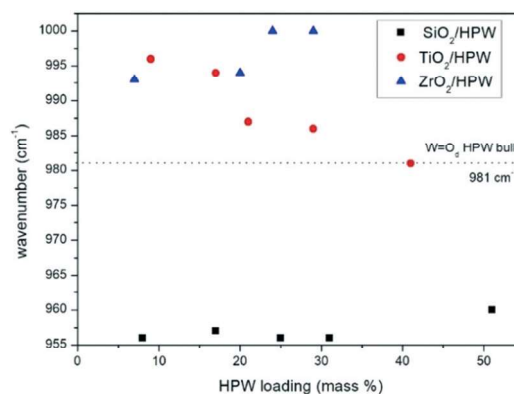


Fig. 1 W=O_d band position observed for the HPW immobilized onto silica, titania and zirconia as a function of HPW effective loading.

The TiO_2/HPW spectra evidenced the presence of three peaks assigned to the stretching of $\text{W}-\text{O}_\text{c}-\text{W}$ at 888 cm^{-1} , $\text{W}=\text{O}_\text{d}$ at around 981 cm^{-1} and $\text{P}=\text{O}_\text{a}$ at 1079 cm^{-1} (Fig. S1b†). Even though the intensity was very weak, a shift of the $\text{W}=\text{O}_\text{d}$ band was observed from its usual position (981 cm^{-1}) up to 995 cm^{-1} (Fig. 1). In the case of ZrO_2/HPW samples, the $\text{W}=\text{O}_\text{d}$ band was present in all the spectra and it was found to shift toward higher wavenumbers ($993\text{--}1000\text{ cm}^{-1}$). More precisely, the $\text{W}=\text{O}_\text{d}$ band shift increased with the increase of HPW content for the ZrO_2/HPW catalysts, while it decreased for the TiO_2/HPW catalysts (Fig. S1b and c†). In the SiO_2/HPW samples the position of the $\text{W}=\text{O}_\text{d}$ band appeared to be almost independent of the HPW wt% (Fig. 1). No significant shift (with respect to the bulk HPW) in the position of the bands corresponding to other HPW bond vibrations was measured, whatever the HPW content or the nature of the support.

Raman spectra were recorded to assess the stability of the immobilized HPW inside the oxide matrices during the calcination at $500\text{ }^\circ\text{C}$ and its presence in the samples after this step. The Raman spectra taken on HPW immobilized onto silica and titania are shown in Fig. S2† together with a comparison with the spectra of HPW and WO_3 . Weak bands assigned to HPW symmetric $\text{W}=\text{O}_\text{d}$ stretching at 1012 cm^{-1} and antisymmetric stretching at 996 cm^{-1} were detected in the spectra of SiO_2/HPW 25, 31 and 51 (broad bands).¹¹ In the spectra of SiO_2/HPW 8 and 17 no signal assignable to HPW was detected. Two bands due to the presence of tungsten oxide (WO_3) were detected in the spectra of SiO_2/HPW 51 (antisymmetric $\text{O}-\text{W}-\text{O}$ stretching at 717 cm^{-1} , symmetric $\text{O}-\text{W}-\text{O}$ stretching at 808 cm^{-1}). WO_3 is a product of HPW degradation due to exposure at high temperature.¹² In the other spectra of the series, no such sign of degradation was detected allowing assumption of HPW stability during calcination and integrity after calcination. The $\text{W}=\text{O}_\text{d}$ antisymmetric stretching signal was found in all the spectra of the TiO_2/HPW catalysts at 996 cm^{-1} and increased proportionally in intensity with the HPW content. HPW was found to be stable when immobilized onto titania even at high loading, since no band assignable to WO_3 was detected. The presence of the $\text{W}=\text{O}_\text{d}$ antisymmetric stretching signal alone in the Raman spectra of the TiO_2/HPW catalyst could be due to reduced symmetry of the WO_6 species caused by stronger interaction of HPW with titania than with silica. SiO_2/HPW 25, 31 and 51 presented both components (symmetric and antisymmetric), because the presence of undeformed octahedra is unlikely when HPW is in contact with a support.¹³ Collection of Raman spectra of ZrO_2/HPW was impossible due to too high sample fluorescence under any conditions operated.

Catalyst structure

The catalyst structure was investigated by X-ray diffraction. The diffraction pattern of solid pure HPW was compared to that of SiO_2/HPW catalysts (Fig. S3a†). Silica was also

reported as a reference and, being an amorphous material, did not show any peak in its pattern. No HPW reflection was observed when it was immobilized inside the silica matrix up to 31 wt%. Conversely, the diffraction pattern of the sample SiO_2/HPW 51 presented some peaks assigned to WO_3 (at 20 , 23.6 , 24.4 , 26.9 , 29.1 , 34.1 and 40.0°), confirming the previous results obtained by Raman spectroscopy (Fig. S3b†). Titania formed by sol-gel synthesis and calcined at $500\text{ }^\circ\text{C}$ showed an anatase crystalline structure (peaks 25.3 , 36.9 , 37.7 , 38.5 , 47.9 , 53.7 , 54.9 , 62.6 and 74.9°) (Fig. S3c†). No peak assignable to HPW or WO_3 could be detected in any pattern of the TiO_2/HPW samples. Using the Scherrer equation on the (101) peak at 25.2° (ref. 14) the size of the anatase crystals was found to decrease with the increasing HPW loading (Table S3†). The zirconia support obtained by sol-gel was a mixture of two phases: the monoclinic (peaks at 24.2° , 28.2° , 31.4° , 34.3°) and the tetragonal (peaks at 30.2° , 35.2° , 50.6° and 60.2°).¹⁵ Diffraction patterns of ZrO_2/HPW showed no peak assignable to HPW (Fig. S3d†). The HPW incorporation in the zirconia matrix promoted the phase transition from monoclinic to tetragonal during the calcination. The size of the zirconia crystals was calculated as well (Table S3†).

Catalyst texture

The three sets of samples presented very different textural features. For the SiO_2/HPW samples, capillary condensation was almost absent (except for the sample with 17 wt% HPW) as a very small hysteresis loop was observed (Fig. S4a†). The adsorption isotherms corresponded to a composite type I-type IV and may be classified as being on the border between the microporous and mesoporous texture.¹⁶ The surface area and pore volume of the decreased with the increasing HPW loading. Simultaneously, the pore diameter remained constant in the range 2.4 to 2.9 nm , except for the last sample at 51% HPW loading for which the pore diameter increased to 3.8 nm (Table S4†). Concerning the TiO_2/HPW series, the anatase crystallites form aggregates during the calcination step. Therefore, what was measured by nitrogen physisorption and is hereafter called ‘pore diameter’ is that of the interparticle void between the crystallite aggregates (Fig. S4b†). The surface area of TiO_2/HPW samples increased as the HPW loading increased and the pore diameter increased (Table S4†). This is well in line with the observed reduction in the size of anatase crystallites (as determined from XRD): the smaller the crystallites, the higher the surface area, the smaller the pore diameter. The pore volume was found to remain almost constant, instead. ZrO_2/HPW catalysts presented a non-porous texture as displaying isotherms without hysteresis (Fig. S4c†) and correspondingly very low surface areas (Table S4†). The structural and textural characteristics of the supports are summarized in Table 1.

Table 1 Structural and textural characteristics of the supports

Support	Structure	Surface area, BET (m ² g ⁻¹)	Pore volume, BJH (cm ³ g ⁻¹)	Pore diameter, BJH (nm)
SiO ₂	Amorphous	901	0.31	2.6
TiO ₂	Crystalline (monophasic, anatase)	15	0.05	6.3
ZrO ₂	Crystalline (biphasic, tetragonal + orthorhombic)	5	—	—

Catalyst surface acidity

The acidity measurements of the catalysts showed the total absence of acid sites for ZrO₂/HPW thus, nothing more is reported about this in the following. Infrared analysis of adsorbed pyridine allowed the identification of Brønsted (B) and Lewis (L) sites at the surface of the other catalysts.¹⁷ The spectra collected over SiO₂/HPW and TiO₂/HPW catalysts after pyridine adsorption and desorption at 100 °C were compared to the spectra obtained on the supports (SiO₂ and TiO₂) (Fig. S5a and c†). A first pair of bands at 1613 and 1450 cm⁻¹ was due to C–C–N stretching of pyridine adsorbed onto Lewis acid sites (L). A second pair of bands at 1637 and 1540 cm⁻¹ is due to the vibrations of pyridine bound onto Brønsted sites (B). Another intense band in the spectrum at 1490 cm⁻¹ is due to pyridine bonded to weak B sites (WB).^{18,19} Finally, a weak band at 1600 cm⁻¹ is due to interaction between pyridine and weak Lewis sites (WL) (Table S5†). Since the absorption bands in the region around 1600 cm⁻¹ were not well resolved, the band at 1450 cm⁻¹ for L sites and the band at 1540 cm⁻¹ for B sites were considered for further calculations. The spectra of both silica and titania showed the prevalence of only Lewis acid sites with the L band at 1450 cm⁻¹. Heteropolyacid insertion in the oxide matrices introduced B sites at the catalyst surface as is visible from the appearance of the corresponding bands.

Pyridine was desorbed from the catalyst surfaces at different temperatures to evaluate the acid site strength through the variation of the respective band intensities. The band intensity evolution of pyridine adsorbed onto SiO₂/HPW17 was reported *versus* the desorption temperature (Fig. S6a–d). The bands at 1540, 1613 and 1638 cm⁻¹ were found first to increase and then to decrease with the increasing desorption temperature, while the intensity of the bands at 1450 and 1490 cm⁻¹ remained stable up to 150 °C before decreasing at higher desorption temperatures. The band intensity trend was found to be the same as that on the other SiO₂/HPW catalysts (Fig. S13†). The band intensity evolution of pyridine adsorbed onto TiO₂/HPW17 was reported *versus* the desorption temperature (Fig. S5d†). In this case, all the bands were found to decrease with the increasing desorption temperature. The same behaviour was observed on the other TiO₂/HPW catalysts (Fig. S7†).

The band intensity assigned to pyridine adsorbed onto strong B sites at 1540 cm⁻¹ and L sites at 1450 cm⁻¹ was more specifically followed during the thermo-programmed desorption for all the catalysts. SiO₂/HPW showed quite strong B sites, as can be seen from the stability of the 1540 cm⁻¹ band intensity during pyridine desorption. On the other

hand, the L sites were found to be weaker, as pyridine started to desorb in consistent quantity from 200 °C (Fig. S8a†). Conversely, TiO₂/HPW catalysts showed both weak B and L sites, as pyridine started to desorb at 50 °C and left the catalyst surface much faster than for the previous samples (SiO₂/HPW) (Fig. S8b†). The relative percentage of B and L sites and (B/L ratio) was calculated for the SiO₂/HPW and TiO₂/HPW catalysts using the intensity of B and L signals (Table 2). It is clear from the calculated B/L ratio that oxides contain only weak Lewis acid sites. With increased loading of HPW, the B/L ratio increased due to generation of new Brønsted acid sites.

The surface density of strong Brønsted acid sites calculated using the data obtained from pyridine adsorption and normalized by the specific surface area (S_{BET}) was correlated with the HPW loading (Fig. 2). The surface density of B sites generally increased with the HPW content. Two distinct tendencies can be seen in the two catalyst groups: B site surface density increases much faster with the heteropolyacid wt% when HPW is immobilized onto silica than onto titania.

4. Discussion

Heteropolyacid immobilization and stability inside the oxide matrices

Calcination at 500 °C was conducted first to remove all traces of solvent and ethylene glycol, which was used as a structure directing agent to promote porosity.²⁰ Calcination also confers mechanical strength to the final material. During the calcination, condensation reactions proceed to completion, the excess water is eliminated and the M–O–M network (M = Si, Ti, or Zr) is formed and reaches stability. The washing step in the Soxhlet extractor was crucial to remove the HPW

Table 2 Percentage of Brønsted and Lewis acid sites based on the total acidity (B + L) and calculated B/L ratio

Catalyst	B sites%	L sites%	B/L sites
SiO ₂	0	100	
SiO ₂ /HPW8	32	68	0.47
SiO ₂ /HPW17	13	87	0.15
SiO ₂ /HPW25	28	72	0.38
SiO ₂ /HPW31	34	66	0.51
SiO ₂ /HPW51	36	64	0.56
TiO ₂	0	100	
TiO ₂ /HPW9	7	93	0.07
TiO ₂ /HPW17	9	91	0.09
TiO ₂ /HPW21	16	84	0.19
TiO ₂ /HPW29	27	73	0.36
TiO ₂ /HPW41	37	63	0.58

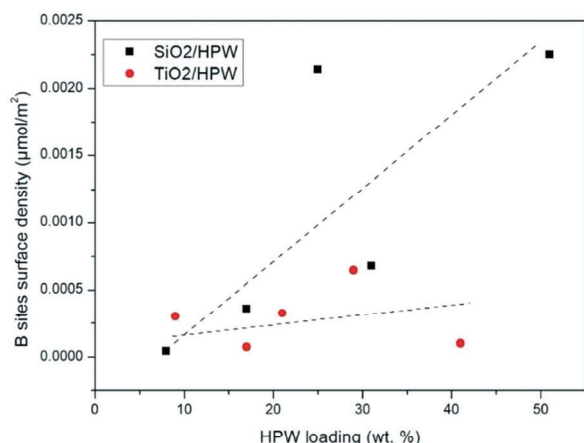


Fig. 2 Surface density of B strong acid sites plotted against HPW loading.

units which did not establish a strong interaction with the catalyst surface. If not removed, these HPW units would leach into the liquid reaction medium and eventually perform homogeneous catalysis. Soxhlet extraction was chosen because it allows continuous contact between the catalyst and fresh solvent, thus overcoming the limitations established by solvent saturation with HPW.

The presence of HPW after catalyst calcination and extraction in ethanol was confirmed by elemental analysis for the HPW immobilized onto SiO₂ and TiO₂. The W/P molar ratio was found to be close to the value of 12:1 (Table S6†), which is the same as found in the Keggin structure, giving already a good index of HPW preservation or at least excluding total HPW decomposition upon exposure to high temperature. However, this is not enough to draw firm conclusions about the HPW state in the solids prepared. Raman spectroscopy and XRD are more appropriate techniques to investigate the HPW stability and structural preservation upon immobilization.

Concerning the ZrO₂/HPW catalysts, the efficiency of HPW encapsulation was investigated by UV-vis spectroscopy. The HPW losses, measured by analysing ethanol after Soxhlet extraction, were 3% of the initial HPW employed during the synthesis for the catalyst ZrO₂/HPW20, but around 23% for the other samples. HPW losses could be due to the very low catalyst surface area, which did not allow enough contact between the Keggin anions and the forming zirconia network. The high immobilization efficiency in the sample ZrO₂/HPW20 could be due to an optimal pH value being reached during the synthesis. For the zirconia to be charged positively, the pH in the reaction medium should be lower than 4.²¹ The quantity of HPW employed during the synthesis of ZrO₂/HPW7 may have been too low, causing the charge on the zirconia network to be not positive enough to immobilize all the Keggin units. Conversely, for the catalysts ZrO₂/HPW24 and 29 the HPW quantity may have been too high, causing the pH value to drop and triggering the redissolution of part of the zirconia network with consequent

release of HPW. However, despite the HPW losses being important, still a good quantity could be immobilized in the oxide matrices allowing loadings up to 51 wt%.

The HPW Keggin structure in the bulk crystalline phase is stable until 465 °C.²² Further increase in temperature provokes the progressive decomposition of the Keggin structure to tungsten oxide (WO₃) and phosphorous pentoxide (P₂O₅).⁴ P₂O₅ is normally hard to find after catalyst exposure to high temperature because it leaves the sample during thermal treatment due to its high volatility. Conversely, due to its thermal stability, WO₃ crystals could accumulate on the catalyst surface and be readily identifiable. Raman spectroscopy allows clear distinction between the Keggin structures and WO₃ and several studies about the thermal stability of bulk and supported HPW were carried out using this technique.²³ In general Raman spectroscopy on SiO₂/HPW and TiO₂/HPW catalysts gave evidence of HPW stability inside the oxide matrices even after calcination at 500 °C since no peaks typical of WO₃ or P₂O₅ could be detected for any catalyst except SiO₂/HPW51, which featured two distinct WO₃ peaks. The low thermal stability of HPW in SiO₂/HPW51 could be due to the high loading of HPW and low surface area that lead to lower dispersion. For the remaining catalysts, the increased thermal stability of HPW is due to its interaction with the support.^{12,24}

In Raman, the HPW signal strongly depends on the degree of crystallinity and on the environment. The more isolated the HPW in the sample, the lower the signal intensity. The absence of peaks related to HPW in the samples SiO₂/HPW8 and 17 can be considered as a sign of high HPW dispersion in the corresponding silica matrix, indicating that the HPW units may be relatively individually dispersed. Concerning the catalysts SiO₂/HPW31 and 25, the W=O_d stretching signal was visible and its shape was well in agreement with the one of bulk HPW, suggesting that for these two samples HPW crystallites were formed. For the HPW immobilized onto titania, the same band was also present but deformed. This could find its explanation in the different acidic nature of titania with respect to silica. Silica is a neutral support (considering that it presents strong acid sites but in very small amounts), which is considered the best for HPW as this makes it not interact too strongly with the Keggin units, thus allowing HPW to preserve its acidity.²² In contrast, titania being more basic could interact more strongly with HPW, and partially deform its structure. These hypotheses seemed to find further support in the Raman spectra, where the antisymmetric component of the W=O_d stretching was the only one visible for the TiO₂/HPW catalyst, thus allowing assumption of a stronger interaction of HPW with the support which caused their structural deformation and the disappearance of the W=O_d symmetric stretching.

The XRD patterns did not show any peak typical of WO₃, confirming HPW stability for all the catalysts except for SiO₂/HPW51, for which HPW partial decomposition occurred, as is visible from the appearance of reflections typical of WO₃ crystals in the diffraction pattern. In this case, probably the

amount of SiO₂ formed was not enough to allow good contact and dispersion of all the HPW incorporated. This catalyst possessed in fact a low surface area (85 m² g⁻¹) if compared with the other catalysts from the same group (699–277 m² g⁻¹). In all the other diffractograms no peak of HPW was detected, confirming the good dispersion inside the oxide matrices. HPW high dispersion allows better contact of the Keggin units with the support and therefore increased its thermal stability and its leaching resistance in liquid medium. Simultaneously, just as mentioned above, the presence of HPW was proven by Raman spectroscopy. Thus, the combination of Raman and XRD data allows claiming that HPW aggregates are not bigger than 3–4 nm.

While silica-based catalysts were found to be amorphous as expected, titania and zirconia-based catalysts were crystalline materials. Titania crystallized in the anatase form during the calcination. Both degree of crystallinity and crystal size decreased with increasing HPW loading. This behaviour could be due to the decreasing pH in the reaction environment due to the increasing quantity of dissolved HPW.²⁵ Another possible explanation consists in considering a sort of “mechanical” effect during calcination: incorporated HPW prevented TiO₂ crystallites to coalesce and grow. As is visible from the diffraction pattern, the titania crystallization is more and more delayed with the increasing HPW content. Zirconia samples featured a multiphasic structure consisting in a mixture of monoclinic and tetragonal phases, which was unexpected because the tetragonal zirconia phase usually appears at ambient pressure above 1205 °C.²⁶ However, the synthesis of tetragonal zirconia *via* the sol-gel route and calcination at 500 °C was already reported.²⁷ At heteropolyacid loading higher than 7 wt% the tetragonal phase became predominant. So, in this case, the presence of HPW brought the zirconia crystallization in the tetragonal phase forward. This could be due to the decreasing level of pH in the synthesis medium. As reported by Davis *et al.*, tetragonal zirconia precipitates from the precursor solution for pH lower than 4.²⁸ Loading the zirconia with HPW species enhances the crystallinity of the ZrO₂ support as seen from Table S3.† The acidity generated from Keggin-type clusters appear to behave similar to mineralizing agents used in wet-synthesis of inorganic oxides. Under these acidic conditions, the HPW species does not only lead to an improved crystallinity, but promotes an increase of the crystallite size and modification of the crystallographic ordering.²⁹ The application of the Scherrer equation to the diffraction maxima located at 2θ = 30.2 (tetragonal) and 28.2 (monoclinic) reveals that the average size of the zirconia particles increases drastically when going from the pristine support to the ZrO₂/HPW7 sample; this could be due to the incorporation of HPW in the oxide matrix. At the same time, the contribution of the tetragonal fraction to the mixture of crystalline phases notably increases (note the complete disappearance of the diffraction peak at 2θ = 28.2). With further loading of HPW (20, 24 and 27%) tetragonal ZrO₂ becomes the major component with an almost constant crystallite size around 40 nm.

HPW interaction with the supports

The interaction of the heteropolyacids with the supports was investigated by IR spectroscopy. The bonding between HPW and the oxides is made between the hydroxyl groups (OH)⁻ of the oxide matrices and the heteropolyacids in the form (ΞM-OH₂)⁺(H₂PW₁₂O₄₀)⁻, where M is Si, Ti or Zr, and is strong enough to prevent HPW leaching from the solid during the washing step and later during the reaction in liquid phase. The shift difference of the W=O_d band to higher or lower wavenumbers resulted from the interaction between the electron donor (Ti-OH, Si-OH or Zr-OH) and electron acceptor (HPW) species. Inside the silica framework HPW is linked to silanol groups with the electron density on the silica. As already reported by Ramos-Fernandez *et al.*, this causes a shift of the W=O_d band towards lower wavenumbers.³⁰ Titanium is less electronegative than silicon (Si electronegativity = 1.90, Ti electronegativity = 1.54), so the electron density in the case of TiO₂/HPW is more shifted toward the HPW. This makes the W=O_d band shift towards higher wavenumbers. Zirconium is even less electronegative than titanium (Zr electronegativity = 1.33), so the same band is even more shifted upwards. The dependence of the shift on the HPW loading in the case of TiO₂/HPW catalysts could be due to the progressive oxide surface coverage by the HPW units, so that, at high loading, the interactions HPW-HPW become predominant over the TiO₂-HPW interaction and the W=O_d band is found to come back at the same position as in bulk HPW.

Catalyst texture

The surface area and pore volume of the SiO₂/HPW catalysts decreased with the increasing HPW loading. Simultaneously, the pore diameter remained in the range 2–3 nm, except for the sample with 51 wt% for which it increased to 3.8 nm. The decrease in pore volume with increasing HPW loading is not considered to be provoked by pore blocking, as is usually the case when they are immobilized by impregnation of preformed supports. Alternatively, it is seen as an effect of the dropping surface area and supported by the fact that the pore size remained constant, while the pore size distribution is usually found to shift toward bigger pore diameters when little pores are blocked. This indicates that the HPW are probably located partially embedded in the silica pore walls.

Concerning the TiO₂/HPW catalysts, titania does not possess a real porous structure. The anatase crystallites form aggregates during the calcination step. Therefore, what was measured by nitrogen physisorption is the void between the crystallite aggregates. The surface area of TiO₂/HPW samples increased as the crystallite size decreased (*i.e.* as the HPW loading increased). This is well in agreement with the observed reduction in the anatase crystallite size which was, as just mentioned above, an effect of the increased acidity of the synthesis medium provoked by the increasing amount of dissolved HPW in the starting solution or an effect of incorporated HPW which prevented TiO₂ crystallites to grow.

In this case the interparticle empty space size is reduced with increasing HPW loading. From those data, we hypothesized that the Keggin units may be bonded at the outer surface of the anatase crystals. This could further support the hypothesis of progressive titania surface coverage by the Keggin units. However, the definitive proof about the exact location of the HPW inside the oxide matrix was not found, and the explanations provided remain hypothetical. The exact HPW location would need further investigation and could be the subject of future studies.

Conversely, the ZrO_2/HPW catalysts exhibited a very low surface area and non-porous structure. The fact that such a big quantity of HPW could be immobilized without being decomposed during calcination brings us to hypothesize that the Keggin units entered somehow in the crystalline structure. This hypothesis is supported by the absence of HPW peaks in the X-ray diffractograms and from the zirconia phase transitions observed.

Catalyst acidity

Infrared analysis of adsorbed pyridine was performed on SiO_2/HPW and TiO_2/HPW catalysts. The immobilization of HPW into the oxide matrices introduced strong B sites at the catalyst surface. It is worth remembering that HPW does not possess L acidity,³¹ so from now on in the discussion the L sites will be supposed to come exclusively from the support. Concerning the Lewis acid sites on silica, Brinker *et al.* reported them, in amorphous silica, to originate from strained defects as detected by NMR.³² In their paper, empty d-orbital activation of silicon at temperatures higher than 200 °C is evoked. Condensation reactions involving isolated vicinal Si–OH groups cause the formation of rings containing 3 or 4 silicon members: the change in the tetrahedral geometry around silicon activates the d-acceptor orbitals causing Lewis acidity (Fig. 3).

The thermo-desorption program was not the same for the two sets of samples, this was due to the tendency of anatase to be reduced under the analysis conditions, which made the catalyst wafer become dark and very fragile, thus impeding further analysis. Despite this, some comparison between the samples is still possible. Following the evolution of the band

intensity during pyridine desorption at different temperatures it was visible that the site strength was influenced by the nature of the support. In fact, pyridine was found to desorb much slower from SiO_2/HPW than from TiO_2/HPW catalysts, indicating stronger acid sites for the former. In the SiO_2/HPW catalyst spectra the bands assigned to pyridine bonded to L sites at 1613 cm^{-1} and to B sites at 1540 and 1638 cm^{-1} were found first to increase and then to decrease. Flego *et al.* already observed this behaviour for pyridine adsorbed onto zeolites³³ and it was explained as the result of the “pyridine desorption–diffusion process”. Pyridine is hydrogen bonded to the Brønsted acid sites at around room temperature and forms pyridinium ions at higher temperature.³⁴ Pyridine molecules and pyridinium ions are mobile at elevated temperature and they can jump from site to site. As the temperature increases, pyridinium ions desorb as pyridine molecules and jump to adsorb either onto another B site (and transfer again to pyridinium ions) or onto a L site. As the temperature increases further (higher than 150 °C) the pyridine molecule desorption from the catalyst surface becomes predominant. The band intensity being proportional to the amount of pyridine bonded to a specific site, the pyridine molecules moving from one site to another caused the increase and decrease of the band intensity. One should notice that the increase at 150 °C of the bands at 1613 cm^{-1} , 1540 and 1638 cm^{-1} does not correspond to a proportional decrease in the other bands. This phenomenon could be due to pyridine, which can sometimes jump carrying the proton from a B site to another, changing temporarily the proportion between B and L sites, so that is difficult to say from where the pyridine is jumping and where it bonds during the diffusion process.³³

The desorption trend of pyridine from SiO_2/HPW and TiO_2/HPW was observed measuring the two main band intensities at 1450 cm^{-1} (L) and 1540 cm^{-1} (B) with the increasing desorption temperature. For the SiO_2/HPW catalysts, quite strong B sites could be observed, since the intensity of the band at 1540 cm^{-1} was found to be quite stable during the thermal treatment. Lewis sites were found to be weaker, since pyridine was desorbed faster from the surface. Conversely, for the TiO_2/HPW catalysts, both B and L sites were found to be weak. This understanding of the weakness of the B sites of HPW on TiO_2 agrees with the view of Schnee *et al.*,³⁵ and allows to conclude that HPW immobilized onto silica featured stronger B acidity. This is well in agreement with the hypothesis of mild interaction between silica and HPW, which does not affect too dramatically their acidity while ensuring their heterogenization.

The catalysts featured different proportions of Lewis and Brønsted sites at their surface. The correlation of the B site% based on the total acidity (B + L) with the HPW loading allowed distinguishing of two different trends: while the B% over SiO_2/HPW remained almost constant, the same was found to increase almost linearly over TiO_2/HPW . The increasing B% with HPW loading can then be interpreted as a sign of TiO_2 surface coverage by HPW.

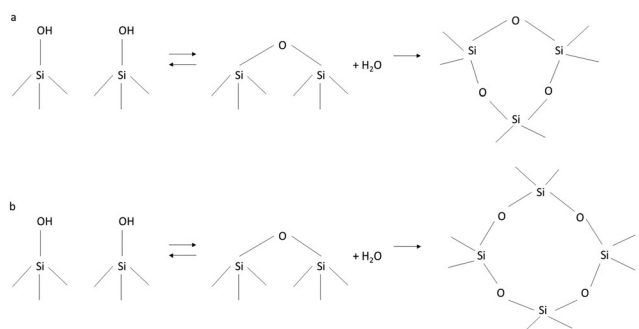


Fig. 3 Defects created on the silica surface caused by condensation reactions during thermal treatment ($T > 200$ °C).

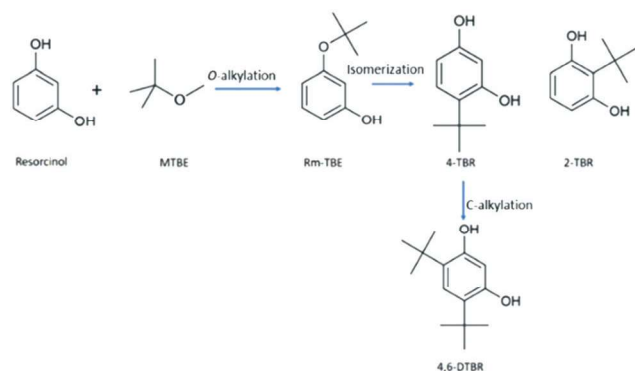
The density of strong B sites per m² of catalyst was calculated using the intensity of the band at 1540 cm⁻¹ and correlated with the HPW loading. In this way, it was possible to take the big difference in surface area between the silica and titania supports into account. Two tendencies could be observed: the density of strong B sites was in most cases higher for the SiO₂/HPW catalysts. Those data again concur to the hypothesis of mild interaction of HPW with silica and stronger interaction of HPW with titania, which would interfere with the HPW acidity and decrease the density of strong B sites. This hypothesis is reinforced if one realizes that the ZrO₂/HPW catalysts showed no acidity at all (which would result in a horizontal straight line at B site surface density). The strong interaction between HPW and zirconia neutralized the HPW acidity because all the HPW protons are employed in the bonds with the support framework.⁹

The SiO₂/HPW total acidity at 25%, 31% and 51% of HPW was measured using ammonia chemisorption and TPD. No straight trend between the acidity and the loading could be found as the total acidity decreased and then increased again. However, this behaviour could be due to HPW partial decomposition into SiO₂/HPW51, thus not reflecting the real HPW loading.

Catalytic activity

The reaction pathway of resorcinol butylation is found to proceed through *O*-alkylation, isomerization and finally *C*-alkylation. (Scheme 1) All the steps in the reaction pathway required the presence of the catalyst to occur. Alkylation at 60 °C formed mono ether (RmTBE) of resorcinol during the early moments of the reaction, which was then converted to 4TBR and 2-TBR.⁴ Upon *tert*-butylation, the aromatic ring was slightly activated, thus undergoing second alkylation to produce 4,6-DTBR.

The resorcinol alkylation with methyl-*tert*-butylether (MTBE) was performed in the liquid phase using MTBE as a solvent. The resorcinol conversion after 24 h of reaction is reported for the three sets of catalysts (Table S7 and Fig. S9†). After 24 h of reaction, the conversion did not increase anymore due to catalyst deactivation. To compare the two



Scheme 1 Proposed reaction pathway for resorcinol butylation with MTBE.

Table 3 Moles of resorcinol converted per strong Brønsted acid site of the catalyst

Catalyst	Total number of strong Brønsted acid sites	Total moles of resorcinol converted	Moles of resorcinol converted per strong B acid site
SiO ₂	0	0	—
SiO ₂ /HPW8	2.15×10^{-2}	2.15×10^{-5}	237
SiO ₂ /HPW17	1.591×10^{-1}	1.59×10^{-4}	52
SiO ₂ /HPW25	4.149×10^{-1}	4.15×10^{-4}	31
SiO ₂ /HPW31	1.471×10^{-1}	1.47×10^{-4}	69
SiO ₂ /HPW51	1.339×10^{-1}	1.34×10^{-4}	100
TiO ₂	0	0	—
TiO ₂ /HPW9	9.3×10^{-3}	9.33×10^{-6}	1022
TiO ₂ /HPW17	2.9×10^{-3}	2.88×10^{-6}	2208
TiO ₂ /HPW21	1.48×10^{-2}	1.48×10^{-5}	900
TiO ₂ /HPW29	3.03×10^{-2}	3.03×10^{-5}	630
TiO ₂ /HPW41	1.44×10^{-2}	1.44×10^{-5}	970

sets of catalysts the moles of resorcinol converted per strong B acid site before catalyst deactivation was calculated (Table 3). TiO₂/HPWxx catalysts could perform more catalytic cycles before deactivation than the SiO₂/HPWxx ones.

The reaction selectivity was reported at 10% iso-conversion for all SiO₂/HPW and TiO₂/HPW (Fig. 4). For all the catalysts, the selectivities to RmTBE (25–90%) and 4TBR (10–70%) were high compared to that to 4,6-DTBR. The selectivity to 2TBR was low, as well as the selectivity to the two unidentified products (less than 20% for their sum).

The reaction selectivity was then reported as a function of the B% of acid sites (Fig. S10†). In general, the selectivity to RmTBE decreased from almost 70 to 25% with the increasing B site%. 4TBR selectivity increased in the range from 30 to 60%. The selectivity to 4,6-DTBR generally increased from 5 to 20%. SiO₂/HPW8 showed an atypical behaviour, with low 4TBR selectivity (10%) and very high selectivity to RmTBE (90%). This observed catalytic activity could also be correlated with the B/L ratio determined for the two sets of catalysts. As the B/L ratio increases with HPW loading, the formation of 4-TBR and 4,6-DTBR improves. At a lower B/L ratio the major product was RmTBE due to the large proportion of L sites compared to B acid sites. This indicates that weak Lewis and Brønsted acid sites catalyse the *O*-alkylation to form RmTBE,

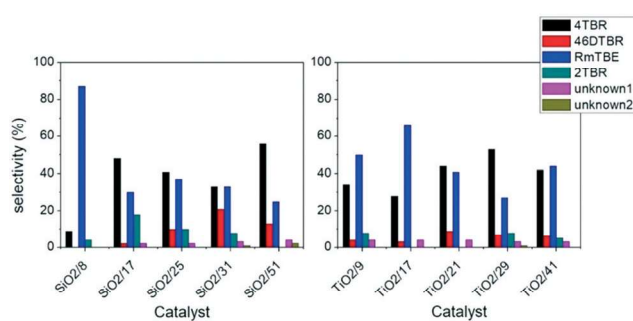


Fig. 4 Reaction selectivity at 10% resorcinol iso-conversion for the two sets of catalysts SiO₂/HPW and TiO₂/HPW (reaction carried out in the liquid phase, at 60 °C and under autogenic pressure).

whereas the isomerization to 4-TBR and further *C*-alkylation to 4,6-DTBR are catalysed by strong Brønsted acid sites.

It is generally accepted that Friedel–Crafts reactions require Lewis acid catalysts when using alkyl halides, but Brønsted acid catalysts when the alkylation reagent is an alcohol or ether. Therefore, considering MTBE as an alkylating agent, it can be assumed that the first synthetic step should take place mainly at the Brønsted acid sites on the catalyst surface.³⁶ The ether formation (RmTBE) observed for this reaction was also reported by other authors. Candu *et al.* associated its formation to both B and L sites.

Q8 Desphande *et al.* reported that in benzylation with benzyl alcohol the etherification was faster than the alkylation reaction, and the generated dibenzyl ether could act as an alkylating agent.³⁷

All the SiO₂/HPW and TiO₂/HPW catalysts were active in the resorcinol alkylation with MTBE. ZrO₂/HPW did not show any activity as was predicted from the total absence of surface acidity. The resorcinol conversion at 60 °C and autogenic pressure was moderate, but in agreement with what was already reported in the literature for the same kind of reaction.⁵ In addition, methanol, which is produced in the first reaction step from MTBE cracking, was found to be a poison for the catalyst, thus reducing their activity in the resorcinol alkylation. To confirm this behaviour, a catalytic test was run using resorcinol and MTBE (1:3 molar ratio) using methanol as a solvent. The catalysts were found to be inactive under such reaction conditions. This was due to the bonding of methanol molecules to HPW and thus blocking of the active protons as already reported by Yamada *et al.*³⁸

The catalyst possessing the highest density of B sites at its surface (SiO₂/HPW51) was not the most active and no clear correlation was found between the sole density of B sites and resorcinol conversion, suggesting that both the acid sites, Lewis and Brønsted types, should be considered as active players.

The resorcinol *tert*-butylation gave a mixture of alkylated molecules, giving as major products RmTBE and 4TBR. The reaction selectivity was correlated to the % of B sites and B/L

ratio at the catalyst surface. As the % of B sites (B/L ratio) increases from 0 to 34% the selectivity to 4TBR and 46DTBR increased in both series of catalysts due to increased Brønsted acid sites that isomerize efficiently RmTBE to 4TBR. As the % of B sites further increases, 4TBR further undergoes *C*-alkylation to 46DTBR. Further increase of the fraction of B sites above 34% for SiO₂/HPW51 and TiO₂/HPW41 catalysts decreased the selectivity to 4,6-DTBR probably due to the approaching ratio of B/L ~0.58 and 0.56 to unity. It is well documented that as the B/L ratio controls the selectivity for 46DTBR, at B/L = 1 the formation of 46DTBR is completely hindered as seen in the case of the Ga/Beta catalyst.⁷ Therefore, the selectivity for 46DTBR is controlled by the B/L ratio, whereas the percentage of Brønsted acid sites controls the conversion of resorcinol.

The role of Brønsted and Lewis acid sites in the resorcinol alkylation with MTBE

The strong B site% at the catalyst surface was plotted against the resorcinol conversion at equilibrium (Fig. 5). The plot between the percentage of weak B sites and resorcinol conversion was also prepared and showed approximately the same trend (Fig. S11†). Coming back to the correlation between conversion and strong B sites, the resorcinol conversion was found to increase and then to decrease with the increasing number of strong B sites. An optimal B site% (B/L ratio) around 26% was found to maximize the resorcinol

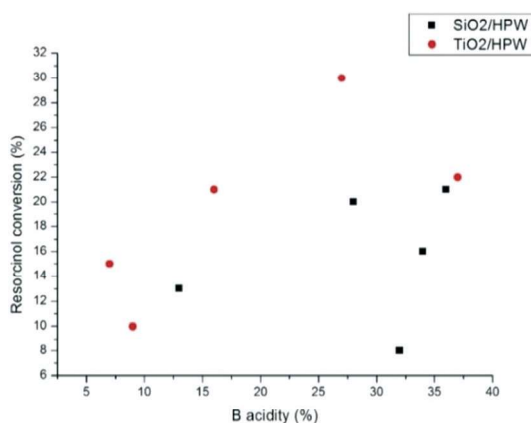


Fig. 5 Resorcinol conversion versus strong B site% based on the total acidity (Brønsted + Lewis strong sites).

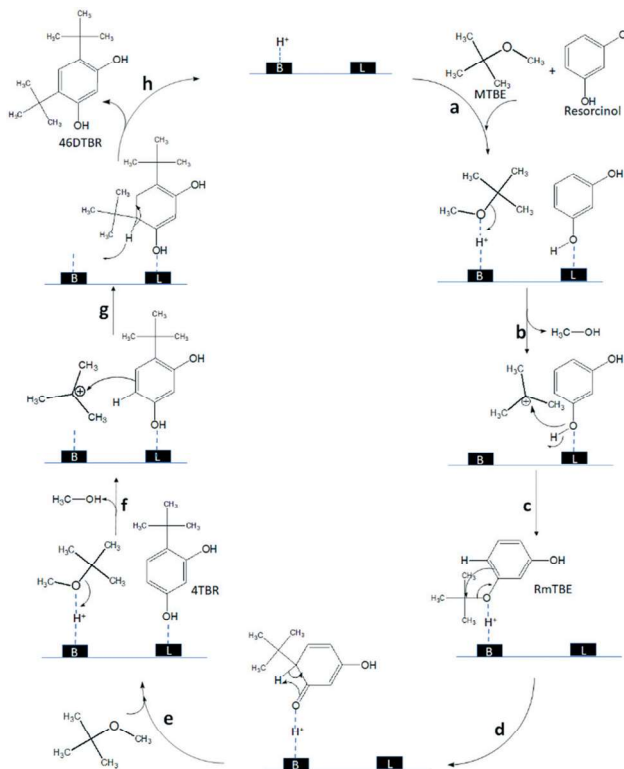


Fig. 6 Proposed reaction mechanism of resorcinol *tert*-butylation on Lewis and Brønsted sites.

Q9 conversion. Nur *et al.*¹ already observed a similar trend for the same reaction carried out using zeolite beta loaded with gallium. This is new information if compared with what is commonly known for the Friedel–Crafts alkylation of dihydroxybenzenes carried out using homogeneous catalysts. In the homogeneous phase, the catalyst role is to activate the alkylating species and the catalyst choice is made depending on the nature of the alkylating agent. In the heterogeneous phase, adsorption of reagents is crucial, since the reaction occurs at the catalyst surface. The catalyst should be then designed not only for the production of alkylating species, but also for the substrate adsorption. Considering this, the reaction mechanism is depicted as follows: in the first reaction step, MTBE is converted to methanol and the *tert*-butyl cation on the catalyst strong Brønsted acid sites (Fig. 6a and b). SiO₂ and TiO₂ supports with only Lewis acid sites were found to be inactive, indicating that the presence of strong Brønsted acid sites is essential to promote the *tert*-butyl cation formation.³⁶ However, Lewis acid sites facilitate the adsorption of resorcinol molecules through weak hydrogen bonding of electronegative O atoms of resorcinol (Fig. 6b). The *tert*-butyl cation then reacts with the resorcinol, which is adsorbed onto L acid sites in proximity (Fig. 6c). This forms RmTBE, which undergoes isomerization to form 4TBR on the B site (Fig. 6d and e). Adsorption of hydroxybenzenes onto oxides was already reported to occur between the phenolic oxygens and the Lewis sites.³⁹ Further C-alkylation of 4-TBR will lead to 46DTBR as seen from Fig. 6f and g. Finally, 46DTBR desorbs leaving behind the B and L acid sites (Fig. 6h). So, for the resorcinol conversion the Brønsted/Lewis acid site ratio is a critical feature. When the B site% (namely the ratio B/L) is too low, which means that the catalyst surface is prevalently covered by Lewis sites, only a small number of MTBE molecules can be converted to the *tert*-butyl cation. Consequently, the resorcinol conversion remains low. Conversely, when the B/L ratio is too high, which means that the catalyst surface is prevalently covered by B sites, the number of adsorbed resorcinol molecules is low, as there are not enough L sites. However, at optimum B/L ratio of 0.5 and 26% B sites the resorcinol conversion remains maximum as discussed earlier. Hence, the role of B sites is to activate the alkylating agent, while the role of L sites is to adsorb the substrate. Even though the L sites do not take part directly in the reaction, this study underlines the importance of considering their role in the mechanism, since resorcinol adsorption in proximity of B sites is crucial to allow good conversion.

Conclusions

This research pointed out the importance of considering both L and B sites as active players in resorcinol alkylation with MTBE. This is a very important parameter to consider when resorcinol alkylation is performed using heterogeneous catalysts. L sites have in fact the role of adsorbing the substrate close to the *tert*-butyl cation, which is formed on B

sites. In this research, resorcinol conversion was found to increase and then to decrease with increasing % of B sites at the catalyst surface, showing that for the resorcinol conversion to be maximized, the L/B ratio is a critical feature.

Conflicts of interest

There are no conflicts to declare.

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