

NanoZeolites – porous nanomaterials for CleanTech, Encapsulation and Triggered-release Applications

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ABSTRACT

Zeolites are well known porous materials established in applications which employ their large surface area, controllable porosity and tuneable surface chemistry. Through a reduction in their particle size by an order of magnitude, significant increases in product performance have been achieved and, more notably, new applications have been accessed which until now were unsuitable for classical zeolite materials.

Keywords: zeolites, porous, encapsulation, triggered release

1 INTRODUCTION

Zeolites were first discovered at the end of the 18th century and came to prominence in the 1960's when synthetically produced zeolites were employed in large industrial applications as molecular sieves for filtration and purification purposes, and as catalysts in the cracking of crude oil. However, recent advances in hydrothermal synthesis techniques [1] and procedures to modify the surfaces of the crystalline particles [2] have led to the development of a new form of these materials – the NanoZeolites, with particle size in the lower sub-micron range (e.g. NanoZeolite-FAU, see Fig.1).

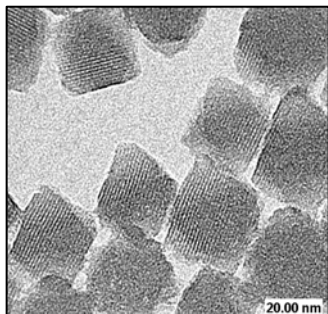


Figure 1: TEM micrograph of crystalline NanoZeolite Faujasite (mean particle size ca. 50nm)

These porous, nanocrystalline materials have breathed new life into an established material class and possess significantly improved properties (such as higher specific surface area), leading to performance enhancement in many known applications.

Furthermore, the availability of nanoscale zeolites has opened up new applications, which were until now unserviceable with microcrystalline particles.

2 NANOZEOLITES

Advancements in synthesis and purification techniques have taken the mean particle size of zeolites down from the few microns range to around 100 nm (an order of magnitude). Furthermore, narrower particle size distributions can be achieved in comparison with classical microcrystalline zeolites which are currently commercially available (see Figure 2). This not only means a more homogeneous material and an increase in the surface area (per gram of particles), but also increases the kinetics of adsorption/desorption processes.

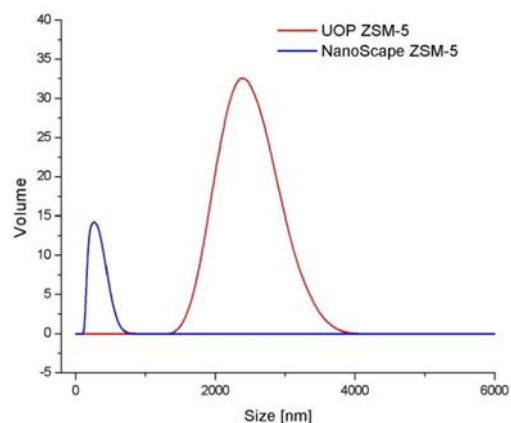


Figure 2: Comparison of particle size distribution of NanoZeolite MFI with a commercial microcrystalline MFI zeolite

This property can be put to good use in the form of thin film adsorber coatings in industrial dehumidification and/or energy recovery systems [3]. The use of nanoscale zeolites means: a reduction in weight (less adsorber material required to coat surfaces effectively); smaller cross-sections (due to thinner films) and thereby lower air stream resistance; enhanced adsorption/desorption kinetics; and a higher overall efficiency of the complete system (through savings in energy). The use of an LTA zeolite structure (with pore diameter 3-5 Å) furthermore imposes a high selectivity towards moisture adsorption, and reduces risk of bacterial contamination. Operational lifetime of the systems is also lengthened due to the better adhesion of the nanoparticles onto the substrate (typically aluminium foil or stainless steel).

3. OPEN-PORE APPLICATIONS

NanoZeolites lend themselves to applications in which the porous material is applied either as a thin-film coating or as an additive dispersed within a matrix. The so-called “open pore” applications include using the zeolite as a filter, adsorber or catalyst. A combination of the pore size and pore-surface chemistry can be employed to effectively and selectively filter out, adsorb, desorb or catalytically convert gas or liquid phase molecules. When coated onto the surfaces of various substrates (aluminium, steel, ceramic, carbon fibres), NanoZeolite thin films have significantly contributed to improving the performance of air purification filters and exhaust-gas catalysts. On fibre mats, these nanoparticle coatings have increased the active surface area without causing a significant loss in porosity (which would reduce airflow rate). For water purification applications NanoZeolites have proven suitable for both polymer and ceramic membranes. In the former case, the inorganic material is used as an additive to an organic polymer matrix; whereas for ceramic membranes a coating is employed, which modifies the effective pore size of the ceramic material.

4. ENCAPSULATION

NanoZeolites can also be employed as hosts for functional molecules such as dyes or catalysts (see Fig. 3). Through a suitable encapsulation process (e.g. impregnation, grafting etc.), the guest molecules are brought into the pore structure of the NanoZeolite and, depending on the size of molecule (in relation to pore dimensions) and the pore wall – guest molecule interactions, reside either in the pore channels or the central cavities of the unit cell. These encapsulated guest molecules exhibit more stability than when solvated and an increased resistance to chemical, mechanical and thermal influences. Furthermore, through encapsulation the application range of the functional molecule can be extended, e.g. organic dyes dispersed in aqueous systems; photochromic dyes in

polymers with high flexural modulus. Through this technique the use of (and reliance upon) organic solvents can be reduced, and the lifetime of certain molecules significantly prolonged.

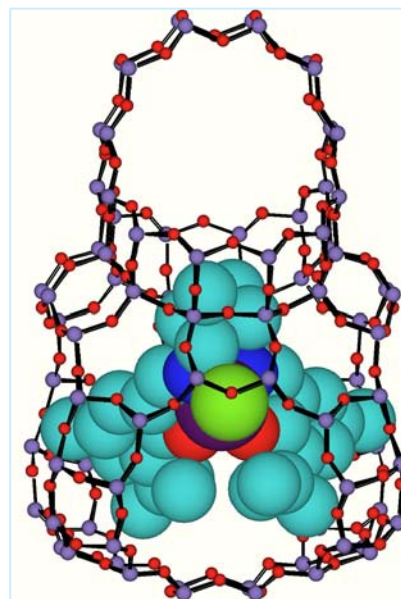
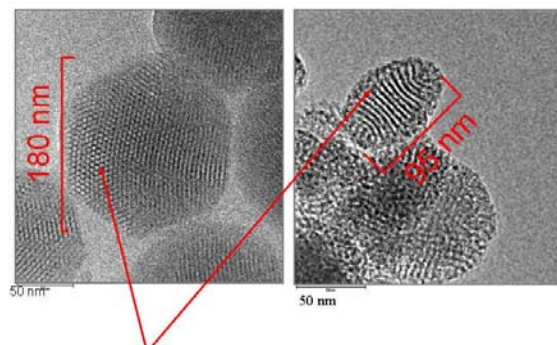


Figure 3: Functional molecule encapsulated within the pore structure of a NanoZeolite host

For certain applications (e.g. catalysts, sensors) it is not the encapsulation, protection or transport of the molecule that is of importance, but its release into a surrounding medium. A slow release can be achieved through careful selection of parameters such as: the strength of host-guest interaction (physical/chemical); and the steric confinements imposed upon the guest through encapsulation. For larger, bulkier molecules a nanoscale mesoporous host is often more appropriate, with pore diameters reaching up to 100Å (see Fig. 4).



Pores with diameter ca. 50-100 Å available for loading with functional molecules

Figure 4: TEM micrographs of nanometre sized mesoporous materials

A controlled or triggered release can be achieved through use of any external stimulus (“trigger”). This can be temperature, pressure or a burst of radiation (e.g. UV light).

Thermal triggers typically focus on the increased vibrations which occur within the zeolite framework when heat is applied. The oscillations of the cage structure can cause a pore mouth to expand to a size large enough to allow the guest molecule to exit the pores. A change in pressure can also force a molecule out through a pore opening, though more commonly the effect is that of varying the equilibrium adsorption state of weakly bound molecules. Attachment of guest molecules to the pore channel walls through special linkers, or the fitting of “flaps” over the pore mouth openings, allows the use of UV light as a trigger. There is scope here not only to control the speed of release but also the wavelength range over which the trigger activates. This leads to a highly sensitive and extremely controllable release mechanism.

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