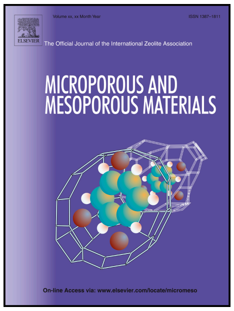

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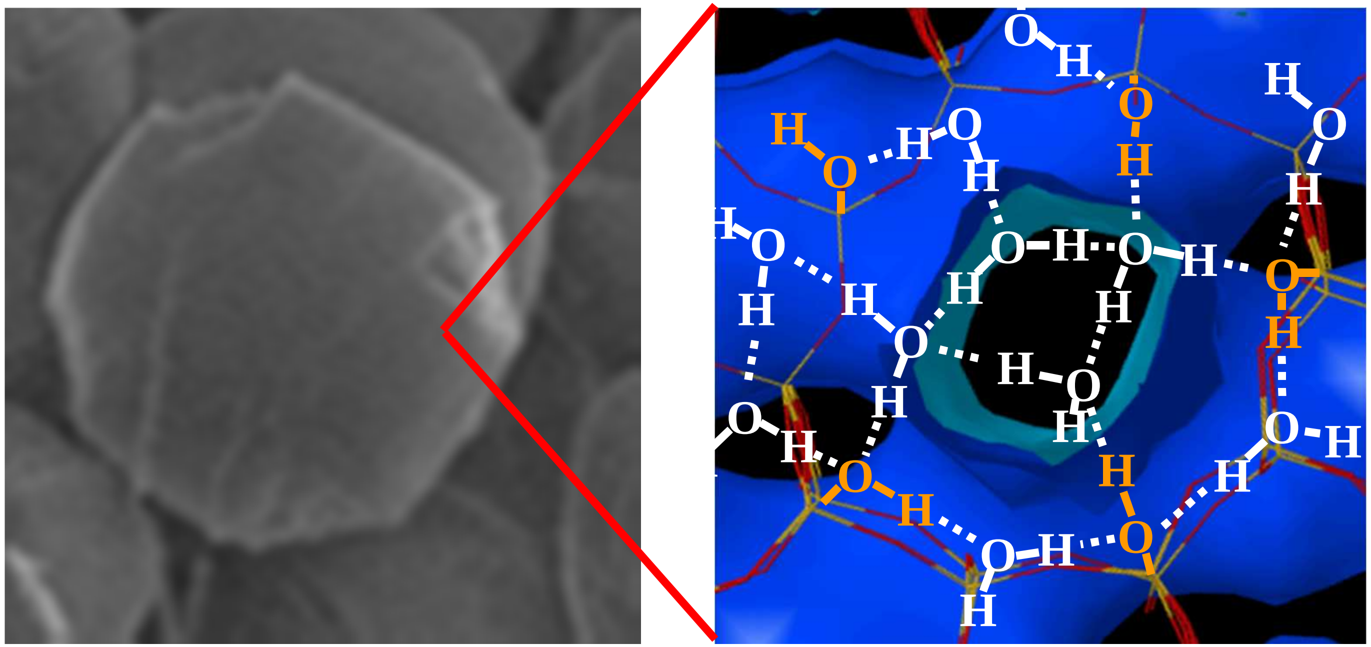

Frozen moisture on silicalite-1 slows down H_2 diffusion

Resistance to the transport of H_2 through the external surface of as-made and modified silicalite-1 (MFI)

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Keywords: Silicalite-1 (MFI) surface barrier; Surface modification; Hydrogen diffusion; Thermal Desorption Spectroscopy; Sievert's apparatus.

Abstract

The adsorption and the thermal desorption of hydrogen in as-made and surface-modified silicalite-1 (MFI) loose crystals has been studied to shed light on the relation between the outer surface barrier and the transport of mass through it. The four different surface modifications can be probed by the change in the contact angle of water, but do not produce any apparent change in the morphology and the structure of the crystals. The H_2 adsorption isotherms in a Sievert's-type apparatus at 77 K and up to 8 MPa on the pristine and the modified silicalite-1 samples are almost overlapping, showing that the modifications involve the external surface of the samples. However the diffusion coefficients of H_2, as derived from the sorption kinetics, evidence different sorption rates of H_2 into the different silicalite-1 samples. In particular the unmodified silicalite-1 sample presents the lowest diffusion coefficient and yields the highest H_2 desorption temperature in Thermal Desorption Spectra acquired at 0.03 K/s. The observed phenomena have been attributed to the surface silanols on the outer surface of the as-

made silicalite-1 crystals, which are either eliminated or greatly reduced in number by the modifying agents. Polar and hydrophilic silanol groups bind frozen water molecules on the outer surface of as-made crystals which hinder the diffusion of hydrogen, and interact more strongly with the H_2 molecules. This provides sorption sites with higher potential energy barriers, and at the same time physically obstruct the pore entrances of the molecular sieve. The surface modification of porous fillers is of interest for the manufacture of mixed matrix membranes, for the improvement of the performance of pressure swing adsorption processes, and for gas storage applications.

1. Introduction

The substitution of energy intensive separation and purification processes (*e.g.* distillation) in the energy and chemical market is potentially able to greatly reduce the global energy demand. Membrane operations lend themselves to this task since their energy requirements are smaller than that of the best thermal processes [1]. However, the expansion of the province of membrane operations requires new tough and resistant materials able to withstand organic solvents and aggressive environments [1,2]. In addition to this, the separation of several gas pairs by polymeric membranes is limited by the well-known performance-limiting trade-off between permeability and selectivity: highly permeable polymers are not very selective and vice versa very selective polymers are not very permeable [3]. Carbon molecular sieve (CMS) [4] and inorganic membranes [5] – made of molecular sieves [6], metals, ceramics [7] or metal organic frameworks [8] – have demonstrated outstanding separation performances beyond the Robeson upper bound [3]. However today they are unfit for most processes: CMS membranes are very expensive, brittle, subject to air oxidation and they strongly absorb water and organic vapours [4,9]; ceramic and metallic membranes are expensive and their low surface-to-volume ratio would determine a huge footprint of the plants and a high energetic cost of the process [1]. Polymer based membranes containing porous filler particles dispersed in the separating layer, also known as hybrid or mixed matrix membranes (MMMs) [2,4,10], are considered one of the viable options available today to obtain the advanced performances required to next generation membranes [1]. MMMs couple the outstanding separation properties of CMS and inorganic materials with the low production cost of polymeric hollow fibres requiring only minor changes in the current manufacturing procedures.

In the case of glassy polymers, the adhesion of ceramic fillers (*e.g.* zeolites) to the polymer matrix is problematic [11] and this usually gives rise to MMMs containing interfacial defects [12,13]. One method to eliminate such defects is the modification of the surface of the filler by grafting suitable groups that improve the chemical affinity to the polymer, even with no covalent bonds between the two phases [14-18].

In the scientific literature the transport of mass through dense MMMs containing porous fillers has been interpreted in terms of the Maxwell model, borrowed from the original work on the electric conductivity of heterogeneous materials made of dispersed spheres in a continuous medium [19], and of modified Maxwell models [20-24]. According to these models, the factors affecting permeability through defect-free MMMs are three: the permeability of the polymer bulk, the permeability of the filler bulk and the volume fraction of the filler. Modified models have taken into account the shape and the orientation of the filler [20-21] and the presence of interfacial effects, such as pore blocking, loosening of the polymer packing or polymer densification at the interface with the filler [22-24]. Moore and Koros pointed out that a reduced permeability region within the sieve surface (case V in their classification of non ideal effects in MMMs) may be observed when a certain impurity selectively sorbs into the zeolite and partly obstructs the pores (*e.g.* moisture in poly(vinyl acetate) - 4A (LTA) MMMs) [25]. The influence of moisture was much less when the more hydrophobic H-SSZ-13 zeolite was used instead of 4A [25].

Although the existence of an outer barrier to the transport of matter in and out of molecular sieves has been evidenced by theoretical [26-30] and experimental [31-40] studies, this aspect has received little attention from the scientific membrane community. One of the few examples is the analysis of the gas permeation data of a series of amorphous perfluoropolymer based MMMs containing silicalite-1 crystals of different size [14,15], giving consistent hints about the presence in those membranes of a shell of loosely packed polymer around them, together with a barrier to the transport of mass through the crystals or on the outer surface of the crystals. The nature of those barriers was not investigated further. There was no evidence whether they were due to the internal structure of the crystals, *i.e.* to pore interruption or blocking caused by twinning and interfaces between parts of the crystal of different orientations [35-40]. Similarly, no investigation was carried out on other possible reasons such as the presence of carbonaceous [33] or amorphous siliceous [31,32,38] residues on the outer surface and on the interfaces between different crystalline domains, the presence of structural faults on the first crystal layers [34,36,38], or the adsorption of moisture on the outer surface of the crystals [37], besides the cited work of Moore et al. [25].

In this study the issues regarding the internal architecture of the crystals and the obstruction of the pores due to non-volatile deposits have been neglected. The attention has been concentrated on the contribution offered by the outer surface of the molecular sieves to the barrier. The outer surface of four samples of a single batch of silicalite-1 (MFI) has been modified in four different ways. The H_2 sorption isotherms and kinetics of the as-made and modified crystals have been determined in a Sieverts type volumetric apparatus (PcT) in the pressure range 0÷8 MPa at 77 K. The volumetric Sievert's type apparatus allows the simultaneous determination of gas total adsorption capacity and diffusion kinetics, with transient behaviours ranging from seconds to hours. The apparent H_2 diffusion coefficients have been calculated under the assumption of diffusional resistance in the pore network. Then, the sorption data have been discussed by assuming the presence of a surface barrier. The same samples have been characterized by Thermal Desorption Spectroscopy (TDS) of hydrogen between 20 and 120 K.

2. Experimental

2.1. *Synthesis and surface modification of silicalite-1 (MFI)*

Silicalite-1 (MFI) has been prepared from a synthesis mixture of the following composition (in oxides):

$8.8\ (C_3H_7)_4NBr : 5\ Na_2O : 0.125\ Al_2O_3 : 100\ SiO_2 : 1250\ H_2O$

obtained by dissolving the right amount of tetrapropylammonium bromide (>99%, Fluka, purum) in a freshly prepared 30% sodium hydroxide solution (pellets, 98,6%, Baker analyzed), followed by the addition of the rest of distilled water, and finally by precipitated SiO_2 (BDH). Aluminium was contained as an impurity mainly in the precipitated silica, and its content in the crystals was measured by means of atomic absorption spectroscopy (Perkin Elmer AAS 380). The homogeneized gel was loaded in a teflon lined stainless steel autoclave and heated at 170 °C for 30 hours. The solid was filtered and washed with plenty of water up to a neutral pH, and dried at 100 °C for 12 hours.

Different samples of the same batch of silicalite-1 were modified with trichloromethylsilane (98%, Fluka), dichlorodimethylsilane (99%, Alfa Aesar), chlorotrimethylsilane (99,5%, Carlo Erba) and 1H,1H,2H,2H-perfluorodecyltrichlorosilane (96%, Lancaster), which are able to graft on the outer surface the following moieties: $\equiv SiCH_3$, $=Si(CH_3)_2$, $-Si(CH_3)_3$ and $\equiv Si(CH_2)_2(CF_2)_8F$. For the sake of clarity, in the following the corresponding samples will be called Me, Me_2, Me_3 and F, respectively. The silylation yielding the Me_3 silicalite sample was carried out with a large excess of $ClSi(CH_3)_3$ in toluene at room temperature. The grafting reactions yielding the Me, Me_2 and F silicalite samples instead were carried out on desiccated zeolites, with a very small excess of the reagents at 0°C in a dry environment. Dry toluene was used as the reaction medium, and the reaction lasted no more than 15 min. After the reaction, the zeolite was immediately filtered and washed with dry toluene in order to remove the unreacted silane.

Chlorosilanes react rapidly at 0°C with the silanols on the zeolite surface (MFI-OH) according to the following overall reaction:

$$\text{MFI-OH} + \text{Cl-SiX}_3 \rightarrow \text{MFI-O-SiX}_3 + \text{HCl} \qquad (1)$$

The minimum amount of di- and trichlorosilanes has to be used in a dry environment because water promotes the self-condensation of the reagent, which in turn may give rise to long grafts of oligomeric species forming a deposit of alkylated silica on the zeolite surface.

2.2. *PcT volumetric apparatus*

PcT isotherms were obtained with a home-made volumetric apparatus described in the recent literature [41]. Approximately 800 mg of each sample were inserted in the sample holder (SH) and were degassed prior to the measurements at 393 K overnight in dynamic vacuum. The system is operating in high vacuum (less than 10^{-7} Pa) obtained by a turbomolecular pump. A series of electric valves divide the reservoir and the sample holder volumes. The system volumes were chosen according to the evaluation of the volume/mass relationship of Wang and Suda [42]. The accuracy of the void system volume is 0.2%. Two Bourdon Haenni pressure transducers - end scale of 0.1 MPa (P1) and 10 MPa (P100) - on the reservoir volume measure the lower and higher pressures ranges respectively (accuracy 0.00001 and 0.001 MPa, respectively). The temperature of the reservoir is measured by a platinum resistor (Pt100) while the SH temperature is measured by a k-type thermocouple which uses the Pt100 measurements as a reference. The temperatures of reservoir and SH are monitored at different points in order to check their uniformity (0.1% error). The whole equipment (pressure and temperature measurements, valves, pumping system, time settings, LN_2 level, data acquisition and analysis) is controlled by a Labview home-made program via a µ-DAQ acquisition card.

2.3. *TDS apparatus*

Thermal desorption spectroscopy (TDS) is a widely applied technique in surface science [43] and in catalysis [44] for the energetic characterization of adsorbates on surfaces. To measure the desorption of physisorbed molecular hydrogen, which typically possesses a small heat of adsorption (~5 kJ mol^{-1}), thermal desorption spectroscopy has been extended down to very low temperatures of about 20 K [45].

Prior to the TDS measurements, the samples have been annealed at 378 K in high vacuum (higher than 10^{-6} kPa) for at least 8 h to remove moisture and contaminations. Afterwards, at room temperature hydrogen pressure of 2.5 kPa was introduced into the chamber and the sample was slowly cooled down to approximately 20 K. The sample was kept at 20 K under hydrogen atmosphere for approximately 30 min and then the chamber was evacuated to remove the non-adsorbed hydrogen molecules. For the measurement the sample was heated (0.03 Ks^{-1}) and the signal of the desorbed hydrogen was recorded by the mass spectrometer. The instrument’s calibration procedure has been previously reported in literature [45].

2.4. *SEM and XRD*

Scanning electron images and Energy Dispersive X-ray (EDX) analysis were recorded using a scanning electron microscope (SEM) Quanta FEG 400 (FEI). The SEM images were acquired with an electron beam of 10 keV.

X-ray diffraction measurements have been made using the Cu K_α radiation (λ = 1.5418 Å) of a Bruker Axs Diffractometer/Reflectometer (D8) equipped with a Dynamic Scintillation Detector NaI and a Gobel mirror. The measurements are made in transmission: the sample powder is put in a special glass capillary (ID = 0.8 mm, wall thickness 0.1 mm, Hilgenberg GmbH) and the latter in a home-made sample holder. All measurements have been carried out at room temperature. The contribution of the empty capillary has been subtracted from the patterns.

2.5. *Thermogravimetric measurement*

Thermogravimetric analysis of the pristine unmodified silicalite-1 sample was carried out in N_2 flow with a Perkin Elmer Pyris 6 TGA. The sample was dried at 115°C in N_2 flow before heating up to 800°C with a heating rate of 2°C/min.

3. Results and discussion

The SEM images (Figure 1) show the typical morphology of silicalite-1 with intergrown structures [46] indicating an average grain size of 18 μm. The details of the surface of the crystals remain unchanged after the outer surface modification, with no visible growth of foreign matter. The XRD patterns of the starting and of the modified materials (Figure 2) show the typical peaks of silicalite-1 with MFI topology [47]. The XRD patterns do not show any cristobalite peak, the most intense of which should appear at $2\theta \sim 10°$ [48]. As expected, X-ray diffraction does not reveal any structural modification of silicalite-1 by organo-silane molecules because the modification takes place on the surface and not in the bulk [49]: the silane molecules can hardly enter the narrow pores of of MFI. Moreover, the silane modifying agents probably react at the entrance of the silanol-rich slits at the interface of two different crystal domains and restrict their size, as found for mesoporous materials [50].

The extent of the modification of the outer surface can instead be followed via the contact angle of water (CAM 200, KSV, Helsinki, Finland) on a layer of crystals adhering to double-sided tape: as an example, the contact angle of silicalite-1 (81±2°) increases to 150±1° after just 10 min reaction with $Cl_3Si(CH_2)_2(CF_2)_8F$, and remains constant for longer reaction times, up to 150 min. The water contact angle of the other samples are 132±1° (Me), 124±1° (Me_2), and 129±2° (Me_3).

The EDX analysis confirms, within the experimental error, the same composition of the silicalite-1after the modification process (see Table 1). PcT H_2 adsorption isotherms have been obtained on the pristine and the modified silicalite-1 samples at 77 K (LN_2 temperature) and from 0 up to 8 MPa (Figure 3).

Table 1: Atomic percentage of modified and as-made silicalite-1 obtained by EDX. The error is about 5% of each value.

Silicalite-1 sample	Si	O	Na	F
As made	35	62	2.0	-
F	38	58	2.0	1.0
Me	37	59	2.0	-
Me_2	36	60	2.0	-
Me_3	35	61	2.2	-

The H_2 sorption capacity of a ZSM-5 (MFI) zeolite reported by Jhung et al. (0.756 wt% at 77 K and 0.100 MPa, Si/Al 140) [52] is about 15 % higher than the values reported for the five silicalite-1 samples of this study. The lower sorption capacity can be related to the lower Al content of MFI samples in this study (Si/Al 800): higher amounts of Al increase the H_2 sorption capacity of zeolites [52] due to the fact that, where tetrahedral Si atoms have a neutral formal charge, a tetrahedral Al atom in a framework position in a zeolite bears a negative formal charge, which has to be compensated by the positive charge of a cation. H_2 molecules interact more effectively with the strong electric field generated by this ionic couple.

The very similar sorption capacity of the MFI samples at high pressure indicates that the surface modification does not change significantly the silicalite-1 adsorption properties. However, the modest differences found in the sorption capacity can be rationalized in terms of the changes in the nature of the external surface of the crystals. In fact the strongest sorption sites reside on the outer surface of the as-made crystals, covered with polar silanols, whereas the internal surface of the pores mainly contains hydrophobic bridging oxygen atoms bound to two different tetrahedral Si atoms. Polar O–H bonds induce stronger electric fields than the O–Si bonds generated by the surface modification, and therefore H_2 molecules are more strongly attracted by O–H bonds than by O–Si bonds. As expected, the as-made MFI shows the highest H_2 sorption capacity and the surface-modified MFI samples from 2 to 5% less.

A simple calculation of the hydrogen surface coverage, although not appropriate in the case of a microporous material [53], may give some qualitative information. When one monolayer (ML) of hydrogen molecules is adsorbed in cryogenic conditions on a flat surface, an upper limit of 7-8 molecules per nm^2 is expected. As pointed out for meso- and macroporous substances [54] a good estimation of the coverage in terms of molecules per nm^2 can be calculated by considering the adsorption capacity together with the surface specific area (SSA) of the samples. Taking into account the results of Figure 3 and by assuming the apparent BET SSA for sample F of 333 m^2/g (Tristar 3020 II, Micromeritics, Norcross, GA, USA) as a constant for all of the samples, the as-made and the modified silicalite-1 adsorb the equivalent of one monolayer of hydrogen molecules in the narrow pores of the samples (0.53-0.57 nm). In particular, the examined samples show a H_2 adsorption equivalent to 0.77 ML at 0.1 MPa.

The results obtained by the analysis of the adsorption isotherms can be combined with the study of the dynamical features obtained from the analysis of the pressure transient status following an abrupt increase of P in the sample holder volume [41].

The rate-determining factors in the sorption-desorption of H_2 in silicalite-1 at 77 K can be several [31-40]: diffusional resistance in the pore network, inner barriers, blocking of the superficial pores which produce a virtually impermeable layer with dispersed holes, frozen moisture and/or grafted moieties obstructing or restricting the size of the open pores. It is possible that two or more of such factors act in parallel opposing non negligible resistances to the overall transport of mass, therefore the rationalization of the experimental results requires a discuss of their effects.

At first it will be assumed that diffusion limitations inside the pore network alone control the sorption kinetics of H_2 at 77 K. If this assumption is true, the pressure decrease can be modelled with a negative exponential function whose time constant τ is related to the diffusion of the hydrogen molecules into the silicalite-1 channels and their adsorption on the zeolite walls. Considering the Fick equation on a zeolite of spherical shape and taking into account the fraction of hydrogen adsorbed (Λ) [55-57], the transient behaviour of the total amount of the diffusing gas is represented by formula (2) below:

$$m_t = (m_0 - m_\infty) \cdot 6 \cdot \sum_{n=1}^{\infty} \frac{\exp(-D p_n^2 t / a^2)}{9\Lambda/(1-\Lambda) + (1-\Lambda)\, p_n^2} + m_\infty \qquad (2)$$

where D is the apparent Fick diffusion coefficient, a is the radius of the spherical zeolite in which the hydrogen molecules diffuse, p_n is a shape dependent factor calculated from boundary condition, m_0 and m_∞ are the moles of gas per unit volume after the opening of the valve between the reservoir and the sample holder volumes and at the equilibrium pressure, respectively. The m_0 value has been calculated considering the expansion of the gas only on the sample holder volume removing the contribution of the sample volume.

The graph of typical fitting results is reported in Figure 4. The cross represents the calculated pressure step due to the expansion of the gas between the reservoir and the sample holder volume [41]. The length *a* considers the average radius of the zeolite particles, therefore the fitted parameter is D/a^2 as reported in the literature [56]. The kinetic curves may include the time to reach the equilibrium temperature, however this effect is the same for all of the samples of silicalite-1 studied here, which only differs for the chemical modification of the outer surface of the crystals. In Figure 5 the diffusion coefficient *vs.* hydrogen coverage (θ) obtained for the different samples is reported.

The D *vs.* θ dependence is related to the 'Darken correction' $D=D_0[\mathrm{dln}P/\mathrm{dln}C]$ [56] and considering the Toth equation [51] the following equation is obtained:

$$D=D_0/(1-\theta^t) \qquad (3)$$

The positive parameter t which appears in equation (3) measures the heterogeneity of the surface of the adsorbent as probed by the adsorbate. In particular, lower values than 1 (perfect homogeneity) indicate increasing heterogeneity. The best fit for the values of t are the following: 0.38 (as made MFI), 0.42 (Me_2), 0,44 (Me_3), 0,46 (Me) and 0.38 (F); with the exclusion of sample F, the order of t – and hence the order of homogeneity – follows the same order of increasing hydrophobic character of the outer surface as revealed by the contact angle. Bearing in mind that the interior of silicalite-1 is hydrophobic, it seems that the capping of silanol groups makes the outer surface more similar to the environment experienced by H_2 in the pore network; the extreme hydrophobicity of the perfluorinated chains instead would restore heterogeneity with respect to the pore network.

The silicalite-1 grafted with $–SiMe_3$ groups displays the highest sorption rate, whereas the as-made and the F (fluorinated tails) samples yield the lowest H_2 diffusion.

The dependence of the sorption rate of H_2 from the chemical nature of the outer surface of the silicalite-1 is an experimental evidence of the role it plays on the overall sorption rate of H_2 inside the crystal at 77 K.

The assumption that diffusion limitations inside the pore network govern the sorption kinetics is in contrast with the findings of Krishna and van Baten on Molecular Dynamics simulations in ideal, defect-free silicalite-1 at 300 K. In that case the intra-crystalline Stefan-Maxwell diffusion coefficient decreases with higher H_2 loadings [58], whereas in this study a faster H_2 diffusion is observed at 77 K in the sorption experiments at higher loadings. This contradiction has been explained in a similar case (C2-C4 hydrocarbons in Zn(tbip) MOF) by considering that self-diffusion relies on the very difficult exchange of molecules in narrow pores, whereas the transport of molecules under the effect of a concentration gradient does not [36]. In this case however the sorption kinetics of H_2 are recorded by imposing several small steps, so that for each of them the diffusion coefficient in the pore network can be considered as a constant. The apparent contradiction with the result of Krishna et al. [58] can instead be explained by the partial immobilization of hydrogen in the pentasil chains of silicalite-1 at low temperatures (*vide infra*).

The D/a^2 values obtained above by fitting the experimental data with eq. (2) can be used to obtain D values at different θ loadings by assuming that all zeolites have the same average radius a equal to 9 μm: they lie in the range $4 \div 10 \cdot 10^{-13}$ m^2 sec^{-1}. The obtained values are more than two orders of magnitude lower than the self-diffusion coefficients of H_2 in the interior of Na-ZSM-5 measured by Bär et al. at 160, 140 and 120 K, equal to about $1.7 \cdot 10^{-10}$, $1.6 \cdot 10^{-10}$ and $1.9 \cdot 10^{-10}$ m^2 sec^{-1} [59]. That study evidenced that the unusually low mobility of hydrogen was induced by the capture in the pentasil chains of a significant fraction of the molecules. Also, both PFG NMR and Quasi Elastic Neutron Scattering measurements reported an increase of the self-diffusion of H_2 at constant temperature with increasing loadings, just as it has been found in this study. It is not possible to draw clear conclusions from the comparison of the two situations because of the differences in the temperatures of the measurements (77 *vs.* 120-160 K) and the different activation procedures of the samples (120 *vs.* 400°C); both the lower temperature and the higher amount of water in the silicalite-1 samples of the present study are expected to decrease the diffusion rate of H_2. Therefore the influence of diffusion limitations inside the pore network on the overall H_2 sorption kinetics cannot be excluded on the basis of this comparison, but it is important to point out that the modification of the chemical nature of the outer surface does not influence the diffusion limitations inside the pore network.

The other extreme assumption will be now adopted: the mobility of H_2 in and out of the silicalite-1 is controlled by the surface only; if the diffusional resistance through the laminar fluid film surrounding the crystals can be neglected, then H_2 diffusion can be limited by means of two possible mechanisms: i) diffusional resistance through a thin barrier of thickness δ at the surface [56], due for example to the presence of frozen moisture at the pore mouth, or ii) by the presence of plugs on a fraction of the pore mouths [39,40]. No one of the two can be excluded on the basis of our experimental data. Therefore, in the assumption that only the surface controls the H_2 sorption kinetics at 77 K, in the simple case when the pressure is kept constant during the experiment, the sorption rate is given by expression (4) below for spherical particles of radius a [56]:

$$m_t / m_\infty = 1 - \exp(-3 D_{barr} t / \delta' a) \qquad (4)$$

where the D_{barr} represents the effective diffusivity through a barrier of effective thickness δ. It is important to realize that $D_{barr}/\ \delta$, also known as the surface permeability [55], is the overall resistance to transport of hydrogen that takes into account both mechanisms, *i.e.* pore plugging and resistance through the open pores: the different localized resistances on the different pore mouths, in fact, can be averaged over the whole crystal surface [39].

In the present study, the reduction of the amount of polar silanols at the outer surface, accompanied by lesser amounts of strongly bound water, is probably the reason why faster hydrogen sorption kinetics are observed. The bulky perfluorinated tails compensate the reduced hydrophilicity of the surface with a much larger sterical hindrance, so that at the end the sorption rate of hydrogen is comparable to what is found in the case of the as-made silicalite-1.

A reasonable additional explanation for the increase of diffusion with the surface coverage is the presence of much stronger sorption sites at the outer surface of silicalite-1 than at the interior of the crystal. Those H_2 molecules adsorbed at the outer surface of silicalite-1 which are hopping to the interior of the crystal probably need to pass a free energy barrier which is higher than the barriers separating different sorption sites inside the pore network. The increase in molecule-molecule interactions at higher pressure may decrease the height of the free energy barrier one molecule has to overcome for diffusing into the crystal. A similar behaviour was described for the modelling of intra-crystalline self-diffusion of methane in all-silica LTA [60].

A hydrogen desorption study by means of TDS was performed to investigate more accurately the modification induced by the surface functionalizations discussed above. In order to observe the different kinetic parameters of modified and unmodified silicalite-1, the TDS spectra acquired with desorption rate of 0.03 K/s are compared in figure 6. All the samples spectra present one main broad structure whose centroid position does not appear at the same temperature. In particular the desorption spectra of the unmodified silicalite-1 and the fluorinated sample have similar maximum temperatures, while in the other samples the maximum desorption rate occurs at lower temperatures.

These variations can be rationalized with the same hypothesis used to explain the differences in the adsorption kinetics: pore plugging/restriction and stronger sorption sites on the outer surface of the as-made silicalite-1, covered with ≡Si–OH groups and frozen moisture, are characterized by a higher free energy barrier for the desorption of hydrogen to the gas phase than in the case of crystals with hydrophobic surface modifications.

Strongly adsorbed water molecules on the outer silanols of unmodified silicalite-1, close to the pore entrance, may effectively hinder the hydrogen desorption from the internal pores. Frozen moisture and higher activation energy may act as a sort of a “stopper” on the pore entrance keeping the desorbing H_2 molecules inside the pore network, and this “stopper” is mostly effective in the non-modified silicalite-1, where the surface silanols are present. This stopping effectiveness decreases in the order –OH > $\equiv SiCH_2CH_2(CF_2)_8F$ > $=Si(CH_3)_2$ > $–Si(CH_3)_3$ ~ $\equiv SiCH_3$. Generally, a high energy barrier is associated with strong adsorbent-adsorbate interactions. The reduction in the number of the surface silanols, caused by the bonding of the silanes, is expected to reduce the amount of moisture and the strength of the sorption sites on the outer surface. Consequently, the maxima of the correspondent TDS spectra are shifted towards lower temperatures. Bulky linear perfluorinated alkyl chains grafted on silica are known to self-assemble, forming compact and tightly packed self assembled monolayers [61]. A similar situation might occur in MFI crystals modified with the fluorinated moiety, giving rise to a physical barrier for the transport of diffusing species yielding the second slowest desorption rate. If the other modifications introduced on the surface of the MFI crystals are considered, it seems that after the modification the size of the group bound to the outer surface of the zeolite governs the desorption rate of H_2 and therefore the dynamic desorption properties of the modified silicalite-1.

When these experimental evidences are compared with the diffusion during sorption (Fig. 5), a fair agreement is found. In fact, the slowest sorption is observed again for the unmodified MFI and the MFI modified with fluorinated chains.

It must be pointed out that the as-made crystals show the highest H_2 sorption capacity and at the same time the slowest H_2 transport rate. The highest number of surface silanol groups on them is probably responsible of both effects: the highest sorption capacity due to the strongest dipolar moment of the terminal hydroxyl group with respect to O-Si bonds; the slowest transport rate due to the highest potential energy barriers for surface diffusion from stronger sorption sites on the external surface, both to the internal surface (the pores of the zeolite, adsorption into the zeolite) and to the gas phase (desorption). An additional effect of the surface silanols is the sorption of water molecules, which can form strong hydrogen bonds: the crystals were activated at 105 °C in order to preserve the organic grafts from decomposition, therefore water linked with hydrogen bonds is still present on silanol groups. Adsorbed water is not expected to decrease the polarity of the surface, and in addition it might reduce the pore size and physically hinder the transport of hydrogen [37].

A confirmation of the presence of adsorbed water after activation at 115°C comes from the thermogravimetric profile of the pristine, unmodified silicalite-1 sample (Figure 7). The overall weight loss from 115 to 800°C is 9.24%, and all of it is due to the loss of water because the zeolite had been calcined already. Most of the water (weight loss 7.24%) was lost between 115 and 325°C, with the highest slope in the TG curve around 236°C: this is water which sticks to the zeolite framework with hydrogen bonds, and/or that is coordinated to the Na^+ ions. In agreement with the findings of Bodart et al., more water is lost from 330 to at least 800 °C, due to the condensation of vicinal silanol groups at crystal defects [62].

In conclusion, the features of the H_2 sorption kinetics and of the TDS experiments are influenced by the polar silanol groups on the outer surface of silicalite-1, which still retain large amounts of water after the activation treatments at 105-120°C. A surface barrier exists around silicalite-1 crystals and the resistance it offers is not negligible; it operates by the action of two possible mechanisms: a) the physical obstruction or reduction of size of the pore entrance due to frozed moisture, and b) the deepening of the free energy barriers for the hopping of H_2 out of the surface layer, either to the gas phase or to the interior of silicalite-1. The silylation of the surface speeds up the sorption process by eliminating the surface silanols or reducing their number. The bulky fluorinated moiety of sample F probably reduces the diffusion of hydrogen by sterical hindrance.

Other resistances to transport are probably present, but their eventual contributions cannot be quantified on the basis of the results of this study. Intra-crystalline diffusional resistance could be revealed by PFG-NMR or neutron scattering experiments at 77 K [59,63,64]. Interference Microscopy and Infra-Red Microscopy [39,40,64] might measure independently the surface permeability and the intra-crystalline diffusivity, and estimate the probability that a generic pore at the surface is not plugged, if the times of H_2 diffusion recorded in this work at 77 K are long enough.

It is probable that for larger molecules than H_2 [56] and for thin zeolite layers [26, 65-67] the effect of surface barriers is more relevant. This study indicates that surface modification is able to modulate the height of the surface barrier to the transport of H_2 in and out of silicalite-1 at 77 K. Surface modification is a tool to obtain better performing membranes, but it can also be tailored to improve pressure swing adsorption processes and the filling/delivery of sorbent loaded gas storage tanks.

5. Conclusions

The external surface of silicalite-1 (MFI) crystals has been modified by grafting four different moieties. The surface modifications do not change significantly the hydrogen adsorption capacity at 8 MPa and 77 K, with a maximum difference of only 5%. The diffusion rate of H_2 in the MFI crystals is influenced by the chemical nature of the surface, therefore the outer surface of MFI is a barrier for the transport of H_2 at 77 K. In particular, since unmodified silicalite-1, with terminal silanols ≡Si-OH, yields the slowest adsorption rate of H_2, the hypothesis has been made that frozen water molecules, forming hydrogen bonds with surface silanols, may physically obstruct the entrance of the pores. In addition to this, the stronger sorption sites for hydrogen offered by silanols are characterized by higher energy barriers for the hopping of H_2 when compared to the outer surface sorption sites of hydrophobically modified crystals. These results are confirmed by the TDS spectra acquired at 0.03 K/s heating rate, which show the highest desorption temperature of hydrogen for the as-made silicalite-1. Again, this difference can be explained by the effect of strongly adsorbed water on surface silanols close to the pore entrance, and by higher energy barriers.

The above findings indicate the presence of diffusional barriers on the outer surface of loose silicalite-1 crystals. It has been demonstrated that the chemical modification of the outer surface of porous fillers is able to modify the diffusivity of penetrants. This strategy in turn may prove viable to enhance the performance of mixed matrix membranes, as well as of pressure swing adsorption processes and of sorbents for the storage of gas.

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Figure Captions

Figure 1: SEM image of silicalite-1.

Figure 2: XRD patterns of silicalite-1 before and after the modifications. a: reference pattern; b: as-made silicalite-1; c: sample F; d: sample Me; e: sample Me_2; f: sample Me_3.

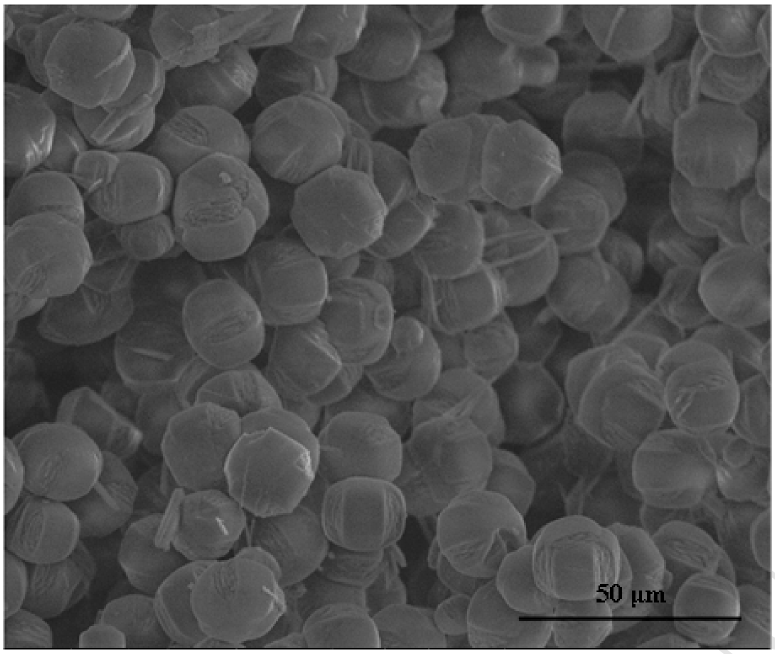
Figure 3: H_2 adsorption isotherms of the different MFI samples obtained at 77 K in the pressure range 0÷8 MPa. The curves represent the fittings of the experimental data (total adsorption) obtained by the Toth model [51].

Figure 4: PcT experimental data fitted by decaying function *vs*. hydrogen diffusion/adsorption time.

Figure 5: Fitting of D/a^2 results of H_2 adsorption kinetics at 77 K in the different silicalite-1 (MFI) samples as a function of the hydrogen coverage θ. Symbols: ■ Me_3, ☐ Me_2, ● Me, ○ F, and ◆ as made MFI. Points fitted by a third-degree polynomial function. D/a^2 error is 3-5%.

Figure 6: H_2 TDS spectra of the different MFI samples in the temperature range 25 - 120 K. The heating rate is 0.03 K/s.

Figure 7: TG and DTG curves for the as-made silicalite-1 sample in N_2 flow, after equilibration in N_2 flow at 115°C. The heating rate is 2°C/min.



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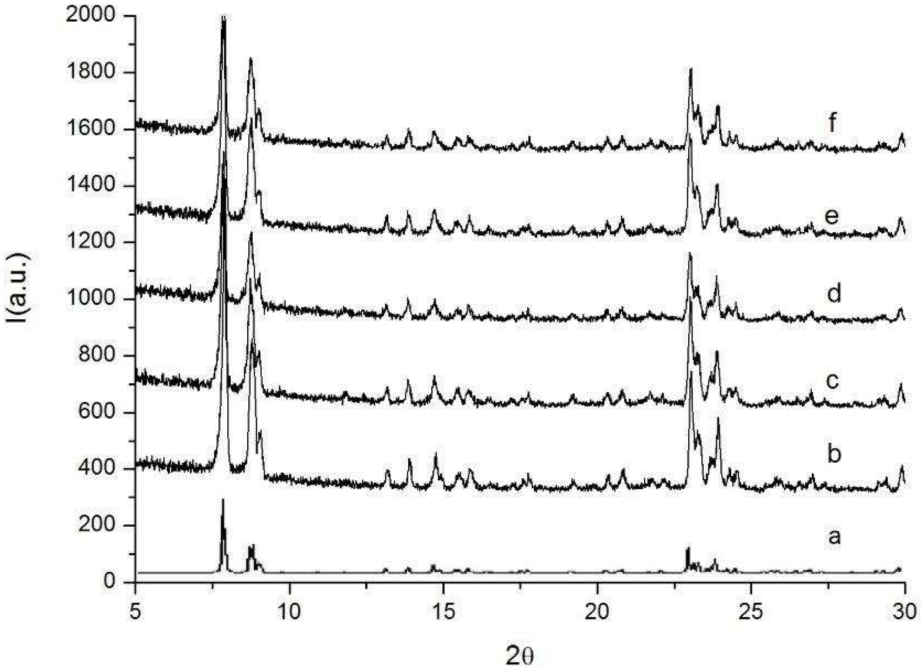
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Figure 2.

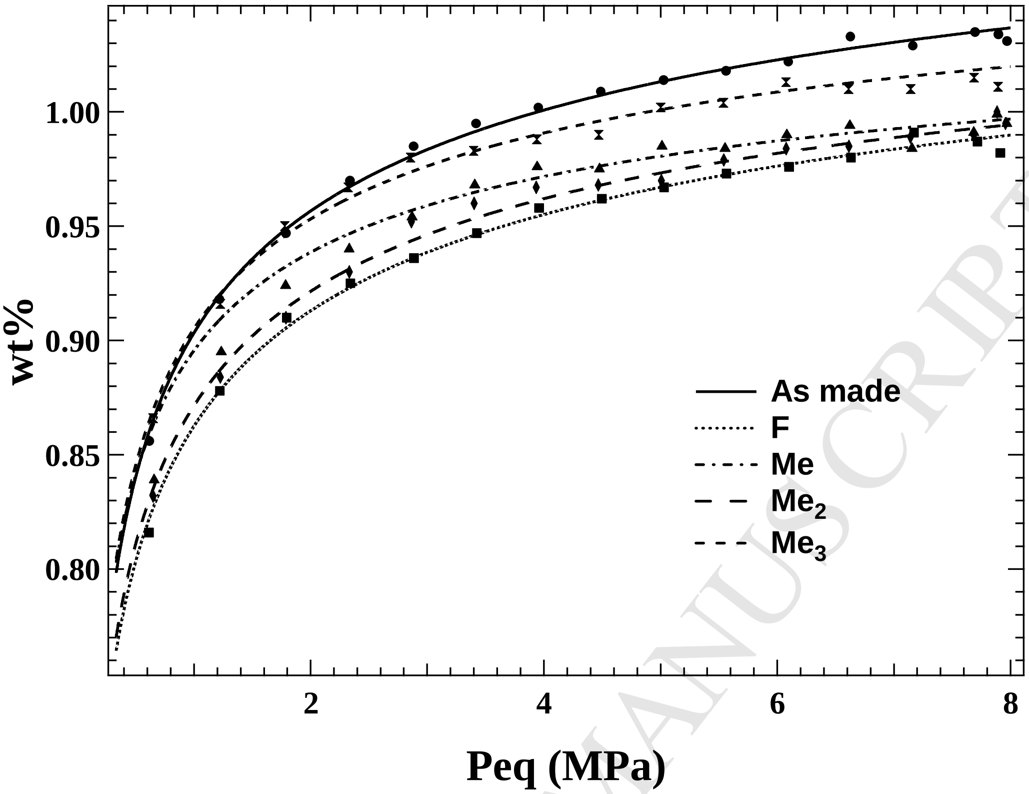
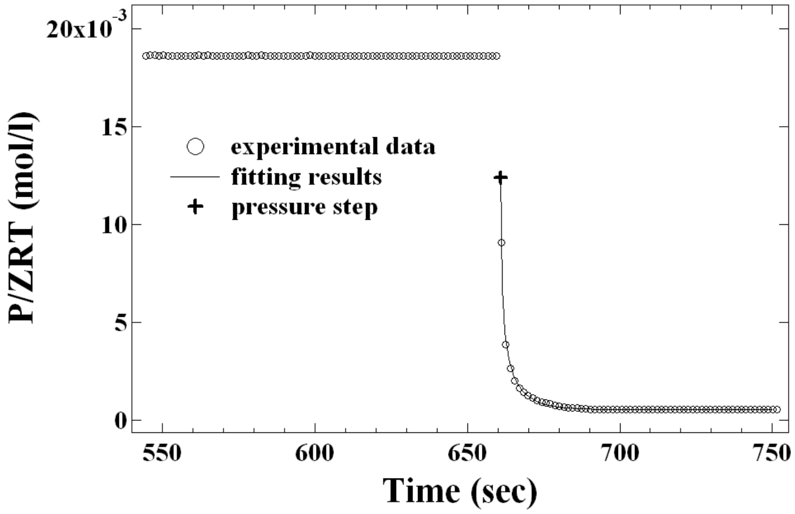


Figure 3.


20x10^{-3}
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P/ZRT (mol/l)
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650
700
750
Time (sec)
experimental data
fitting results
pressure step

Figure 4.

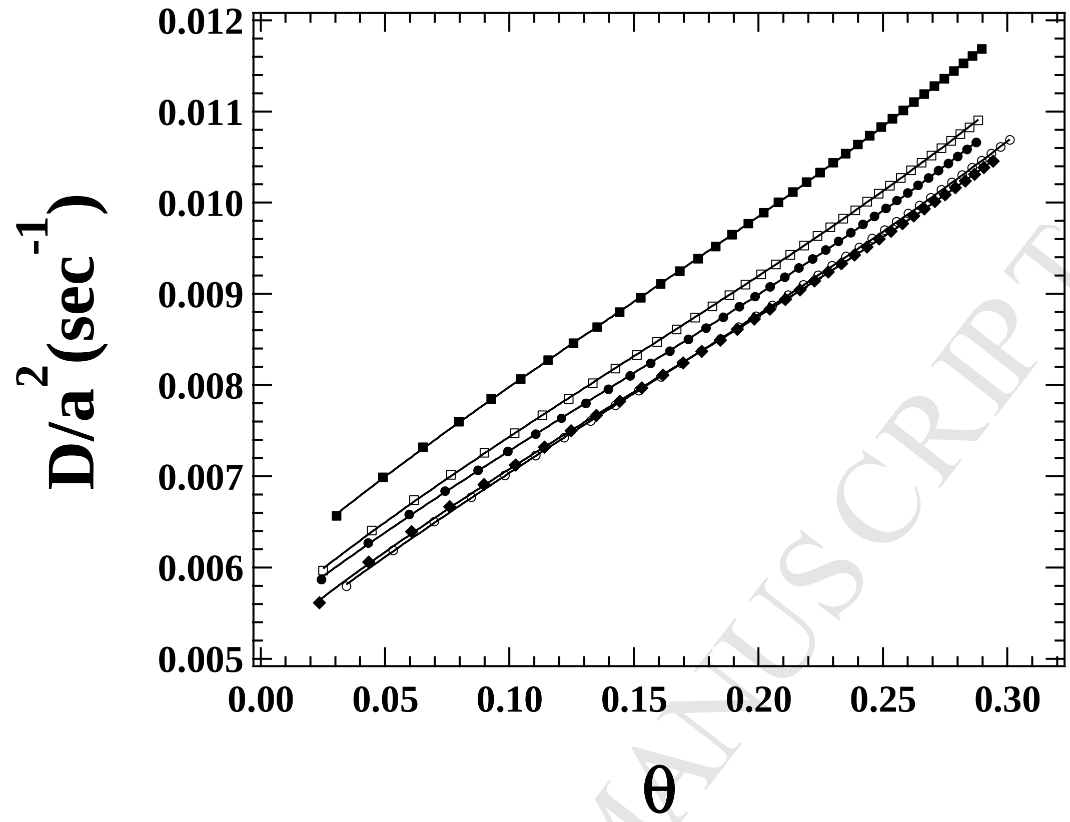
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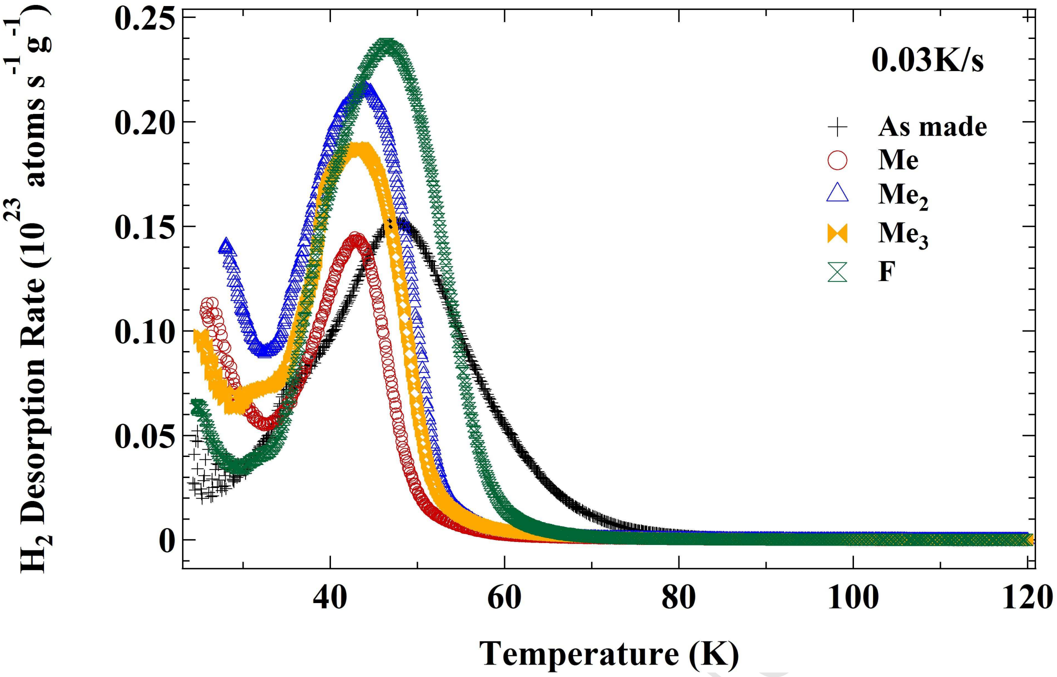
Figure 5.


0.03K/s
As made
Me
Me2
Me3
F
H2 Desorption Rate (10^23 atoms s^-1 g^-1)
0.25
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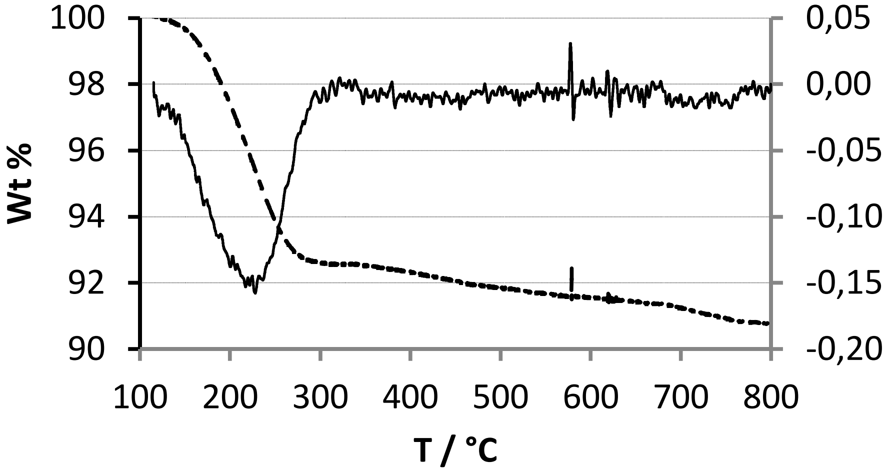
0.15
0.10
0.05
0
40
60
80
100
120
Temperature (K)

Figure 6.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Wt %
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800
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Figure 7.

Highlights

- A surface barrier for the transport of H_2 at 77 K is evidenced on silicalite-1
- Surface modification of MFI crystals speeds up H_2 sorption and desorption
- Surface silanols trap moisture and enhance the surface barrier
- Pore obstruction and stronger sorption may explain the enhancement of the barrier
- Surface modification can tailor the transport properties of fillers and adsorbents