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ChemComm
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Preparation of highly accessible mordenite coatings on ceramic monoliths at loadings exceeding 50% by weight

M. A. Ulla,[b] E. Miro,[b] R. Mallada,[a] J. Coronas[a] and J. Santamaría*[a]
[a] Department of Chemical Engineering, University of Zaragoza, 50.009 Zaragoza, Spain.
E-mail: iqcatal@unizar.es; Fax: 34 976 762142; Tel: 34 976 761153
[b] INCAPE (FIQ,UNL-CONICET), Santiago del Estero 2829, 3000 Santa Fe, Argentina

Received (in Cambridge, UK) 1st December 2003, Accepted 22nd December 2003
First published as an Advance Article on the web 29th January 2004

A mordenite layer with a high accessibility has been synthesised on cordierite monolith supports; substantial loadings of mordenite were achieved (above 50 wt%) under the synthesis conditions used.

Ceramic and metallic monoliths have been used as catalytic supports for a wide variety of gas-phase reactions such as catalysis in automotive applications, ozone abatement in aircrafts, selective reduction of NO_x and catalytic combustion. Cordierite is often the material of choice for ceramic monoliths, being a thermally resistant material, amenable to deposition of a catalytic support layer such as silica or alumina. As Heck *et al.*[1] noted in their review, the usual coating techniques such as dip-coating, slip-coating and spin-coating yield catalyst loadings that are considerably lower than those attainable in a fixed bed for a given reactor volume. This leads to larger volumes in monolith-based catalytic reactors, and has spurred a strong interest in the development of methods to attain higher catalyst loadings.

A possible alternative to solve this problem would be the deposition of the active phase directly on the support (*i.e.*, without a previous washcoat, and ideally also without binders). Zeolites are excellent candidates for this approach in view of their catalytic properties and of the considerable experience gathered in recent years concerning the synthesis of zeolite films on different substrates.[2] A number of recent works,[3,4] have addressed the preparation of zeolite coatings on ceramic monoliths and foams. These investigations face two main problems: on the one hand, in spite of a recent report[3] where MFI zeolite loadings up to 30% by weight were attained, high zeolite loadings are difficult to achieve, even with repeated hydrothermal synthesis processes. In fact, most investigations in the literature report zeolite loads between 5 and 20% by weight. On the other hand, increasing the zeolite load on a support normally involves synthesis of a thick zeolite layer where crystals are highly intergrown. Diffusion rates of reactants into and of products out of this zeolite layer could be strongly lowered, therefore decreasing the accessibility, and the degree of utilisation of the catalyst.

In this work, the synthesis of mordenite coatings at high loadings and with a good accessibility on monolith supports has been attempted using a seeded synthesis method. The objective was to obtain a layer of closely packed individual crystals, in such a way that easy accessibility to each crystal could be preserved.

The zeolite layers were prepared in several steps. First, the Cordierite monolith supports (Corning™, 400 cells per square inch, 0.1 mm average wall thickness) were cleaned by immersion in deionized water for 20 min in an ultrasound bath, then subjected to seeding using a 30 s dip-coating treatment by immersion in a 20 g l^{-1} suspension of mordenite seeds (Tosoh™ Co., Si/Al ratio = 5, 1 μm particle size). After drying at 298 K the seeding procedure was repeated twice, then the seeded support was subjected to hydrothermal synthesis to promote the growth of the mordenite seeds. The weight gain during the seeding step was < 0.15 wt%, referred to the monolith weight. Synthesis was conducted at 175 °C, for either 14 or 24 h, using a gel with the following molar composition: $H_2O:SiO_2:Na_2O:Al_2O_3 = 80:1:0.38:0.025$. Ludox™ AS40 and sodium aluminate were used as the silica and alumina sources, respectively. After synthesis, the mordenite-coated monoliths were rinsed in distilled water and immersed in an ultrasound bath for 20 min to remove any loosely adhering material.

DOI: 10.1039/b315386j

The accessibility of the zeolite material grown on the monolith using the procedure given in this work was compared with other possibilities, namely, a 15-micron thick mordenite membrane supported on porous alumina, and mordenite powder. Kinetic adsorption experiments were carried out in a thermobalance (CI Electronics) using water as the adsorbate. To this end, a known amount of mordenite material was calcined to remove any adsorbed compounds, then cooled to room temperature and exposed to a N_2/water vapour mixture at 50% relative humidity, while the weight change was continuously monitored.

Table 1 gives information concerning the synthesis conditions used on different samples and the results obtained regarding mordenite loading on the support and the synthesis selectivity, defined as the ratio between the amount of mordenite deposited on the substrate and the total amount of mordenite produced (the remainder appears as crystals collected at the bottom of the autoclave).

XRD analysis (not shown) indicated that well-crystallised, pure mordenite was the only zeolite phase present in measurable quantities both on the monolith surface and on the crystals collected after synthesis at the bottom of the autoclave. Crystal growth occurred preferentially along the [001] axis. The data in Table 1 indicate that the main factor controlling the synthesis selectivity is the ratio of the volume of synthesis solution to mass of substrate used (V_{sol}/M_{subs}), rather than the duration of synthesis. The selectivity is highest (82%) at the lowest value of V_{sol}/M_{subs}. For a given synthesis time, as V_{sol}/M_{subs} increases, the weight gain of mordenite on the support increases although the synthesis selectivity decreases. This indicates that some nucleation in the bulk of the solution takes place, and therefore the proportion of crystals formed in the bulk increases with the synthesis volume. Table 1 also shows that under the conditions used in this work it is possible to attain high zeolite loadings (up to 53% by weight), at a reasonable selectivity level (65%), in a single 24 h synthesis process.

Fig. 1 shows scanning electron microscopy (SEM) views of mordenite coatings on cordierite monoliths. The top micrograph is a cross-section of the monolith, at the boundary shared by four monolith channels. The thickness of the mordenite coating is variable, in part owing to the roughness of the monolith support. In

Table 1 Synthesis conditions, weight gain and synthesis selectivity for different mordenite-coated supports

Sample no.	Synthesis time/h	$(V_{sol}/M_{subs})^a$/ $cm^3\ g^{-1}$	$M_{MOR}/M_{subs}{}^b$	Weight gain (%)	Synthesis selectivity (%)
1	24	19.8	0.573	47	82
2	24	28.1	0.657	48	73
3	24	31.5	0.800	52	65
4	24	34.3	0.815	53	65
5	14	22.4	0.513	38	74
6	14	30.5	0.600	39	65

[a] Ratio of volume of synthesis solution to mass of substrate. [b] Ratio of total mass of mordenite produced to mass of substrate.

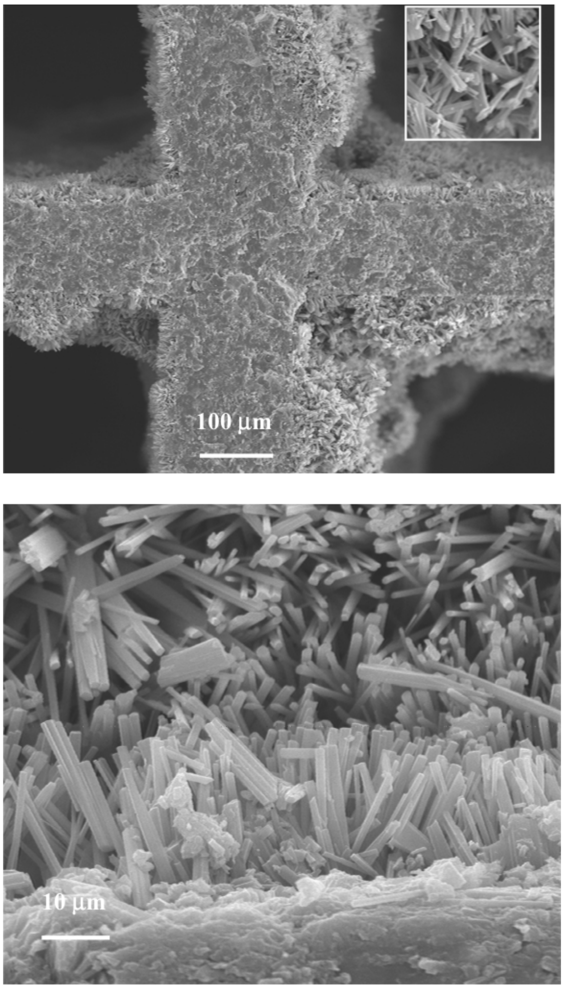

Fig. 1 Different views of mordenite crystals on cordierite monoliths. Top: general view of a monolith cross section. Bottom: A closer view of crystals grown at the junction of horizontal and vertical monolith walls.

most cases, the thickness was between 40 and 100 microns, although thicknesses exceeding 130 microns were not uncommon. It can also be seen that at a first level, the crystals grow from the mordenite seeds mainly in a direction that is roughly perpendicular to the support surface, until a height of 15–30 microns is reached. On top of this first layer, there is less ordered material, and clusters of mordenite crystals can be observed, consisting of crystals that grow in all directions (see inset in top micrograph). These are probably formed from crystals that first nucleate in the bulk and then precipitate on top of the first level of mordenite coating, where they continue to grow. Interestingly, there is little intergrowth of the crystals inside the clusters, and crystal individuality is maintained, with ample space between crystals, as illustrated in the inset of the top micrograph. The bottom micrograph shows crystals grown on two perpendicular monolith walls. The crystals growing on both walls are clearly separated from each other, to the point that individual crystals can be easily differentiated. It can again be concluded that crystal individuality is largely preserved.

Table 2 Evolution of water uptake (expressed as percentage of saturation level) during adsorption kinetic experiments

Time/s	Powder	Membrane	Monolith
3704	44.5	87.4	92.3
4473	54.5	88.6	96.7
6680	77.2	91.2	99.2
8747	89	93.3	99.6
10672	94.9	95.2	99.9

Preserving the individuality of crystals is important because of accessibility reasons. A high catalyst loading may obviously be obtained with a layer of intergrown mordenite crystals having a thickness of tens of microns. However, this would present a considerable transport resistance to molecules from the fluid phase. In contrast, in the mordenite coatings developed above, the reactants can easily reach the voids between crystals, then diffuse across the 2 micron thick crystals utilising the 0.48 × 0.34 nm channels in the [010] direction. In this way, the maximum diffusion path inside the zeolite would be around one micron on average for the mordenite coated monoliths in this work.

The better accessibility of the mordenite material on the monolith was proven in kinetic diffusion experiments where water adsorption was continuously monitored (Table 2). While initially water uptake was very rapid in the three systems studied, as water adsorption progressed the differences became more evident. The higher accessibility corresponded to the mordenite crystals on the monolith, followed by the mordenite membrane, and finally by the powder (3 micron in size, 86 mg of mordenite powder supported as a bed on a nonporous plate), which showed the highest diffusion resistance.

Financial support from Spain (MCYT) is gratefully acknowledged.

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