ELSEVIER

The effect of different slurry compositions and solvents upon the properties of ZSM5-washcoated cordierite honeycombs for the SCR of NO$_x$ with methane

Juan M. Zamaro, Maria A. Ulla, Eduardo E. Miró *

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL-CONICET) Santiago del Estero 2829, 3000 Santa Fe, Argentina

Abstract

ZSM5-washcoated monoliths were prepared using different slurry compositions and the following solvents: water, methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ethyl acetate, and acetone. The effect of the different solvents on the coating characteristics was studied and two of their properties, viscosity and volatility, were used to analyze the results obtained. The solvents giving rise to high-viscosity slurries – butyl alcohol, ethyl acetate, and acetone – were not effective for the washcoating process. In the case of the other solvents, when viscosity and vapor pressure increased the load obtained was higher, probably due to a combined effect of viscosity and partial evaporation during the blowing step. Water yielded zeolite coatings with the best mechanical stability, measured by ultrasonic test. When water was used as solvent, the zeolite load increased linearly with the square root of viscosity. Finally, an In/HZSM5-coated honeycomb was tested for NO$_x$ reduction with methane under excess oxygen. It showed a behavior very similar to that of the powder catalyst, which is one of the main objectives pursued when coating monoliths.
© 2005 Elsevier B.V. All rights reserved.

Keywords: ZSM5 washcoating; Cordierite honeycombs; Slurry solvents; SCR of NO$_x$ with CH$_4$

1. Introduction

The monolithic reactor is the most widely used catalytic system for environmental applications. Ceramic catalytic monoliths can be obtained by means of extrudates in which the catalytically active material is used to manufacture the monolith, or by the deposition of powder as a coating on a ceramic honeycomb substrate [1].

Zeolites are attractive materials to be used in environmental applications and the literature reports emerging technologies for the selective reduction of NO$_x$ with ammonia in stationary sources using metal-exchanged zeolites as catalysts [2]. Among other examples of environmental applications, the selective reduction of NO$_x$ with hydrocarbons under lean conditions has been a topic of great research activity during the last decade [3,4] while the

adsorption of VOC's appears as another promising application [5].

In the case of zeolites, the coating layer can be made in either of two ways: by hydrothermal synthesis [6,7] or by deposition from a slurry of zeolite particles. The first one of these methods has the advantage of achieving a stronger adhesion to the support but, on the other hand, it is considerably more complex than slurry-coating and can give rise to diffusion limitations if a dense layer is formed. However, a recent publication reports a highly accessible mordenite coating obtained by hydrothermal synthesis, apparently overcoming this latter negative aspect [8].

In previous works [9,10], we reported the effect of different binders on the SCR of NO$_x$ with methane using CoFerrierite and CoZSM5 washcoated on cordierite honeycombs. The said reaction consists in two main parallel paths: the oxidation of methane with NO$_x$ and with oxygen. If the second one is preferred, the system is not effective because the reductant is consumed by the usually-in-excess oxygen.

* Corresponding author. Fax: +54 42 571162.
  E-mail address: emiro@fiqus.unl.edu.ar (E.E. Miró).

Boix et al. [9] reported that $Al(NO_3)_3$ added to a CoZSM5 slurry inhibits the NO_x reduction due to the formation of a non-stoichiometric spinel which expels Co ions from exchange positions. Notwithstanding, the use of silica as a binder was reported to have a beneficial effect in the same reaction, increasing the selectivity towards NO_x reduction when CoFerrierite is washcoated onto a ceramic monolith [10].

The final characteristics of a washcoat are complex functions of the type of monolith used, the properties of the slurry, and the preparation conditions. In their review of monolith coatings, Nijhuis et al. [1] presented an excellent, thorough description of washcoating methods for common materials. However, to our knowledge, no systematic study of washcoating methods for zeolites has yet been reported in the literature and only a few articles on the subject have been published so far.

The properties of the slurry can be governed by selecting three main variables: (i) the properties of the solid particles, (ii) the solids weight percent in the slurry, and (iii) the type of solvent used for stabilizing the slurry. The first two aspects have been recently addressed in the open literature [11,12]. With respect to the third aspect, the solvent most widely used is water. Nevertheless, fundamental properties of the slurry such as viscosity and particle dispersion can be modified by selecting different solvents. Viscosity and surface tension could affect the flow pattern originated when the suspension excess is eliminated from the channels during the blowing stage. However, as far as we know, the effect of the use of different solvents has not yet appeared in the open literature. The only way to change the solvents properties that has been explored is the addition of a surfactant agent or an electrolyte. For example, Beers et al. reported the case of 1.8% of Teepol to disperse BEA zeolite crystals in water [13].

In this work, we report an experimental study of the preparation and characterization of ZSM5 washcoated onto a cordierite honeycomb using the method of deposition from a slurry. We mainly focus on the use of different solvents and compositions in the slurry preparation and on their effect upon the coating properties. Washcoated monoliths were characterized by scanning electron microscopy (SEM), optical microscopy, mercury intrusion porosimetry (MIP), and laser particle size analysis. The adhesion of the washcoats was evaluated using an ultrasonic technique [14,15]. Finally, an In/HZSM5 monolithic catalyst was prepared and tested for the selective catalytic reduction (SCR) of NO_x with methane in the presence of excess oxygen, exploring the effect of different operation variables such as temperature, concentration of reactants, and the effect of water in the feed.

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 area (GSA) were 0.42 g cm^{-3} and 27.4 cm^2 cm^{-3}, respectively. The monoliths were washcoated with aqueous suspensions of 15, 25, 30, 35, and 40 wt.% of zeolite (NH_4–ZSM5 Zeolyst with Si/Al = 15). The effect of different solvents was also explored using methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ethyl acetate, and acetone. Among them, we were only able to prepare slurries with an appropriate viscosity using the first three solvents. In order to compare them with water, we used the same solid and solvent weight as those used to obtain 30 wt.% in the aqueous slurry.

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.

2.2. Morphology observations

A Nikon Optiphot (50–400×) metallurgical microscope with halogen lamps was used to perform optical observations of the samples. The microscope had a Microflex AFX-DX photo-micrographic attachment with an FX-35 DX dark box. Samples of monoliths were transversally cut with a CSi disc and carefully polished in order to measure the characteristic dimensions of coatings. Additionally, a Leica Stereozoom 2000 stereomicroscope was used in order to perform inspections of the zeolite coating. Pictures of the samples were processed with the Image Tool program in order to obtain the open frontal area (OFA) and the roundness (4π × section × perimeter^{-2}). Roundness varied between 0 and 1, the greater the value the rounder the object.

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

The particle size distribution of some powder samples was determined with Laser Particle Size Analysis (LPSA) through a Malvern Mastersizer X instrument equipped with a sample suspension unit. Typically, suspension concentrations between ca. 0.004 and 0.02% (w/w) were used, with obscurations between 15 and 35%. The as-received ZSM5 sample was under the form of nearly spherical aggregates of ca. 3 μm in average size, while the ZSM5 crystals had a size between 0.1 and 0.3 μm. Pore size distributions of the monolith samples were measured by mercury intrusion porosimetry using an Micromeritics Autopore II 9220 V1.04 unit.

2.4. Washcoat adherence

The adherence of zeolite coatings was evaluated using a method described in the patent literature [14] which consists in the measurement of weight loss caused by exposing the sample to ultrasound. This method was recently applied by Valentini et al. [15] for alumina layers on ceramic and metallic supports and by Beers et al. [16] 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 or water 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 during 2 h at 120 °C. The weight of the sample both before and after the ultrasonic treatment was measured. This method was employed to measure the washcoating adherence of different samples for comparison purposes.

2.5. Catalytic measurements

A 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 [17]. 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 [1]. The activation was carried out in air flow at 750 °C during 2 h in order to develop the $(InO)^+$ active sites by solid-state reaction between impregnated In_2O_3 and zeolite protons [17].

This monolithic catalyst was evaluated in a continuous flow system with a total flow rate of 208 cm^3/min. The typical composition of the reacting stream was 500, 1000, 2000, and 3000 ppm NO, 1000 ppm CH_4, 2, 4, 7, and 10% O_2, in He balance. The reaction was performed at atmospheric pressure, temperatures between 300 and 600 °C and GHSV: 30,000 h^{-1} (lineal velocity: 5.4 cm/s). The washcoated monolith (1 cm × 1cm × 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 only nitrogen oxide species detected were NO and NO_2. N_2O was not detected in the catalytic runs.

3. Results and discussion

Various solvents with different viscosity an volatility were tested for washcoating ZSM5 on ceramic honeycombs. Table 1 shows the results obtained with water, isopropyl

Table 1
Properties of slurries prepared with different solvents and the zeolite loads obtained

Solvent	γ[a]	Zeolite washcoat (wt.%)	μ (calculated)[b]	P (20 °C)[c]
Water	0.53	7.6	6.6	17.5
	0.46	5.7	4.7	
Isopropyl alcohol	0.53	–[d]	14.2	35
	0.46	16.0	10	
	0.37	9.6	6.8	
Ethyl alcohol	0.53	21.0	9.3	41.5
	0.46	12.0	6.6	
Methyl alcohol	0.53	23.9	3.9	91
	0.46	10.8	1.4	

[a] Volume fraction of solids measured after centrifugation.
[b] Theoretical viscosity calculated with equation $\eta(\gamma)$ (centipoise) = $\eta°/(1 - \gamma)^{2.5}$.
[c] Solvent vapor pressures in mm Hg.
[d] It was not possible to washcoat the monolith due to the high viscosity of the slurry.

alcohol, ethyl alcohol, and methyl alcohol. It can be seen that the amount of zeolite load increases with the concentration of the slurry and with the increase of both the viscosity and volatility of solvents.

It is known that viscosity is a fundamental property of the slurry which strongly affects the characteristics of the coating [1]. Viscosity is a function of the solvent employed and the volumetric fraction of solids in the slurry, and it can be easily estimated using equation $\eta(\gamma)/\eta° = 1/(1 - \gamma)^{2.5}$ [18], were γ is the volume fraction of solids and $\eta°$ is the viscosity of the pure solvent. In Table 1, it can be seen that when viscosity and vapor pressure increase, the load obtained is higher probably due to a combination effect of viscosity and partial evaporation during the blowing step. An exception is the case of methanol, for which, in spite of its low viscosity, the load is still high. This is probably due to the fact that methanol has the highest volatility among the solvents employed, and most likely this effect prevails.

For a given solvent (water) with different amounts of zeolite, there is a linear dependence between zeolite loading in the washcoat and the square root of its theoretical viscosity (Fig. 1). This effect is due to the fluid-dynamic characteristics of the system; the rate of blowing air and the slurry viscosity affect the load, thickness and shape of the films [19]. It has been reported that the coating load is proportional to the non-dimensional capillary number (Ca) thus explaining the linear function observed in Fig. 1A. It should be pointed out here that the capillary number is proportional to the square root of viscosity.

Another important property of the slurry that strongly affects the washcoat characteristics is the solids concentration. In Fig. 1B, the zeolite load is plotted against the solids content in the slurry. The increase in weight obtained in each immersion at a given slurry concentration is not a function of the number of previous immersion steps, suggesting that once the first layer of zeolite crystals is formed, the surface
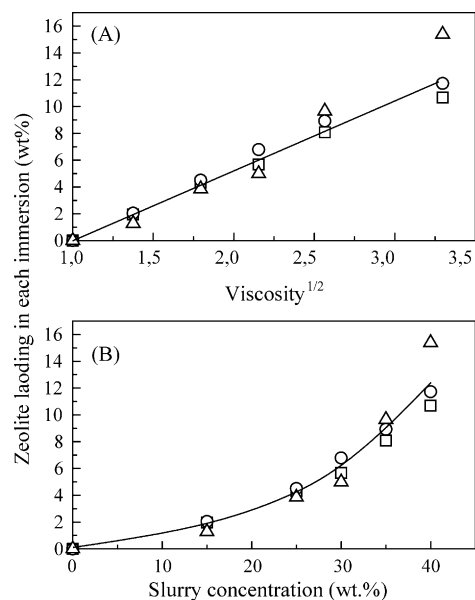
Fig. 1. Weight percent (wt.%) of ZSM5 loaded onto cordierite monolith after each immersion as a function of: (A) slurry theoretical viscosity and (B) slurry ZSM5 concentration. (○) One immersion; (□) two immersions; (△) three immersions.

rugosity remains invariant and very similar to the bare monolith rugosity.

Fig. 2 depicts a SEM picture of a ZSM5 washcoated monolith, using water as a solvent, showing a homogeneous, compact film with the zeolite particles well anchored to cordierite macropores. Mercury Intrusion Porosimetry results (not shown) indicate that the bare cordierite monolith presents a macropore distribution with a maximum centered at 1.5 μm and does not show pores at sizes smaller than 0.1 μm. 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.

The solids concentration in the slurry, the viscosity, and the air flow rate during the blowing stage also affect the geometry of the channels. The film shape correlates with the flow lines of a viscous fluid displaced by an air bubble moving inside a square section capillary [19]. 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 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, the accumulation at the vertices gets smaller and smaller until the transverse symmetry of the channel becomes circular (see Fig. 3). The open frontal area (OFA) and roundness, which are also important variables in coated-monolith design, are calculated from the processed optical micrographs. The changes of these two parameters with immersion numbers are presented in Fig. 4. The roundness increases whereas the OFA decreases with the increments of the immersion numbers, in line with the above discussion. Note that the roundness value can vary from 0 to 1 and that the greater the value the rounder the object.

Fig. 5(A and B) shows pictures of cross-sections of monoliths coated with slurries made with water and ethyl
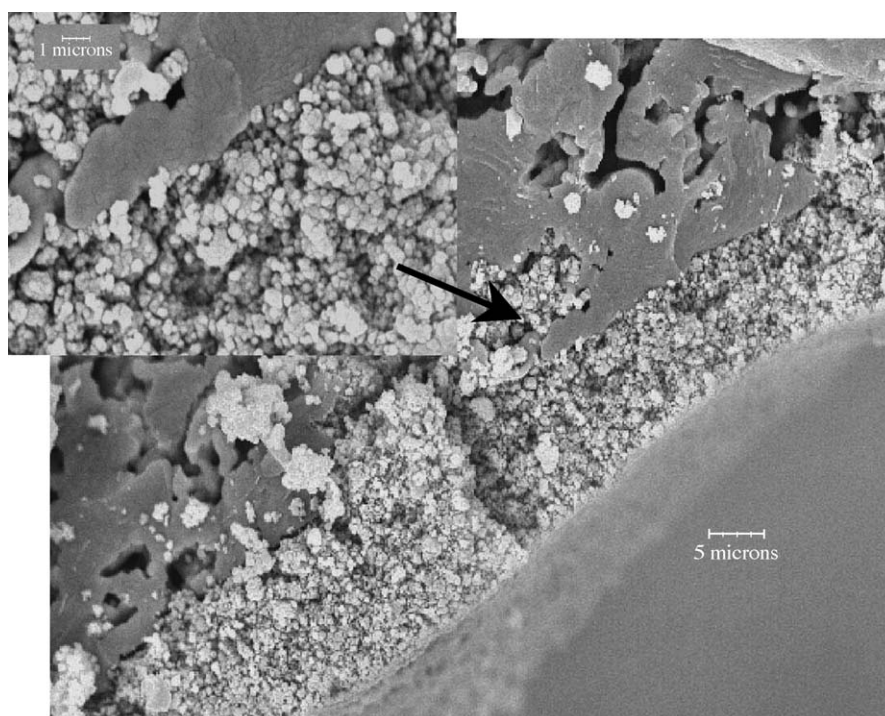

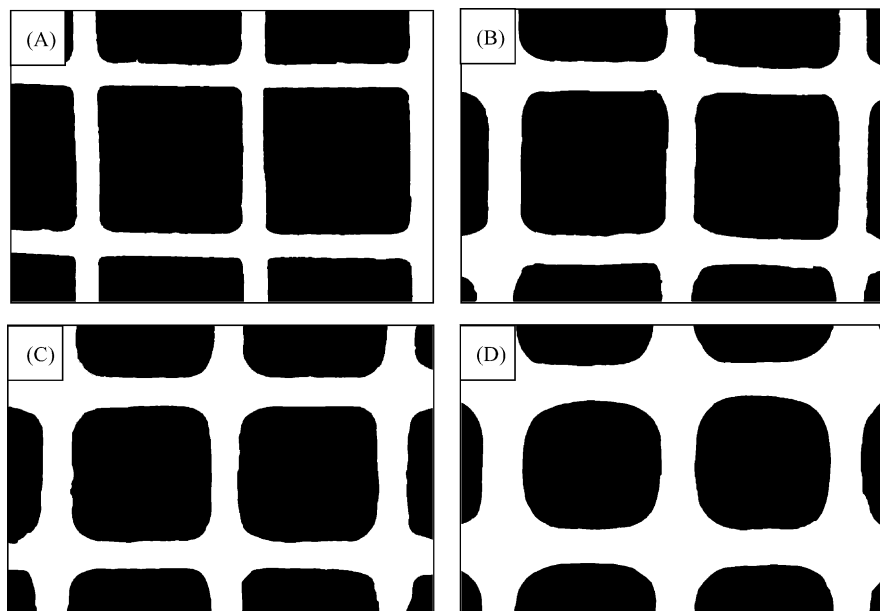Fig. 2. Cross-section micrograph (SEM) of ZSM5 washcoated monolith (water was used as solvent).

Fig. 3. Processed images of cross-sections of ZSM5 washcoated monolith with: (A) one immersion, (B) two immersions, (C) three immersions, and (D) four immersions. Images were taken with an optical microscope. Thirty percent of aqueous slurry was used.

alcohol, respectively. A different geometry of the washcoat can be seen in the channel corner, the roundness of the washcoat made with water being bigger. This fact could be originated in the different viscosity and surface tension of ethyl alcohol which affect the interface between the slurry and bubbles of air during the blowing step.

One of the least studied and most important variables to be optimized is the washcoat stability [12]. We performed stability tests with air flow rates and temperatures similar to the ones employed in environmental applications. However, we could not observe any zeolite loss under these conditions.
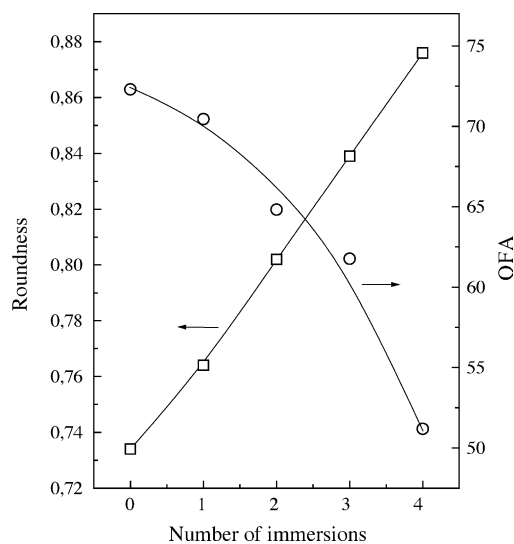

Fig. 4. Changes in the open frontal area (OFA) and the roundness of the monolith channels with the increment of immersion numbers.
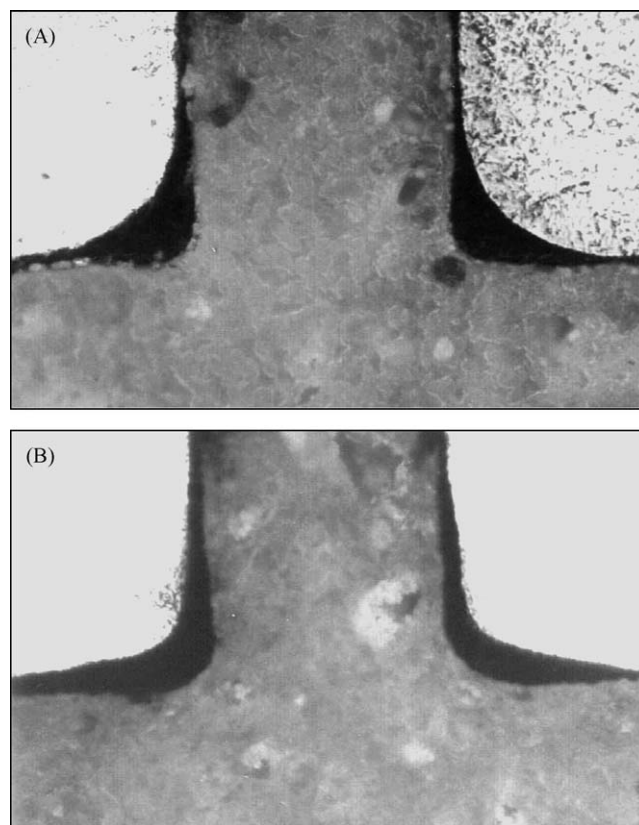

Fig. 5. Cross-sections of ZSM5 washcoated monoliths obtained from slurries prepared with two different solvents: (A) water and (B) ethyl alcohol. Images were taken with an optical microscope.

Table 2
ZSM5 loss after ultrasonic test (see Section 2)

Solvent	Zeolite load (%wt.)	Zeolite loss[a] (%wt.)
Water	21.8	2.9
Methyl alcohol	23.9	29.1
Ethyl alcohol	21	21.7
Isopropyl alcohol	16	43.2

[a] Weight percent of zeolite detached after ultrasound test performed with water for 1 h.

Thus, a more severe stability test was employed, which consists in an accelerated ultrasonic test reported in the patent literature [14]. Results of this test are shown in Table 2 for the different solvents employed in this work. It can be observed that the better stability is obtained with water as solvent. The lack of dispersion of the zeolite particles and the formation of aggregates is probably the cause of this behavior. Taking into account this observation, a search for better solvents will be conducted in the future.

Finally, an In/HZM5 catalyst was washcoated on a cordierite monolith in order to test it for the NO_x reduction with methane in excess oxygen. The slurry was made using water as solvent. The typical curves of NO_x conversion against temperature, with a maximum in the 450–550 °C range, are shown in Figs. 6–8. These curves were obtained at a volume space velocity of 30,000 h^{-1}, calculated with the flow/zeolite volume relationship. NO_x concentration is varied in Fig. 6A, showing that NO_x conversion decreases
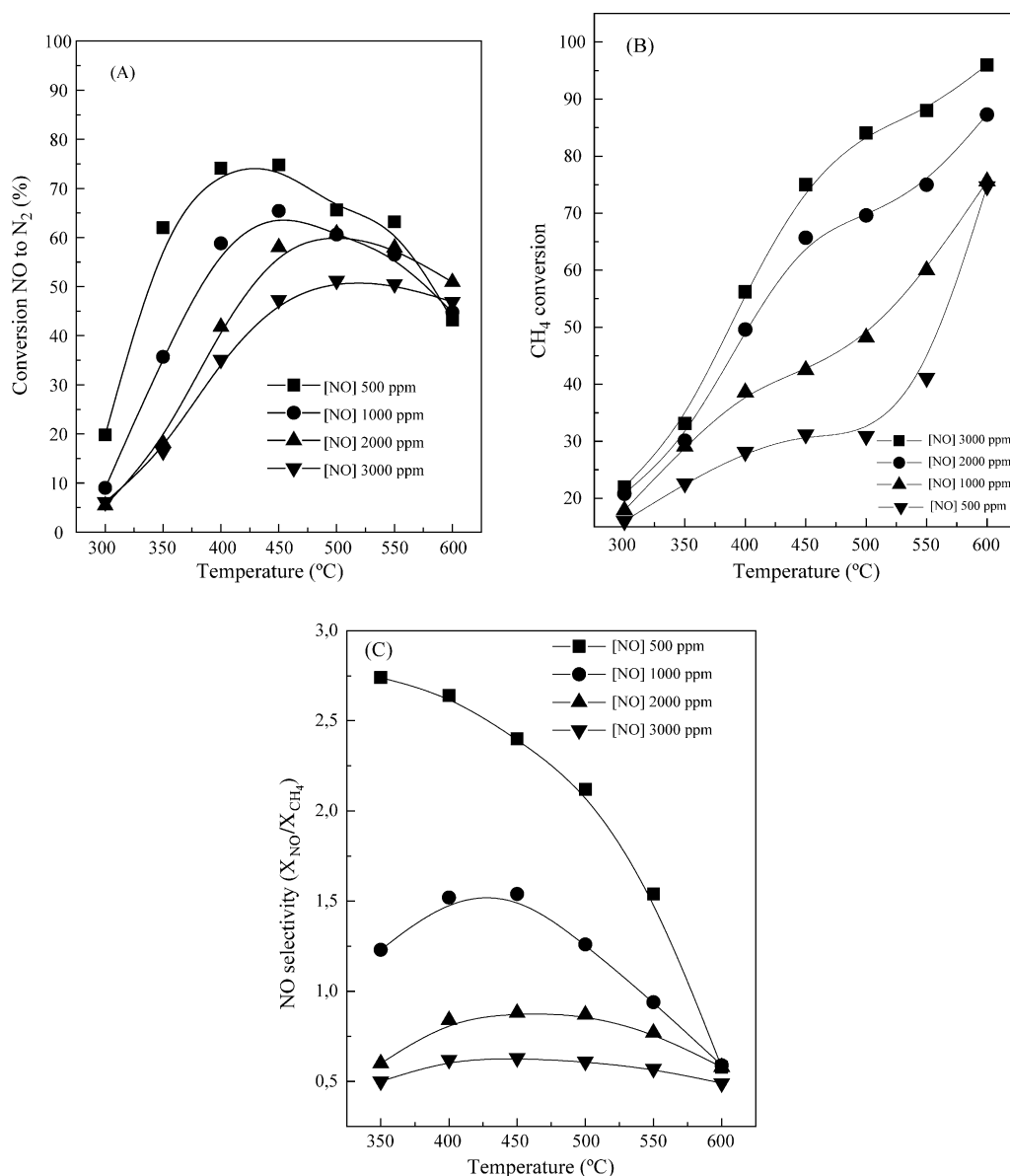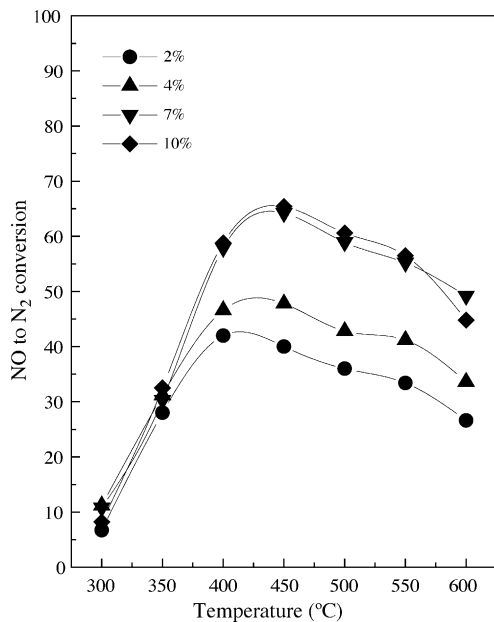

Fig. 6. Catalytic activity of the In/HZSM5 washcoated monolith for NO_x SCR with CH_4 in excess O_2. Effect of NO_x concentrations. (Reaction conditions: 500, 1000, 2000, and 3000 ppm NO, 1000 ppm CH_4, 10% O_2, in He balance. GHSV: 30,000 h^{-1}). (A) NO to N_2 conversion, (B) CH_4 conversion, (C) selectivity defined as: (NO to N_2 conversion)/methane conversion.

Fig. 7. Catalytic activity of the In/HZSM5 washcoated monolith for NO_x SCR with CH_4 in excess O_2. Effect of O_2 concentrations. (Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 2, 4, 7, and 10% O_2, in He balance. GHSV: 30,000 h^{-1}).

when NO_x concentration increases, which is a typical kinetic behavior of an order smaller than one. Fig. 6(B and C) shows methane conversion and selectivity defined as (NO to N_2 conversion)/(methane conversion). It can be seen that selectivity decreases with temperature due to the increase in methane conversion and the decrease in NO conversion.
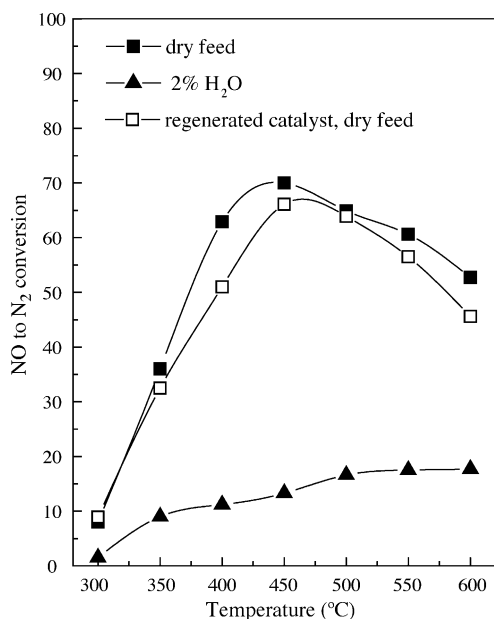

Fig. 8. The effect of water (2%) on the catalytic activity of the In/HZSM5 washcoated monolith for NO_x SCR with CH_4 in excess O_2. Regenerated catalyst means that after deactivation it was oxidized in air at 750 °C. (Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 10% O_2, in He balance. GHSV: 30,000 h^{-1}).

By varying oxygen concentration, an increase in NO_x conversion up to 7 vol.% is observed, reaching a plateau for higher concentrations (Fig. 7). The addition of 2% water results in a strong decrease in activity (Fig. 8), which is a well-known fact for In-zeolite catalysts [17]. This is due to the strong adsorption of water on the active $(InO)^+$ sites. This effect is partially reversible; once water is stopped conversion is restored but not completely, probably due to the partial destruction of $(InO)^+$ active sites. However, as shown in the same figure, a treatment in air at 750 °C almost restores the initial activity. The above described behaviors are well known for the In/HZSM5 catalyst in powder form. The most important point here is that the monolithic catalyst behaves as the powder, indicating that an optimal coating procedure has been achieved. This is not an easy task; as a matter of fact, in previous studies [9,10] we found that the coating procedure could negatively affect the catalytic activity and selectivity for NO_x reduction.

Reaction orders were calculated at low conversions (350 °C) for both NO and CH_4 reaction velocities. Since the SCR of NO_x is a complex reaction system, they are apparent kinetic orders. For NO to N_2 reaction velocity, kinetic orders for NO and O_2 are 0.6 and 0.4, respectively. For methane reaction velocity, 0.2 and 0.3. These values are similar to those reported in [20].

4. Conclusions

When different solvents are used, viscosity and vapor pressure strongly affect the obtained zeolite loading. When viscosity and vapor pressure increase, the load obtained is higher probably due to a combined effect of viscosity and evaporation during the blowing step. An exception is the case of methanol, for which, in spite of its low viscosity, the loading is still high. This is probably due to the fact that methanol has the highest volatility among the solvents employed, and most likely this effect prevails.

It has also been shown that the geometry of the zeolite coating can be changed using different solvents. For example, in the case of ethyl alcohol there is a smaller amount of material accumulated in the corners, the roundness of the washcoat being bigger when water is used. This is an interesting result, showing that different solvents can be chosen in order to obtain different washcoat geometries. Unfortunately, in all the alcohols used in this work for replacing water, the stability during the ultrasound tests was lower.

When water is used as a solvent, the viscosity of the slurry exponentially increases with the solid volume percent. A similar behavior follows the zeolite load when plotted against slurry concentration. Besides, the load increases linearly with the square root of viscosity. These are important features in designing zeolite coatings onto ceramic honeycombs when the washcoating method is employed. Another interesting feature is that the increase in weight obtained in each immersion at a given slurry

concentration is not a function of the number of previous immersion steps, probably due to a similar rugosity of the surface after the immersions.

The activity and selectivity obtained for a InH/ZSM5 catalyst washcoated on cordierite show that the properties of the powder are maintained after the coating process, which indicates that an optimal procedure has been adopted.

Acknowledgements

References

[1] T.A. Nijhuis, A.E.W. Beers, T. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, Catal. Rev. 43 (4) (2001) 345.

[2] I.-S. Nam, S.T. Choo, D.J. Koh, Y.G. Kim, Catal. Today 38 (1997) 181.

[3] J.N. Armor, Catal. Today 26 (1995) 147.

[4] H. Hamada, Catal. Surv. Jpn. 1 (1997) 53.

[5] N.R. Burke, D.L. Trimm, R.F. Howe, App. Catal. B: Environ. 4 (1) (2003) 97.

[6] J. Caro, M. Noack, P. Kölsch, R. Schäfer, Microporous Mesoporous Mater. 38 (2000) 3.

[7] M.A. Ulla, R. Mallada, J. Coronas, L. Guitérrez, E. Miró, J. Santamaría, Appl. Catal. A: Gen. 253 (1) (2003) 269.

[8] M.A. Ulla, E. Miró, R. Mallada, J. Coronas, J. Santamaría, Chem. Commun. (2004) 528.

[9] A. Boix, E.E. Miró, E.A. Lombardo, R. Mariscal, J.L.G. Fierro, Appl. Catal. A: Gen. 276 (2004) 197.

[10] A.V. Boix, J.M. Zamaro, E.A. Lombardo, E.E. Miró, Appl. Catal. B: Environ. 46 (2003) 121.

[11] C. Agrafiotis, A. Tsetsekou, J. Mater. Sci. 35 (2000) 951.

[12] C. Agrafiotis, A. Tsetsekou, A. Ekonomakou, J. Mater. Sci. Lett. 18 (1999) 1421.

[13] A.E.W. Beers, T.A. Nijhuis, F. Kapteijn, J.A. Moulijn, Microporous Mesoporous Mater. 48 (2001) 279.

[14] S. Yasaki, Y. Yoshino, K. Ihara, K. Ohkubo, US Patent 5,208,206 (1993).

[15] M. Valentini, G. Groppi, C. Cristiani, M. Levi, E. Tronconi, P. Forzatti, Catal. Today 69 (2001) 307.

[16] A.E.W. Beers, T.A. Nijhuis, F. Kapteijn, J.A. Moulijn, Microporous Mesoporous Mater. 48 (2001) 279.

[17] E. Miró, L. Gutiérrez, J. Ramallo, F. Requejo, J. Catal. 188 (2) (1999) 375.

[18] V. Starov, V. Zhdanov, M. Meireles, C. Molle, Adv. Colloid Interface Sci. 96 (2002) 279.

[19] W. Kolb, R.L. Cerro, Chem. Eng. Sci. 46 (9) (1991) 131.

[20] A. Ribotta, M. Lezcano, M. Kurgansky, E. Miró, E. Lombardo, J. Petunchi, C. Moreaux, J.M. Dereppe, Catal. Lett. 49 (1997) 77.