Modification of the Adsorption and Catalytic Properties of Molecular Sieves by Reaction with Organometallic Complexes

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Molecular sieves can be modified by organometallic complexes using two different methods: (i) OMCVD (organometallic chemical vapor deposition), where a multilayered organometallic fragment is calcined and transformed into an oxide of rather indefinite composition, and (ii) SOMC (surface organometallic chemistry), where an organometallic fragment is grafted with retention of its molecular integrity. Both methods may lead to a grafting, which can occur at the external surface and/or inside the channels of the zeolites. In the case of SOMC, by judicious choice of both the reaction conditions and the organometallic complexes, it is possible to modify only the external surface of the sieve, for example, of a mordenite. This can lead to a decrease of the surface acidity, allowing greater selectivity in catalytic reactions (such as xylene isomerization). Another application is the modification of the pore openings of the channels by grafting organometallic compounds near the pore entrances. This results in a modification of the adsorption characteristics of the molecular sieve, allowing a fine tuning of its properties. Depending on the size of the adsorbed molecule, two effects can be observed: (i) a total exclusion of the molecule from the channels of the molecular sieve, due to steric effects ("thermodynamic" control); (ii) a modification of the adsorption kinetics of the adsorbed molecule, depending greatly on its size and on the size of the organometallic fragment ("kinetic" control). Finally, the grafting reaction can, in some cases, occur inside the channels, thereby leading to effects similar to those described above and to a reduction of the adsorption capacity due to the presence of the grafted organometallic moieties within the pores.

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Introduction

Molecular sieves, and more specifically zeolites, offer many applications, including catalysis (e.g. catalytic cracking, isomerization of xylenes, alkylation of aromatic compounds), separation processes (e.g. the preparation of oxygen or the removal of water from gases, solvents, etc.), not to mention one of their most important applications as bulk materials to replace phosphate compounds in detergents. Their cage-like structures of precise geometry, with pores of uniform shape running throughout the entire crystal, render them very useful for all these applications. Indeed, the limited size of the channels may prevent the formation of certain intermediates in catalytic reactions, thereby leading to unexpected selectivities (shape−form selectivity). Furthermore, the fixed dimensions of the channels lead to similar properties over the whole crystal.

Although more than fifty naturally occurring species have been characterized and more than 120 synthetic zeolites have been prepared,[1] it is not yet possible to vary the size of the pores and of the cages in a continuous, systematic manner. A zeolite is mainly composed of SiO_4 and AlO_4 tetrahedra and has a well-defined crystallographic structure. For a given zeolite, the size of the pores can be varied by cation exchange or by replacement of the Si or Al atoms by other atoms. This has led to numerous techniques for modification of the zeolitic pore system in a controlled manner, with the aim of improving their performances in catalysis and/or molecular separations. These techniques can generally be classified into three groups:[2]

(i) Modification by a Cation-Exchange Process: The zeolitic pore size can be altered, in a controlled manner, by a replacement of the exchangeable cations, which are normally located near the pore openings. This can lead to a significant alteration of the zeolitic pore structure.[3] A typical example is the adsorption of 2-methylpentane and 2,2-dimethylbutane on mordenite: both alkanes are adsorbed on a calcium mordenite, but only 2-methylpentane is adsorbed on a strontium- or barium-exchanged mordenite.[4] This observation can be simply explained in terms of a pore size reduction on going from the calcium-exchanged mordenite to the strontium and barium ones. As 2,2-dimethylbutane has a kinetic diameter slightly larger than that of 2-methylpentane, it will be excluded from the strontium- and barium-exchanged mordenites.

(ii) Modification by Preadsorption of Polar Molecules: Another method for modifying the molecular sieving effect of a zeolite is to preadsorb polar molecules. Indeed, these molecules will bind around the exchangeable cations and thereby modify the diffusion of adsorbed hydrocarbons. A typical example is the adsorption of butanes on a CaA zeolite, which shows a marked dependence on the amount of preadsorbed water or amines.[5]

(iii) Modification of the Zeolite Framework: Finally, pore size "engineering" in zeolites can be achieved by a modification of the zeolitic framework. This can be performed in various ways:

(a) Firstly, crystallographic changes can be obtained by thermal treatment. For example, thermal treatment of zeolites in the presence of water results in a modification of the pore sizes.[6] Indeed, steam treatment leads to migration and hydrolysis of the exchangeable cations. We will not describe this process in more detail here, as such modifications are not relevant in the realm of organometallic compounds.

(b) Another method is the internal and external structure modification of the zeolite framework by the incorporation of additional atom groups. Various methods have been described in the literature[7] such as silylation, disilylation, boration, etc. As silanes are organometallic compounds, we will briefly discuss these methods in the final part of this review, but we will describe more extensively the reactions of organotin compounds with cloverite, a recently discovered gallophosphate.[8]

(c) A third way of modifying the zeolite framework is to selectively modify the external surface of the zeolite crystal, leaving the internal channels or cavities unaffected. This is typically achieved by reaction with organometallic compounds (including silicon compounds) and will be reported in detail in the next section, in particular the modification of mordenite by reaction with organotin or -germanium compounds.

Modification of the External Surface of Zeolite Crystals

The first example of a variation of the properties of a zeolite by modification of the external surface was reported by Niwa et al. in 1984.[9] The principle of the method was relatively simple, its purpose being the deposition of an organometallic moiety on the zeolite surface that could not enter the pore system. The great advantage of this modification method was that the internal properties of the zeolite remained unchanged after the grafting reaction, in contrast to what was observed when the modification occurred inside the pores as well (see the next part of this review). In most cases, the zeolite used in these studies was mordenite. Indeed, mordenite has monodimensional channels (Figure 1)[6] and so, even if not all the pore openings were modified, an effect could still be observed. Indeed, modification of only 50% of the pore openings should lead, statistically, to 25% of the channels remaining unmodified, 25% of them being modified at both ends, and 50% of them having only one extremity modified. For zeolites with bi- or tri-dimensional channel systems (e.g. ZSM-5 or faujasite), modification of 50% of the channel apertures will have no effect on the adsorption properties since the molecules can enter via the unmodified channel apertures and occupy all the voids in the solid. Significant effects can only be observed when more than 95% of the pore openings are modified, a result which in practice is difficult to achieve. This accounts for the fact that, in most cases, the studies have been carried out on mordenite.

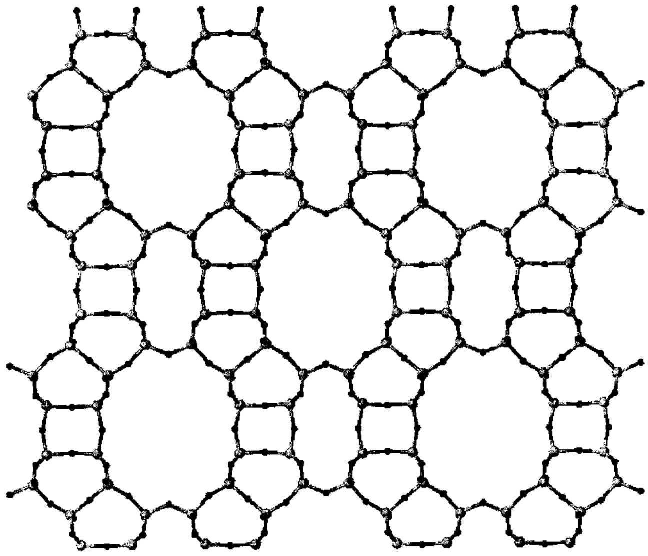


Figure 1. Schematic representation of the channels of mordenite

Niwa et al.[9] deposited $Si(OCH_3)_4$ on mordenite by chemical vapor deposition (C.V.D.). The C.V.D. technique differs quite significantly from surface organometallic chemistry (S.O.M.C.), which will be discussed later. In C.V.D., there is no control of the grafting process at the molecular level. Once one, or more typically, several layers of an organometallic have been grafted on a surface, thermal or chemical treatment leads to an inorganic material (usually an oxide, but possibly also a carbide, a nitride, etc.), which has a definite composition. In S.O.M.C., only one (or less than one) monolayer of an organomolecular fragment is grafted onto the surface, which thus retains, at least in part, its molecular integrity. In the case of the Niwa approach by OMCVD, $Si(OCH_3)_4$ was allowed to react with the hydroxy groups present on the external surface of the zeolite, thereby leading to a surface organometallic complex:

$$\equiv T{-}OH + Si(OCH_3)_4 \rightarrow \equiv T{-}O{-}Si(OCH_3)_3 + CH_3OH$$

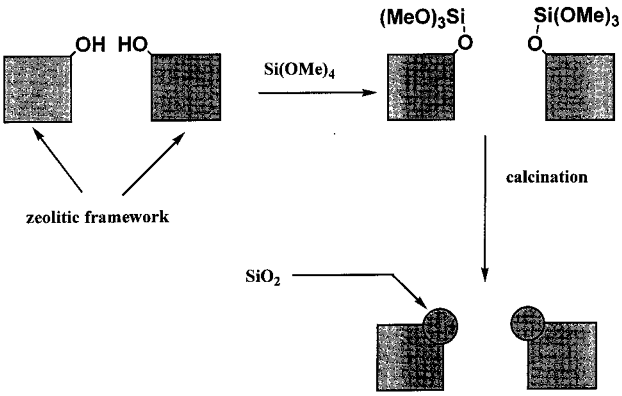
where T represents a framework atom such as Si or Al. This surface complex was then able to undergo further reactions with the hydroxy groups of the surface, leading to multigrafted species:

$$\equiv T{-}O{-}Si(OCH_3)_3 + x \equiv T{-}OH \rightarrow (\equiv T{-}O)_{1+x}Si(OCH_3)_{3-x} + x\, CH_3OH$$

$$T = Si, Al;\ x = 1, 2$$

The resulting materials were subsequently calcined under oxygen, leading to the formation of silica-coated zeolites by the elimination of the hydrocarbon residues (ligand and alcohol) as shown in Scheme 1.

Repetition of this process reduced the dimensions of the pore entrances by 0.1 nm for a single-step modification or by 0.2 nm for a multistep OMCVD modification. Adsorption of *p*-xylene was greatly modified on these materials; while this molecule was easily adsorbed on unmodified mordenite (Large pore from Norton), it was totally excluded from the same zeolite modified by grafting $Si(OCH_3)_4$ (2.7 wt.-% complex) and subsequent calcination. A study of the reaction on the surface of mordenites with various Si/Al ratios was carried out, the results of which showed that the amount of adsorbed methoxysilane depended on this parameter, the "epitaxial" growth of the SiO_2 layer on the external surface being perturbed by the aluminium atoms.[10]



Scheme 1. Modification of the pore entrance of a zeolite by reactions with $Si(OMe)_4$

Various other silicon-containing molecules have been used, for example $(C_3H_7)_3Si(OCH_3)$, which led only to a monografted complex, the Si−C bond being very stable,[11] or chlorosilanes.[12] With the latter, the reaction led to the formation of hydrochloric acid, thus it was necessary to use zeolites with a high Si/Al ratio in order to avoid the local destruction of the framework by HCl.

As these modifications did not affect the internal catalytic properties of the zeolites, the modified solids could be used in catalysis, often showing increased selectivity for the desired products. There have been numerous reports of such applications, although most of them deal with the formation of dibranched aromatic compounds and the production of *para*-substituted aromatic compounds. For example, such systems are used in the alkylation of toluene by methanol.[13] The deposition of silica onto the zeolite leads to a large decrease in the catalytic activity, but to a concomitant marked increase in the *p*-xylene selectivity. These results were explained in terms of a decrease of the diffusivity inside the channels due to the silica deposit, together with a deactivation of the acid sites on the external surface due to reaction with the silicon compound. Similar results were obtained for toluene disproportionation and *o*-xylene isomerization;[9c] the larger the amount of silica deposited on the catalyst, the higher the selectivity towards *p*-xylene and the lower the catalytic activity.

However, the main problem of these studies was that the reaction of the organometallic compound with the surface was performed by OMCVD, which does not offer control at the molecular level. Numerous surface species were most probably obtained which, by calcination and migration, gave rise to poorly defined solids. It was thus difficult to correlate the catalytic properties with the modification of the zeolite.

More recently, numerous studies have been undertaken using the SOMC technique, which preserves the molecular structure on the surface. Various organometallic compounds have been reacted with mordenite and the grafted fragments thus obtained have been fully characterized by in situ IR spectroscopy, volumetric measurements, elemental analysis, and ^{13}C-CP-MAS solid-state NMR.[14−18] The grafting of organometallic derivatives of various metals has also been studied, including magnesium ($MgNp_2$), zirconium ($ZrNp_4$), germanium ($GeBu_4$), and, most thoroughly, tin (SnR_4 compounds with R = Me, Et, *i*Pr, *n*Pr, *n*Bu, Ph, Cy; $HSnBu_3$). In the case of the alkyltin compounds, the solids were also characterized by ^{119}Sn-MAS-NMR. In each case, reaction of the organometallic compound with the external surface hydroxy groups occurred, which can be described in terms of the following equations:

$$\equiv Si{-}OH + MR_4 \rightarrow \equiv Si{-}O{-}MR_3 + RH$$

M = Sn, Ge, Zr; R = Me, Et, *n*Pr, *i*Pr, *n*Bu, Np, Cy, Ph

$$\equiv Si{-}OH + HSnBu_3 \rightarrow \equiv Si{-}O{-}SnBu_3 + H_2$$

$$\equiv Si{-}OH + MgNp_2 \rightarrow \equiv Si{-}O{-}MgNp + NpH$$

These results were confirmed by further studies on various oxides (silica, alumina, silica/alumina, etc.).[19] For all organometallic compounds, the reaction occurred only at the external surface and near the pore entrances, the starting organometallic compounds being too large to enter inside the channels (with the sole exception of $SnMe_4$, which probably reacted very rapidly at the pore entrances, thereby preventing other molecules of tetramethyltin from penetrating inside the channels, XPS showing a considerable tin enrichment on the surface). The main interest in this approach stemmed from the fact that the organometallic compounds were not calcined after the grafting reaction. As a consequence, the reduction of the pore openings was under a *strict molecular control* and was also much larger than that achieved in the previously mentioned studies, where calcination and formation of an oxide layer typically resulted in only a ca. 5% decrease in the dimensions of the pore entrance. Figure 2 shows a pore entrance of mordenite after grafting of a tributyltin organometallic fragment. It can readily be seen that the pore entrance is reduced by ca. 30−40%. This significant obstruction of the pore entrance results in a marked change in the adsorption properties of the modified zeolite. In studies of these systems, the adsorption capacities were determined by a dynamic method, the apparatus being shown in Figure 3. It could be described as a chromatographic method, the zeolite being placed in a small chromatographic column. Pulses of the desired hydrocarbon were introduced at the entrance of the column and the gaseous phase was analyzed at the output. The adsorption capacity was determined from the quantity of hydrocarbon present in the pulses that did not appear in the output from the column.

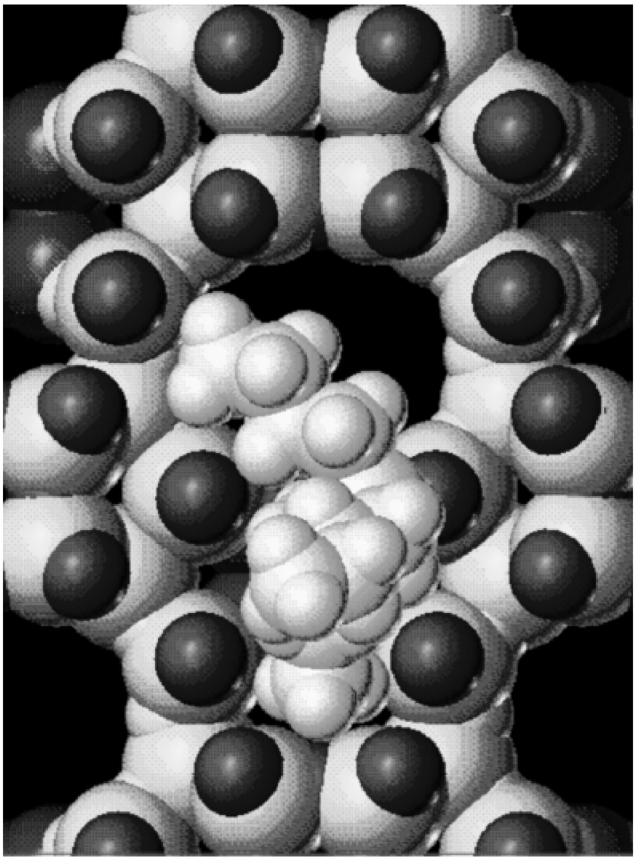


Figure 2. Molecular modelling representation of the pore entrance of mordenite after the grafting reaction of an organometallic tributyltin fragment

Figure 4 shows the adsorption capacities for *n*-hexane, 2-methylpentane, 2,3-dimethylbutane, and isooctane (2,2,4-trimethylpentane) of mordenite and of mordenite modified by grafting various organometallic complexes. Clearly, the adsorption capacities (as determined by this method) were greatly modified after the grafting reaction, although the data were not so easy to explain quantitatively. In principle, the role of the organometallic fragment should be very simple; the incoming molecule either can or cannot enter the pore system, depending on the bulkiness of the organometallic fragment. This may be evaluated, for example by molecular modelling. Experimentally, however, the results are more complicated:

In some cases, molecules which were experimentally found to enter into the pore system of mordenite (e.g. isooctane) could no longer penetrate into mordenites modified by bulky organotin compounds (e.g. SnR_3; R = Cy, *n*Bu).

In other cases, molecules experimentally found to enter the pore system of mordenite were also found to penetrate mordenite modified by organotin fragments, albeit more slowly. This was the case for 2,3-dimethylbutane. Here, the actual adsorption capacity of the mordenite was not modified by the grafting reaction, which occurred only on the external surface of the solid without modification of the bulk.

These results are best explained as follows:

(a) A “thermodynamic” effect is observed when a hydrocarbon molecule, which can be adsorbed by the unmodified

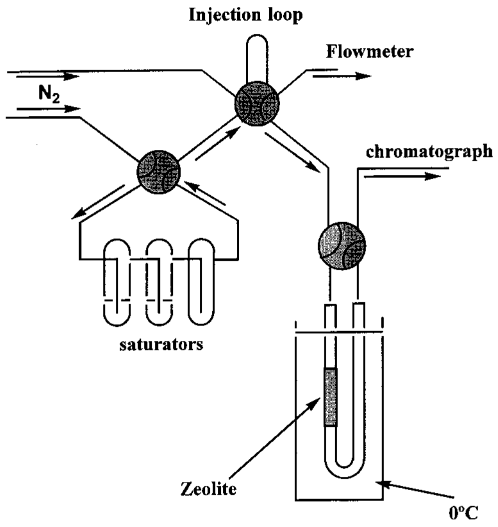


Figure 3. Schematic representation of the apparatus used for the determination of adsorption capacities by a dynamic method ("pulse" method)

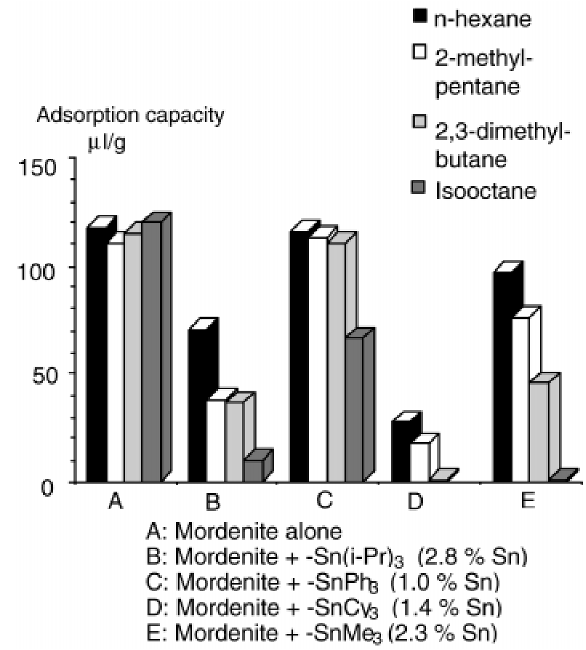
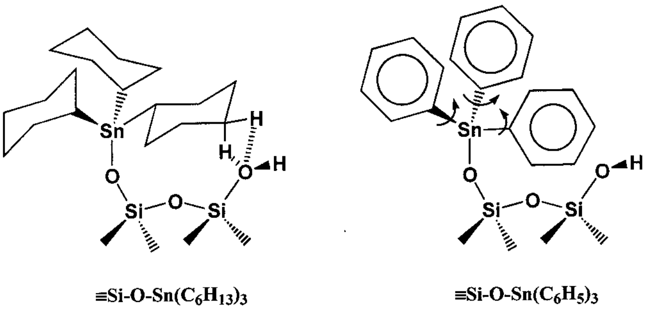


Figure 4. Adsorption capacities (determined by the pulse method) of *n*-hexane, 2-methylpentane, 2,3-dimethylbutane, and isooctane in unmodified mordenite and in mordenite modified by grafting various organometallic complexes

zeolite, can no longer pass through the partially obstructed pore entrance following grafting of the complex, due to steric interactions. A typical example is provided by isooctane, which is adsorbed by mordenite, but is totally excluded from mordenite modified by trimethyltin or tricyclohexyltin. In this case, the new adsorption capacity is zero.

(b) A "kinetic" effect, which is attributable to a decrease in the diffusion rate of molecules able to pass through the modified pore entrances. Indeed, at the pore entrances, the hydrocarbon molecules can interact with the alkyl ligands of the grafted organometallic complexes, resulting in a decrease of their diffusion rate and so to an apparently lower adsorption capacity. These effects were relatively straightforwardly predicted by Monte Carlo theoretical calculations.[20]

Another interesting conclusion of these studies was obtained by comparing the effects of the tricyclohexyltin and triphenyltin grafted fragments (Figure 4). While mordenite modified by tetracyclohexyltin readily discriminated the four hydrocarbons, no effect was observed for the samples modified by reaction with tetraphenyltin. This was explained by assuming, in agreement with ^{13}C-CP-MAS NMR data,[19c] that the phenyl ligands were able to rotate freely about the C−Sn bonds, while the cyclohexyl moieties interacted with remaining hydroxy groups on the surface, thereby leading to a more efficient reduction of the dimensions of the pore entrances (Scheme 2).



Scheme 2. Structure of ≡Si−O−SnR$_3$ (R = C_6H_{13}, C_6H_5) grafted on mordenite

Most of the modified zeolites were found to be unstable at high temperature (decomposition of the organometallic fragment at temperatures above 200 °C). However, a significant exception to this rule was observed with mordenite modified by organogermanes; the grafted fragment was stable up to ca. 400 °C, allowing the possibility of using this material for practical applications.[15]

These materials were also studied with regard to the direct separation of a mixture of the aforementioned four hydrocarbons. For this purpose, a different experimental setup was used (Figure 5). The mixture of hydrocarbons was passed continuously through the zeolite in the form of chromatographic column and the gases were analysed sequentially by GC. Figure 6 shows typical results obtained by this method: while the four hydrocarbons (*n*-hexane, 2-methylpentane, 2,3-dimethylbutane and isooctane) were not discriminated by unmodified mordenite, they were easily separated by mordenite modified by grafting organometallic complexes. These experiments thus represented a real case of separation of hydrocarbon mixtures by a zeolite. It should be pointed out that, with the exception of isooctane, even if the hydrocarbons could enter the pores, they were discriminated by their van der Waals interactions with the grafted organometallic fragment (combination of thermodynamic and kinetic effects).

Finally, a study was undertaken of the zeolite properties as a function of the organometallic loading, in order to gain a better understanding of the grafting mechanism.[21] Vari-

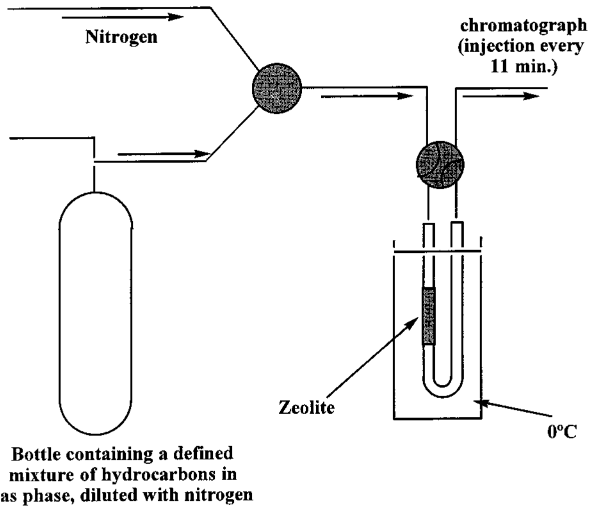


Figure 5. Schematic representation of the apparatus used for the separation of mixtures of hydrocarbons

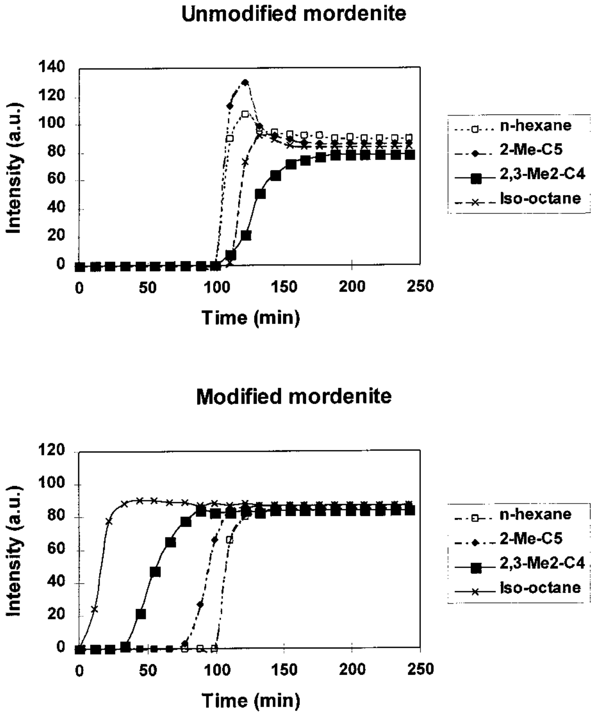


Figure 6. Separation of a mixture of hydrocarbons (*n*-hexane, 2-methylpentane, 2,3-dimethylbutane, and isooctane) by unmodified mordenite and by mordenite modified by grafting tributyltin fragments

ous organometallic complexes of tin (SnR_4; R = Me, Et, *n*Pr, *n*Bu) were used. The adsorption properties of these modified materials towards *n*-hexane, 2-methylpentane, 2,3-dimethylbutane, and isooctane were studied (Figure 7).

It was shown that a total exclusion of isooctane could be achieved with tin loadings greater than 0.5 wt.-%, while 2-methylpentane and 2,3-dimethylbutane were only discriminated with tin loadings in excess of 0.9 wt.-%. No detectable effect was observed in the case of *n*-hexane, even with tin loadings as high as 1.5 wt.-%. These results can be interpreted by assuming that the grafting reaction of the tin fragments occurs on different hydroxy sites of the mordenite, depending on the degree of tin loading. There are four possible grafting sites on an idealized external surface of mordenite (Figure 8), reaction at which should lead to differential reductions of the pore sizes. It has been proposed that for low tin loadings (below 0.5 wt.-%), the grafting reaction occurs only at site 1. A molecular modelling study showed that under these conditions only isooctane would be totally excluded and that the other hydrocarbons would still be able to enter. For tin loadings between 0.5 and 1.0 wt.-%, it is proposed that the grafting reaction occurs at sites 3 or 4, resulting in the exclusion of both 2-methylpentane and 2,3-dimethylbutane.

These modified mordenites have also been used in catalysis experiments, for the selective isomerization of C_8 aromatic mixtures to xylenes.[16] These C_8 aromatic mixtures contained *ortho*-, *meta*- and *para*-xylenes and a non-negligible amount of ethylbenzene (10−40%), of which *para*-xylene is the most useful component. This is removed from the reaction mixture in an aromatic separation unit and the *p*-xylene-depleted mixture is then fed to a unit where the *o*- and *m*-xylenes are isomerized into an equilibrium mixture of *p*-, *o*- and *m*-xylenes. This mixture is then recycled to the *p*-xylene recovery unit together with fresh feed. As the C_8 mixture contains ethylbenzene, the catalyst has to be able to convert it with a minimum loss of xylenes, in order to avoid an increase of its concentration in the recycle loop. Consequently, the objectives of the isomerization units are to isomerize xylenes and to convert ethylbenzene into valuable products. Usually, this is accomplished industrially by the use of a bifunctional catalyst consisting of a large-pore acid zeolite (typically mordenite) and a hydrogenating metal (platinum). It was thus interesting to study the applicability of mordenites modified by organometallic complexes in this reaction. However, such reactions are performed at high temperatures (410°C) and under these conditions the organometallic fragment is not stable: a dealkylation of the grafted species occurs, resulting in a mordenite bearing only dealkylated species. The modified mordenites were therefore calcined prior to use. They were then mixed mechanically with a hydrogenation catalyst, in the form of Pt/Al_2O_3 (0.3 wt.-% Pt). Mordenites modified by various organometallic complexes [$MgNp_2$, $ZrNp_4$, Sn(*n*Bu)$_4$, Ge(*n*Bu)$_4$] were used. It was observed that the disproportionation reactions, which lead to undesirable products and to a loss of some of the xylenes, were, in some cases, greatly reduced compared to the situation using an unmodified mordenite. When the mordenite was modified by Ge(*n*Bu)$_4$ or $ZrNp_4$, the isomerization selectivity (between xylenes, and for the transformation of ethylbenzene into xylenes) was increased, while the disproportionation reactions became less significant. When mordenite was modified by Sn(*n*Bu)$_4$ or $MgNp_2$, no difference was observed compared to unmodified mordenite.

These results were compared to XPS data: XPS showed that in the case of magnesium and tin complexes there was migration of these metals into the interior of the zeolite

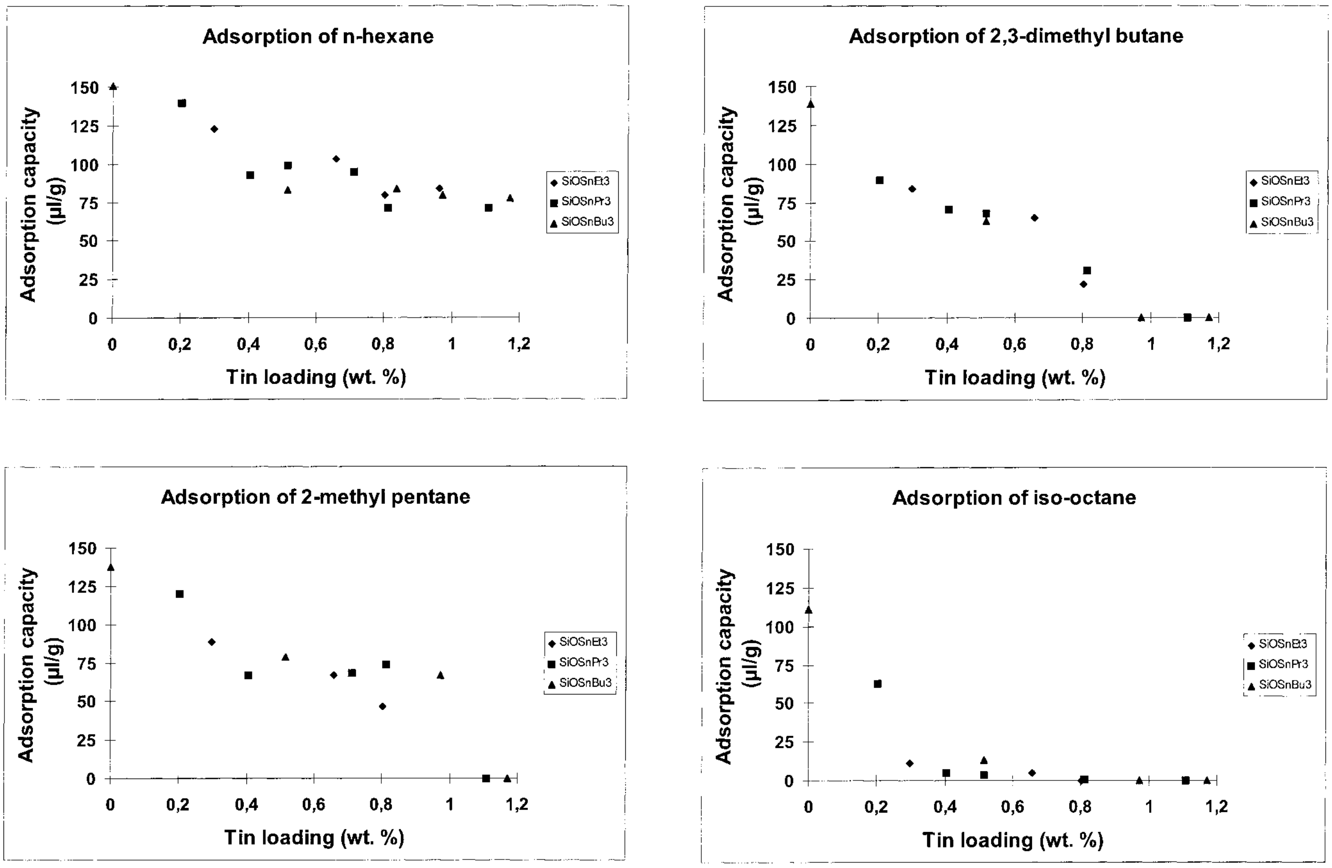


Figure 7. Adsorption capacities towards various hydrocarbons, determined by the pulse method, of mordenite modified by reaction with tetraalkyltin complexes, as a function of the tin loading

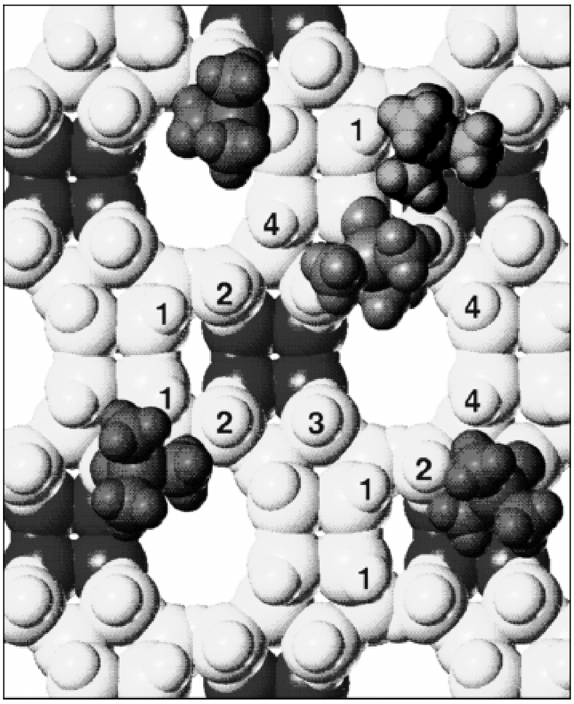


Figure 8. Grafting sites at the pore entrances of mordenite

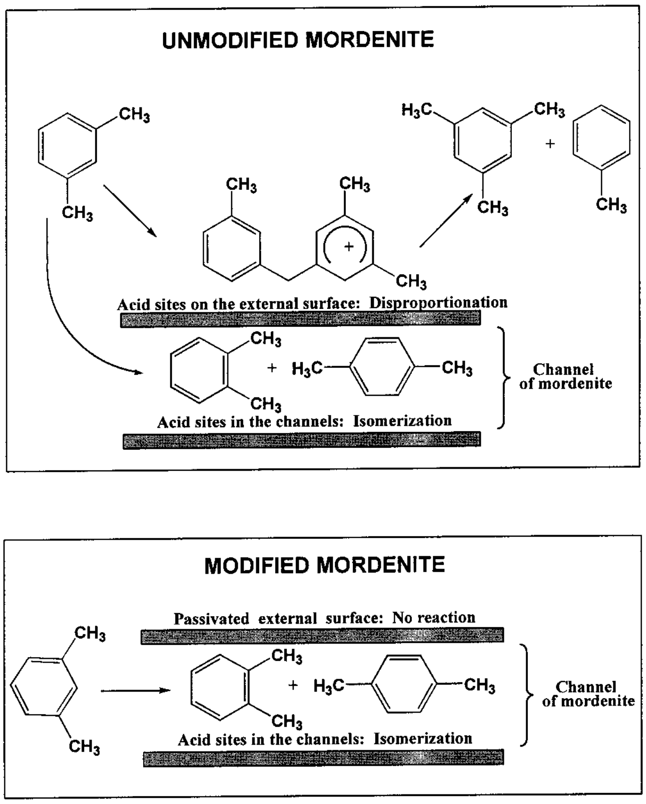
grains during calcination, whereas in the case of germanium and zirconium there was no migration, resulting in the formation of a disperse layer of Ge or Zr "oxide" on the external surface of the zeolite crystals. It was thus logical to suppose that the disperse layer was responsible for the observed decrease in disproportionation.

The interpretation of this experimental correlation between catalytic and XPS results is shown in Scheme 3. The disproportionation reaction is bimolecular; it requires the formation of a bulky reaction intermediate. This intermediate, in view of the channel dimensions of the mordenite zeolite framework, should be formed preferentially by the intervention of the acid sites present at the channel entrances, or preferably at the external surface of the zeolite crystals. The grafting of the organometallic complexes at the external surface leads to the elimination or poisoning of such "non-selective" acid sites, which leads to an overall reduction of the disproportionation reactions.

These studies were also extended to other microporous materials, such as mesoporous silicas and cloverite. However, in these cases, the modification occurred not only on the external surface but also inside the channels. These results are presented in the following part of this review.

Modification of the Internal and External Surfaces of Molecular Sieves

Before describing the modification of the properties of molecular sieves by true organometallic compounds, we will



Scheme 3. Isomerization of xylenes on unmodified and modified mordenite

briefly overview the modification by the other compounds, essentially silanes and boranes.[2,22]

Acidic zeolites can be modified by reaction with silanes, due to the reactivity of the Si−H bond. Reactions with hydroxy groups of the zeolite can thus be written as:

$$\equiv T{-}OH + SiH_4 \rightarrow \equiv T{-}O{-}SiH_3 + H_2$$
$$\equiv T = Si, Al$$

This chemisorbed group can react further with another hydroxy group, resulting in a silicon dihydride species linked to the surface via two σ-bonded oxygen atoms:

$$\equiv T{-}OH + \equiv T{-}O{-}SiH_3 \rightarrow (\equiv T{-}O)_2SiH_2 + H_2$$
$$\equiv T = Si, Al$$

In all cases, the samples were further hydrolyzed in order to obtain stable compounds that could not react with the adsorbents:

$$(4-x)\,H_2O + (\equiv T{-}O)_xSiH_{4-x} \rightarrow (\equiv T{-}O)_xSi(OH)_{4-x} + (4-x)\,H_2$$
$$\equiv T = Si, Al;\ x = 1, 2$$

Thus, a total of 4 hydrogen molecules were evolved per grafted silicon. In principle, the greatest number of silanes that could react with the zeolite (very often a mordenite) could not exceed the number of hydroxy groups (typically around 2 mmol per gram). In practice, the experimental value was invariably lower, owing to several factors: (i) heterogeneous reactivity of the hydroxy groups (depending on their crystallographic localization), (ii) a decrease of the diffusion rate of the silane molecules in the channels, following the reduction of the dimensions of the pore openings after modification by an initial SiH_4 molecule (this effect is somewhat analogous to that described above as a kinetic effect in the case of zeolites modified only at the external surface).

Another modification method involved the use of disilanes such as $H_3Si{-}SiH_3$ rather than simple silanes of the type SiR_4. Two reactions occurred simultaneously, depending on whether the Si−Si or an Si−H bond was broken:

$$2 \equiv T{-}OH + Si_2H_6 \rightarrow H_2 + 2 \equiv T{-}O{-}SiH_3$$
$$\equiv T{-}OH + Si_2H_6 \rightarrow H_2 + \equiv T{-}O{-}Si_2H_5$$

In the case of silanes, the chemisorbed species could undergo further reactions with the hydroxy groups, leading to multigrafted species. Finally, the residual ≡Si−H and ≡Si−Si≡ bonds were hydrolysed to ≡Si−OH groups:

$$\equiv Si{-}H + H_2O \rightarrow H_2 + \equiv Si{-}OH$$
$$\equiv Si{-}Si\equiv + 2\,H_2O \rightarrow H_2 + 2 \equiv Si{-}OH$$

The resulting solids were often characterized by adsorption kinetics of Xe, Kr, O_2 or N_2. In all cases, a pore size reduction was observed, leading to a decrease of the pore volume. It was also observed that the hydrolysis reaction led to a marked decrease in the pore volume, resulting, in some cases, in a complete exclusion of *n*-butane. This was not due to a destruction of the framework, since smaller molecules such as rare gases and oxygen could still fill the pores, but solely due to the reduction of the pore size by the grafted fragments (thermodynamic effect).

Similar modifications of zeolites were carried out using B_2H_6 but, as above, changes in the adsorption properties were only significant after treatment under severe conditions.[2]

Recently, the reaction of organometallic compounds with the internal hydroxy groups of molecular sieves has been studied. Due to the non-negligible size of the organometallic complexes, only some molecular sieves could be used, namely cloverite[23] and mesoporous silica (MCM-41 or MS-1).[24]

Cloverite is a synthetic microporous gallophosphate with a 20-tetrahedral pore opening, the synthesis and structure of which was reported in 1991.[8] Its crystal structure contains two non-intersecting channel systems with 8-ring (8-T, 3.8 Å) and 20-ring (20-T, 13.2 Å) pore openings. The diagonal dimension of the supercages formed at the intersections of the 20-ring channels amounts to 23−30 Å (Figure 8).[25] Furthermore, hydroxy groups can only be found at the windows of these supercages (4 hydroxy groups per window, 6.2 Å apart). The reactions of $SnMe_4$, $SnEt_4$ and $HSnBu_3$ with this solid were studied by numerous methods and the resulting materials were fully characterized by physicochemical techniques such as ^{13}C-CP-MAS- and ^{119}Sn-MAS-NMR, EXAFS, X-ray powder diffraction, XPS, etc.[23] In all cases, it was shown that the grafting reaction had occurred both on the external surface and inside the channels, most of the tin being found in the bulk. Depending on the starting organometallic species, different solids were obtained, with a mean value of one grafted organometallic fragment per window of the supercages when $SnEt_4$ or $HSnBu_3$ were used (corresponding to ca. 3.5 wt.-% tin) or four grafted organometallic fragments per window in the case of $SnMe_4$ (corresponding to ca. 14 wt.-% tin). In the latter case, all hydroxy groups in the solid had reacted. For all samples, the grafted organometallic fragment was fully characterized as a $\equiv T-O-SnR_3$ complex, in which tin was tetracoordinated. The reaction was not selective and both $\equiv P-OH$ and $\equiv Ga-OH$ hydroxy groups reacted:

$$\equiv T-OH + SnR_4 \rightarrow \equiv T-O-SnR_3 + RH$$
$$R = Me, Et$$
$$\equiv T-OH + HSnBu_3 \rightarrow \equiv T-O-SnBu_3 + H_2$$

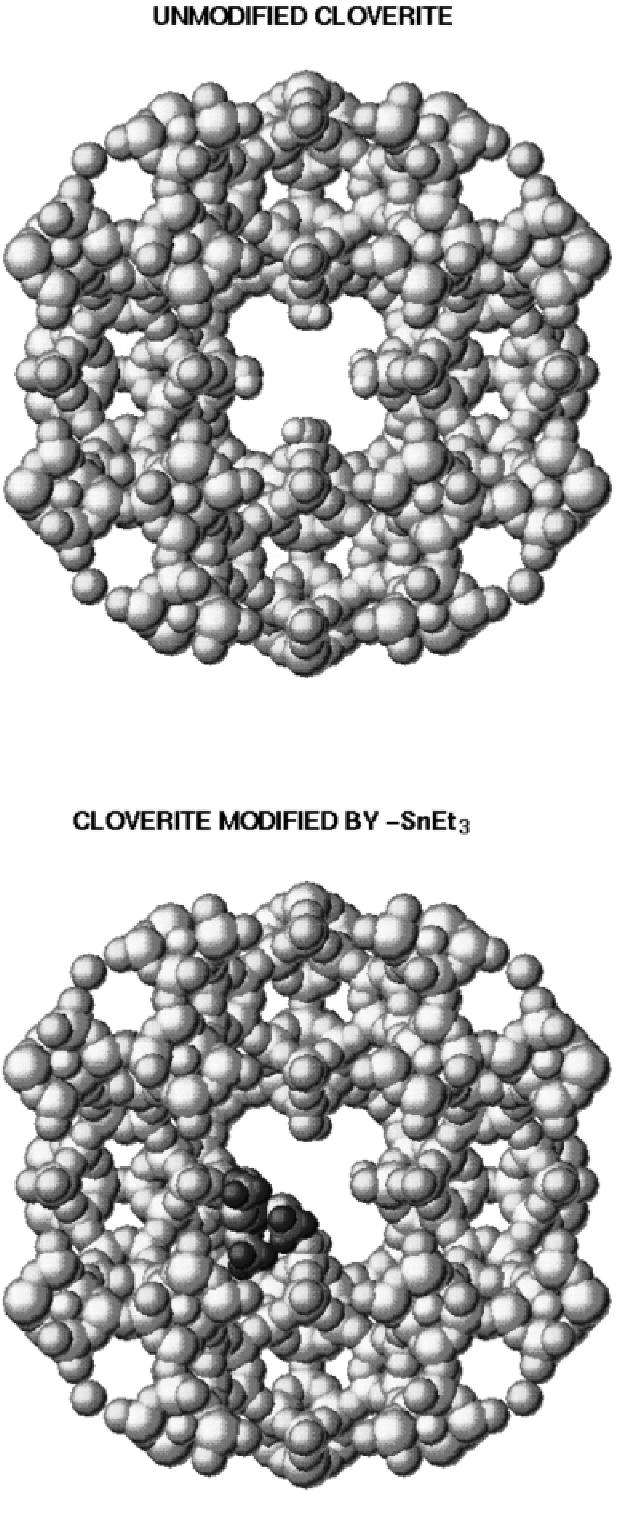
As an example, Figure 9 shows a molecular modelling representation of a supercage window before and after modification by $SnEt_4$.

The adsorption properties of unmodified cloverite and of cloverite modified by grafted $-SnR_3$ fragments were studied. The adsorption properties towards *n*-hexane, benzene and isooctane were determined using a static method. The apparatus used for these studies is shown schematically in Figure 10. The cloverite sample was connected to a pressure gauge and a vacuum line via a break-seal. A known amount of the appropriate hydrocarbon was introduced into the system as a liquid and immediately vaporized. The break-seal was then broken and the variation of the hydrocarbon pressure was analyzed as a function of time, thereby allowing determination of the adsorption capacity.

The values obtained for unmodified cloverite showed that benzene and isooctane filled only the 20-T channel system, while *n*-hexane filled both the 8-T and 20-T channel systems. When cloverite was modified by tetramethyltin (14 wt.-%), tetraethyltin, or tributyltin hydride (3.5 wt.-%), the following features were observed: (a) Total exclusion of isooctane from all materials. (b) Reduction of the adsorption capacities towards *n*-hexane and benzene, which became very similar after the grafting reaction.

The exclusion of isooctane was explained in terms of the reduction of the size of the windows of the supercages, which prevented passage of this molecule. This was also the case for butane after reaction with disilane. These observations are nicely predictable by molecular modelling.

The reduction of the adsorption capacities towards *n*-hexane and benzene was due to two factors: (i) *n*-Hexane could only fill the 20-T channel system, owing to a blocking of the pore openings of the 8-T channels by the organometallic fragments grafted onto the external surface. (ii) The decrease of the adsorption capacity corresponds to a reduction in the pore volume due to the presence of the grafted organometallic complexes inside the channels. This effect was also predictable by simple molecular modelling calculations.


UNMODIFIED CLOVERITE

CLOVERITE MODIFIED BY $-SnEt_3$

Figure 9. Molecular modelling representation of a supercage window of cloverite before and after modification by reaction with tetraethyltin

Unfortunately, no difference was observed between cloverites modified by reaction with tetramethyltin, tetraethyltin, or tributyltin hydride, even though the sizes of the windows were reduced to varying extents. This was probably related to the limited range of hydrocarbons adsorbed on these materials. However, such a modification of the adsorption characteristics of a molecular sieve is very interest-

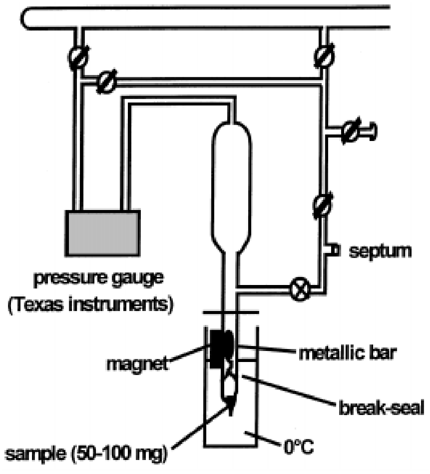


Figure 10. Schematic representation of the apparatus used for the determination of the adsorption capacities by a static method

ing as there are many more steric interactions between the adsorbed molecule and the grafted organometallic complex than in the case of mordenite, where the grafting reaction occurs only on the external surface (there is not just one interaction with the organometallic compound as the hydrocarbon is adsorbed onto the solid, but numerous interactions along the channels).

Analogous studies were also performed on MCM-41, a recently discovered mesoporous silica.[26] MCM-41 has pores with a very sharp diameter distribution, rendering this material useful for separation processes of large molecules. Depending on the template used during the synthesis, the diameter of the pores can be varied from ca. 20 to 100 Å. The reactions of various alkyltin complexes with this solid were studied using the same physicochemical techniques as mentioned above.[24] As with mordenite and cloverite, a reaction was observed with the surface hydroxy groups. However, in contrast to what was observed in the previous examples, the main surface product when the mesoporous silica was pretreated at 200°C was not $\equiv Si-O-SnR_3$ but $(\equiv Si-O)_2SnR_2$, obtained by reaction of two hydroxy groups with SnR_4. This result was tentatively attributed to the concavity of the walls in the pores, which probably induced a stabilization of the multi-grafted species. When the mesoporous silica was initially dehydroxylated at 500°C, the mono-grafted species was predominant (more than 90% of the tin was present in the form of $\equiv Si-O-SnR_3$ species) and all the hydroxy groups were consumed. For this material, the grafting reaction completely modified the shapes of the hydrocarbon adsorption isotherms (Figure 11). Indeed, the isotherm of unmodified mesoporous silica showed a great increase of the adsorbed alkane (for example, *n*-hexane) at low P/P_0 ratios, while the isotherm of the modified material increased only slowly as a function of P/P_0. This phenomenon was independent of the hydrocarbon, all alkanes with the same number of carbon atoms giving the same curves. It was explained by assuming that for the unmodified material the adsorption curve was due to hydrogen bonding between the hydroxy groups of the surface and the C−H bonds of alkanes, while in the modified material the hydroxy groups were absent and the aforementioned interactions were replaced by van der Waals interactions between the alkyl groups of the grafted organometallic fragments and the hydrocarbons.

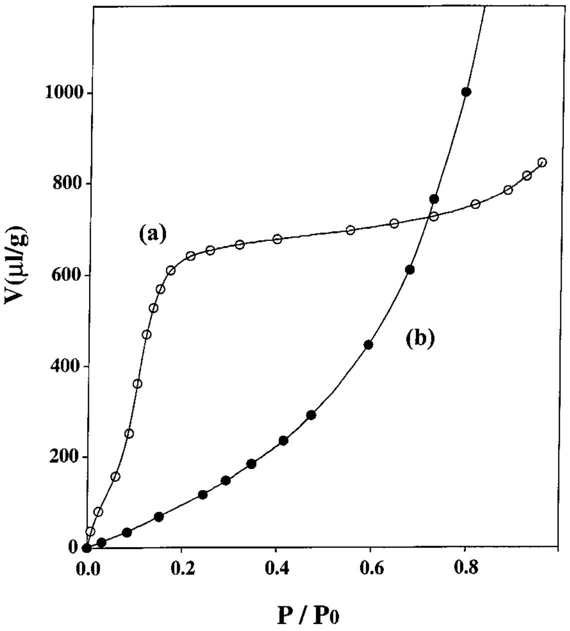


Figure 11. Adsorption isotherms at 0°C of *n*-hexane on MCM-41 dehydroxylated at 500°C before (a) and after (b) reaction with tetrabutyltin

Conclusion

This short review article has shown the great advantages of the modification of molecular sieves by grafting organometallic compounds. Two different methods can be used: OMCVD, where the grafted organometallic fragment is calcined and transformed into an oxide of rather indefinite composition, and SOMC, where the grafted organometallic fragment is well-characterized and retains its molecular integrity. Both methods can lead either to a grafting reaction only on the external surface, or to grafting inside the channels of the molecular sieve as well, depending on the reaction conditions and on the size of the organometallic complex used for the modification. In the case of SOMC, it is possible to modify only the external surface of molecular sieves such as mordenites, leading to an increased selectivity, e.g., in xylene isomerization. Grafting of the organometallic complex near the pore entrances permits a fine tuning of the adsorption properties of the zeolite. Two effects can be observed, depending on the size of the adsorbed molecule: (i) a total exclusion of the molecule from the channels of the molecular sieve, due to steric constraints ("thermodynamic effect"); (ii) a retardation of the adsorption kinetics of the adsorbed molecule, due to steric interactions with the grafted organometallic fragments at the pore entrances ("kinetic control").

These properties of the modified materials can be envisaged as being useful in catalysis. For this purpose, it would be necessary to first introduce the catalytically active species into the channels of the molecular sieve and then to graft the organometallic complex onto the external surface in order to reduce the dimensions of the pore entrances. Two effects could then be expected: (i) The leaching of the catalyst could be completely avoided, allowing easy recycling. (ii) By judicious choice of the organometallic complex, only some reaction products could be desorbed from the molecular sieve containing the homogeneous catalyst, resulting, in line with the principle of microreversibility, to an increase in the selectivity towards these products.

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