

Highly porous hybrid metallosilicate materials prepared by non-hydrolytic sol-gel: hydrothermal stability and catalytic properties in ethanol dehydration

Ales Styskalik,^{a,b,c} Imene Kordoghli,^a Claude Poleunis,^a Arnaud Delcorte,^a Carmela Aprile,^d Luca Fusaro,^d Damien P. Debecker^{*a}

^aInstitute of Condensed Matter and Nanoscience (IMCN), UCLouvain, Place Louis Pasteur 1,
1348 Louvain-La-Neuve, Belgium

^bMasaryk University, Department of Chemistry, Kotlarska 2, CZ-61137 Brno, Czech Republic

^cMasaryk University, CEITEC MU, Kamenice 5, CZ-62500 Brno, Czech Republic

^dDepartment of Chemistry, Unit of Nanomaterials Chemistry, University of Namur, 5000 Namur,
Belgium

*Corresponding author (damien.debecker@uclouvain.be).

ABSTRACT

Herein, we present novel phenylene- and xylylene-bridged silica and metallosilicate materials prepared by non-hydrolytic sol-gel. The hybrid silica are highly porous, chemically similar to periodic mesoporous organosilica (PMO), but amorphous without any pore ordering. Analogous hybrid metallosilicates are obtained by directly incorporating Al, Nb, or Sn in the hybrid silica framework. Exhibiting open texture, surface acidity and tunable hydrophobicity, these materials are excellent candidates for catalytic alcohol dehydration reactions. The gas-phase hydrothermal and thermal stability of these materials is examined. While the hybrid silica is expectedly stable, a stark decrease in stability is observed for phenylene bridged silsesquioxanes upon metal introduction. The extent of the hydrolytic Si-C(sp²) bond cleavage is quantitatively followed by ²⁹Si MAS NMR, TG analysis, and GC-FID analysis of effluent coming from samples exposed to water vapor. Two important features affecting the hydrothermal and thermal stability are identified: (i) the homogeneity of metal dispersion within the silica matrix, and (ii) the electronegativity of the incorporated metal. The stability of hybrid metallosilicates is significantly improved by replacing the phenylene bridges with xylylene bridges, due to the presence of more stable Si-C(sp³) bonds. Interestingly, the latter hybrid metallosilicate proves to be an active catalyst for the dehydration of ethanol to ethylene. Unlike the other hybrid materials presented here, it reaches high ethylene yields without undergoing degradation and deactivation.

Keywords: non-hydrolytic sol-gel, hybrid metallosilicate; hydrothermal stability; heterogeneous catalysis; ethanol dehydration

1. Introduction

Hybrid organic-inorganic materials based on silica have recently attracted considerable attention because of their possible application in catalysis, adsorption, gas sensing, etc. [1]. The thermal stability of these materials depends on the nature of the organic group which is incorporated, e.g. ethylene bridges ($-\text{CH}_2\text{CH}_2-$) are stable up to 300 °C, methylene bridges ($-\text{CH}_2-$) up to 400 °C, and phenylene bridges ($-\text{C}_6\text{H}_4-$) up to 550 °C [2–4]. Hydrothermal (HT) stability was tested thoroughly in batch (boiling water, various pH,...) [5]. HT stability of periodic mesoporous organosilica networks (PMO) is generally evaluated by boiling the samples in water for up to several days and monitoring the mesostructural order by X-ray diffraction and is reported to be higher than for plain inorganic silica materials [5]. Dral et al. suggested, that the improved hydrothermal stability of silica with organic bridges is caused by the higher connectivity of Si precursors and by the relaxation of strained siloxane bonds (due to the incorporation of flexible bridges) rather than by increased hydrophobicity [5].

Hydrothermal stability tests in flow (gas phase) were reported only scarcely. It was shown that both methylene and phenylene bridged silica start to decompose at 400 °C in a flow of humid air [3,6]. The degradation was observed by ^{13}C and ^{29}Si MAS NMR: methylene and phenylene bridges transformed to terminal methyl and phenyl groups, respectively, and Q signals of silicon appeared at the expense of T signals in ^{29}Si NMR spectra. It was concluded that the hydrolysis of Si–C bonds is responsible for the degradation [3,6].

The catalytic activity is brought to hybrid silica materials in most cases by grafting or co-condensation of organosilanes with reactive organic groups (e.g. benzene sulphonic acid, propyl

sulphonic acid, propyl amine, metal porphyrin complexes, etc.) [7–10]. These materials were shown to be very promising catalysts in many liquid phase reactions performed in batch (e.g. transesterification of fatty acids, condensation of aldehydes with alcohols, alkylation of phenols, etc.). Hydrophobic catalysts exhibited improved performance, when bulky organic molecules need to be transformed, while water should be repelled [7,8]. As a rare example of catalysis in gas phase, Rác et al. performed the alkylation of phenol by isopropyl alcohol over sulfonated phenylene bridged silica at 150 °C; the studied materials were stable under these conditions [11].

The incorporation of a catalytically active metal into the structure of hybrid silica-based materials is less common. On the first hand, a recent field of research is focused on hybrid zeolites [12,13]. These materials require elaborate procedures and precise conditions and are relatively unstable, possibly owing to the rapid hydrolysis of Si–C bonds by water molecules trapped in the pores of zeolites [14]. On the second hand, amorphous hybrid metallosilicates are also attracting a lot of attention. Al, Ti, V, and Zr were successfully incorporated in ethylene-bridged silica [15–22]. Remarkably, these hybrid metallosilicates showed high hydrothermal stability in boiling water, even higher than corresponding metal-free mesoporous organosilica. Phenylene-bridged silicas with Al and Zr were also prepared and their stability in boiling water was again improved in comparison to plain hybrid silica [23,24]. The generally accepted explanation of this phenomenon is based on a lower amount of Si–O–Si bonds (unstable in hot liquid water); these bridges are substituted by Si–O–M and Si–C–Si linkages in hybrid metallosilicates [25]. Catalytic applications included epoxidation of cyclooctene, alkylation of 2,4-di-tert-butylphenol, methanolysis of palm oil, etc. [17,19,21,23]. However, to the best of

our knowledge, the gas phase stability and catalytic performance of hybrid metallosilicates have not been assessed yet.

Here, our intention was to apply hybrid metallosilicates (Al, Nb) in the gas phase dehydration of (bio)ethanol to (bio)ethylene – an important reaction in the perspective of integrated biorefineries [26] – and to study the effect of hydrophobicity on catalytic performance. To do so, highly porous hybrid metallosilicate catalysts were prepared by non-hydrolytic sol-gel chemistry (NHSG) [27–29]. The introduction of organic groups and of the metal took place directly during the polycondensation reactions, using either the acetamide elimination route or the alkyl halide elimination route. Phenylene bridged materials were selected because of the well-known high thermal stability of this organic moiety. However after performing some preliminary catalytic experiments, it appeared that the (hydro)thermal stability of these materials was very low in comparison to reported data on hybrid silica without metal [3]. Therefore we conducted a systematic study on the stability of hybrid metallosilicates. Using XPS and ToF-SIMS, we show here that the homogeneity of active metal sites distribution is the key property which dictates both the catalytic activity and the (hydro)thermal stability of these hybrid catalysts. We also propose a strategy to obtain more stable hybrid catalysts, active in ethanol dehydration.

2. Experimental

2.1 General. All manipulations were performed under high vacuum or dry N₂ atmospheres using Schlenk techniques or in a dry box with H₂O and O₂ levels below 1 ppm. Diisopropylether and benzene-d₆ were dried over Na metal. CH₂Cl₂ was dried with P₄O₁₀. All solvents were distilled,

and stored in a glovebox over molecular sieves. Aluminum chloride (ABCR, AlCl_3 , 99.999 %), niobium(V) chloride (ABCR, NbCl_5 , 99.99%), tris(dimethylamido)aluminum (Aldrich, $\text{Al}(\text{NMe}_2)_3$), niobium(V) ethoxide (ABCR, $\text{Nb}(\text{OEt})_5$, 99.9 %), tetrakis(diethylamido)tin (ABCR, $\text{Sn}(\text{Net}_2)_4$, 99.99 %), and 1,4-bis(triethoxysilyl)benzene (ABCR, 95 %) were stored in a glovebox and used as received. Ethanol absolute (AnalaR NORMAPUR, 99.95 %), acetic acid anhydride (Acros, 99 %), α , α' -dichloro-p-xylene (TCI 98.0 %), tripropylamine (TCI, 98 %), thionyl chloride (Roth, 98 %), and trichlorosilane (Sigma, 99 %) were used as received. 1,4-Bis(trichlorosilyl)benzene was prepared from 1,4-bis(triethoxysilyl)benzene according to a patent [30]. 1,4-Bis(trichlorosilylmethyl)benzene was prepared from trichlorosilane and α , α' -dichloro-p-xylene according to literature [31]. 1,4-Bis(triacetoxysilyl)benzene and 1,4-bis(triacetoxysilylmethyl)benzene were prepared from their corresponding trichlorosilyl-derivatives by an action of acetic acid anhydride [32,33]. Silica-alumina catalyst support (grade 135, $\text{SSA} = 600 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.76 \text{ cm}^3 \text{ g}^{-1}$, Si/Al ratio ~ 8) was purchased from Sigma-Aldrich.

2.2 Characterization. Transmission IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) were recorded on a Bruker Equinox 55 spectrometer from KBr pellets or on a Bruker Alpha-Platinum ATR system. The same instrument in combination with pyridine adsorption was used for acid sites number estimation. Wafers based on ca. 30 mg of analyzed sample were pressed and evacuated at 350°C . Then pyridine was adsorbed at its autogenous pressure at RT. Physisorbed pyridine was removed by evacuation at 150°C and IR spectra were collected. Molar extinction coefficients according to Emeis were used for calculations for absorption bands at 1455 cm^{-1} (Lewis acid sites) and at 1545 cm^{-1} (Brønsted acid sites).[34] Strength of acid sites was estimated by further evacuation/IR measurement steps at 250 and 350°C . Thermal analysis (TG/DSC) was performed

on a Mettler Toledo TGA/DSC 3+ apparatus in the stream of air ($100\text{ cm}^3\text{ min}^{-1}$) with a temperature ramp of $5\text{ }^{\circ}\text{C min}^{-1}$ to $1000\text{ }^{\circ}\text{C}$, in an alumina crucible. Surface areas (SA) and pore volumes were determined by nitrogen adsorption at 77.4 K by volumetric techniques [35,36] on a Tristar 3000 instrument (Micromeritics, USA). Prior to measurement, the samples were degassed at $150\text{ }^{\circ}\text{C}$ for at least 8 h. The specific surface area was determined by the multipoint BET method with at least five data points with relative pressures between 0.05 and 0.30. Aluminum and silicon contents were determined on an ICP optical emission spectrometer iCAP 6500 Duo (Thermo, UK) equipped with a solid-state generator with a frequency of 27.12 MHz and a maximum power input of 1350 W . The measurements of Al were performed at 167.0 , 308.2 , and 309.2 nm . For Si analysis, wavelengths 212.4 and 251.6 nm were used. Powder X-ray diffraction analyses were performed on GNR Europe 600 diffractometer with a $\text{CoK}\alpha$ ($1.7903\text{ \AA}$) radiation source. The xerogels were measured on a diffraction-free silicon holder in reflection mode. Solution NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer at frequencies 299.8 MHz for proton and 75.4 MHz for carbon with deuterated solvents as the external lock. The proton and carbon NMR spectra were referenced to the residual proton signals or carbon resonances of benzene- d_6 (7.15 and 128.0 ppm , respectively). Solid-state ^{27}Al , ^{29}Si , and ^{13}C solid state MAS NMR spectra were acquired on Bruker Avance-500 NMR spectrometer with a 4 mm CP-MAS Bruker probe at frequencies 99.4 MHz for silicon, 130.3 MHz for aluminum, and 125.8 MHz for carbon. Magic angle spinning rates were 8 kHz for ^{29}Si and ^{13}C (CP)MAS and 10 kHz for ^{27}Al MAS spectra. Quantitative ^{29}Si MAS spectra were recorded using a 300 s relaxation delay, a $3\text{ }\mu\text{s}$ (90°) excitation pulse, and a 52 ms acquisition time. Chemical shifts were referenced externally to ^{29}Si $\delta[3\text{-(trimethylsilyl)-1-propanesulfonic acid sodium salt}$

(DSS)]: 1.53 ppm; ^{13}C δ [adamantane] 38.68 ppm; ^{27}Al δ [[Al(H₂O)₆]³⁺ (aq. solution)]: 0.0 ppm.

The quantitative analysis of ^{29}Si MAS NMR spectra (exponential line broadening value = 0) was performed as follows: (i) phase correction; (ii) baseline correction using least squares method; (iii) deconvolution of signals to T¹, T², T³, Q², Q³, and Q⁴ peaks with 100 % Gaussian shape until RMS deviation characterizing the fit between calculated and measured data was below 0.05; (iv) integration. The relative integrated areas of mentioned peaks were used to calculate the percentage of T sites and degree of condensation (sum of weighed ratios of peak areas vs. total peak area). TEM micrographs of ground xerogels were acquired on a Tecnai G2 F20 instrument. X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a SSI X probe spectrometer (model SSI 100, Surface Science Laboratories, Mountain View, CA) equipped with a monochromatized Al-K α radiation (1486 eV). The sample powders, pressed in small stainless troughs of 4 mm diameter, were placed on an insulating home-made ceramic carousel. The pressure in the analysis chamber was around 10⁻⁶ Pa. The analyzed area was approximately 1.4 mm² and the pass energy was set at 150 eV. The C1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale [37]. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK) and spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after baseline was subtracted. Time of flight secondary ion mass spectrometry (ToF-SIMS) analyses were carried out by using a TOF.SIMS⁵ instrument (IONTOF GmbH, Münster, Germany). A pulsed Bi₅⁺ metal ion source was used to produce a primary beam using an acceleration voltage of 30 kV. An AC target current of 0.07 pA with a bunched pulse width lower than 1 ns was used. Both positive and negative secondary ion species were analysed. For spectra, a raster of 128 x 128

data points over an area of $250 \times 250 \mu\text{m}^2$ was used. The total primary ion beam dose for each analysed area was always kept below $5 \cdot 10^{10}$ ions cm^{-2} , ensuring static conditions. Lateral resolution of $\sim 3 \mu\text{m}$ and mass resolution $m/\Delta m > 4000$ at 29 m/z were maintained for positive and negative spectra acquisition. Charge compensation was done by interlaced electron flood gun ($E_k = 20 \text{ eV}$). All data analyses were carried out using the software supplied by the instrument manufacturer, SurfaceLab (version 6.5). Sample powders were pressed onto adhesive part of Post-it® papers. The SAXS data sets were collected using the BioSAXS-1000, Rigaku at CEITEC (Brno, Czech Republic). Data were collected at room temperature with focused (cofocal OptiSAXS optic, Rigaku) Cu K α X-ray ($1.54 \text{ \AA}$). Sample to detector (PILATUS 100K, Dectris) distance was 0.48 m covering a scattering vector ($q=4\pi\sin(\theta)/\lambda$) range from 0.008 to 0.6 $\text{\AA}^{-1}$. Samples were placed in 1.5 mm quartz capillaries (Hilgenberg). Ten separate two-dimensional images were collected for buffer and sample (1 min exposure per image, 10 min total exposure). Radial averaging was performed using SAXSLab3.0.0r1, Rigaku.

2.3 Xerogel synthesis – acetamide elimination route (Scheme 1). 4.565 g (9.383 mmol) 1,4-bis(triacetoxysilyl)benzene was loaded in an autoclave in a glove box and dissolved in 25 cm^3 CH_2Cl_2 . In a separate vial, a CH_2Cl_2 solution (5 cm^3) of 0.1931 g (1.213 mmol) $\text{Al}(\text{NMe}_2)_3$ was prepared and stirred at RT for 5 min. The solution of $\text{Al}(\text{NMe}_2)_3$ was then added to the solution of the 1,4-bis(triacetoxysilyl)benzene with vigorous stirring (5 min). The autoclave was sealed and kept in an oven at $130 \text{ }^\circ\text{C}$ for 72 hrs. During this time, gelation occurred. After cooling down, the autoclave was put back into the glovebox, opened and the gel was transferred into a Schlenk vessel. The gel was then dried under vacuum at $60 \text{ }^\circ\text{C}$ overnight in order to remove the solvent

and volatile condensation products (N, N'-dimethylacetamide and acetic acid anhydride). The resulting powder was annealed in flow of dry nitrogen at 250 °C (1 °C min⁻¹, 6 hrs) yielding a pale brown xerogel sample (**Al-8SiPhSi-Ac**, Fig. 1S), where 8 is the molar ratio between the silicon precursor and the aluminum precursor (nominal Si/Al ratio = 16), “Ph” stands for the phenyl bridges and “Ac” stands for “acetamide elimination route”. Samples **Nb-8SiPhSi-Ac** and **Sn-8SiPhSi-Ac**, were prepared using the same procedure, but with Nb(OEt)₅ or Sn(NMe₂)₄ respectively as the metal precursors. Nb(OEt)₅ was used instead of niobium dialkylamides due to their poor stability (i.e. in this case ethyl acetate was eliminated upon condensation between Si and Nb precursors). As a benchmark, **SiPhSi-Ac** (plain, no metal) was prepared without addition of metal precursor. Also, one xylylene bridged sample was prepared with bis(triacetoxysilylmethyl)benzene instead of bis(triacetoxysilyl)benzene (**Al-8SiXySi-Ac**) (Table 1). Higher temperatures (160-190 °C) were needed for **SiPhSi-Ac**, **Sn-8SiPhSi-Ac**, and **Al-8SiXySi-Ac** in order to obtain gels.

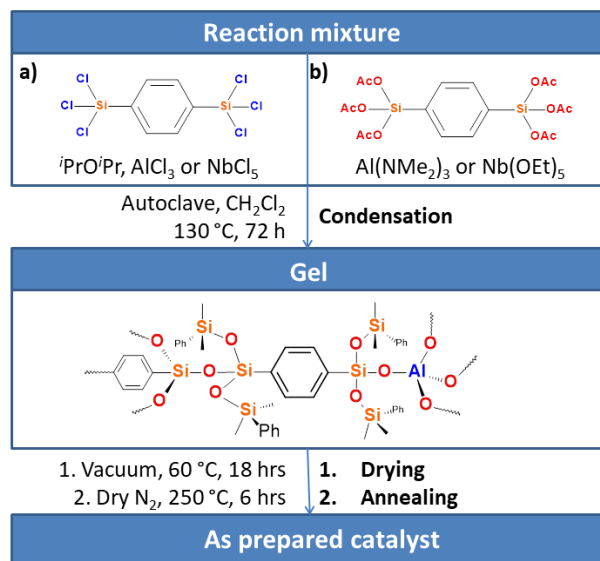
Table 1: Synthesis (amount on precursors introduced in the preparation) and characterization of phenylene bridged metallosilicate catalysts by XPS, and ICP-OES.

Sample	n _{Si} (mmol)	n _M (mmol)	n _{DIPE} (mmol)	Si/M ratio (-) Theor ^a /ICP/XPS
SiPhSi-Ac	8.910	-	-	-/-/-
Al-8SiPhSi-Ac	9.383	1.213	-	15.5/16.4/15.3

Al-8SiPhSi-Et	9.386	1.170	30.00	16.0/15.6/18.3
Nb-8SiPhSi-Ac	9.392	1.171	-	16.0/15.2/19.3
Nb-8SiPhSi-Et	9.670	1.223	32.51	15.8/16.8/42.9

^aThe nominal Si/M ratio is 16; the theoretical value presented in the table is the value calculated from the precise masses of reactants introduced during the synthesis (n_{Si} , n_{M} , n_{DIPE}).

2.4 Xerogel synthesis – alkylhalide elimination (ether) route (Scheme 1). 3.238 g (9.386 mmol) 1,4-bis(trichlorosilyl)benzene was loaded in an autoclave in a glove box and dissolved in 25 cm³ CH₂Cl₂. In a separate vial, a CH₂Cl₂ solution (5 cm³) of 0.1560 g (1.170 mmol) AlCl₃ and 3.065 (30.00 mmol) diisopropylether (DIPE) was prepared and stirred at RT for 15 min. This solution was then added to the solution of the 1,4-bis(trichlorosilyl)benzene with vigorous stirring (5 min). The autoclave was sealed and kept in an oven at 130 °C for 72 hrs for gelation. After cooling down, the autoclave was put back into the glovebox, opened and the gel was transferred into a Schlenk vessel. The gel was then dried under vacuum at 60 °C overnight in order to remove the solvent and volatile condensation product (isopropylchloride). The resulting powder was annealed in flow of dry nitrogen at 250 °C (1 °C min⁻¹, 6 hrs) yielding a pale yellow xerogel (**Al-8SiPhSi-Et**, Fig. 1S, Et stands for ether route). Sample **Nb-8SiPhSi-Et** was prepared in the same way with NbCl₅ as the metal precursor. Pure inorganic benchmarking catalyst with the same Si/Al nominal ratio was prepared in the same way utilising SiCl₄ as silicon precursor (**Al-16Si-Et**).



Scheme 1: Preparation procedure of hybrid metallosilicate catalysts by alkylhalide elimination route (a) and acetamide elimination route (b).

2.5 Spectroscopic characterization data (IR and NMR). Complete summary can be found in the supporting material to this manuscript (ESI). These may be accessed via journal website.

2.6 Hydrothermal stability test – dynamic. The xerogel samples (0.192 g, 0.20–0.40 mm particle size) were diluted with glass beads (0.5–1 mm) in order to keep the volume of the catalyst bed constant. The void space of the reactor was filled with silica beads. Stability testing was carried out by feeding 0.216 g h^{-1} of liquid H_2O by means of NE-300 syringe pump in $40 \text{ cm}^3 \text{ min}^{-1}$ of N_2 (10 mol% of water in N_2). The tests were carried out at atmospheric pressure, $\text{WHSV} = 1.1 \text{ h}^{-1}$. Temperature was varied stepwise in the range from 205 to 415°C by steps of 35°C . One step consisted of (i) heating ramp and stabilization at the temperature (21 min) and (ii) steady temperature state (35 min). The analysis of effluent gas containing products of hydrolysis was carried out by VARIAN 3800 Gas Chromatograph (5 injections at each temperature) equipped

with a flame ionization detector (FID) and a Cydex B column (25 m long, internal diameter 0.22 mm, film thickness 0.25 μm).

2.7 Hydrothermal stability test – static. The fixed bed reactor was prepared in the same way as for the dynamic test. 0.216 g h^{-1} of H_2O in 40 cm^3 N_2 was fed for 24 h, temperature of the bed was kept at 240 $^\circ\text{C}$. Sample was collected after cooling down and analyzed by TGA, MAS NMR, and N_2 physisorption.

2.8 Thermal stability was assessed simply by calcination of the xerogel at 400 $^\circ\text{C}$ in a flow of dry air (flow ca. 40 cm^3 min^{-1} , fixed bed, ramp 1 $^\circ\text{C min}^{-1}$, 4 hrs) followed by analysis of calcined sample.

2.9 Catalytic dehydration of ethanol. The fixed bed reactor was prepared in the same way as for hydrothermal stability tests. 0.192 g of phenylene bridged samples was used; the mass of catalyst was normalized based on inorganic part in the case of samples with significantly different mass fraction of organic groups (**Al-16Si-Et** and **Al-8SiXySi-Ac**) so that the amount of metal is the same in all experiments. Catalytic testing was carried out by feeding 0.212 g h^{-1} of absolute ethanol by means of NE-300 syringe pump in a N_2 flow of 40 cm^3 min^{-1} (4.4 mol% of ethanol in N_2). The tests were carried out at atmospheric pressure, WHSV = 1.1 h^{-1} . Temperature was varied stepwise in the range from 205 to 415 $^\circ\text{C}$ by steps of 35 $^\circ\text{C}$. One step consisted of (i) heating ramp and stabilization at the temperature (21 min) and (ii) steady temperature state (56 min). The analysis of reactants and products in the effluent gas was carried out by VARIAN 3800 Gas Chromatograph (8 injections at each temperature) equipped with a flame ionization detector (FID) and a Cydex B column (25 m long, internal diameter 0.22 mm, film thickness 0.25 μm).

3. Results and discussion

3.1 Phenylene bridged silsesquioxane (no metal) – synthesis, characterisation, and stability

Sample without any metal (**SiPhSi-Ac**) was synthesized by NHSG as a benchmark (eq. 1) and annealed in flow of dry N₂ (250 °C, Scheme 1). This material exhibited very similar structural properties to previously reported hybrid silica with phenylene bridges prepared by conventional hydrolytic sol-gel methods [3]. ²⁹Si and ¹³C CPMAS NMR spectra of the as prepared sample (annealed in N₂ at 250 °C) confirmed presence of intact phenylene bridges (Fig. 1 and 2S), only signals in the T region (CSiO₃) were observed for ²⁹Si species. These signals originate from the presence of 3 overlapping contributions centered at -62, -72, and -78 ppm which can be attributed respectively to CSi(OSi)(OH)₂ (T1), CSi(OSi)₂(OH) (T2), and CSi(OSi)₃ (T3) species, where C stands for an aromatic carbon of a phenylene group bound to silicon [3]. The absence of Qⁿ signals (i.e. Si(OSi)_n(OH)_{4-n} species) in region comprised between -90 and -110 ppm is a clear indication of the good performance of our synthesis strategy [3]. Thus we can state that sample **SiPhSi-Ac** indeed was a phenylene bridged silsesquioxane (amorphous, no pore ordering, Fig. 3S) with no traces of SiO₂. XPS further attested the presence of aromatic moieties: the intensity of C1s peak was very high and accompanied by a shake-up satellite peak characteristic for aromatic groups (Fig. 4S). Furthermore Si 2p peak was shifted by 1 eV from SiO₂ [38] and NHSG-prepared purely inorganic sample (Fig. 5S) supporting the fact that the close Si environment can be described as CSiO₃. Finally, surface area and pore volume reach 140 m² g⁻¹ and 0.082 cm³ g⁻¹ respectively (Table 3), which is lower than previously reported

phenylene bridged PMOs [2]. The isotherm (Fig. 3) shows hysteresis that does not close in the low p/p_0 range indicating that the adsorption is partially irreversible under the experimental conditions. Similar isotherms have been reported [39–42] for xerogels based on cubic Si_8O_{12} units cross-linked with alkane and alkyl silane bridges and for microporous silicophosphates where this behavior was attributed either to micropores with the same width at the pore entrance as that of the adsorbate molecules resulting in irreversible uptake, or to flexibility in the networks associated with swelling of a non-rigid porous structure. Both explanations are possible for the samples described here. For those specific samples, where the hysteresis does not close (**SiPhSi-Ac**, **Al-8SiPhSi-Ac**, and **Nb-8SiPhSi-Ac**, for hybrid metallosilicates see discussion below), the BET model may not be fully valid and the SA values should be considered with care.

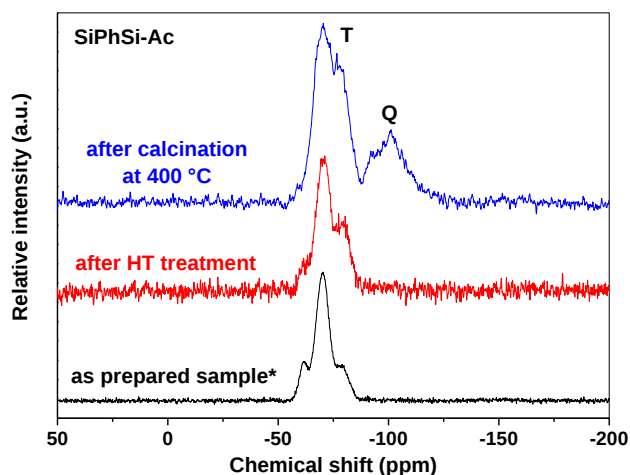


Fig. 1: ^{29}Si (CP)MAS NMR spectra of **SiPhSi-Ac** after various treatment, *denotes CPMAS spectrum.

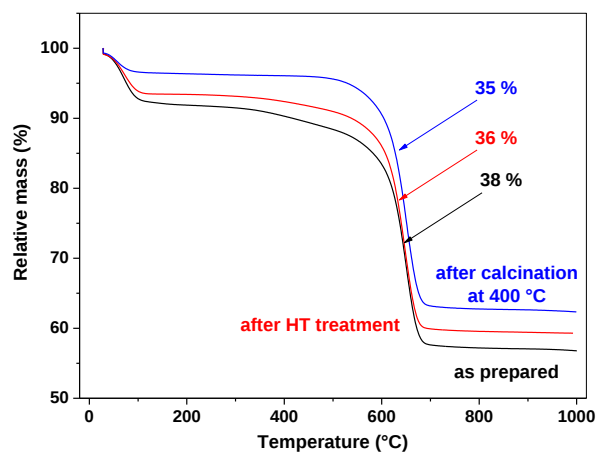


Fig. 2: TG curves of **SiPhSi-Ac** after various treatment.

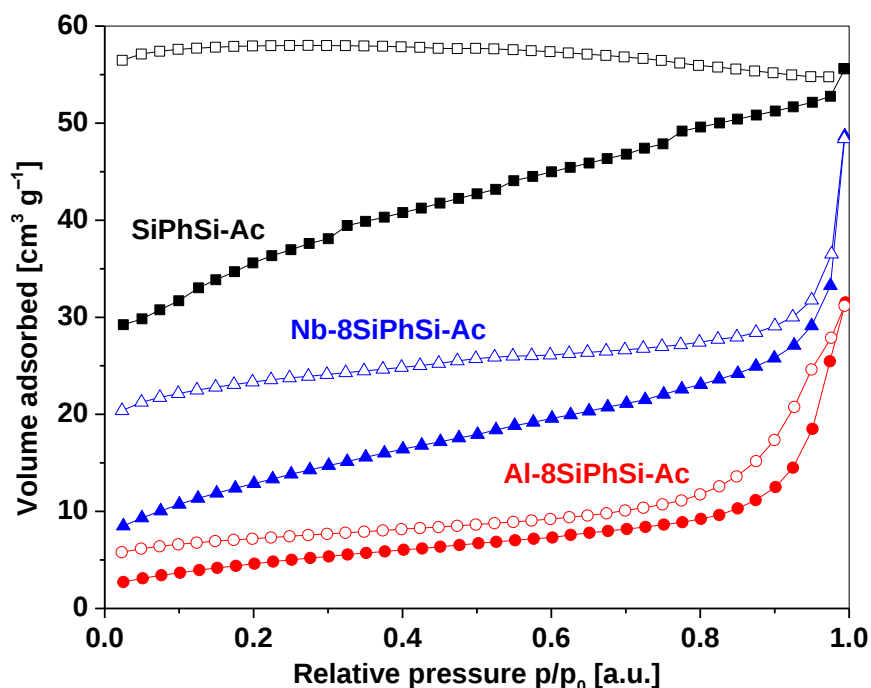


Fig. 3: N₂ adsorption-desorption isotherm of phenylene bridged materials prepared by acetamide elimination route.

Importantly TGA showed high thermal stability of **SiPhSi-Ac** (up to 500 °C) similar to reported data (Fig. 2) [3]. The mass loss due to the burning of phenylene bridges (500-725 °C) accounted for 38 % of the mass which is in a good agreement with the theoretical value (33 %, Fig. 2). This mass loss is slightly higher than expected presumably due to the presence of some unreacted acetoxy- groups, which burn at the same temperature range as phenylene bridges. For the sample calcined at 400 °C in dry air, the mass loss was virtually the same (35 %), showing that the organic species survived the calcination step. However, a partial cleavage of Si-C bonds was observed by ²⁹Si MAS NMR spectroscopy, as evidenced by the presence of a combination of Q², Q³, and Q⁴ sites at -93, -100, and -109 ppm, respectively, with an overall proportion of Q sites equal to 25 % (Fig. 1, Table 2). Since the mass loss did not change after calcination, it can be concluded, that the predominant reaction is a conversion of bridging phenylene moieties to terminal phenyl groups (eq. 2). This transformation has been already reported [3] and is here

reflected in the ^{13}C CP MAS spectrum where a shoulder of the main peak (134 ppm) characteristic for a terminal phenyl group emerged at 128 ppm (Fig. 2S) [3]. Water necessary for this hydrolytic reaction (eq. 2) is either adsorbed in the pores or comes from the oxidation of residual organic groups. Thus, the data presented above confirm that NHSG preparation led to phenylene bridged silsesquioxane materials exhibiting similar thermal stability as conventional hydrolytic sol-gel technique [3].

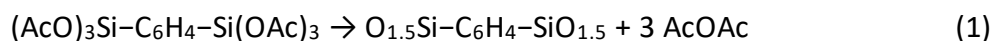


Table 2: Evaluation of thermal and hydrothermal stability by TGA and ^{29}Si MAS NMR.

Sample	As-prepared (annealed at 250 °C, dry N_2)		Calcined at 400 °C, dry air		After static HT stability test	
	ML (%) ^a	Proportion of T sites (%) ^b	ML (%) ^a	Proportion of T sites (%) ^b	ML (%) ^a	Proportion of T sites (%) ^b
SiPhSi-Ac	38	100 ^c	35	75	36	100
Al-8SiPhSi-Ac	42	79	22	0	28	22
Al-8SiPhSi-Et	34	40	19	0	31	12
Nb-8SiPhSi-Ac	38	73	15	10	30	45
Nb-8SiPhSi-Et	33	78	21	21	28	58

^aMass loss between 250 and 800 °C in TGA; ^bSum of the peak areas belonging to T sites (CSiO₃, –61–77 ppm) and Q sites (SiO₄, –90–110 ppm) was set as 100 %; ^cBased on ²⁹Si CPMAS NMR (no hint of Q sites).

Table 3: Textural properties of the hybrid metallosilicate samples after different treatments

Sample	As-prepared (annealed at 250 °C, dry N ₂)			Calcined at 400 °C, dry air			After static HT stability test		
	SA _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	D (nm)	SA _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	D (nm)	SA _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	D (nm)
SiPhSi-Ac	140	0.082	1.3	<10	-	-	90	0.066	1.7
Al-8SiPhSi-Ac	18	0.039	4.8	380	0.12	1.3	<10	-	-
Al-8SiPhSi-Et	460	1.0	9.8	430	1.27	12	320	0.47	8.3
Nb-8SiPhSi-Ac	49	0.051	2.2	130	0.036	1.1	<10	-	-
Nb-8SiPhSi-Et	880	1.40	7.4	650	0.49	6.2	710	0.76	6.7



Since water is unavoidably one of the products of ethanol dehydration, we aimed for studying the gas phase hydrothermal stability of prepared materials in more detail. Two types of tests were performed. In the first test (dynamic), the sample was exposed to a wet N₂ flow (10 mol% of water) in a fixed bed reactor, the temperature was raised from 205 to 415 °C in steps of 35 °C. The product of the hydrolysis (benzene; coming from the hydrolysis of both Si–C bonds of phenylene bridges in hybrid silica as presented in eq. 2 and 3) was observed and quantified by GC-FID (Fig. 4). Thus, we were able to identify the temperature at which the hydrolysis starts to occur. The second hydrothermal stability test (static) was performed to probe the long term stability. The samples were placed in the same humid flow at 240 °C (typical reaction temperature for EtOH dehydration) for 24 hrs. The treated catalyst was then characterized.

Sample **SiPhSi-Ac** showed high hydrothermal stability. It started to release benzene only from 345 °C during the dynamic HT treatment (Fig. 4). Note, however, that this temperature is much lower than the first signs of degradation observed in dry air (see TGA results in Fig. 2). Long-term stability at 240 °C in humid atmosphere was excellent: the ²⁹Si MAS NMR spectrum did not exhibit any hint of Q signals and mass loss remained virtually same as compared to the fresh catalyst (Fig 1 and 2).

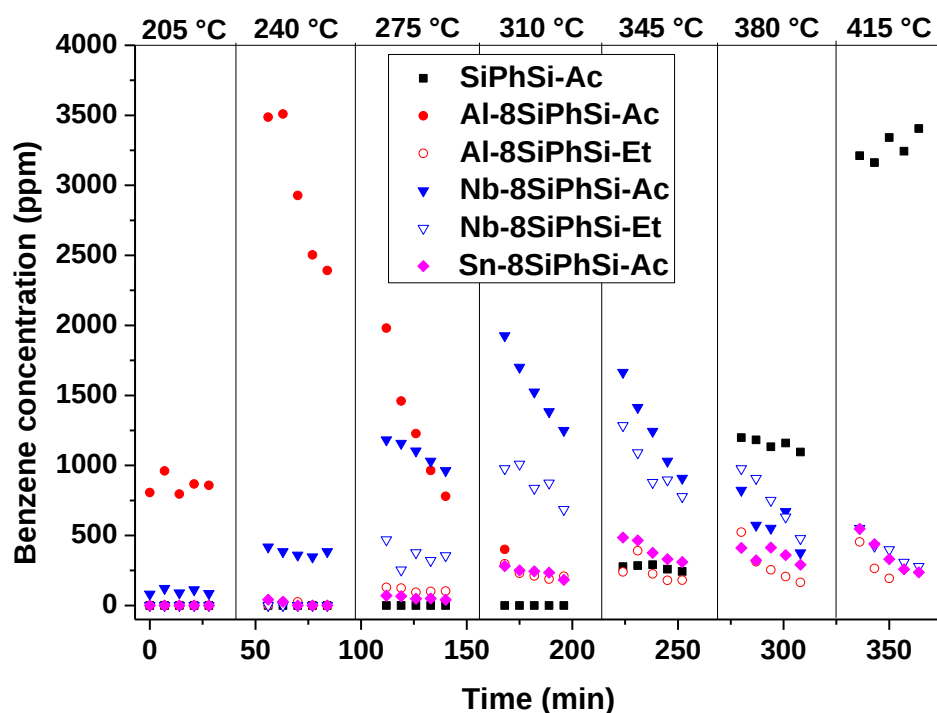
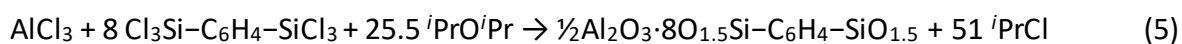
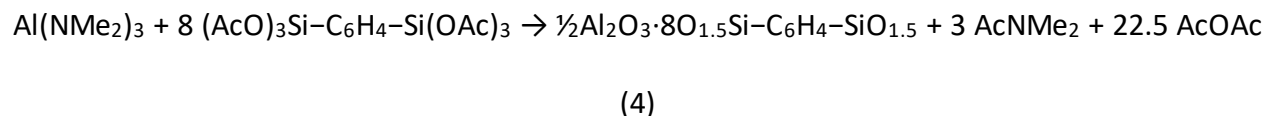


Fig. 4: Benzene release from phenylene bridged metallocatalysts during dynamic HT stability test.

3.2 Phenylene bridged metallocatalysts – synthesis, characterization, and stability

Hybrid metallocatalysts were prepared by NHSG (Scheme 1). This technique is known to yield highly porous mixed metal oxides [33,43–45]. Another advantage is that the kinetics of condensation of different metal precursors are levelled off in NHSG (as compared to classical hydrolytic sol-gel) and therefore it allows for a good control over the homogeneity of the formed mixed metal oxide [27–29]. Here, two NHSG pathways were applied: the acetamide elimination route [43,46] and the alkylhalide elimination (ether) route [44,45] (eq. 4 and 5). Reactions were performed at 130 °C in autoclaves in order to get high condensation degrees

and obtain gels (Scheme 1). This was necessary mainly in the case of acetamide elimination route, where homocondensation of two acetoxy- groups resulting in acetic acid anhydride and $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bridge formation (eq. 4) was reported to occur slowly at lower temperatures [47,48].



The formation of Si–O–M bridges was clearly evidenced by ToF-SIMS analyses. Mixed oxide clusters (AlSiO_3^- , $\text{AlSi}_2\text{O}_5^-$, NbSiO_5^- , and $\text{NbSi}_2\text{O}_7^-$) were unambiguously observed in mass spectra upon bombardment of catalyst surface with Bi_5^+ . The detection of such ions is an indication of the presence of species with Si–O–M bonds at the surface of the analyzed material.[49] Relative intensities of peaks associated to these masses and its consequences on homogeneity of prepared materials are discussed in detail below (see section 3.3) Another strong evidence of Si–O–Nb bridges formation was found in IR spectra of niobium silicate samples: absorption band at 920 cm^{-1} originating in valence vibrations of Si–O–Nb bridges as well as Si–OH bonds[50] increased significantly in its intensity upon Nb incorporation indicating an extensive formation of Si–O–Nb bridges (Fig. 6S). Other IR absorption bands (e.g. ν Si–O–Al and ν Si–O–Si at $1030\text{--}1050 \text{ cm}^{-1}$) or NMR signals (e.g. $(\text{C}_{\text{ar}}\text{Si}(\text{OSi})(\text{OH}/\text{Al}/\text{Nb})_2$ at -61 ppm and $(\text{C}_{\text{ar}}\text{Si}(\text{OSi})_2(\text{OH}/\text{Al}/\text{Nb})$ at -71 ppm) overlapped strongly and could not be used as unambiguous M–O–Si bridges formation evidence.

IR (ESI), ^{13}C (Fig. 7S) and ^{29}Si NMR (Fig. 6) spectra and XPS (Fig. 5S and 8S) confirmed presence of phenylene bridges in the hybrid metallosilicate materials, similar to **SiPhSi-Ac**. In XP spectra phenylene bridged metallosilicates exhibited very intense C 1s peak with a shake-up satellite peak characteristic for aromatic groups (Fig. 8S). The position of Si 2p peak was shifted again by 1 eV from SiO_2 and NHSG-prepared purely inorganic benchmark [38]. However in this case some Si-C bond cleavage already occurred in the as-prepared samples as reflected by the larger peak width (higher FWHM) of Si 2p peak in XP spectra (Fig. 5S). Quantification of this cleavage was performed by ^{29}Si MAS NMR and discussed in detail (see below).

Textural properties (Table 3) of prepared materials strongly depended on the chosen synthetic route. While materials prepared by the acetamide elimination route were mostly microporous, their hysteresis loop did not close (similar to metal free **SiPhSi-Ac**), and their surface areas and pore volumes reached up to $49 \text{ m}^2 \text{ g}^{-1}$ and $0.051 \text{ cm}^3 \text{ g}^{-1}$ respectively (Fig. 1), materials synthesized by the ether route were mesoporous and reached markedly higher surface areas and pore volumes (up to $880 \text{ m}^2 \text{ g}^{-1}$ and $1.4 \text{ cm}^3 \text{ g}^{-1}$, respectively, Fig. 5). All samples were XRD amorphous and did not exhibit any pore ordering according to SAXS analyses (Fig. 3S); the TEM micrographs revealed only ill-defined and non-organized aggregates in a broad agreement with XRD and textural analyses (Fig. 9S).

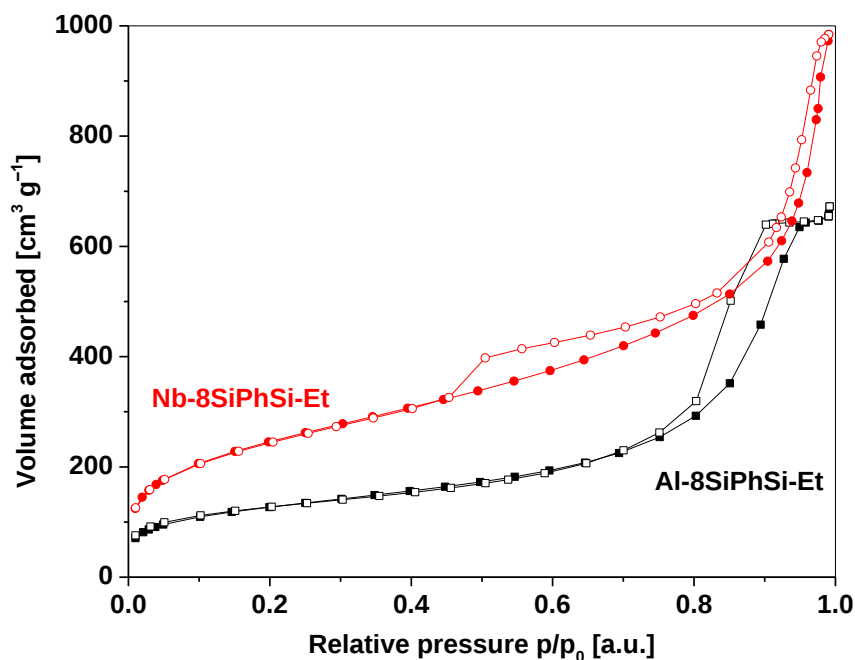


Fig. 5: N_2 adsorption-desorption isotherm of phenylene bridged metasilicates prepared alkyl halide elimination (ether) route.

The stability of phenylene bridges was found to be markedly affected by metal introduction. As prepared **Al-8SiPhSi-Ac** (annealed at 250 °C in dry N_2) already displayed an extensive cleavage of Si-C bonds (T site proportion was only 79 %, compare to 100 % for **SiPhSi-Ac**, Fig. 6). It is worth noting that mass loss of as prepared **Al-8SiPhSi-Ac** was higher than the expected value (42 % vs. 32 %). It can be explained by the presence of residual acetoxy- groups, which is clearly reflected in IR and NMR spectra (bands representing asymmetric valence COO vibration in IR spectra at 1535 and 1710 cm^{-1} , signals of methyl and carboxyl groups in ^{13}C CPMAS NMR spectra at 21, and 169–177 ppm, respectively; Fig. 7S). The presence of broad signals in ^{13}C CPMAS NMR spectra in the chemical shift range comprised between 169 and 177 ppm suggests that some of the acetoxy- groups are in the bidentate form [42]. This assumption can be further supported by the observation of two sets of bands originating from symmetrical and asymmetrical vibrations of COO groups in IR spectra (ESI) [51,52]. The bidentate acetoxy- groups are coordinated to the

aluminum atoms and make them predominantly six-coordinated. ^{27}Al MAS NMR spectra corroborate this hypothesis; a major contribution comes from AlO_6 species in as-prepared sample, while signal for AlO_4 moieties becomes the most intense peak after calcination at 400 °C (when most of the acetoxy- groups is burned, Fig. 10S.). As another consequence, these bidentate acetoxy- groups are very stable and lower the catalytic activity of **Al-8SiPhSi-Ac** (see below).

TG analysis showed that thermal decomposition of **Al-8SiPhSi-Ac** started already at ca. 400 °C in dry air (Fig. 7), ca. 100 °C earlier than for metal-free **SiPhSi-Ac**. ^{29}Si MAS NMR analysis confirmed that the damage to the material was deeply progressing with thermal treatment: no T signal was observed after calcination at 400 °C (only Q signal coming from SiO_4 species between -90 and -120 ppm, Fig. 6). Yet, the mass loss of calcined sample during TGA was still relatively high (22 %, Fig. 7, Table 2). The possible contribution to high mass loss is coke formation by carbonization of phenylene bridges and residual acetoxy- groups; sample after calcination at 400 °C is black.

The dynamic HT stability test allowed to highlight an important release of benzene already at 205 °C for sample **Al-8SiPhSi-Ac** (Fig. 4). ^{29}Si MAS NMR spectra further evidenced the very low hydrothermal stability of **Al-8SiPhSi-Ac**: T sites proportion after static HT stability test was only 22 %. (Table 2, Fig. 6). Moreover the amount of organic groups after static HT treatment decreased significantly in comparison to as-prepared sample as can be deduced from TG analyses (Fig. 7, Table 2). Similar to what is observed with the calcined sample, the mass loss after static HT stability test was higher than expected on the basis of ^{29}Si MAS NMR spectra. It is

probably caused by carbonization of organic groups. Finally, the poor HT stability was observed also by a loss of porosity: the solid was nonporous after static HT treatment (Table 3).

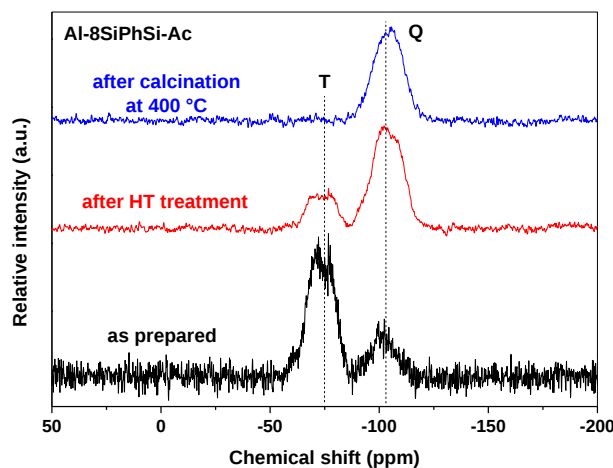


Fig. 6: ^{29}Si MAS NMR spectra of **Al-8SiPhSi-Ac** after various treatment.

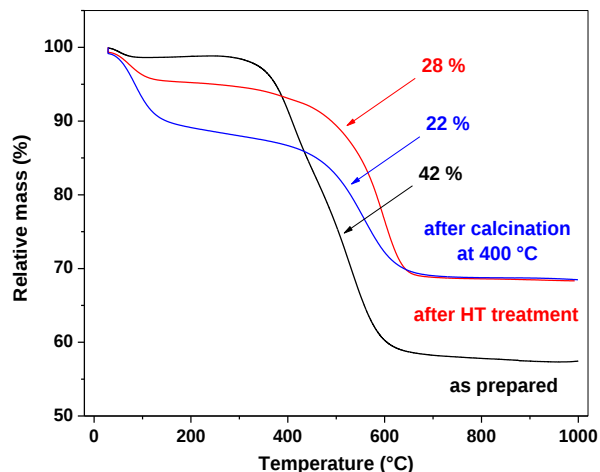


Fig. 7: TG curves of **Al-8SiPhSi-Ac** after various treatment.

The sample with identical composition prepared by the ether route (**Al-8SiPhSi-Et**) displayed also a significant stability drop. Similar to **Al-8SiPhSi-Ac** the as-prepared sample **Al-SiPhSi-Et** (annealed at 250 °C in dry N_2) exhibited considerable Si-C bond cleavage based on ^{29}Si MAS NMR spectra, T site proportion was 40 % (Fig. 8, Table 2). However most of the organic groups were preserved within **Al-SiPhSi-Et** – not as phenylene bridges, but as terminal phenyl moieties – these were observed as a very intense peak in ^{13}C NMR spectrum (Fig. 7S). Moreover the TGA mass loss was close to the theoretical value (34 % vs. 32 %, Fig. 9) and the as-prepared sample was only slightly yellowish indicating the absence of coke coming from carbonization of organic groups.

Thermal stability of **Al-SiPhSi-Et** was very poor: no T signal was observed in ^{29}Si MAS NMR spectra after calcination at 400 °C (only Q signal, Fig. 8). Mass loss exhibited by calcined sample (19 %) can be thus ascribed to coke formed by carbonization of phenylene and phenyl groups (sample after calcination at 400 °C is black, Fig. 9, Table 2).

Interestingly, **Al-8SiPhSi-Et** displayed somewhat higher stability during dynamic HT treatment in comparison to **Al-8SiPhSi-Ac**. While the sample from acetamide elimination route (**Al-8SiPhSi-Ac**) released benzene already at 205 °C, the sample from ether route (**Al-8SiPhSi-Et**) showed first hints of benzene at 275 °C (Fig. 4). Sample **Al-SiPhSi-Et** showed similar extensive Si-C bond cleavage to **Al-8SiPhSi-Ac** after static hydrothermal stability test at 240 °C; T site proportion in ^{29}Si MAS NMR spectra dropped to 12 % (Table 2). Textural properties were deteriorated after static HT treatment, surface area and pore volume dropped by 29 and 54 %, respectively (Table 3). Unlike **Al-8SiPhSi-Ac**, sample **Al-SiPhSi-Et** retained some porosity again pointing at its somewhat higher HT stability.

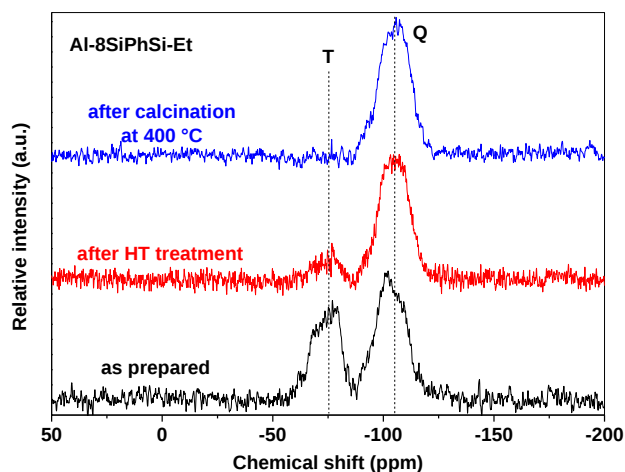


Fig. 8: ^{29}Si MAS NMR spectra of **Al-8SiPhSi-Et** after various treatment.

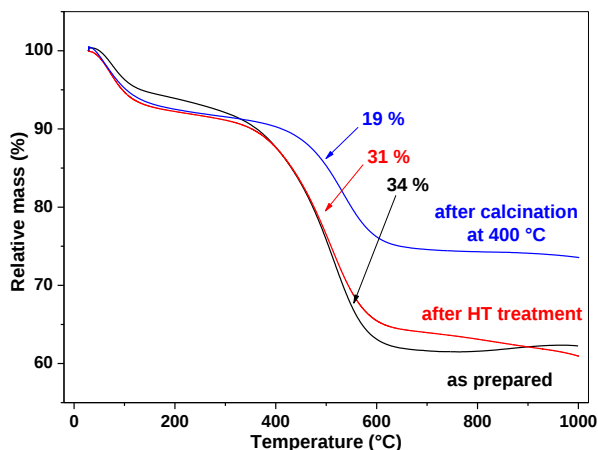


Fig. 9: TG curves of **Al-8SiPhSi-Et** after various treatment.

In order to better understand the observed hydrolytic reactions and release of benzene from phenylene bridged metallocsilicates, Nb containing samples were prepared in the same manner by acetamide elimination and ether route. The obtained results closely resemble those obtained for samples containing Al. Both as-prepared samples exhibited already some Si–C bond cleavage; T site proportions were 73 and 78 % for **Nb-8SiPhSi-Ac** and **Nb-8SiPhSi-Et**, respectively (Fig. 10 and 11, Table 2). Thermal stability was much lower for both samples than in the case of metal free **SiPhSi-Ac** (Table 2). ²⁹Si MAS NMR spectra after static HT stability test revealed that the Si–C bond hydrolysis was considerably progressing, T site proportions decreased to 45 and 58 % for **Nb-8SiPhSi-Ac** and **Nb-8SiPhSi-Et**, respectively (Fig. 10 and 11, Table 2). All these data were in a good agreement with TG analyses (Fig. 11S and 12S). Static HT stability test also provoked a porosity loss. Similar to Al samples **Nb-8SiPhSi-Ac** was completely nonporous after static HT treatment. **Nb-8SiPhSi-Et** kept some surface area and pore volume (80 and 54 %, respectively, as compared to the as-prepared sample, Table 3). Finally benzene release was observed at 205 °C for sample **Nb-8SiPhSi-Ac**; sample from ether route (**Nb-8SiPhSi-Et**) started to release benzene at 275 °C (Fig. 4). It is noteworthy that the sample prepared by acetamide elimination route displays more extensive Si–C bond cleavage after all types of treatment (as-prepared, calcination, static HT treatment). Moreover it starts to release benzene at lower temperature than **Nb-8SiPhSi-Et**. Finally, after static HT stability test, the textural properties of **Nb-8SiPhSi-Ac** are affected more deeply than for **Nb-8SiPhSi-Et**. Thus **Nb-8SiPhSi-Ac** clearly appears less stable than the corresponding hybrid material prepared by the ether route.

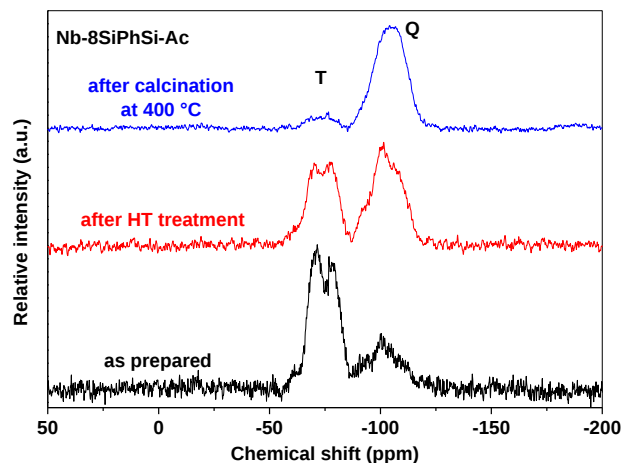


Fig. 10: ^{29}Si MAS NMR spectra of **Nb-8SiPhSi-Ac**

after various treatment.

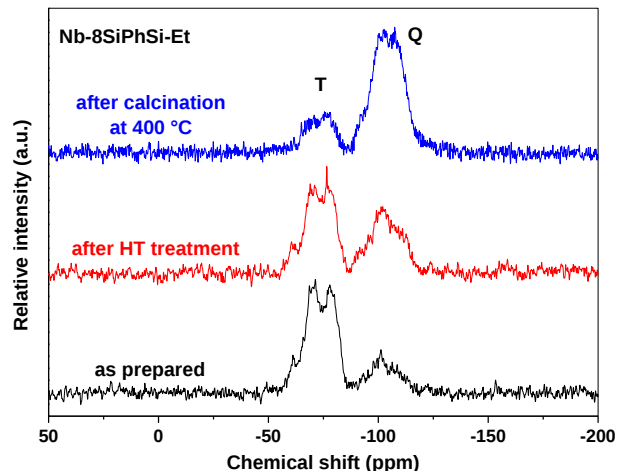


Fig. 11: ^{29}Si MAS NMR spectra of **Nb-8SiPhSi-Et**

after various treatment.

3.3 Identification of stability drop cause – homogeneity of M/Si mixing and electronegativity

To identify the possible reasons for the different stability of samples prepared by ether and acetamide elimination route, we inspected their properties as revealed by a variety of characterization techniques. **Al-8SiPhSi-Et** and **Al-8SiPhSi-Ac** both had similar Si:Al ratios and they both contained comparable amount of phenyl and/or phenylene groups. The degree of condensation was also very similar based on ^{29}Si MAS NMR spectra (Table 1S). The less stable **Al-8SiPhSi-Ac** had a lower surface area than more stable **Al-8SiPhSi-Et** (Table 3). Thus, higher surface area as a cause for lower hydrothermal stability can be ruled out. Both samples could in principle exhibit different amounts of Brønsted acid sites (H^+ could promote Si-C bond scission by an electrophilic aromatic substitution) [53]. A possible role of acidic protons on the instability of the hybrids was however excluded by a specific experiment: **Al-8SiPhSi-Ac** and **Al-8SiPhSi-Et**

were exposed to a mixture of EtOH and 2,6-ditertbutyl pyridine (a strong base known to interact selectively with H^+ due to its steric constraints) [54] and compared to a catalytic run with EtOH only. For both catalysts, while activity in ethanol dehydration decreased (i.e. Brønsted acid sites were selectively poisoned), the production of benzene remained unaffected (Fig. 13S).

The homogeneity of these hybrid Si-Al materials (which can be viewed as the degree of dispersion of Al in the hybrid silica matrix) was clearly different, depending on the synthesis route. For **Al-8SiPhSi-Ac** the surface molar Si:Al ratio determined by XPS fitted almost perfectly with the bulk molar Si:Al ratio determined by ICP-OES, indicating a high homogeneity for this material. For **Al-8SiPhSi-Et**, the amount of Al detected at the surface layer was slightly lower, hinting at its lower homogeneity (Table 1).

The homogeneity of Al mixing within silica matrices was further studied using ToF-SIMS. Peaks of $(AlSiO_3)^-$, $(AlSi_2O_5)^-$, $(Al_2O_4)^-$, and $(AlO_2)^-$ were followed at $m/z = 102.94$, 162.92 , 117.95 , and 58.967 , respectively (relevant parts of mass spectra Fig. 14S). These signals were well resolved, without any overlap, and undoubtedly assigned. The peak area for the first two masses is taken as an indication of the presence of homogeneously dispersed Al in silica. The peak area of the third mass is taken as an indication of the presence of alumina clusters (poorly dispersed Al oxide species). Finally the peak area of the last mass is a function of Al concentration in the surface layer. Reporting the peak areas of the Al-Si moieties vs. alumina clusters it appears that the sample prepared by acetamide elimination route (**Al-8SiPhSi-Ac**) shows relatively more mixed Al-Si clusters than the sample prepared by the ether route (**Al-8SiPhSi-Et**) (Fig. 12a and b). In a very good agreement, the peak area ratio of $(Al_2O_4)^-$ vs. $(AlO_2)^-$ shows a higher proportion of alumina clusters per aluminum atoms in surface layer for **Al-8SiPhSi-Et** in

comparison to **Al-8SiPhSi-Ac** (Fig. 12c). Therefore we suggest that Al dispersion in hybrid silica in sample **Al-8SiPhSi-Ac** is better than in **Al-8SiPhSi-Et**. Thus, it seems that the homogeneity of Si-Al mixing has a direct influence on Si-C bond hydrolytic stability. We propose that the more homogeneous distribution of Al in phenylene silsequioxane matrices, the less stable these materials are. Our hypothesis works with the fact that a homogeneous Al dispersion implies higher amount of Si-O-Al bridges, which introduce instability into hybrid metallosilicates similar to pure inorganic metallosilicates and zeolites under gas-phase hydrothermal conditions [25]. Unlike inorganic materials, where the highly polar Al-O bond is reported to have the lowest stability (leading in turn to dealumination) [25], we observe the most striking difference in Si-C bond stability upon Al introduction in hybrid metallosilicates.

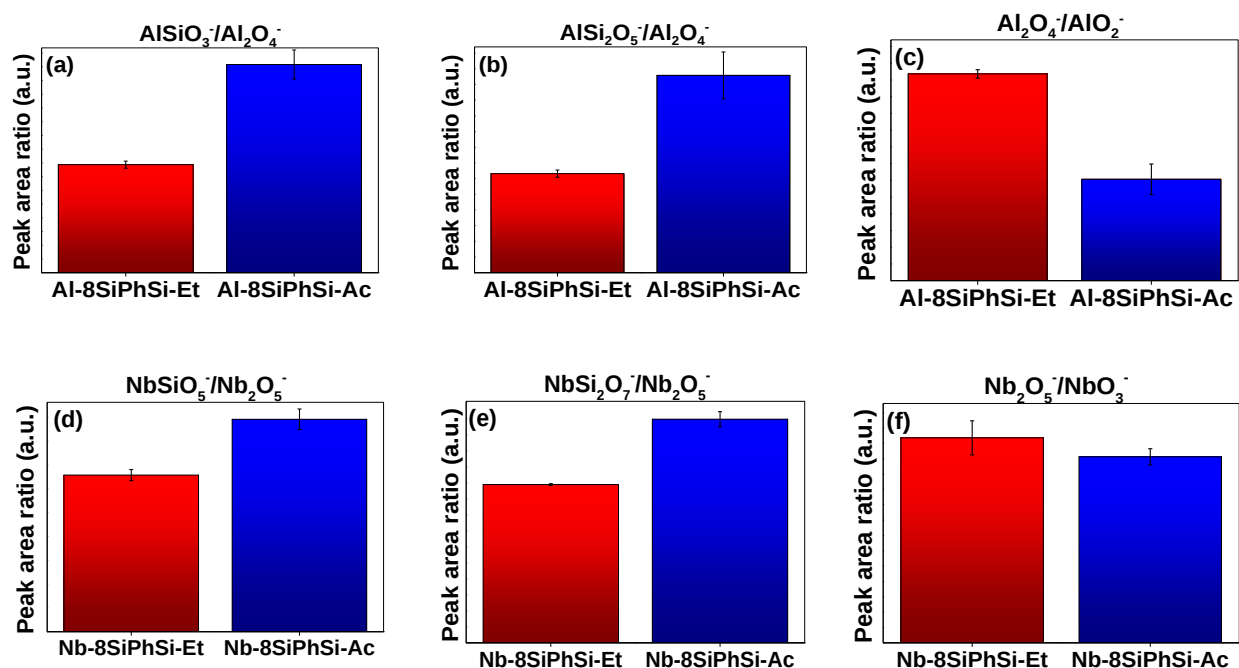


Fig. 12: Comparison of samples prepared by acetamide elimination (blue) and ether route (red) in terms of peak area ratios of various masses in mass spectra obtained by ToF-SIMS. Plots a, b, and c refer to Al containing samples, plots d, e, and f to Nb containing samples.

The possible reasons for different hydrothermal and thermal stabilities of **Nb-8SiPhSi-Ac** vs. **Nb-8SiPhSi-Et** were also analyzed. On the one hand, influence of degree of condensation (which is similar for both samples according to ^{29}Si MAS NMR, Table 1S) and surface area (which is lower for less stable material) was ruled out, similar to Al containing samples. On the other hand, striking difference in Nb dispersion within hybrid silica matrices was again observed. Nb content in the surface layer was much lower than in bulk material in the sample prepared by ether route, while well corresponding values were observed for the sample prepared by acetamide elimination route (XPS, ICP-OES, Table 1). Moreover ToF-SIMS revealed that **Nb-8SiPhSi-Et** contained less mixed Nb-Si moieties (NbSiO_5^- and $\text{NbSi}_2\text{O}_7^-$, $m/z = 200.89$ and 260.86 , respectively) and more niobia clusters (Nb_2O_5^- , $m/z = 265.81$) per Nb atoms in surface layer (NbO_3^- , $m/z = 140.90$) in comparison to **Nb-8SiPhSi-Ac** (Fig. 12d, e, and f). Thus it is possible to suggest again that the degree of homogeneity plays a significant role in hydrothermal and thermal stability of hybrid metallosilicates (based on the results for both Al and Nb containing samples).

It is noteworthy, that the abrupt decrease of gas phase HT stability of phenylene bridged silsesquioxane matrices upon metal introduction is in striking contrast to what was observed in boiling water, where an improvement of HT stability was observed upon metal insertion (based on BET and XRD analyses) [23,24]. Moreover the bonds reported to cleave in boiling water are Si–O–Si bridges, while in our case we observe the hydrolysis to occur at the expense of Si–C bonds. However it is useful to realize that gas phase and liquid phase hydrothermal stabilities of

zeolites are also two completely different cases with Al–O bonds being cleaved in the former, while the latter causes the Si–O–Si or Si–O–M bridges to hydrolyze (depending on pH) [25].

At this point we intend to identify the cause of such an abrupt decrease of (hydro)thermal stability upon introduction of metals into the silsesquioxane matrices. While Al and Nb have very similar electronegativities (1.61 and 1.60 according to Pauling, respectively), Si exhibits different electronegativity value (1.90). The differences in electron withdrawing properties between Si and guest elements (Al, Nb) can introduce partial charges into the silsesquioxane matrices making them prone to attack by polar water molecules. This is in a good agreement with our hypothesis that the higher content of polar Si–O–Al/Nb bridges in materials with better metal dispersion causes their lower stability.

To prove the effect of electronegativity phenylene bridged silsesquioxane with tin was synthesized by acetamide elimination route (**Sn-8SiPhSi-Ac**; details on synthesis and characterization in ESI). Tin has an electronegativity value close to silicon (1.96). Indeed, sample **Sn-8SiPhSi-Ac** was more stable than its corresponding Al and Nb derivatives. The as-prepared sample contained intact phenylene bridges as deduced from ^{29}Si MAS NMR spectra where only signals of T sites were observed (compare with T site proportion ranging from 44 to 85 % for Al and Nb containing samples, Fig. 13). Calcination at 400 °C only led to a mild Si–C bond cleavage in comparison to **Al-8SiPhSi-Ac** and **Nb-8SiPhSi-Ac** (T site proportion 41 %, Fig. 13). Finally, **Sn-8SiPhSi-Ac** started to release low amounts of benzene at 275 °C (Fig. 4) during dynamic HT treatment (compared to substantial evolution of benzene from **Al-8SiPhSi-Ac** and **Nb-8SiPhSi-Ac** already at 205 °C). In a good agreement, lower amount of Si–C bonds was cleaved after static HT stability test in comparison to **Al-8SiPhSi-Ac** and **Nb-8SiPhSi-Ac** (T site proportion 77 %

according to ^{29}Si MAS NMR spectra, Fig. 13). Electronegativity of inserted metal was thus identified to be a second important parameter (after homogeneity of M/Si dispersion) influencing stability of hybrid metallosilicates.

3.4 Increasing stability of hybrid metallosilicates – xylylene bridged material

It is known that $\text{Si-C}(\text{sp}^3)$ bonds are more resistant towards both electrophilic and nucleophilic substitution than $\text{Si-C}(\text{sp}^2)$ bonds [53,55]. In order to increase the stability of our materials, but retain hydrophobic aromatic groups, aluminum-containing *p*-xylylene ($-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$) bridged silsesquioxane was prepared by acetamide elimination route (**Al-8SiXySi-Ac**; details on synthesis and characterization in ESI). SS NMR unambiguously proved the presence of $\text{Si-CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{Si}$ moieties in the as-prepared sample, new intense signal ascribed to methylene species was observed at 22 ppm in ^{13}C CP MAS NMR spectra. N_2 physisorption measurements (Fig. 15S) indicated presence of both micro- and mesopores in contrary to phenylene bridged samples prepared by acetamide elimination route, which were completely microporous. Surface area reached $520 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.33 \text{ cm}^3 \text{ g}^{-1}$, and average pore diameter 2.5 nm for **Al-8SiXySi-Ac**. According to t-plot analysis 46 % of pore volume was microporous with meso and larger pores accounting for the rest. Varying bridging groups (length and flexibility) has been already reported as a way to change textural properties in hybrid materials made via NHSG [33]. Finally, similar to **Al-SiPhSi-Ac** two sets of signals of acetoxy- groups were observed in IR spectra and COO peak was broadened towards lower field in ^{13}C NMR spectra indicating the presence of bidentate acetoxy- moieties. Again, these groups

coordinated to Al atoms, made them predominantly six-coordinated (^{27}Al MAS NMR spectra Fig. 10S), and impaired catalytic activity of **Al-8SiXySi-Ac** (see below).

The as-prepared sample contained solely well preserved xylylene bridges (no SiO_4 moieties, compare with T site proportion of 79 % for **Al-SiPhSi-Ac**, Fig. 14). On the contrary, Si-C bonds in the sample calcined at 400 °C were almost completely cleaved (Fig. 14). Importantly, the first hints of xylene (product of hydrolysis of Si-C bonds) were observed at 345 °C only during the dynamic HT stability test (not shown); moreover no Si-C bond hydrolysis was observed after 24 hrs at 240 °C on stream (static HT treatment, Fig. 14). Based on these results it can be concluded that the hydrothermal stability of **Al-8SiXySi-Ac** was significantly improved in comparison to phenylene bridged metallosilicates and was close to **SiPhSi-Ac** (metal free phenylene bridged sample). The hydrothermal as well as thermal stability limit temperature is ca. 345 °C for xylylene bridged hybrid metallosilicates. It is worth noting that this value is close to the temperature (400 °C), at which a transformation of bridging methylene moieties to terminal methyl groups was observed in metal free hybrid silica samples [6]. At the same time, it is above the thermal stability limit (300 °C) of ethylene bridged silsesquioxanes (no metal) [2].

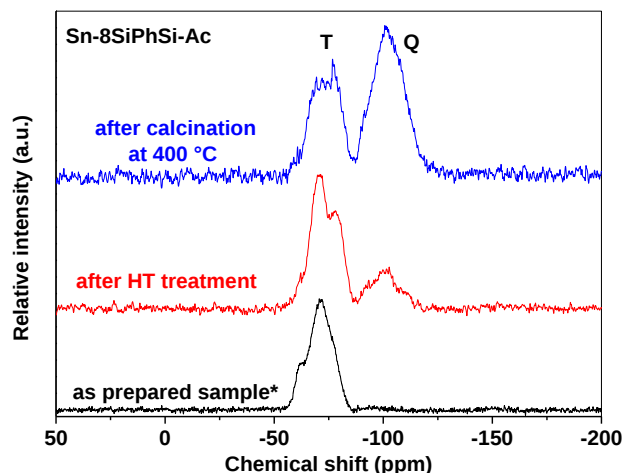


Fig. 13: ^{29}Si (CP)MAS NMR spectra of **Sn-8SiPhSi-Ac**

after various treatment, *denotes CPMAS spectrum.

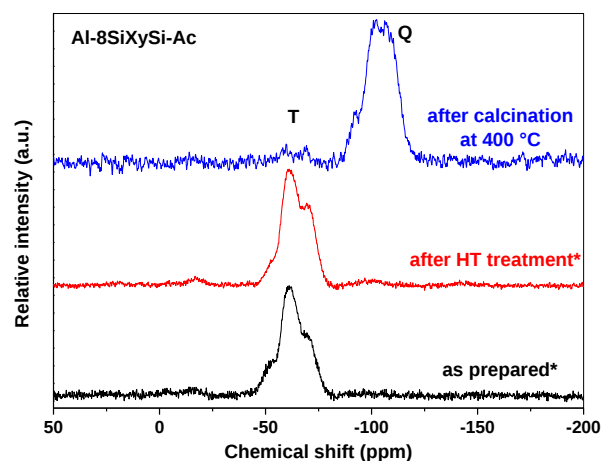


Fig. 14: ^{29}Si (CP)MAS NMR spectra of **Al-8SiXySi-Ac**

after various treatment, *denotes CPMAS spectra.

3.5 Catalysis

As-prepared materials were tested as catalysts for the gas-phase ethanol dehydration in the temperature range between 205 and 400 °C. The major products of catalytic reaction were ethylene and diethylether; other observed products in very low amounts were acetaldehyde, butenes, and butadiene (mainly at higher temperatures). Taking the experimental variability into account, the carbon balance is almost equilibrated (92 to 106 %). Ethylene selectivity was high and similar for all samples prepared by NHSG (75–100 %) and was substantially higher than for commercial benchmarking catalyst (Silica alumina catalyst support grade 135), which was the only sample producing vast amounts of diethylether. A comparison of selectivity to ethylene and diethylether is given in Table 4 for all samples close to full ethanol conversion (80–90 %). While NHSG prepared catalysts displayed selectivity to ethylene up to 95.5 %, commercial silica-alumina gives only 56.7 %. The opposite trend was observed for diethylether selectivity – silica-

alumina showed the highest number (30.8 %), while NHSG prepared catalysts exhibited much lower diethylether selectivities (2.00–18.0 %).

Table 4: Ethylene and diethylether selectivities for NHSG prepared catalysts and commercial benchmark catalyst close to full ethanol conversion (80–90 %).

Sample	Conversion [%]	Temperature [°C]	Ethylene selectivity [%]	Diethylether selectivity [%]
Commer. Al-Si	86.6	310	56.7	30.8
Al-16Si-Et	84.5	275	95.5	8.54
Al-8SiPhSi-Ac	84.5	310	75.8	14.2
Al-8SiPhSi-Et	90.6	275	88.6	18.0
Nb-8SiPhSi-Ac	94.0	390	95.3	2.00
Nb-8SiPhSi-Et	87.3	400	95.1	4.87
Al-8SiXySi-Ac	80.4	345	73.4	5.24

The activity of hybrid Al samples was as follows: **Al-8SiPhSi-Et** > **Al-8SiPhSi-Ac** > **Al-8SiXySi-Ac** (Fig. 15). While higher activity was expected for samples prepared by acetamide elimination route (since they display high homogeneity of Si-Al mixing, and therefore putatively a high density of active sites for dehydration), one factor strongly impaired their performance: the strong binding of acetoxy- groups to aluminum causing high amounts of six-coordinated Al atoms (Fig. 10S).

Hybrid Al-containing samples were compared to pure inorganic catalyst prepared by the ether route (**Al-16Si-Et**). Similar high catalytic activity and ethylene yields were observed for hybrid **Al-8SiPhSi-Et** and pure inorganic **Al-16Si-Et**. The commercial benchmarking silica-alumina exhibited

slightly lower ethanol conversion than the best NHSG catalysts (**Al-8SiPhSi-Et** and **Al-16Si-Et**), however due to its low ethylene selectivity the ethylene yields were much lower.

Niobium samples exhibited lower catalytic activity than their Al analogues, as expected, due to generally lower acid strength of niobium silicates in comparison to aluminosilicates [56,57]. In this case, more homogeneous sample (**Nb-8SiPhSi-Ac**) was more active than the less homogeneous catalyst (**Nb-8SiPhSi-Et**). The amount of acetoxy- groups in as-prepared **Nb-8SiPhSi-Ac** was much lower than in **Al-8SiPhSi-Ac** meaning that the affinity of acetoxy- groups to Nb atoms is not as high as it is in the case of aluminum.

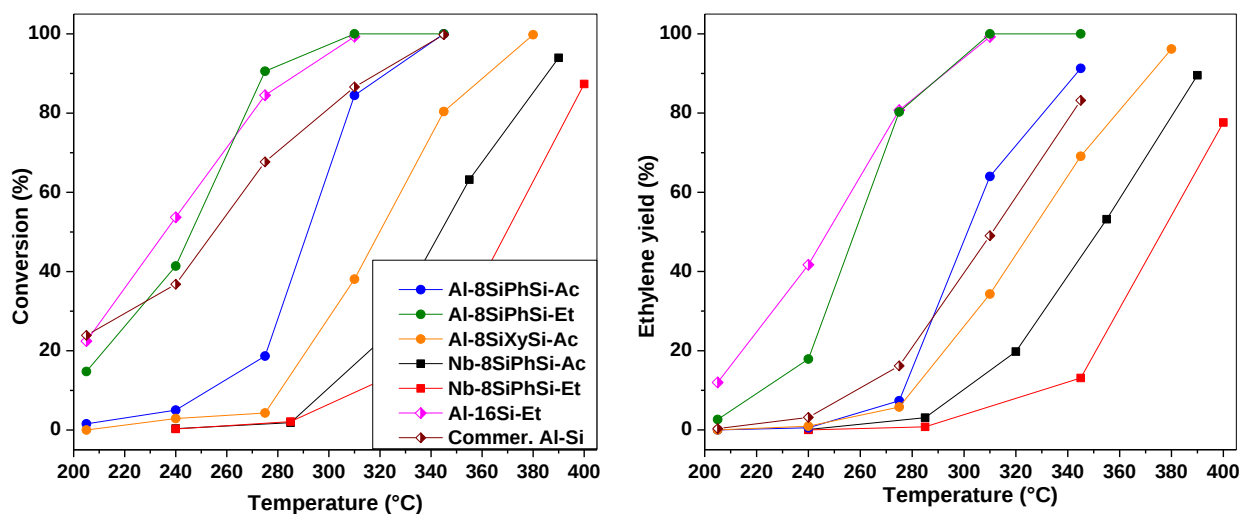


Fig. 15: Ethanol conversion and ethylene yield at different temperatures over hybrid metallosilicate catalysts.

In order to better understand the observed catalytic activity and selectivity, we attempted to compare the catalysts in terms of acid site loading, strength, and nature. Data for fully inorganic catalysts (**Al-16Si-Et** and commercial **Al-Si**) obtained via combination of IR spectroscopy with pyridine adsorption are given in Table 5. For hybrid samples it was not possible to record

reproducible and reliable data due to their poor thermal stability (dehydration step lead to the catalyst degradation).

Table 5: Acid site loading, strength, and nature for NHSG prepared Al-16Si-Et and commercial benchmark catalyst.

Sample	Total acid sites (mmol g ⁻¹)	B/L ratio (-)	Acid sites after desorption at 350 °C ^a (%)	B/L ratio ^a (-)
Commer. Al-Si	0.14	0.24	33	0.05
Al-16Si-Et	0.027	0.83	72	0.17

Commercial catalyst had 5 times higher acid site loading than NHSG prepared sample (one of the reasons being higher Al concentration), these acid sites were mostly weak and Lewis in nature. On the contrary **Al-16Si-Et** exhibited much stronger acid sites (72 vs. 33 % of pyridine kept after evacuation at 350 °C) with higher fraction of Brønsted acid sites. This can tentatively be attributed to a better homogeneity in the aluminosilicate made by NHSG. Both acid site strength and nature have been already reported to influence significantly alcohol dehydration (stronger acid sites provide more ethylene due to more pronounced dehydration),^[58,59] therefore it can be argued that these properties present the decisive advantage of NHSG prepared samples leading to outperformance of commercial benchmark (mainly in the ethylene selectivity). The reasons for lower catalytic activity in the case of samples prepared by acetamide elimination route and Nb-based have been already discussed (strong acetate binding and lower strength of Nb acid sites in comparison to Al sites).

Finally, it is important to make a connection between the HT stability and catalytic activity. **Al-8SiXySi-Ac** (xylylene bridged material) was the only hybrid catalyst which was able to reach high

ethanol conversion without any observation of hydrolytic products (xylene); substantial release of benzene was observed for all phenylene bridged metallosilicates during catalytic experiments. The improved hydrothermal stability of xylylene bridges makes **Al-8SiXySi-Ac** promising as a starting point for further studies (e.g. lower loading of hydrophobic organic groups, etc.).

4. Conclusions

In this paper we have described the synthesis of homogeneous and highly porous hybrid silicate and metallosilicate materials via non-hydrolytic sol-gel routes. We show that the hydrothermal gas-phase and thermal stability of hybrid phenylene bridged silica materials abruptly decrease upon metal introduction (M = Al, Nb, Sn). The degradation of hybrid materials was reflected mainly in the hydrolysis of Si-C bonds, which was revealed by the evolution of benzene in reaction conditions, by a mass loss in TGA and by the formation of Q sites detected in ^{29}Si MAS NMR spectra. While the first hint of Si-C bonds cleavage was observed at 345 °C for metal free silica, extensive hydrolysis took place between 205 and 275 °C already for hybrid metallosilicates. These results differ from the previously reported data on hydrothermal stability of Al and Zr containing PMOs in boiling water where an improvement of stability was observed upon metal insertion [23,24]. The gas phase HT stability of hybrid metallosilicates with aromatic groups was improved by the introduction of xylylene instead of phenylene bridges due to better stability of Si-C(sp²) bonds.

Among the phenylene bridged metallosilicates studied, Sn-containing sample was the most stable. It was concluded that this is due to its electronegativity value, close to that of Si. Al and Nb differ more in electronegativity from Si, thus introducing higher partial charges into the silsesquioxane networks and making them prone to attack by polar water molecules. Homogeneity of metal dispersion in hybrid silica (and consequently the number of Si–O–M bridges) was identified as the other key factor influencing stability. The potential influence of surface area, degree of condensation, and Brønsted acid sites was discarded.

In the gas-phase ethanol dehydration reaction, the most active hybrid catalysts made by NHSG markedly outperformed a commercial silica-alumina benchmark catalyst, mainly owing to a much higher ethene selectivity. Yet, a similar catalytic activity was also achieved with a purely inorganic catalyst prepared in the same way. Also, in terms of stability, we show that all phenylene bridged metallosilicates hydrolyzed in the course of the reaction and released benzene. The only stable hybrid metallosilicate able to achieve high ethanol conversion under reaction conditions was the xylylene bridged aluminosilicate. It is suggested that this functionality should be investigated further – possibly with a lower degree of organic groups content – in a search for higher performance in ethanol dehydration.

Funding Sources

Marie Skłodowska-Curie grant agreement No 751774.

F.R.S.–F.N.R.S project "EQP U.N030.18.

Communauté française de Belgique, ARC programme 15/20-069.

Notes

The authors declare no competing financial interest.

Acknowledgements

A.S. acknowledges funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 751774. F.R.S.–F.N.R.S. is thanked for the acquisition of the physi-chemisorption equipment used here (project "EQP U.N030.18"). Authors acknowledge the 'Communauté française de Belgique' for the financial support through the ARC programme (15/20-069). This research used resources of the "Plateforme Technologique Physico-Chemical Characterization" – PC², the SIAM platform (Synthesis, Irradiation & Analysis of Materials) and the MORPH-IM platform (Morphology & Imaging) located at the University of Namur. Authors thank L. Simonikova for performing ICP-OES analyses and V. Vykoukal for TEM micrographs. CIISB research infrastructure project LM2015043 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements at the CF Cryo-electron Microscopy and Tomography and at the CF X-ray Diffraction and Bio-SAXS. This research has been financially supported by the MEYS CR under the project CEITEC 2020 (LQ1601). François Devred and Jean-François Statsyns are acknowledged for the technical and logistical support.

References

- [1] M. Faustini, L. Nicole, E. Ruiz-Hitzky, C. Sanchez, *Adv. Funct. Mater.* 28 (2018) 1704158.
- [2] D. Esquivel, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, *Mater. Lett.* 65 (2011) 1460–1462.
- [3] D. Esquivel, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, *J. Mater. Chem.* 21 (2011) 724–733.
- [4] P. Van Der Voort, D. Esquivel, E. De Canck, F. Goethals, I. Van Driessche, F.J. Romero-Salguero, *Chem. Soc. Rev.* 42 (2013) 3913–3955.
- [5] A.P. Dral, C. Lievens, J.E. Ten Elshof, *Langmuir* 33 (2017) 5527–5536.
- [6] T. Asefa, M.J. MacLachlan, H. Grondey, N. Coombs, G.A. Ozin, *Angew. Chemie - Int. Ed.* 39 (2000) 1808–1811.
- [7] C. Bispo, P. Ferreira, A. Trouvé, I. Batonneau-Gener, F. Liu, F. Jérôme, N. Bion, *Catal. Today* 218–219 (2013) 85–92.
- [8] S. An, Y. Sun, D. Song, Q. Zhang, Y. Guo, Q. Shang, *J. Catal.* 342 (2016) 40–54.
- [9] J.A. Melero, R. van Grieken, G. Morales, *Chem. Rev.* 106 (2006) 3790–3812.
- [10] J. Manayil, A. Lee, K. Wilson, *Molecules* 24 (2019) 239.
- [11] B. Rác, P. Hegyes, P. Forgo, Á. Molnár, *Appl. Catal. A Gen.* 299 (2006) 193–201.
- [12] A. Corma, U. Díaz, T. García, G. Sastre, A. Velty, *J. Am. Chem. Soc.* 132 (2010) 15011–15021.
- [13] R. Millini, G. Bellussi, *Catal. Sci. Technol.* 6 (2016) 2502–2527.
- [14] S. Zanardi, W.O. Parker, A. Carati, G. Botti, E. Montanari, *Microporous Mesoporous Mater.* 172 (2013) 200–205.
- [15] Y. Xia, W. Wang, R. Mokaya, *J. Am. Chem. Soc.* 127 (2005) 790–798.
- [16] B.J. Hughes, J.-B. Guilbaud, M. Allix, Y.Z. Khimyak, *J. Mater. Chem.* 15 (2005) 4728–4733.

- [17] J.A. Melero, J. Iglesias, J.M. Arsuaga, J. Sainz-Pardo, P. de Frutos, S. Blazquez, J. Mater. Chem. 17 (2007) 377–385.
- [18] S. Shylesh, P.P. Samuel, A.P. Singh, Microporous Mesoporous Mater. 100 (2007) 250–258.
- [19] S. Shylesh, P.P. Samuel, A.P. Singh, Catal. Commun. 8 (2007) 894–898.
- [20] W. Guo, X.S. Zhao, Microporous Mesoporous Mater. 85 (2005) 32–38.
- [21] Q. Yang, Y. Li, L. Zhang, J. Yang, J. Liu, C. Li, J. Phys. Chem. B 108 (2004) 7934–7937.
- [22] S.-R. Zhai, S.S. Park, M. Park, M.H. Ullah, C.-S. Ha, Eur. J. Inorg. Chem. 2007 (2007) 5480–5488.
- [23] R. Sánchez-Vázquez, C. Pirez, J. Iglesias, K. Wilson, A.F. Lee, J.A. Melero, ChemCatChem 5 (2013) 994–1001.
- [24] Q. Yang, J. Yang, Z. Feng, Y. Li, J. Mater. Chem. 15 (2005) 4268.
- [25] R. Gounder, Catal. Sci. Technol. 4 (2014) 2877–2886.
- [26] C. Angelici, B.M. Weckhuysen, P.C.A. Bruijninx, ChemSusChem 6 (2013) 1595–1614.
- [27] A. Styskalik, D. Skoda, C.E. Barnes, J. Pinkas, Catalysts 7 (2017) 168.
- [28] D.P. Debecker, V. Hulea, P.H. Mutin, Appl. Catal. A Gen. 451 (2013) 192–206.
- [29] D.P. Debecker, P.H. Mutin, Chem. Soc. Rev. 41 (2012) 3624–3650.
- [30] D.E. Katsoulis, M.E. Kenney, P.E. Vassilaras, Alternative Methods for the Synthesis of Organosilicon Compounds, WO2013137904A1, 2013.
- [31] M. Motevalli, D.L. Ou, A.C. Sullivan, J. Organomet. Chem. 445 (1993) 35–38.
- [32] J.H. Balthis, E.G. Rochow, D.G. White, in: J.C.B. Jr (Ed.), Inorg. Synth., John Wiley & Sons, Inc., 2007, pp. 45–47.
- [33] A. Styskalik, D. Skoda, Z. Moravec, M. Babiak, C.E. Barnes, J. Pinkas, J. Mater. Chem. A 3 (2015)

7477–7487.

- [34] Emeis C. A., *J. Catal.* 141 (1993) 347–354.
- [35] J. Rouquerol, F. Rouquerol, K.S.W. Sing, *Adsorption by Powders and Porous Solids*, Academic Press, 1998.
- [36] S. Lowell, *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*, Springer, 2004.
- [37] D.A. Shirley, *Phys. Rev. B* 5 (1972) 4709–4714.
- [38] C.D. Wagner, A. V Naumkin, A. Kraut-Vass, J.W. Allison, C.J. Powell, J.R. Rumble Jr, *Natl. Inst. Stand. Technol. Gaithersburg, MD* 20899 (2003).
- [39] J.J. Morrison, C.J. Love, B.W. Manson, I.J. Shannon, R.E. Morris, *J. Mater. Chem.* 12 (2002) 3208–3212.
- [40] Y. Hagiwara, A. Shimojima, K. Kuroda, *Bull. Chem. Soc. Jpn.* 83 (2010) 424–430.
- [41] A. Styskalik, J.G. Abbott, M.C. Orick, D.P. Debecker, C.E. Barnes, *Catal. Today* (2018) 1–9.
- [42] A. Styskalik, D. Skoda, Z. Moravec, J.G. Abbott, C.E. Barnes, J. Pinkas, *Microporous Mesoporous Mater.* 197 (2014) 204–212.
- [43] D. Skoda, A. Styskalik, Z. Moravec, P. Bezdicta, M. Babiak, M. Klementova, C.E. Barnes, J. Pinkas, *RSC Adv.* 6 (2016) 24273–24284.
- [44] V. Lafond, P.H. Mutin, A. Vioux, *Chem. Mater.* 16 (2004) 5380–5386.
- [45] D.P. Debecker, K. Bouchmella, M. Stoyanova, U. Rodemerck, E.M. Gaigneaux, P. Hubert Mutin, *Catal. Sci. Technol.* 2 (2012) 1157.
- [46] A. Styskalik, D. Skoda, J. Pinkas, S. Mathur, *J. Sol-Gel Sci. Technol.* 63 (2012) 463–472.

- [47] D. Skoda, A. Styskalik, Z. Moravec, P. Bezdicka, J. Bursik, P.H. Mutin, J. Pinkas, *RSC Adv.* 6 (2016) 68739–68747.
- [48] D. Skoda, A. Styskalik, Z. Moravec, P. Bezdicka, J. Pinkas, *J. Mater. Sci.* 50 (2015) 3371–3382.
- [49] M. Caillot, A. Chaumonnot, M. Digne, C. Poleunis, D.P. Debecker, J.A. van Bokhoven, *Microporous Mesoporous Mater.* 185 (2014) 179–189.
- [50] A. Corma, F.X. Llabrés I Xamena, C. Prestipino, M. Renz, S. Valencia, *J. Phys. Chem. C* 113 (2009) 11306–11315.
- [51] G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227–250.
- [52] M. Nara, H. Torii, M. Tasumi, *J. Phys. Chem.* 100 (1996) 19812–19817.
- [53] C. Eaborn, *J. Organomet. Chem.* 100 (1975) 43–57.
- [54] R.T. Carr, M. Neurock, E. Iglesia, *J. Catal.* 278 (2011) 78–93.
- [55] C. Eaborn, J.G. Stamper, G. Seconi, *J. Organomet. Chem.* 204 (1981) 27–45.
- [56] P. Brandão, A. Philippou, J. Rocha, M.W. Anderson, *Catal. Letters* 80 (2002) 99–102.
- [57] A. Philippou, P. Brandão, A. Ghanbari-Siahkali, J. Dwyer, J. Rocha, M.W. Anderson, *Appl. Catal. A Gen.* 207 (2001) 229–238.
- [58] T.K. Phung, L. Proietti Hernández, A. Lagazzo, G. Busca, *Appl. Catal. A Gen.* 493 (2015) 77–89.
- [59] T.K. Phung, G. Busca, *Catal. Commun.* 68 (2015) 110–115.