

GROWTH OF ZEOLITES FIRMLY ATTACHED TO METAL SURFACES FOR USE IN CATALYSIS

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ABSTRACT

Synthesis of clusters of acicular MFI zeolites from porous silica layers strongly attached to stainless steel surfaces is reported. The porous silica layers are prepared by pyrolysis of silicone rubber layers applied from solutions in ethylacetate or dimethylether. The surface area of the silica is about 100 m²/g of silica, the pore volume about 0.13 ml/g of silica. XPS spectra indicate the metal to be completely covered by the silica. The template solution is impregnated into the pore volume of the silica layer, after which the coated steel plate is treated hydrothermally for at least 18 hours at 170°C in a solution of silica in ammoniumhydroxide.

The resulting MFI crystallites have been deposited on the surface of the stainless steel as clusters of about 1.5 µm consisting of small acicular crystallites. The density of clusters depends on the thickness of the initial silica layer. The X-ray pattern is that of MFI and indicates some preferred orientation. The clusters are strongly adhering to the metal surface provided that grease and oxide layer have been completely removed by rinsing and polishing.

The open structure of the clusters of zeolite crystallites leads to a large external surface area facilitating transport into the pore structure of the zeolites.

INTRODUCTION

The relatively narrow pores of small zeolite crystallites call for utilization of small bodies to minimize transport limitations during catalytic reactions. Although zeolites can be synthesized in some cases as very small (less than 1 µm) crystallites, application of these small bodies in fixed catalyst beds leads to a high pressure drop. With liquid-phase reactions utilizing suspended catalyst bodies separation of the catalyst from the liquid is usually performed by filtration or centrifuging. Effective separation asks for bodies of at least about 3 µm. Since the size of zeolite crystallites is too small, binders, such as amorphous silica-alumina, are generally utilized to produce bodies of some mm's for fixed beds, between 50 and 150 µm for fluidized beds, and 3 to 50 µm for suspended catalyst applications. However, transport limitations cannot be avoided when bodies this large are involved, especially when bodies larger than about 10 µm are used.

Transport limitations with zeolites can be significantly alleviated when small zeolite crystallites are anchored to solid surfaces. Jansen et al. [1] have deposited zeolite crystallites on solid surfaces. During the zeolite synthesis most of the crystallites are deposited on the surface by sedimentation. The procedure can therefore only be applied on surfaces oriented horizontally.

We investigated the growth of layers of zeolites with an adjustable thickness strongly adhering to a solid surface. We started from a silica layer, prepared by pyrolysis of a silicone rubber layer [Geus 2,3], which was firmly attached to a metallic surface. A solution of silicone rubber in an organic solvent, such as ethylacetate, was applied onto the surface to be covered. After drying, the silicone rubber layer, which is strongly adhering to the surface, is pyrolyzed in air at a temperature of about 450°C. The surface area of the obtained silica is of the order of 100 m² per g of silica. It is important to note that the template is impregnated into the pore volume of the silica layer. Subsequently the thus covered surface is brought into an alkaline synthesis solution and kept at elevated temperatures under autogenous pressure.

The thus formed zeolite monolayer is grown from the porous silica layer, which is very strongly adhering to the metal surface. The advantage of this result is the easy separation and no contamination of the products with traces of catalyst.

The zeolite layers can be applied, for instance, on the surface of Sulzer packings, on the blades of stirrers and baffles and on the walls of monoliths. Since a agreeable flow can be established along the surfaces covered with zeolite crystallites, both external and internal transport limitations can be avoided. It can be expected that application on a solid surface can suppress deactivation of zeolite catalysts, resulting in higher selectivities.

The aim of this research is the impregnation of porous amorphous silica layers applied onto metal surfaces with an appropriate template and to nucleate and grow zeolite crystallites from the porous silica layer. In this research we will concentrate on the growth of MFI.

EXPERIMENTAL

A stainless steel 304 disk is polished to remove surface pollution and oxide layers. Subsequently a thin film of silicone rubber dissolved in ethylacetate (5 wt.%) is spin-

coated onto the clean metal surface. After drying, the remaining silicone rubber film is pyrolyzed in air at 450°C for 30 minutes. The resulting porous silica layer is impregnated with tetrapropylammoniumbromide (TPABr) dissolved in water or in ethanol after which the impregnated film was aged for 30 minutes. An alkaline solution of SiO₂ (Aerosil 200), TPABr, and ammoniumhydroxide is prepared [4,5,6,7]. The molecular composition of the solution is SiO₂ : TPABr : NH₄OH : H₂O = 10:1:7:100.

The solution and the impregnated disk are placed in a PTFE-lined steel vessel. The disk is supported by a teflon aid for vertical positioning. The vessel is placed in a furnace, heated to 170°C and kept at this temperature for varying periods of time with or without rotating the vessel at 10 rotations per minute. After the synthesis quenching is effected by placing the vessel into cold water.

To remove the remaining solution and unreacted amorphous silica the covered disks were treated ultrasonically. The zeolite crystals are examined by XRD (Nonius Enraf) with Co K_α radiation and SEM. A Philips XL30 FEG SEM (equipped with a field-emission tip) operated at 10 kV is used. The mechanical strength of the layers is tested by scratching with rods.

RESULTS AND DISCUSSION

The thickness of the porous silica layer is adjustable by changing the concentration of silicone rubber in the solution which is spin-coated or by consecutively depositing several layers onto the surface. The attachment of the porous layer is tested by scratching the silica layer with rods of different material having a conical end of about 0.1 mm. Only with a metal rod the layer is affected, whereas wooden or PVC rods have no effect. To obtain strongly adhering silica layers it is important that the metal surface has been completely freed from grease and thick oxide layers.

XPS measurements with a Vacuum Generators instrument show that the surface is completely covered with SiO₂. The spectra did not contain traces of iron, chromium or nickel. Elemental analysis in the SEM using X-ray photons indicated besides silicon, the presence of chromium, iron and nickel, as can be expected for stainless steel. The surface area and the porous structure of the pyrolyzed silicone rubber is determined

Figure 1



Figure 2

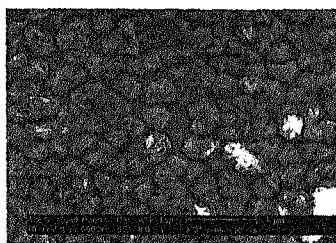


Figure 3

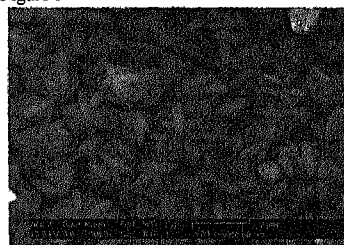


Figure 1: Layer of zeolites grown from a relatively thin silica layer. Clusters of small acicular zeolite crystallites.

Figure 2: Layer of zeolites grown from a relatively thin silica layer. Lower magnification of same specimen as represented in Figure 1.

Figure 3: Layer of zeolites grown from a thicker silica layer. Higher density of clusters of small acicular zeolite crystallites.

from a sample removed from the metal surface by measuring the extent of nitrogen adsorption as a function of pressure. The BET surface area is 100 m^2 per g of silica. The total pore volume is 0.13 ml per g of silica and the micropore volume 0.09 ml per g of silica. Impregnation of the porous silica layer with TPABr is performed with a 20% solution of the salt in water or in ethanol (96%). There was no difference in the final result using these solvents. After synthesis for 18 hours at 170°C zeolite crystallites strongly adhering to the surface of the stainless steel have formed. Increasing the synthesis time to 48 and 96 hours does not change the appearance of the zeolite crystallites. The zeolites are present as acicular crystallites assembled in clusters of about $1.5 \mu\text{m}$ on the surface of the stainless steel, as can be seen in Figure 1. In this figure the result obtained with a thin silica layer is represented. The structure of the metal surface, especially the profile arising from the polishing treatment, can be distinguished underneath the zeolite crystallites. A micrograph at a lower magnification is shown in Figure 2. It is evident that a fairly open structure exposing an extended external surface area has been achieved. With thicker initial silica layers the metal surface is completely covered with a monolayer of small clusters of zeolite crystallites.

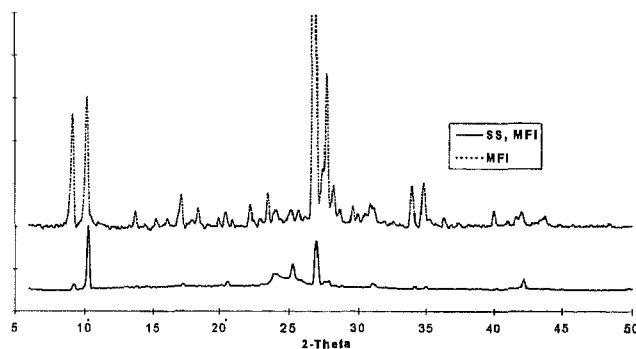


Figure 4: XRD pattern of MFI (dotted) and MFI grown on a metal disk (line).

Some larger crystallites ($3 \times 10 \mu\text{m}$) have been deposited on top of the layer of small clusters. Figure 3 represents a micrograph of a thicker initial silica layer. The density of the cluster of zeolite crystallites is higher. The above mentioned scratching procedure indicates the same adherence of the zeolite crystallites and the initial silica layer. A good adherence is also evident from the fact that the ultrasonic treatment does not affect the zeolite clusters.

The X-ray diffraction pattern of the zeolite layer corresponds to that of MFI. The intensity of the diffraction maxima indicates some preferred orientation (Figure 4). Relative to the bulk MFI pattern, some reflections are strongly enhanced. The reflections at 10.3, 20.6 and 31.3 degrees 2 theta correspond with hkl respectively 020, 040 and 060. It is clear that the b-axis is perpendicular to the metal surface. So the straight pores are facing the surface.

CONCLUSIONS

Clusters of zeolite crystallites strongly adhering to stainless steel surfaces can be produced starting from a porous silica layer prepared by pyrolysis of silicone rubber. The thickness of the initial silica layer determines the density of the resulting clusters of zeolite crystallites. The large external surface area of the clusters of zeolite crystallites

results in a rapid mass transport into the pore system of the zeolites. Application of the zeolite crystallites to a metal surface enables one to achieve a fast transport from the bulk of a liquid phase to the external surface of the zeolite crystallites. With gas phase reactions application of a layer of zeolites on special metal structures, such as metallic monoliths, can also offer excellent transport properties.

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