

## Cobalt-Exchanged Mordenite onto a Cordierite Honeycomb for SCR-NO

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*Structured catalysts were prepared by deposition of cobalt-exchanged mordenite films on the walls of cordierite monolith channels either by wash coating or by hydrothermal synthesis. The aim of this work is to analyze different deposition techniques and their influence on the catalytic activity. The catalytic activity of the structured materials is compared with that of zeolite powder. The hydrothermal synthesis was performed in situ in a pressured autoclave reactor varying the reaction conditions (time, stirring degree). This technique consists in the crystallization of mordenite on the cordierite honeycombs employed as a substrate. In order to analyze the stirring effect, some of the samples were synthesized by stirring while others were treated in a stagnant medium. The influence of time on reaction was estimated by sampling at regular time intervals. Deposition by impregnation (wash coating) was also performed by immersing the monolith into a suspension (20–40 wt.%) with Co-exchanged mordenite. The wash coating was performed under different conditions (suspension concentration, incorporation of agglutinants, number of immersions) to obtain a zeolite coating active and selective as catalyst for nitric oxide selective reduction with hydrocarbons. The samples obtained by either method were characterized by scanning microscopy, TPR, XRD, and catalytic activity for the SCR of NO<sub>x</sub> with propane.*

**Keywords** Co-MOR catalyst; Structured catalyst; SCR-NO with propane; Zeolite wash coating

### Introduction

Structured catalysts have found many applications in combustion and environmental uses. Some important industrial applications of these materials are the control of car exhaust emissions, the removal of nitrogen oxides from flue gases, and the control of industrial emissions (Cybulsky and Moulijn, 1994, 1998; Heck and Farrauto, 1995; Saracco and Specchia, 1994). The commercial catalyst is used in the form of monoliths, with geometry and design specific for the different applications. The main advantages of monolithic catalysts with respect to conventional packed beds are: very low pressure drop, higher geometric surface areas (specifically advantageous

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for the selective catalytic reduction (SCR) process), attrition resistance, and a low tendency to ash plugging.

Honeycomb monoliths consist of a monolithic matrix made of cordierite coated with catalytic material. Different authors (Iwamoto and Hamada, 1991; Armor, 1995; Jansen et al., 1993) have shown that metal-exchanged zeolites are effective for the SCR of NO by hydrocarbons. The use of zeolite catalysts for NO<sub>x</sub> reduction with distinct structures has been covered in the patent literature, namely, mordenite, clinoptilolite, and pentasil, but few articles have been published in the scientific literature.

There are three ways to prepare the monoliths: zeolite films grown on cordierite by synthesis in situ (Basaldella et al., 2001; Wang et al., 2001), catalytic materials wash coated on cordierite (Irandoost and Andersson, 1988; Zamaro and Miró, 2003; Zamaro et al., 2005), and massive extruded zeolite monoliths (Jansen et al., 1993; Bahamonte et al., 2003).

In this work, honeycomb monolith catalysts were prepared by deposition of cobalt-exchanged mordenite films on the walls of cordierite monolith channels either by wash coating or by hydrothermal synthesis. The goal of this work was to analyze different deposition techniques and their influence on the catalytic activity for SCR-NO with propane.

## Experimental Section

### *Preparation of Wash-Coated Monolith*

Cordierite monoliths with a density of 62 cells/cm<sup>2</sup> of square section were dipped in slurry composed of a solution of 17 to 30% w/w Na-mordenite. The preparation of suspensions was carried out by water addition (exact amount) on solid components and subsequent homogenization by magnetic stirring at room temperature. The characteristics of the prepared slurry are reported in Table I.

The predetermined wash-coat loading was reached with successive dipping-blowing cycles, followed by drying at 120°C and calcinations at 450°C for 2 h in O<sub>2</sub> stream. After each impregnation the suspension excess was removed in air current, and the monolith was weighed to evaluate the catalyst load. By means of this process, monoliths with loads between 17% and 30% were obtained. Finally, catalysts were exposed to an accelerated test for one hour in an ultrasound bath with water to evaluate film stability, according to the method of Zamaro (2005). Film

**Table I.** Characteristics of the suspension

Suspension denomination	I	II	III	IV
H <sub>2</sub> O (mL)	14,0	12,62	23,74	10,0
Zeolite (g)	6,0	5,41	4,7	2,24
Ludox HS-40 (g)	0,0	5,86	5,09	1,06
% Zeolite	30,0	22,6	14,0	16,8
% SiO <sub>2</sub>	0,0	9,7	6,0	3,1
SiO <sub>2</sub> /zeolite	—	0,43	0,43	0,19
%Total solids	30,0	32,3	20,0	20,0

stability was determined by weighing the sample before and after the ultrasound treatment. The test was performed on ultrasound cleaning equipment, Sonicator SC-120, of 60 kHz frequency, 0.5 ampere, and 220 volts. Colloidal SiO<sub>2</sub> (39.5% of SiO<sub>2</sub>, Ludox HS-40, DuPont) was used as a binder in order to obtain a wash coat of zeolite anchored to the cordierite surface.

### ***Preparation of Zeolitic Film by Hydrothermal Synthesis***

A mordenite/cordierite monolith was in situ synthesized by the hydrothermal technique. This technique consists in the crystallization of zeolite on the cordierite employed as a substrate.

The zeolite was grown on the small monolith (nine channels, 2 cm length) within controlled and selected time and temperature conditions. A piece of cordierite monolith was coated with a layer of aluminosilicate gel having a molar composition 6 Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>:30SiO<sub>2</sub>:780 H<sub>2</sub>O. Then, the hydrogel was transferred to a 50 mL stainless steel autoclave and the cordierite modules were added to it. Previously, the monolith was immersed in the solution and treated with ultrasound for 3 min to promote zeolite uniform growth on the monolith wall. The autoclave was placed in an air-heated oven at 170°C operated with and without stirring for one to four days. After crystallization, the monoliths were washed with water, dried at 120°C, and exposed to ultrasound to remove the material excess of the channels. The zeolite load on the cordierite substrate was determined from the difference in mass of the substrate before and after synthesis. In order to analyze the stirring effect, some of the samples were synthesized by stirring while others were treated in a stagnant medium. The influence of time on reaction was estimated by sampling at regular time intervals.

### ***Catalyst Preparation***

The Na-mordenite film onto the monoliths was exchanged with Co<sup>+2</sup> active phase. A 0.025 M solution of Co acetate was used, which was maintained in stirring for 24 h, at room temperature and pH = 7. Then the samples were filtered, washed with deionized water, and dried at 120°C for 24 h. Finally, catalysts were calcined at 450°C following a predetermined heating program.

For comparison, the same process was followed to exchange Co<sup>+2</sup> in the mordenite powder obtained as residue from the hydrothermal synthesis and from the suspension used to impregnate monoliths.

### ***Characterization of Powder and Structured Catalysts***

The morphology and the homogeneity of the zeolitic films on the cordierite were characterized by scanning electro microscopy (SEM) (Philips model SEM 505 with analyzer EDAX). The purity and identification of the synthesized mordenite were determined by X-ray diffraction (XRD) (Philips PW 1732/10).

The mordenite load on a cordierite substrate was determined from the difference in mass of the substrate before and after the deposition or synthesis.

Temperature programmed reduction (TPR) determined the Co active species. The measurements were carried out in conventional flow equipment fed with a gaseous mixture containing 10% hydrogen in nitrogen. Experiments were performed by

using a quartz reactor containing 0.03 g of catalyst in a flow of  $20 \text{ cm}^3 \text{ min}^{-1}$ . The temperature was increased from room temperature up to  $1000^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . The  $\text{H}_2$  consumption was analyzed by a thermal conductivity detector (TCD). The effluent gas was passed through a trap placed before the detector in order to remove water from the exit stream.

### *Catalytic Evaluation*

Powder and monolithic catalysts were evaluated in a fixed-bed reactor built in quartz, for the selective catalytic reduction (SCR) of NO with propane. A wash-coated monolith of  $3 \times 3$  cells and 2 cm length was placed inside the reactor and the free space between the monolith and the walls of the reactor was filled with silica carbide to avoid flow maldistribution. The temperature range chosen was from  $200^\circ$  to  $700^\circ\text{C}$  and the gas hourly space velocity (GHSV) was between 15000 and  $31000 \text{ h}^{-1}$ , calculated by the catalyst mass in the monolith. In this way, catalytic results obtained with monoliths can be compared with the powder zeolites. The composition of the reacting stream was 1000 ppm of propane, 1000 ppm of NO, and 2–10% of  $\text{O}_2$ . The water effect on the conversion was determined by addition of 6% water vapor in the reactor feed. The gaseous mixtures were analyzed in a chromatograph on-line using a CTR1 (Alltech) column at  $40^\circ\text{C}$ , using a thermal conductivity detector and a He flow of  $20 \text{ cm}^3/\text{min}$ .

The conversions of NO ( $X_{\text{NO}}$ ) and hydrocarbon ( $X_{\text{CH}_4}$ ) were calculated from  $\text{N}_2$  and  $\text{CO}_2$  production, respectively.

## Results and Discussions

### *Wash-Coated Catalyst*

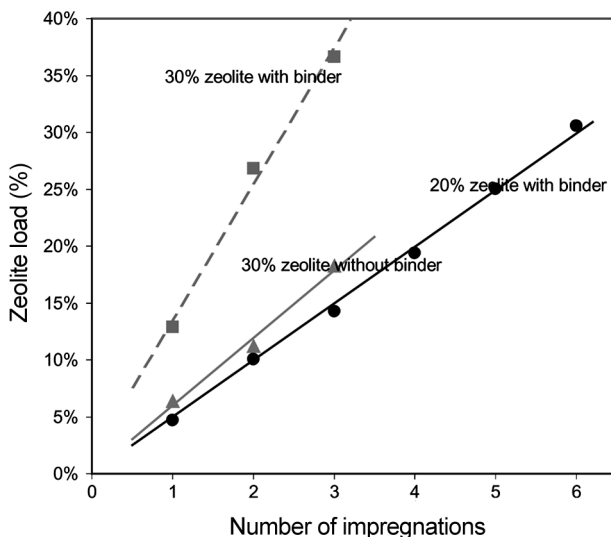
The amount of zeolite loaded on the monolith is an important trend in the preparation of structured catalyst. Table II summarizes the amounts of zeolite wash-coating after calcinations at  $450^\circ\text{C}$ . By operating with different zeolite concentrations in the slurry and by varying the number of impregnations, it is possible to regulate the zeolite loaded in the monolith. In this work, monoliths with zeolite loads between 4% and 37% were obtained by varying the wash-coating procedure conditions.

**Table II.** Amounts of zeolite load on wash-coated monoliths

Monolith	Impregnation steps	Zeolite load %	Film thickness $\mu\text{m}$
M I <sup>a</sup>	2	17.5	
M-II-1	1	12.8	16
M-II-2	2	26.0	32
M-II-3	3	33.3	56
M-III-3	3	14.2	
M-III-6	6	30.5	
M-IV-4	4	19.8	

Roman number corresponds to slurry composition.

<sup>a</sup> Impregnation without binder.

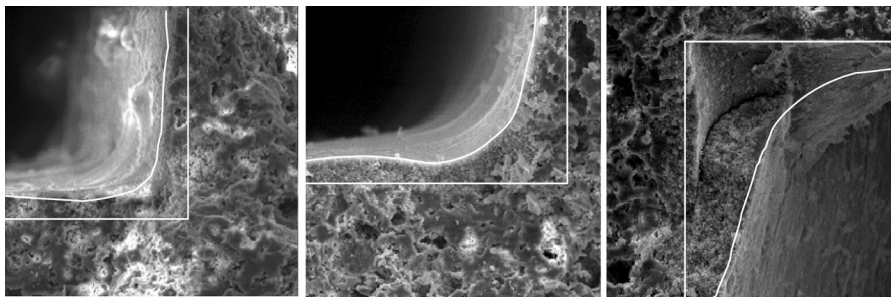


**Figure 1.** Total zeolite load as a function of the number of impregnations.

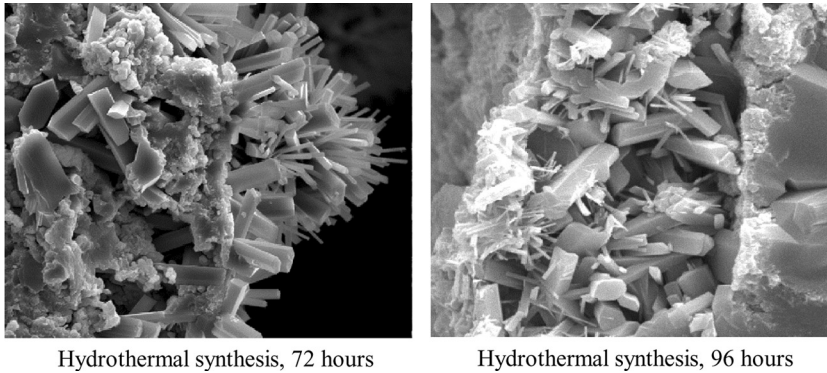
The binder addition was a necessary requirement to obtain a stable film. The zeolite wash coating without binder proved to be unstable when it was treated with ultrasound for 1 h, with the almost total loss of the zeolitic film. Previous studies (Boix et al., 2003) indicate that the addition of colloidal silica improves the adherence of ferrierite wash coat.

Figure 1 shows the effect of the number of immersions, the solid contents of slurry, and the absence or presence of the binder on the zeolite loaded in the monolith, with a lineal ratio among variables. The binder addition increases the zeolite content onto the monoliths for equal solid concentration. These results are coincident with those previously obtained by Zamaro and Miró (2003).

The morphology of the zeolitic film was determined by SEM, noting that in order to obtain higher film homogeneity, it is more convenient to use lower suspension concentration and larger number of immersions. Figure 2 shows the image of the zeolitic film obtained by impregnation of a monolith by using different numbers of immersions in a suspension of equal solid concentration. It is possible to see that material accumulation in the channel corners was generated by successive immersions; the channel form varies progressively from the initial square form up to forms more



**Figure 2.** Morphology variation with the number of impregnations.



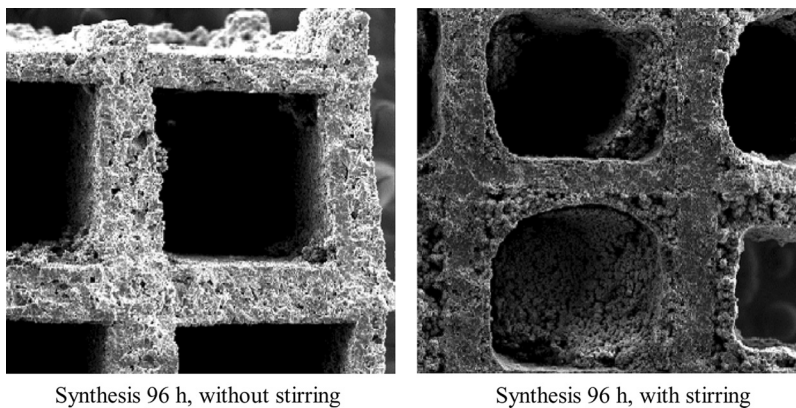
**Figure 3.** Effect of synthesis reaction time over mordenite crystallization.

or less circular. This behavior can be explained by the flow lines of the shift of a viscous fluid by an air bubble inside a capillary of square section (Kolb and Cerro, 1991).

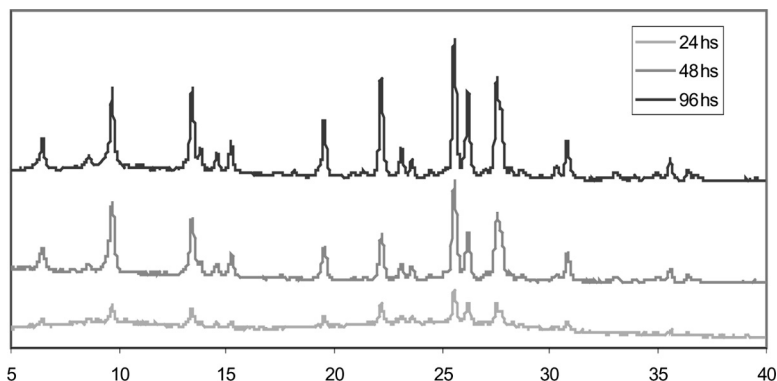
### *In Situ Hydrothermal Synthesis*

The crystallization of mordenite using cordierite as substrate was performed by an in situ hydrothermal synthesis method. During the preparation of the zeolite film by this technique, the reaction time and the stirring strongly affect the morphology. The zeolite film is highly influenced by the reaction time. Working at 170°C, the crystallization starts with formation of isolated crystalline aggregates, while the compact film was obtained after 96 h. Figure 3 shows the film morphology as a function of the reaction time for 72 and 96 h.

Another variable affecting the characteristic of the synthesized film was the stirring, which had an effect on the material load and its distribution. Thus, the coating thickness is larger when operating with stirring (Figure 4), but, in these conditions, the obstruction of some channel was observed. This behavior could be explained by a higher access of the reagents to the interior of the channels by the effect of stirring, which would favor the reaction advance. The most uniform films thicknesses were obtained by zeolite synthesis without stirring, which is attributed to a more



**Figure 4.** Load variation with stirring.



**Figure 5.** Evolution of XRD spectra for different synthesis times.

controlled reaction rate when the system operates in these conditions. By this technique, it is very difficult to control the zeolite film thickness.

The sample synthesized during 96 h without stirring shows a zeolite load of 40% and a film thickness in the range of 30 to 50  $\mu\text{m}$ . Good adherence between the zeolite film and cordierite was achieved in this sample. The film was stable during the catalytic test.

Figure 5 shows the evolution of the diffractograms of the synthesized film on monoliths at different reaction times. It can be observed that mordenite was the only crystalline phase grown during the synthesis. When comparing bibliography data (Szostak, 1992) it is possible to note that in the samples of shorter reaction time, the film presented a crystalline structure like that of the mordenite. The mordenite load increases with the reaction time. The relatively lower intensity of the mordenite XRD peaks indicates a lower zeolite load on the monoliths.

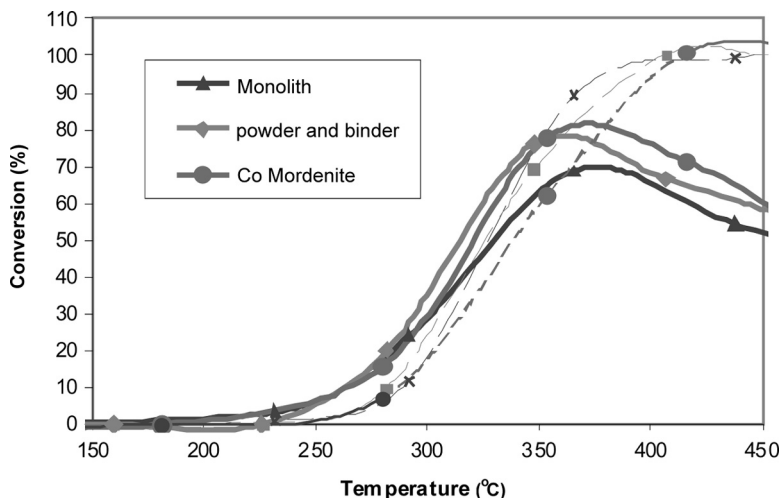
In the operated conditions, the mechanical resistance of the synthesized films was very high, resisting with success accelerated deterioration tests performed by treatment with ultrasound.

### ***Catalytic Evaluation of Monoliths***

In order to determine the catalytic behavior of monoliths obtained by both techniques, the reaction of SCR of NO with propane in oxygen excess was used. The monolithic catalyst activities were compared with the zeolite powder as residue of the hydrothermal synthesis, with the (mordenite + binder) powder and with a commercial mordenite. All zeolitic materials were exchanged with  $\text{Co}^{+2}$ , which is the active phase for the reaction.

In Figure 6, the catalytic activities of wash-coated monolith and the powder catalysts with and without binder are compared, for the same residence time. The residence time for the monolith was related to the zeolitic film mass. An important similarity in the catalytic behavior of the three samples was observed.

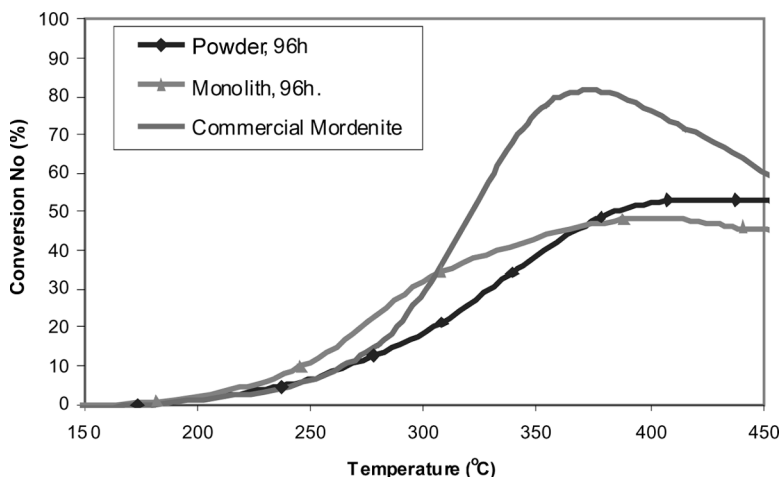
With respect to the maximum conversion of NO to  $\text{N}_2$ , it was proved that obtained values are within usual values for the Co-MOR catalyst (Correa et al., 2003), with a value slightly lower for the monolith with respect to the catalyst in powder. These results indicate that the catalyst supported on the monolith neither significantly modifies its activity nor presents diffusion limitations while it allows



**Figure 6.** Catalytic performance of wash-coated Co-MOR catalysts. NO conversion (solid line) and propane combustion (dashed line). Gas composition: 1000 ppm NO, 1000 ppm propane, 2% O<sub>2</sub>, balance: He;  $m_{\text{cat}} := 0.1 \text{ g}$ ., total flow rate:  $30 \text{ cm}^3 \cdot \text{min}^{-1}$ .

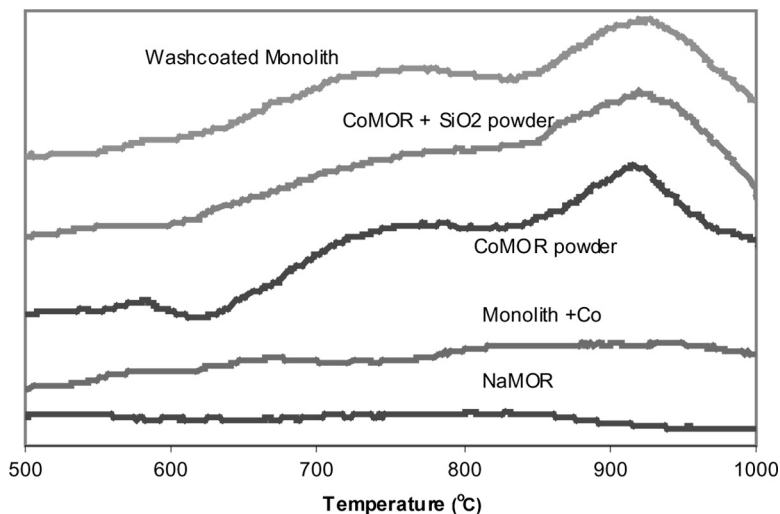
the use of operational advantages of these supports. On the other hand, from the curves for powder and binder and Co-mordenite, it can be deduced that the colloidal silica addition as binder does not significantly affect the catalyst performance. This fact was attributed (Boix et al., 2003) to the interaction of small silica particles with zeolite, thus avoiding the formation of cobalt oxides during the reaction.

Figure 7 shows the catalytic activities of the monolith film obtained by 96 h hydrothermal synthesis without stirring, of the mordenite powder during this same experimental run, and of the Co catalyst on commercial mordenite. Again, the residual powder and the monolith obtained by synthesis present similar activities. However, NO conversion values are slightly lower in synthesized than in the wash-coated films.



**Figure 7.** Catalytic performance of Co-MOR catalyst. Gas composition: 1000 ppm NO, 1000 ppm propane, 2% O<sub>2</sub>, balance: He;  $m_{\text{cat}} := 0.06 \text{ g}$ ., total flow rate:  $18 \text{ cm}^3 \cdot \text{min}^{-1}$ .





**Figure 8.** Temperature programmed reduction of Co-MOR catalysts.

The active species present in tested catalysts were characterized by TPR. Figure 8 shows thermograms for particulate matter, the monoliths studied, the commercial zeolite, and the cobalt supported on cordierite. It can be observed that all samples of Co-mordenite present two signals at 750° and 900°C, attributed to  $\text{Co}^{+2}$  exchanged and located in different channels of the zeolite crystalline structure (Bustamante et al., 2002). The similarity between thermograms of the powder and the monoliths would indicate that the exchange level in both materials is equal. In the Co/cordierite, as in the case of the commercial Na-mordenite, no signals were observed, indicating that the Co is supported in its major part on the zeolite and not on the ceramic support. On the other hand, the commercial zeolite does not add signals to the thermogram of the Co-MOR.

In the thermogram of the in situ synthesized material (not shown) three signals are observed, two of them already described for the exchanged  $\text{Co}^{+2}$  although shifted toward higher temperature and a peak at 550°C attributed to CoO. The CoO presence can be responsible for the lower catalytic of the in situ synthesized film than the commercial zeolite.

## Conclusions

In the operation conditions used in this work, more homogeneous and stable monoliths coated with mordenite are obtained when a binder is added to the suspension to obtain the material by wash coating and when the zeolite synthesis is performed in a medium without stirring. The binder addition increases the zeolite content deposited for equal suspension concentration, and the addition of colloidal  $\text{SiO}_2$  improves the film adherence. In the zeolite obtained by hydrothermal synthesis, the reaction time and the stirring strongly affect the film morphology.

The catalytic performance of Co-mordenite monoliths obtained by both techniques was as good as those for the powder form, which indicates that there are no diffusive restrictions in the film.

The main disadvantage of zeolite hydrothermal synthesis is the complexity of this method as compared with the wash-coating technique.

### Acknowledgments

The authors wish to acknowledge the financial support received from UNLP, UNL, CONICET, and ANPCYT.

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