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Molecular engineering of oxides and zeolites [1]

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1. Introduction

The ability of porous solids to adsorb gases was recognized in the eighteenth century but its practical application to separation and purification of industrial process streams has undergone an explosive growth over the last 20 years.

The present review will be focused on physical adsorption because almost all adsorptive separation processes are controlled by this adsorption phenomenon. In the physical adsorption the interaction energy reflects the strength of the bonding between the sorbate and the surface [1–3,3–8].

The selection of a proper sorbent useful for adsorption and separation purposes is based on:

(i) A high equilibrium capacity and/or high selectivity of the sorbent. The capacity and selectivity are controlled by the pore volume, pore size distribution, surface area and surface composition of the sorbent.

(ii) Good kinetic properties. A correct selection of the crystal size, particle size, macroporosity and binder type is essential.

(iii) Good physical properties, reflecting a high bulk density, a high crush strength and a good erosion resistance of the sorbent.

(iv) Good lifetime performance. The sorbents need to have a high chemical, thermal and mechanical stability.

Taking into account these requirements, oxides and zeolites are potentially important substrates for adsorption and separation purposes [9].

2. Zeolites

Since their discovery more than one century ago, many studies on zeolite minerals have been carried out. Moreover, in the late 1940's the preparation of synthetic zeolites was the start of a large range of zeolitic materials reflecting the complete range of framework substituted tectosilicate including phosphates [10–21].

From their structural formula

$$\frac{x}{n} M^{n+} \left[(AlO_2)_x (SiO_2)_y \right] wH_2O$$

adsorption and ion exchange properties were recognized as their specific characteristics. The possibility of zeolites to adsorb molecules of relative small size over molecules of larger size formed the basis for the introduction of the term molecular sieves.

The first generation of zeolites (1940–1950) reflects the zeolites with low silica to alumina ratios ($SiO_2/Al_2O_3 \leq 10$), prepared from a crystallization of reactive aluminosilicate gels with alkali and alkaline earth metal hydroxides. Such zeolites are characterized by a high ion-exchange capacity, an extremely hydrophillic

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surface and many acid sites with a wide variety of acid strength. Such frameworks show different thermal and hydrothermal stabilities, depending on structural and compositional factors. Typical zeolites are zeolite A, X, Y, chabazite, erionite and mordenite.

The second generation of zeolites were prepared by using all possible quaternary ammonium ions and resulted in many new materials with a new structure type and different chemical compositions. More in particular, aluminosilicates with $SiO_2/Al_2O_3 \geq 20$ were synthesized, out of which ZSM-5 became the most prominent (1960–1970).

The extensive size of organic amines as structure-directing templates or pore filling agents, coupled with a new gel chemistry resulted in the discovery of a third generation of zeolites containing Al^{3+} and P^{5+} as lattice atoms (1982). These aluminophosphate materials are a family of molecular sieves.

The three properties of zeolites which have industrial potential are their capacities to adsorb gases, vapours and liquids; to catalyse reactions and to act as cation exchangers.

The ability of several zeolites such as zeolite A, X, Y, and mordenite to take up large amounts of several guest molecules had been known for a considerable time to use them as drying agents and depending on the pore size as adsorbents for separation purposes.

Furthermore, the unique properties of zeolite frameworks causing unusually high catalytic activity and selectivity has added a new dimension to the field of heterogeneous catalysis and catalytic process engineering.

The cation exchange properties of the zeolites has been studied for a variety of reasons. In general, the parameters controlling the zeolite cation exchange properties are:

(1) The nature of both the competing ions with respect to their relative sizes and to their states of solvation inside and outside the zeolite.

(2) The charge on the zeolite framework coupled with framework geometry.

(3) The heteroenergetic nature of the cation sites available for occupation inside the framework.

(4) The temperature at which exchange is carried out, this can influence the removal of water of hydration, and the accessibility of sites and improve exchange kinetics.

(5) The concentration of the external solution coupled with the presence (or absence) of ligands other than water molecules.

Depending on the nature and valency of the exchangeable cations together with their positions, important selectivity (electrical field) and molecular sieving effects can be created inside the zeolite framework.

In order to improve the performance of zeolites as molecular sieves, several modification techniques were developed to vary in a controlled way the zeolitic pore system: pore size engineering [22]. In practice, pore size engineering in zeolites can be the result of modification by cation exchange process, modification by a preadsorption of polar molecules, or modification of the zeolitic framework.

2.1. Modification by a cation exchange process [10,11]

Changing the cations in a zeolite may effectively enlarge the pore openings by diminishing the cation population and/or a resiting of cations which are normally located near these openings. In zeolite A, divalent ion exchange opens the aperture to full diameter, whereas exchange with a larger univalent ion diminishes the aperture size. It is known that an exchange of potassium for sodium in zeolite A changes the sieving properties. The pore size reduction does not occur gradually with increasing extent of exchange but rather suddenly at a level of about 25% potassium exchange. Also, an increase in the adsorption can be observed by a calcium exchange in NaA and again it does not occur in a linear fashion but rather abruptly. Similar effects are exhibited by the zeolites mordenite, chabazite, zeolite X and offretite.

2.2. Modification by a preadsorption of polar molecules [12]

Another method for altering the molecular sieving effect of a zeolite is the preadsorption of polar molecules. If small amounts of polar molecules, such as water or ammonia, are preadsorbed in a dehydrated zeolite, the adsorption of a second absorbate can be drastically reduced. It is assumed that the strong interaction between the zeolite cation and the dipole moment of the polar molecules produces a diffusion block by clustering the polar molecules around the exchangeable cations in the zeolite channels.

2.3. Modification of the zeolitic framework

Pore size engineering in zeolites can also be achieved by a modification of the zeolitic framework resulting from: (1) crystallographic changes by a thermal treatment, (2) internal and external structural modification by implantation of additional atom groups, or (3) external surface modification of the zeolite crystal (coating process).

2.3.1. Pore size modification by crystallographic changes [13]

The molecular sieve behaviour of zeolites can be controlled by a hydrolytic process at elevated temperatures. Water vapour in contact with zeolite crystals at elevated temperatures results in a variation of the zeolitic adsorption characteristics. The amount of water vapour, the pretreatment temperature and the pretreatment time, can control the effective pore size of zeolites. It appears, that a steam treatment causes a cation migration and a cation hydrolysis of the exchangeable cations or a structural transformation of the zeolite. However, the effect of steam on the adsorption behaviour of zeolites is influenced by the nature of the initial exchangeable cations. For example, Ca chabazite converts to a phillipsite structure and Na chabazite to an analcime.

2.3.2. Internal and external modification of the zeolite structures [21–28]

Silane and diborane show a high reactivity towards zeolitic hydroxyl groups. Treatment of H-zeolites with silane results in a permanent change of their structural properties.

The reaction scheme can be divided into: *primary reaction*, involving accessible zeolitic OH-groups:

$$\equiv\text{Si–OH} + \text{SiH}_4 \rightarrow \equiv\text{Si–O–SiH}_3 + \text{H}_2 \qquad (1)$$

secondary reactions, in which chemisorbed groups may react further with other OH-groups in the zeolite:

$$\equiv\text{Si–O–SiH}_3 + \text{HO–Si}\equiv \rightarrow \equiv\text{Si–O–SiH}_2\text{–O–Si}\equiv + \text{H}_2 \qquad (2)$$

hydrolysis reaction, in which the chemisorbed groups ($-\text{SiH}_3$, $-\text{SiH}_2-$) can be hydrolysed with water to give $-\text{Si(OH)}_3$, $-\text{Si(OH)}_2$ groups:

$$\equiv\text{Si–O–SiH}_3 + 3\text{H}_2\text{O} \rightarrow \equiv\text{Si–O–Si(OH)}_3 + 3\text{H}_2 \qquad (3)$$

$$\equiv\text{Si–O–SiH}_2\text{–O–Si}\equiv + 2\text{H}_2\text{O} \rightarrow \equiv\text{Si–O–Si(OH)}_2\text{–O–Si}\equiv + 2\text{H}_2 \qquad (3')$$

Any combination of reactions (1), (2) and (3) or (3′) will give a ratio evolved H_2/consumed SiH_4 of 4.

Fig. 1 shows the influence of the silanation degree on the pore narrowing effect in mordenite tested by the adsorption of krypton and xenon at 273 K.

A similar behaviour was observed with a diborane modification. Diborane is also reactive towards surface hydroxyl groups, and because of its electron deficient character reactive towards the oxygen bridges $\equiv\text{Si–O–Si}\equiv$ in the zeolite structure, the primary and secondary reactions on H-zeolites can be summarized as:

$$2(\equiv\text{Si–OH}) + \text{B}_2\text{H}_6 \rightarrow 2(\equiv\text{Si–O–BH}_2) + 2\text{H}_2$$

Scheme 1

Because of the reactivity of the chemisorbed groups, a hydrolysis reaction can be carried out

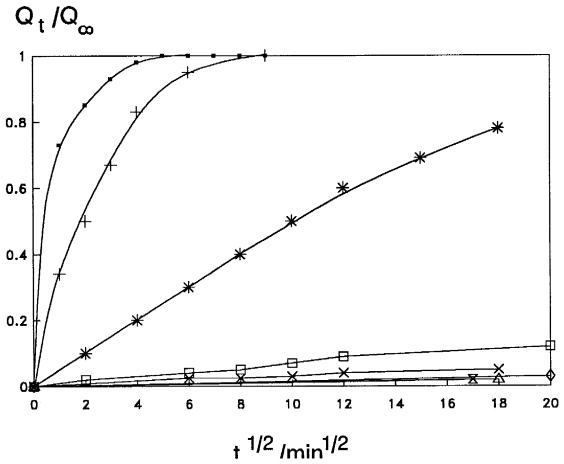


Fig. 1. Krypton and Xenon sorption at 273 K on mordenite LP: ■ Kr parent sample, + Xe parent sample, ∗ Kr silanated with 0.48 mmol SiH_4/g dry, □ Kr silanated with 1.01 mmol SiH_4/g dry, × Xe silanated with 0.48 mmol SiH_4/g dry, ◇ Kr silanated with 1.40 mmol SiH_4/g dry, △ Xe silanated with 1.01 mmol SiH_4/g dry, ⋈ Xe silanated with 1.40 mmol SiH_4/g dry.

not only with water, but also with other molecules such as CH_3OH:

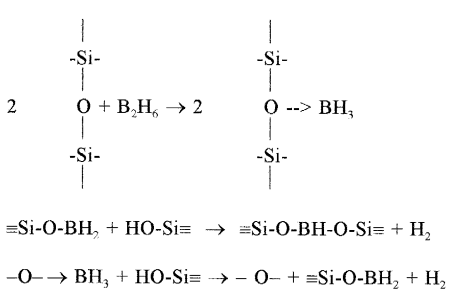
$$\equiv Si{-}O{-}BH_2 + 2H_2O \rightarrow \equiv Si{-}O{-}B(OH)_2 + 2H_2$$

$$\equiv Si{-}O{-}BH{-}O{-}Si\equiv + H_2O \rightarrow \equiv Si{-}O{-}B(OH){-}O{-}Si\equiv + H_2$$

$$\equiv Si{-}O{-}BH_2 + 2CH_3OH \rightarrow \equiv Si{-}O{-}B(OCH_3)_2 + 2H_2$$

Similar reactions can occur with the modifying agents X_nR_m where $x =$ Si, B, Ge and $R =$ H, Cl, etc.

Modification of zeolites, based on chemisorption of silane or diborane and subsequent hydrolysis of the chemisorbed hydride groups can also be applied for encapsulating gas molecules in zeolites. For example, krypton and xenon can be encapsulated in mordenite combining the modification process with a physical adsorption of the noble gases at moderate pressures and temperatures (e.g., 100 kPa, 300 K). The encapsulates are homogeneous and stable towards acids, mechanical grinding and γ-irradiation. By controlling the pore size reduction however, the thermal stability can be controlled. In Fig. 2, the thermal release of two Kr-encapsulates is compared. In one case (a) silanation was carried out at 273 and 393 K and a pressure of 40 kPa. A chemisorption of 1.4 mmol SiH_4/g was obtained. The other sample (b) was silanated with 1.56 mmol SiH_4/g at 373 K and a pressure of 300 kPa. The sample (b), containing more additional Si-groups, shows a higher thermal stability than the sample (a). It is thus possible to control the release rate of encapsulated gases by changing the degree of modification.



Scheme 1.

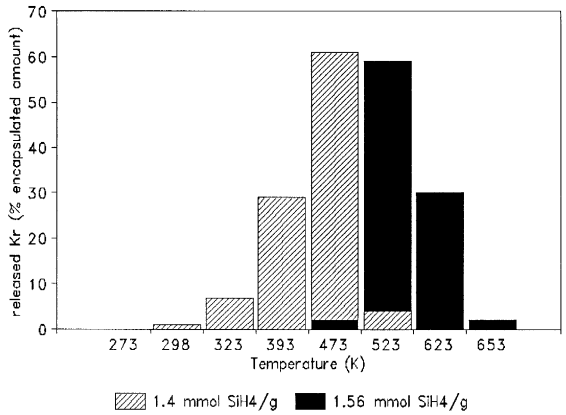
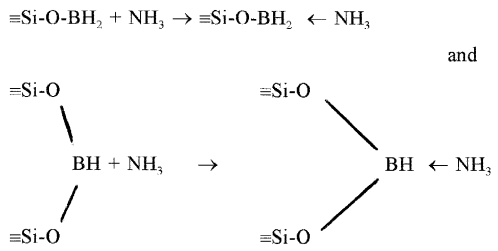


Fig. 2. Thermal release of Kr from two encapsulations, performed by silanation of mordenite.

Furthermore, the implantation of various boron–nitrogen compounds inside the zeolite framework can reduce, in a controlled way, the effective pore size of zeolites. When NH_3 is added to the boranated zeolite (before hydrolysis reaction), at room temperature, the formation of amine–boranes can be detected, which changes the molecular sieving properties of the zeolite (Scheme 2).



Scheme 2.

A gradual increase of the reaction temperature will accentuate the pore-blocking effect for the adsorption of Xe in mordenite LP. Depending on the reaction temperature polymeric amino–boranes $(H_2N \rightarrow BH_2)_n$ and borazines $(B_3N_3H_6)$ were observed in the zeolites.

2.3.3. External surface modification of the zeolite crystals [29,30]

In order to control the pore-opening size without affecting the internal pore system of the zeolite, modifications were carried out using modifying agents with a molecular size larger than that of the zeolite pores so that they can not enter the pores and interact only with the external surface. It has been shown that $Si(OCH_3)_4$ is deposited irreversibly on the H-zeolite. The alkoxide can be deposited by reaction with surface hydroxyl groups, thus covering the external surface of the zeolite crystal after subsequent reactions. Calcination with oxygen removes the hydrocarbon residue and produces silica-coated zeolites. The deposition of SiO_2 at the external surface of the zeolite reduces the size of the pore opening without changing the internal properties of the zeolite. Similar observations were found using methylchlorosilanes, as modifying agents, forming silica-polymers at the external surface of the zeolites. This modification method is very useful in the field of shape-selective catalytic reactions and sorption. Depending on the degree of the SiO_2 deposition at the zeolite crystals the adsorption behaviour can be influenced.

The most obvious approach to obtain controlled mesoporosity is the extension of zeolite-like three-dimensional framework structures to larger pore-sizes.

For a long time, however, these attempts failed to enlarge the pore size of zeolite-like solids. Zeolites X/Y maintained their position as the largest-pore materials in the class of zeolites. The change from aluminosilicate gels to alumino- and gallophosphate gels was the start in the synthesis of large-pore materials. The aluminophosphate VPI-5 and gallophoshate cloverite clearly demonstrated structures in the mesoporous range (13 and 30 Å-diameter cavities, respectively). The synthesis of ultra-large pore (ULP) molecular sieves, named MCM-41, announced a new group of materials characterized by pore diameters that can be adjusted between 18 and 200 Å.

Other important porous material in the region of micro- and mesoporosity for adsorption and separation purposes are the layered structures [31–40] [41–50] [51–60] [61–70] [71–76].

3. Clays

Clays are aluminosilicates with a two-dimensional or layered structure including the common sheet 2:1 alumino- and magnesium- silicates (montmorillonite, hectorite, micas, vermiculites) and 1:1 minerals (kaolinites, chlorites). These materials swell in water and polar solvents, up to the point where there remains no mutual interaction between the clay sheets. After dehydration below 120°C, the clay can be restored in its original state, however dehydration at higher temperatures causes the irreversible collapse of the structure in the sense that the clay platelets are electrostatically bonded by dehydrated cations and exhibit no adsorption.

4. Layered double hydroxides

Layered double hydroxides (LDH) are complex hydroxides of general formula

$M_n^{2+}M^{3+}(OH)_{2+2n}X$ where $n = 2–5$ and X is a charge balancing anion. The anions are located in the interlamellar space but do not fill it. The LDH may be considered as the inverse of the swelling smectite clays because the layers are positively charged, balanced by anions, whereas the clays have negative charged layers balanced by cations in the interlamellar region.

5. Layered phosphates

The general formula of layered phosphates is $M^{IV}(HPO_4)_2 \cdot H_2O$ and the layers consist of a central octahedrally coordinated metal layer sandwiched between tetrahedral phosphate layers. Zirconium and Titanium phosphates are intensively studied.

The major difference from the clays is the lack of swelling of this class of compounds.

6. Pillared interlayered compounds (PILC)

Pillared interlayered compounds have a virtually constant distance between the layers and therefore interlayer space. It is probably the most interesting group of new stable micro- and meso-porous materials available for adsorption and separation applications (Fig. 3). The great diversity of layered compounds and pillar combinations so far used in PILC synthesis were recently reviewed by Vaughan [31]. Pillared interlayered compounds are prepared by swelling the layered compounds in water or by amine intercalation and the exchanging of the interlayer cations or anions with a large polymeric inorganic cation or anion. After filtration, washing and drying, a calcination at about 500°C is required to cross-link the pillars with the layers (Fig. 4). The overall process is quite complicated and can be tuned according to the utilization of the material.

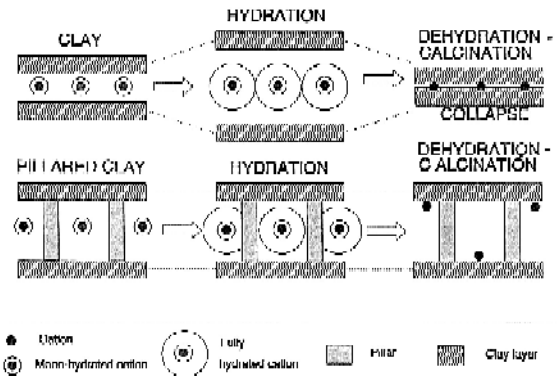


Fig. 3. Swelling effects in normal clay and dimensional stability in pillared clays.

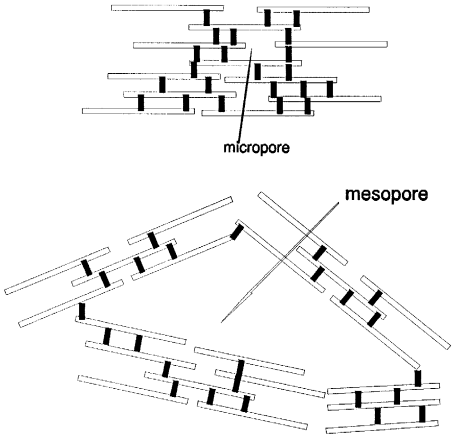


Fig. 4. Schematic representation of pores in pillared clays.

7. Supergallery pillared compounds

Of all known lamellar compounds, smectite clays are particularly well suited for forming pillared derivatives. In most of the pillared lamellar solids, the interlayer distance is comparable to the Van der Waals thickness of the host layers. The term ‘supergallery’ has been proposed to describe derivatives in which the interlayer distance is substantially larger than the thickness of the host layers. The host structures of interest include mainly smectite clays and layered double hydroxides. Recently, Imogolite, a tubular aluminosilicate, has been successfully intercalated as a regular monolayer into smectite [77].

Besides crystalline and semi-crystalline inor-

ganic porous materials, amorphous materials are also potentially important for adsorption.

Materials, having no ordered structure in the X-ray analysis sense, can reflect an important well-controlled and high microporosity. The pore structure in these materials can be controlled by the manufacturing process, reflecting a large pore size distribution, however a poor size selectivity is obtained.

8. Silica gel

Silica gel is one of the synthetic amorphous silicas with a rigid, continuous network of spherical particles of colloidal silica [78]. The two typical types of silica gel are known as regular-density and low-density silica gels, although they have the same densities. The regular-density gel has a surface area of 750–850 m^2/g and an average pore diameter of 22–26 Å, whereas the respective values for the low-density gels are 300–400 m^2/g and 100–150 Å.

9. Alumina-activated alumina

Various forms of alumina (activated alumina) can be prepared (α-, β-, γ-, η- alumina), depending on the manufacturing procedure, with interesting hydrophillic properties and large surface area. Besides an important micropore volume, a considerable number of pores with sizes greater than 50 Å can be found.

Alumina, along with activated alumina, is a desirable sorbent for drying because of its high affinity for water.

10. Gels and colloids

These materials can be divided into different groups [79], after having similar initial preparation techniques, but different post treatments:

- Randomly crosslinked inorganic polymers.
- Packed amorphous colloidal spheres.
- Crystalline colloidal particles.
- Mixed crosslinked colloid-gel agglomerates.

The synthesis and use of gels, mainly based on silica, essentially inorganic randomly crosslinked polymers, is well established [16]. Furthermore a tailoring of such materials with a specific narrow pore size distribution between 30 and 200 Å is possible. Also a wide range of multi-metallic oxide gels can be made with controlled final properties in terms of composition, pore volume, pore size distribution. The wide range of silica–metal oxide materials have been reviewed by Tanabe [80].

11. Composite materials

Many of these materials are recently reviewed [81,82] and these porous materials include

- Mixed crystal forms, -shape, structure, composition.
- Spindal and semi-crystalline glasses.
- Chemically modified glasses (Vycors).
- Differentially calcined and reacted clays.
- Organic bound matrices.

Mixing and packing crystalline materials of different sizes, shapes and composition facilitates the control of the volume and size range of the intercrystal or interparticle voids for controlling the meso- and macro-porosity. The void volume can be further manipulated by differentially melting or reacting one or more components in the composite. A series of controlled pore ‘Vycor’ glass with a narrow pore distribution in the range from 100 to 1000 Å can be obtained by leaching boron from the silica matrix.

An alternate approach to leaching is burning. In these cases, the inorganic matrix is mixed with an organic polymer which is burned out by heating in the air or oxygen. The porosity is determined by the concentration, molecular weight, or size and shape of the organic additive.

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