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

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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 obstructs 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

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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):

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

obtained by dissolving the right amount of tetrapropylammonium bromide (>99%, Fluka, purum) in a freshly prepared 30% sodium hydroxide solution (pellets, 98,6%, Baker analysed), 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 h. The solid was filtered and washed with plenty of water up to a neutral pH, and dried at 100 °C for 12 h.

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:

$$MFI - OH + Cl - SiX_3 \rightarrow MFI - O - SiX_3 + HCl \qquad (1)$$

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