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Zeolite washcoating onto cordierite honeycomb reactors for environmental applications

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Abstract

The preparation conditions to obtain zeolite washcoats with optimum loading and homogeneous distribution are studied for mordenite, ferrierite and ZSM5. The slurry concentration and the number of immersions were combined to obtain different coating thickness and geometry. The solid concentration increases the viscosity of the slurry resulting in an exponential growth of the zeolite loading. In order to obtain more homogeneous washcoatings it is preferable to use diluted suspensions and perform more than one immersion. It was found that the washcoating adherence increases with the decrease in the size of the aggregates deposited on the monolith. This improves the packaging and interaction between particles and facilitates a convenient filling of the surface cordierite macropores, producing a more effective anchorage. In this vein, the order of washcoat stability tested with an ultrasound method is ZSM5 > mordenite > ferrierite. The addition of SiO_2 as a binder improves the adherence of the three zeolites under study probably due to an improvement in the interparticle cohesion. The performance of an In-ZSM5 washcoated monolith was tested for the selective reduction of NO_x with methane under oxygen excess. It was observed that the activity of the monolithic catalyst was as good as those for the In-ZSM5 powder, which indicates that there are no diffusive restrictions due to coating thickness.

Keywords: Zeolite washcoating; Cordierite honeycombs; Adherence; SCR of NO_x with CH_4

1. Introduction

Zeolites are among the most promising materials for the abatement of atmospheric pollutants, e.g. the oxidation of volatile organic compounds and the selective reduction of NO_x. Numerous studies have been performed in microreactors using powder catalysts [1–4]. Nevertheless, for practical environmental applications, these catalysts should be shaped as honeycomb monoliths. Low pressure drop and good tolerance to plugging by dust are essential requisites that lead to the use of catalytic monoliths [5–7]. However, the conventional procedures for preparing catalysts cannot be simply applied to monolithic catalysts. Different procedures can be performed from coating the monolith walls with a support material like alumina or silica, followed by the impregnation of the active phase to the coating of a ready-made catalyst [8].

Zeolite monoliths can be obtained under the form of extrudates [9] in which the catalytically active material is used to manufacture the monolith, although this presents problems regarding the mechanical stability of the final product. Another possibility consists in the deposition of the zeolite as a coating onto a ceramic honeycomb substrate. The most widely used material for monolithic structures is cordierite (a ceramic material consisting of magnesia, silica and alumina in the ratio of 2:3:2) because of its high mechanical strength and its low thermal expansion coefficient [10]. The macropores of the cordierite structure allow the anchoring of the zeolite layer.

There are two ways for coating the zeolite: hydrothermal synthesis (direct synthesis, seeded growth or vapor phase

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synthesis) [11,12] and the deposition from a slurry of zeolite particles followed by a stabilizing thermal treatment. The first method has the advantage of a stronger adhesion of the coating to the support. The main disadvantages of this method, however, are that it is considerably more complex than slurry-coating and that a dense layer can be formed with small intercrystalline pores in which diffusion limitations can occur.

The coating from a slurry, commonly called ‘washcoating’, is usually carried out with a slurry of particles of a comparable size to that of the macropores of the support [8]. The main advantage of this method are a shorter diffusion distance to the active catalyst species for the reactants flowing through the channels and the fact that ready-made catalysts can be directly deposited from the slurry. The preparation of the finished catalysts always involves dipping the monolith into the slurry, blowing air to remove the excess liquid, drying, and calcination. The last step is very important since the calcination binds the washcoat to the monolith walls, and is usually done at temperatures of 550 °C or higher [13]. Besides, a binder can be used in order to improve the binding strength. However, for the washcoating of powder with small particle size, which is the case of zeolite, it has been reported that the use of a binder is not essential [14].

This work focuses on the preparation and characterization of different zeolites (ZSM5, mordenite, ferrierite) washcoated onto a cordierite honeycomb monolith. The method of deposition from a slurry was chosen because of its simplicity and versatility. Silica as a binder was used in some preparations. The said zeolites were selected in view of their activity for the SCR of NO_x reaction when exchanged with cations like Co, Cu, In. Zeolite powders and washcoated monoliths were characterized by scanning electron microscopy (SEM), optical microscopy, mercury intrusion porosimetry (MIP) and laser particle size analysis. The adhesion of the washcoat was evaluated using an ultrasonic technique [14,15]. The main goal of this study was to find out a good preparation route to obtain a mechanically stable washcoated cordierite monolith with catalytic activity at least as good as the powder catalyst. For this purpose, different washcoating strategies are analyzed. Finally, an In/H-ZSM5 monolithic catalyst was prepared and tested for the selective catalytic reduction of NO_x with methane.

2. Experimental

2.1. Preparation of washcoated monolithic catalysts

Cordierite honeycomb monoliths (Corning, 400 cps, 0.17 mm average wall thickness) were used as substrates. The apparent monolith density and its geometric surface were 0.42 g/cm^3 and 27.4 cm^2/cm^3, respectively. The monoliths were washcoated with aqueous suspensions of 25, 30, 35 and 40 wt.% of different zeolites (NH_4-ZSM5 with Si/Al = 15; NH_4-mordenite with Si/Al = 10 and K-ferrierite with Si/Al = 6.5) all of them obtained from Zeolyst. The basic characteristics of these zeolites are summarized in Table 1. Portions of monoliths containing 64 channels were used in these preparations, their dimensions being 1 cm × 1 cm of section and 2 cm long. The outer faces were covered so that the depositions were performed only inside the channels. After each immersion, the suspension excess was blown in a reproducible form, and the zeolite-coated monoliths were dried in a stove at 120 °C and finally calcined at 550 °C for 4 h. One to three immersions of the monolith were performed, so that 12 preparations were obtained with different zeolite loadings.

Table 1
Characteristics of the zeolite particles used in this work

Zeolite	Si/Al	*D* mean[a]	*d* 0.5[a]	*d* 0.9[a]	Mean crystal size[b]
ZSM5	15	5.3	3.9	8.7	0.2
Mordenite	10	5.5	2.6	13	0.5
Ferrierite	6.5	63.7	62.5	115.3	1

D mean (μm): average diameter of spherical equivalent volume of aggregates; *d* 0.5 (μm): 50% of the aggregates have a volume lower than the corresponding to *d* 0.5; *d* 0.9 (μm): 90% of the aggregates have a volume lower than the corresponding to *d* 0.9.

[a] Measured with laser diffraction analysis.

[b] Measured with SEM.

2.2. Morphology observations

A metallurgical microscope Nikon Optiphot (50–400×) with halogen lamps was used to perform optical observations of the samples. The microscope has a photo-micrograpic attachment Microflex AFX-DX with a dark box FX-35 DX. Samples of monoliths were transversally cut with a CSi disc and carefully polished in order to measure the characteristic dimensions of coatings. Additionally, a stereomicroscope Leica Stereozoom 2000 was used in order to perform inspections of zeolite coatings quality and for the determination of washcoat erosion after mechanical stability tests.

The samples morphology was also examined with a scanning electron microscope (SEM) Jeol JSM-35C operated at accelerating voltages of 20–25 kV. The samples were glued to the sample holder with silver paint and covered with a thin gold layer to improve the images.

2.3. Particle size and pore size distributions

Particle size distribution of some powder samples was determined with laser particle size analysis (LPSA) through a Malvern Mastersizer X equipped with a sample suspension unit. Typically, suspension concentrations between ca. 0.004 and 0.02 wt.% were used, with obscurations between 15 and 35%. Pore size distributions of the monolith samples were measured by mercury intrusion porosimetry (MIP) using an Autopore II 9220 V1.04 unit.

2.4. Washcoating adherence

The adherence of zeolite coatings was evaluated using a method described in the patent literature [15], which consists in the measurement of weight loss caused by exposing the sample to ultrasound. This method was recently applied by Valentini et al. [16] for alumina layers on ceramic and metallic supports and Moulijn et al. [17] for checking adherence of in situ zeolite growth on monoliths.

In this work, the coated monoliths were subjected to ultrasound by immersing them in acetone inside a glass vessel and then in an ultrasonic bath (Cole Parmer, 47 kHz and 130 W) for 1 h at 25 °C. After that, the samples were dried for 2 h at 120 °C. The weight of the sample both before and after the ultrasonic treatment was measured. Microscopic observations of the washcoat erosion caused by the ultrasound, were also performed. This method was employed to comparatively measure washcoating adherence of different zeolites with and without silica binder. The effect of differing thermal expansions was also tested by cycling a ZSM5 washcoated monolith between 500 °C and room temperature. The monolith was introduced in a oven at 500 °C and kept for 60 s at this temperature. Then it was quenched at room temperature. The procedure was repeated 10 times; after that the ultrasonic test was performed.

2.5. Catalytic measurements

An ZSM5-coated monolith was selected to load In as the active phase for the SCR of NO_x with methane. The impregnation was carried out with a solution of $In(NO_3)_3$ (5 wt.%). The impregnation procedure for powders is described elsewhere [18]. In this work, the ZSM5 washcoated monolith was immersed in the solution and the excess was blown, repeating this process until obtaining the desired loading (4% of indium). Between blowing steps, the monolith was subsequently dried in a microwave oven and in a stove to obtain uniform distributions of the indium precursor [8]. The activation was carried out in air flow at 750 °C for 2 h in order to develop the $(InO)^+$ active sites by solid-state reaction between impregnated In_2O_3 and zeolite protons [18].

This monolithic catalyst was evaluated in a continuous flow system. The typical composition of the reacting stream was 1000 ppm NO, 1000 ppm CH_4, 10% O_2, in He balance. The reaction was performed at atmospheric pressure and temperatures between 300 and 600 °C with different flow/catalyst weight ratios. The washcoated monolith (1 cm × 1 cm × 2 cm) was placed inside a quartz reactor between quartz wool plugs, and the free space between the monolith and the quartz tube was filled with CSi particles to avoid bypass flow. The gaseous mixtures were analyzed before and after reaction with an on-line FTIR Thermo Mattson Genesis II equipped with a gas analysis cell. The gas-hourly space velocity, GHSV = flow rate × zeolite apparent density/zeolite mass was calculated on the basis of the mass of zeolite loaded in the monolith. In this way, catalytic results obtained with washcoated monoliths can be compared with those of the powder zeolites.

3. Results and discussion

3.1. Morphology of zeolite particles in powders and washcoated monoliths

The shape and size of zeolite particles to be washcoated was studied by SEM and LPSA. Fig. 1 shows SEM pictures of the three zeolites used. It can be seen that the as-received ZSM5 sample is under the form of nearly spherical aggregates of ca. 3 μm in average size, while ZSM5 crystals have a size between 0.1 and 0.3 μm (Fig. 1A). The laser diffractogram (Fig. 2A) shows a distribution between 0.1 and 10 μm, in agreement with the SEM pictures. The mordenite sample has similar features, but the size dispersion is broader (Fig. 2A) and the shape of aggregates is somehow less uniform (Fig. 1B). The morphology and size of the ferrierite powder is totally different. As can be seen in Fig. 1C, crystals are sheet-like of ca. 0.1 μm × 1.0 μm, forming big spherical aggregates. Particle size distribution shows an average size of 60 μm and a wide and asymmetrical dispersion between 0.5 and 100 μm (Fig. 2A). When suspensions of zeolite aggregates are subjected to ultrasound, the size distribution is altered (Fig. 2B), showing the partial rupture of the big aggregates, which produce a shifting of the curve towards smaller sizes. This is indicative of the aggregate stability, the order being ZSM5 > mordenite > ferrierite.

Fig. 3 shows SEM pictures of washcoated monoliths. While ZSM5 and mordenite-coated samples show homogeneous and compact films with zeolite particles anchored into cordierite macropores (Fig. 3A and B), the ferrierite sample shows a non-homogeneous aspect with only a few particles inside the pores (Fig. 3C). It can also be seen that the size of aggregates remains unchanged after the washcoating procedure.

The results obtained with MIP for a ZSM5-coated monolith are depicted in Fig. 4. The bare cordierite monolith presents a macropore distribution with a maximum centered at 1.5 μm, and does not show pores at lower sizes than 0.1 μm (Fig. 4A). When cordierite is washcoated with ZSM5 (13.7 wt.%), the more accessible superficial cordierite macropores are blocked by zeolite crystals, the intrusion volume being lower for this size range. A second type of pores with sizes smaller than 0.1 μm is now observed due to the space between zeolite crystals (Fig. 4B).

3.2. Study of preparation conditions upon the washcoat geometry

3.2.1. Zeolite loading and washcoat thickness

Regulating the load of the material deposited on monoliths is one of the most important preparation aspects [19]. Fig. 5

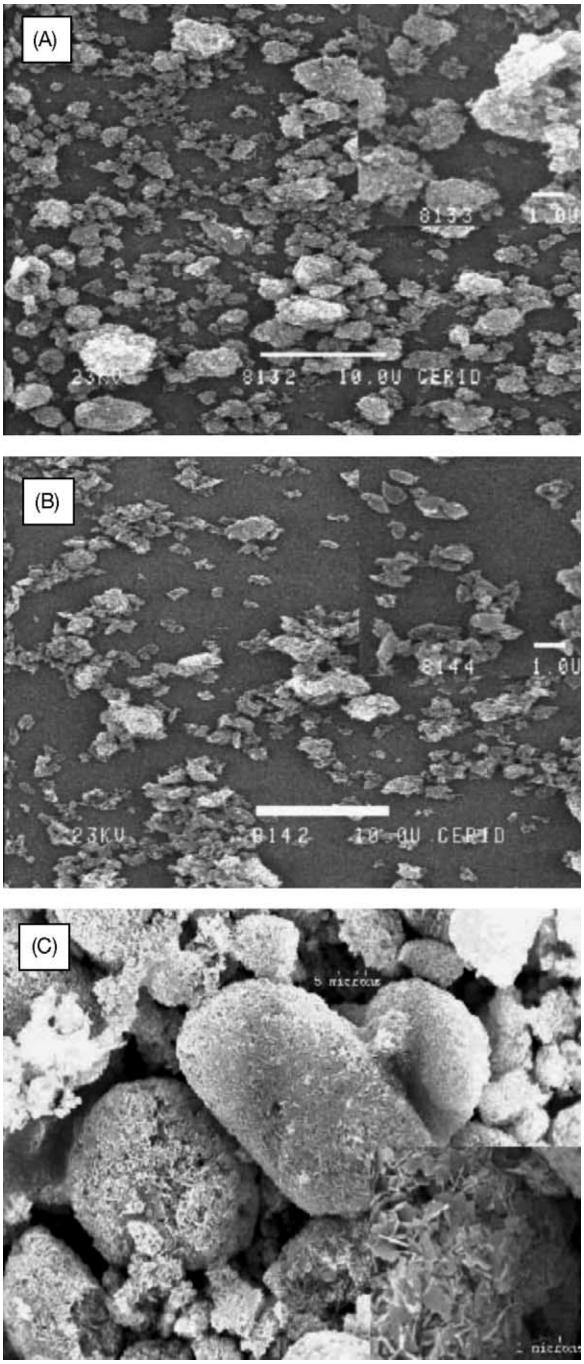

Fig. 1. SEM pictures of the three zeolites used in this work (as received): (A) NH_4-ZSM5; (B) NH_4-mordenite; (C) K-ferrierite.

presents a cross-section cut of a ZSM5-coated monolith, seen with a metallurgical microscope. The characteristic dimensions of the coating are indicated (min. *t*: minimum thickness, max. *t*: maximum thickness). The amount of material loaded during the washcoating procedure and the characteristic dimensions strongly depend on the zeolite concentration in the slurry and the number of immersions. By varying these conditions, the desired zeolite loading and thickness can be adjusted.

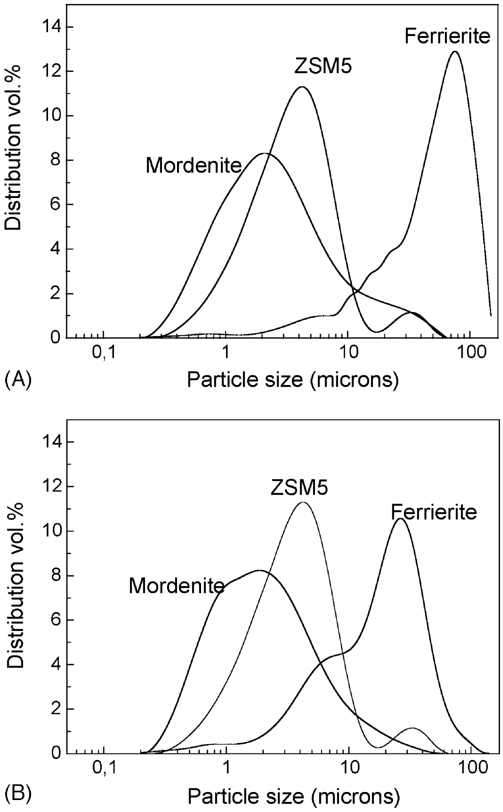

Fig. 2. Particle size distribution measured by laser particle size analysis (LPSA): (A) as-received zeolites; (B) zeolites treated in an ultrasonic bath.

In order to study the influence of the above mentioned washcoating conditions upon the washcoat characteristics, monoliths with different ZSM5 zeolite content, between 4 and 27 wt.%, were prepared by combining different suspension concentrations and a number of immersions. Within this range, a non-linear increase of the load with the suspension concentration was observed (Fig. 6A). A similar trend was observed for the loads achieved at each immersion stage for different concentrations (Fig. 6B), which explains the different slopes of the curves in Fig. 6A. This load was calculated as the increase in weight after each immersion. It is worth noticing that the increase in weight is not a function of the number of previous immersion stages, suggesting that once the first layer of zeolite crystals is formed, the surface rugosity remains invariant and very similar to the bare monolith rugosity. However, during the third immersion, the load increase is considerably higher for concentrated suspensions, due to the combination of a reduced section of the channel (due to the previous depositions) with the high viscosity of the suspension. In this vein, the combination of three immersions and 40% concentration, generates obturation of some channels. Thus, within the 20–30% range of zeolite concentration in the slurry, the latter is sufficiently concentrated not to require an excessive number of immersions, having an adequate viscosity to form a homogeneous layer onto monolith walls.

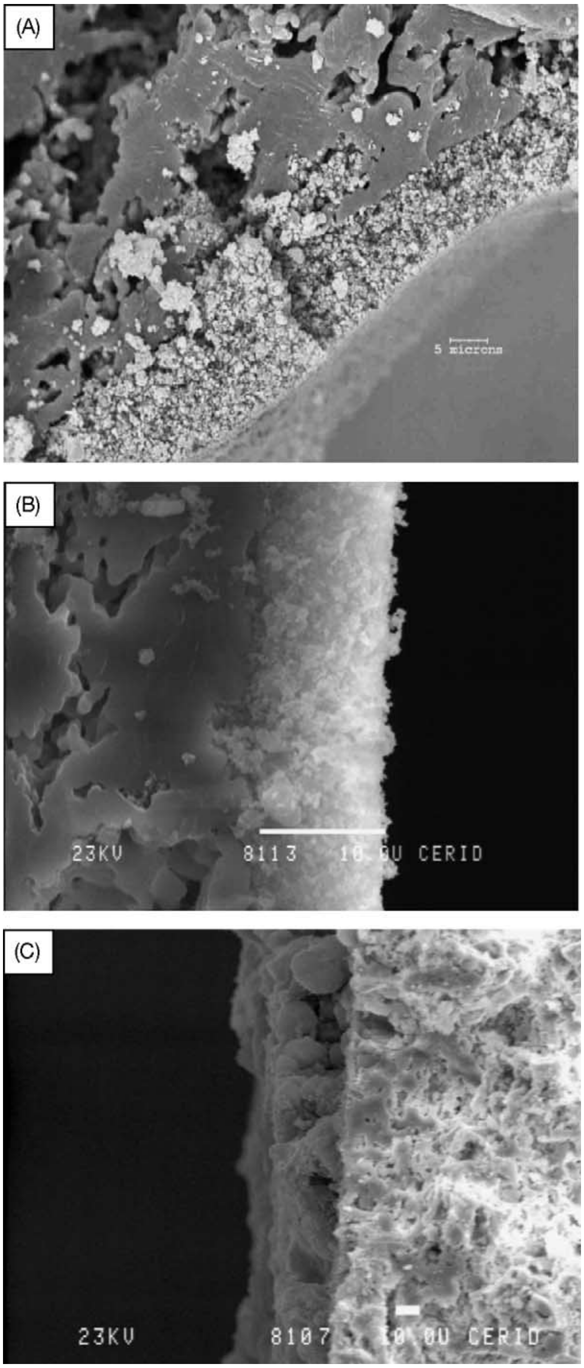

Fig. 3. SEM pictures of washcoated monoliths: (A) ZSM5; (B) mordenite; (C) ferrierite.

A fundamental property of the zeolite slurry is its viscosity (η), which can be simply related to the solids concentration through equation [20]:

$$\frac{\eta(\gamma)}{\eta^0} = \frac{1}{(1-\gamma)^{2.5}}$$

where γ is the volume fraction of solids and η^0 is the viscosity of pure water. The volume fraction of solids can be easily calculated from the density of particles and the concentration of the slurry. A plot (not shown) of the relative viscosity versus the slurry concentration gives a curve which is qualitatively similar to the curves shown in Fig. 6A and B, which indicates that the characteristics of washcoats are strongly related to this property.

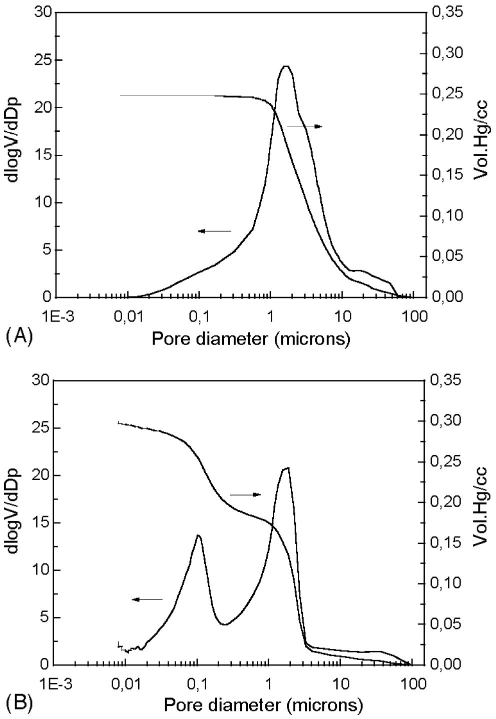

Fig. 4. ZSM5 pore size distribution obtained by mercury intrusion porosimetry (MIP): (A) cordierite monolith; (B) washcoated monolith.

An important characteristic related to the loading is the film thickness. As shown in Fig. 5, the coatings obtained with the washcoating method have two thickness regions. In Fig. 7, it is observed that the minimum thickness varies linearly with the load ($r = 0.98$), whereas the maximum thickness does not, the latter reaching a plateau with high loadings. The greater variability of maximum thicknesses is reflected in the dispersion of the values and it can be easily seen how this impinges on the accurate control of the average film thickness.

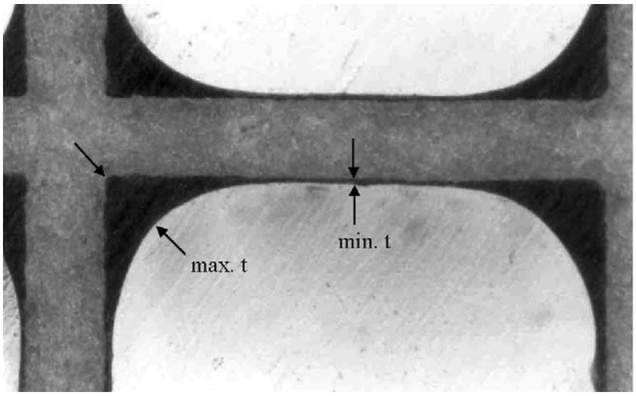

Fig. 5. Cross-section cut of a ZSM5-coated monolith seen with a metallurgical microscope.

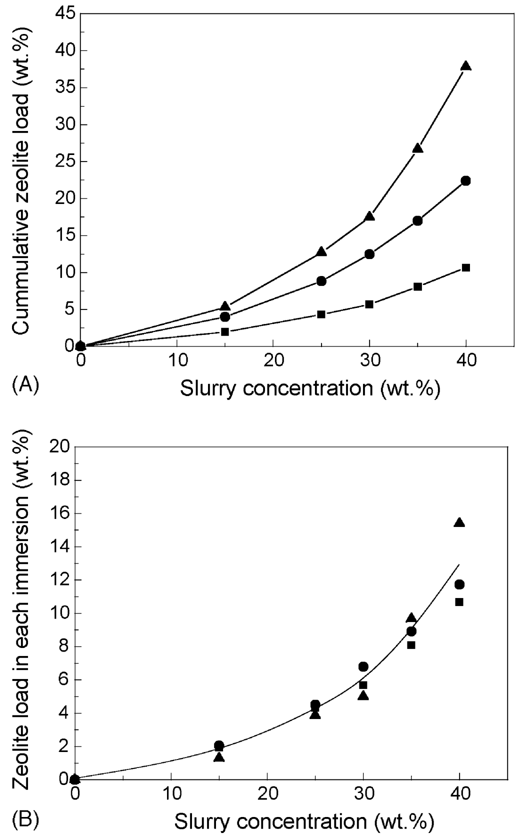

Fig. 6. Effect of slurry concentration upon zeolite loading in the washcoat: (A) cumulative loadings; (B) zeolite loaded in each immersion; (■) one immersion; (●) two immersions; (▲) three immersions.

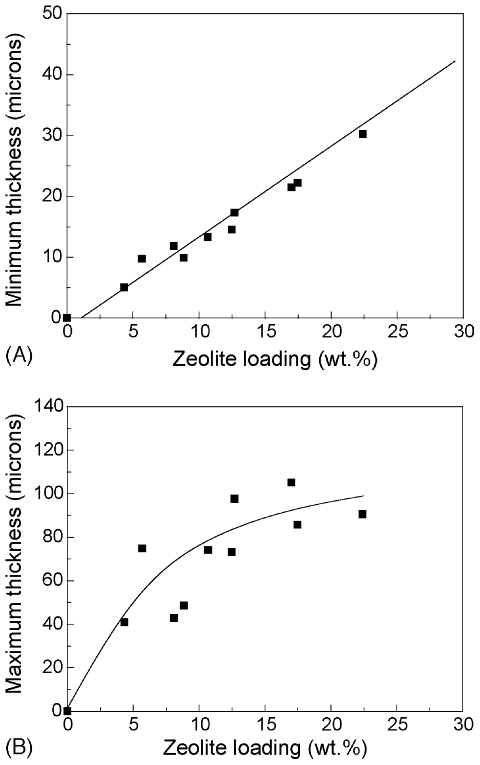

Fig. 7. Washcoat thickness for different loaded monoliths: (A) minimum thickness (min. *t*); (B) maximum thickness (max. *t*).

The minimum thickness (min. *t*) obtained under these preparation conditions could be regulated between 5 and 30 μm corresponding to material loads between 4 and 27%.

From Figs. 6 and 7, it can be inferred that coating thickness is a function of the suspension concentration and of the number of immersions (for the other conditions kept constant). On the other hand, the relative degree of homogeneity of the different preparations can be evaluated, calculating the relative standard deviation of the coatings thicknesses, which is a measure of their variability. It was found that for monoliths with similar loadings, the relative deviations increase with the use of few immersions and concentrated suspensions, if compared to a greater number of immersions with more diluted suspensions (Table 2).

It is interesting to note that even though a very good homogeneous distribution of the zeolite was obtained, a local non-homogeneity in each channel would continue to exist in the monolith. This effect is inevitable when the immersion method is used and is a negative factor since for its use under reaction conditions, the limitations in mass transfer will be critical at the channel corners.

Table 2
Standard deviation of washcoat minimum thickness

Zeolite load (wt.%)	Slurry concentration (wt.%).	Number of immersions	Minimum thickness[a] S.D. (%)
12.7	25	3	19.6
10.7	40	1	47.0

[a] Relative to the average minimum thickness.

Another variable affecting the characteristics of the coatings is the nature of the solvent employed to make the suspension [8], which has an incidence on the material load and its distribution, since its viscosity and surface tension affect the flow originated when the suspension excess is eliminated from the channels during the blowing stage. The effect of different solvents will be analyzed in subsequent studies.

3.2.2. Channel geometry after washcoating

The former variables, which define the distribution of the material inside the monolith channels and the thickness, also determine the shape of the deposit. It was observed through microscopy that as the material is being deposited in successive immersions, the geometry of the channel becomes progressively more circular. This fact is known, and the film shape correlates with the flow lines of a viscous fluid displaced by an air bubble moving inside a square-section capillary [21]. The rate of blowing air and the viscosity of the suspension affects the load, thickness and shape of the films. Since we used a relatively low air flow, the suspension–air interface on the transverse plane of the channels generated during the suspension excess blowing is asymmetrical. Accumulation at the vertices is due to higher viscous strengths in this zone. When this sector is filled with the first material deposition, the channel adopts a more circular geometry. In subsequent depositions, it can be observed that the accumulation at the vertices gets smaller and smaller until the transverse symmetry of the channel becomes circular (Fig. 7).

3.3. Washcoat stability

This is one of the least studied and most important variables to be optimized [14], given the demands of high flows and temperatures used in environmental applications. An accelerated ultrasonic test, reported in the patent literature [15], was performed in order to evaluate the washcoat adherence. The treatment originated different degrees of erosion in the various monolithic samples. The degree of erosion was measured by weighing the sample before and after the ultrasonic treatment under an atmosphere with controlled humidity and also by visualizing the surface through miscroscopic observations. It was found that the mechanical stability is a function of the zeolite type, the order being ZSM5 > mordenite > ferrierite (Table 3 and Fig. 8A). This order correlates well with the sizes and stability of aggregates; higher adhesion is obtained with lower sizes and more stable aggregates. The former effect is due to the anchorage of the particles on the cordierite surface. Bigger aggregates cannot

Table 3
Washcoat stability

Zeolite	Without binder (wt.%)	With SiO_2 binder (wt.%)
ZSM5	4.6 (3.7)[a]	1.8
Mordenite	13	2.3
Ferrierite	26.1	11

Weight percent of zeolite detached after ultrasound test.

[a] After cycling 10 times between 500 °C and room temperature.

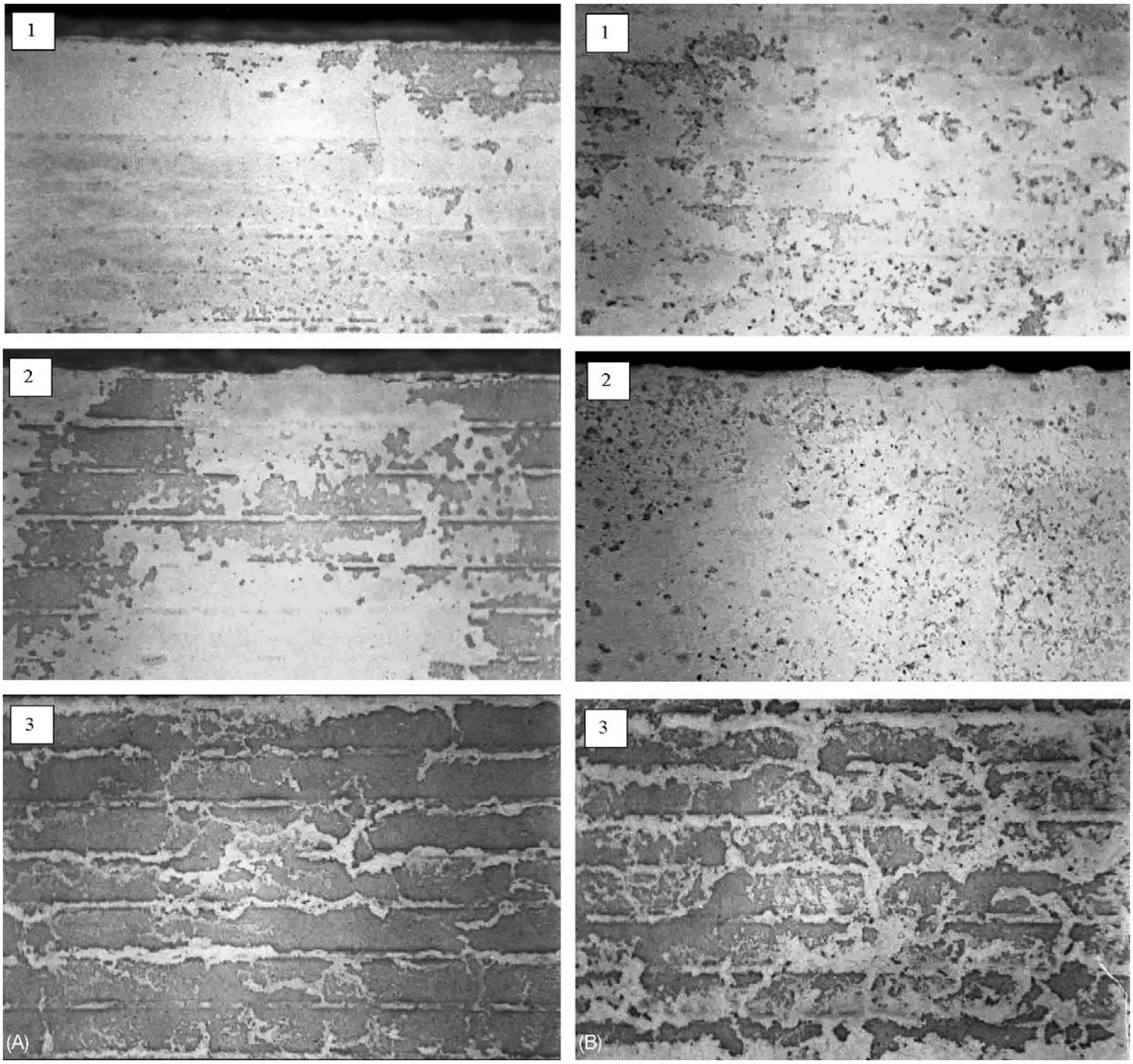

Fig. 8. Washcoat stability. Stereomicroscopic observation of the zeolite film after ultrasound treatment: (A) washcoat without binder; (B) washcoat with silica as a binder; (1) ZSM5; (2) mordenite; (3) ferrierite.

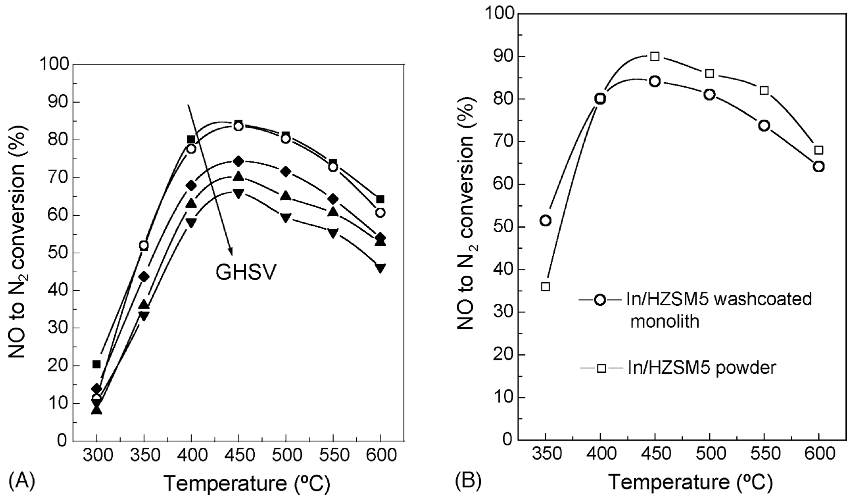

Fig. 9. Selective NO_x reduction with methane with oxygen excess: (A) In-ZSM5 washcoated monolith. Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 10% O_2 and GHSV (h^{-1}): 7500, 15,000, 22,500, 30,000, and 37,500. (B) Comparison between In-ZSM5 powder and washcoated monolith, GHSV: 7500 h^{-1}.

enter inside the pores; thus, a poor adhesion is obtained. It should be reminded here that the size of the aggregates does not change after the washcoating procedure. Table 3 shows the results obtained when a ZSM5 washcoated monolith was subjected to 10 thermal cycles between 500 °C and room temperature and, after that, the ultrasonic test was performed. This experiment was done to test the possible deleterious effect of the different thermal expansion coefficients of the coating and the monolith. The results show that the adhesion was not affected by this thermal treatment.

We have previously found [13] that the addition of colloidal silica improves the adherence of ferrierite washcoats. With the purpose of studying the effect of silica, mordenite, ZSM5 and ferrierite washcoated monoliths were prepared using a 3 wt.% ratio (with respect to zeolite) of colloidal SiO_2 cabosil. The adhesion tests demonstrated that the stability is greatly improved for the three zeolites employed in this study (Table 3 and Fig. 8B). The binder has two important effects: (i) the small size particles fill out the space between aggregates thus increasing the contact between particles and (ii) silica cabosil has a high concentration of hydroxyl groups on its surface, allowing the formation of bondings with zeolite crystals after calcination.

3.4. *Selective catalytic reduction of NO_x with CH_4 on an In-ZSM5 washcoated monolith*

In order to test a washcoated monolith under reaction conditions, the NO_x reduction with methane was performed under dry and wet conditions. In Fig. 9, the conversion of NO_x to N_2 is depicted as a function of the temperature for different GHSV values, calculated as the ratio between zeolite loading volume and the gaseous flow. The monolithic catalyst behaves as well as the powder (Fig. 9B), indicating a good coating procedure. Note that, at low temperature, the NO_x conversion is somewhat higher for the monolith, being the opposite when the temperature increases. Anyway, the differences in conversions are rather small, and the behavior is quite similar. This result also suggests that there are no diffusion limitations inside the catalytic layer, which is an advantage of the washcoating technique if compared with hydrothermal synthesis. With the latter method, a dense layer is usually obtained, which could result in a poor accessibility of the reacting molecules to active sites. However, it should be pointed out that in the case of mordenite this limitation has been recently overcome [22]. In Fig. 9, it can also be seen that for the high spatial velocity used, which is typical of stationary sources of power generation, the maximum conversion remains above 60%. These results are under dry conditions. When water is added in the feed a strong decrease of conversion is observed (not shown) which is a typical and well-known effect. The addition of small amounts of a noble metal helps to overcome the negative effect of water [23] and will be explored in further studies with monolithic catalysts.

4. Conclusions

In order to obtain zeolite washcoats with optimum loading, thickness, and homogeneous distribution, the accurate control of certain preparation variables is mandatory. The results obtained with ZSM5 demonstrate that the solids concentration of the slurry is strongly connected with the viscosity, and together with the number of immersions and blowing conditions, it defines the characteristics of the film deposited. By combining those variables, different loadings, coating thickness, films distribution and geometries can be obtained. With concentrated suspensions, fewer immersions are needed in order to obtain a desired load but the non-homegeneity in the zeolite distribution increases. In order to get more homogeneous washcoatings, for the same load it is preferable to use diluted suspensions and perform more than one immersion even though this modifies the geometry of the channel. Within the 20–30% range of zeolite concentration in the slurry, the latter is sufficiently concentrated not to require an excessive number of immersions, having an adequate viscosity to form a homogeneous layer onto monolith walls. A low flow rate during the channel blowing improves the geometry generating less accumulation at the vertices. Other variables that can be controlled to improve the aspects mentioned above are the solvent and the careful adjustment of the air distribution during blowing.

The washcoating adherence increases with the decrease in the size of the aggregates deposited on the monolith. This improves the packaging and interaction between particles and facilitates a convenient filling of the surface cordierite macropores, producing an effective anchorage. Thus, the greater adherence of mordenite and ZSM5 with respect to ferrierite is explained. At the same time, the higher the own stability of the aggregates, the higher the washcoating stability. Therefore, the ZSM5-coated monoliths are more stable than the mordenite ones. The addition of an additive such as SiO_2, even in a low proportion of 3 wt.%, improves the adherence of the three zeolites under study, probably due to an improvement in the interparticle cohesion. The results obtained in the present work are useful to optimize load, thickness homogeneity, geometry and adherence of zeolitic washcoatings on ceramic monoliths.

Finally, the performance of an In-ZSM5 washcoated monolith is tested for the selective reduction of NO_x with methane under oxygen excess. It is observed that the activity of the monolithic catalyst is as good as the ones for the In-ZSM5 powder, which indicates that there are no diffusive restrictions due to coating thickness.

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