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Preparation of supported Cu/ZSM-5 zeolite films for DeNO$_x$ reaction

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Abstract

This work reports the in situ synthesis of ZSM-5 zeolite films on cordierite and the performance of a Cu/ZSM-5-coated monolithic catalyst in the lean NO$_x$ reduction reaction. At the end of the hydrothermal crystallization, a zeolite/cordierite composite was obtained which consists of a continuous zeolite film that strongly attaches to the sustrate surface. The monolithic catalysts so prepared are active for the reduction of NO. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: ZSM-5 zeolite; Films; Copper; NO$_x$ reduction

1. Introduction

The role of zeolites as adsorbents and catalysts in environmental technology is rapidly expanding, and it is known that copper-containing ZSM-5 zeolites show special NO$_x$ converting properties for the Selective Catalytic Reduction of NO (SCR) with hydrocarbons in excess of oxygen [1]. However, the practical application of this process requires efficient gas and solid contact and a low-pressure drop. Monolithic reactor configurations usually overcome these operational problems and they are the reasons that they are employed extensively in controlling automobile [2] and industrial NO$_x$ emissions [3,4]. Zeolite films supported on honeycomb structures are examples of these types of catalysts, so great interest has been directed to the preparation of zeolite films on different substrates owing to their uniform pore size, resistance to high temperature and the low pressure drop it causes [5].

Despite such advantages, monolithic catalysts involving zeolite coatings in situ have not been studied extensively in relation with the SCR reduction of NO.

This paper reports the results of investigations of the formation of ZSM-5 zeolite films on cordierite and the catalytic performance of Cu/ZSM-5-coated monolithic catalysts in the lean reduction reaction of NO$_x$.

2. Experimental

2.1. Catalyst preparation

The crystallization of ZSM-5 zeolite using cordierite as sustrate was performed by the method of "in situ" synthesis.

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Table 1
Applied molar composition for hydrothermal synthesis

Na/ (Na + TPABr)	TPA/ SiO_2	OH/ SiO_2	Na/ SiO_2	H_2O/ SiO_2	Si/ Al	Al/ Na
0.58	0.1	0.14	0.14	4.1	∞	0

The cordierite samples used in this work consisted of small monoliths (nine channels cross-section, 1 cm long) having a density of 62 channels per square centimeter.

To obtain the appropriate material, the zeolite was grown on the support within the controlled conditions of time and temperature selected from a previous contribution [6]. The hydrothermal synthesis of ZSM-5 zeolite films was performed as follows: a commercial water glass solution (SiO_2, 26.8 wt.%; Na_2O, 9.2 wt.%; and H_2O, 64 wt.%) was added to a stirred mixture of tetrapropylammonium bromide and sodium hydroxide in solution, to find a hydrogel whose composition is shown in Table 1. Then, the hydrogel was transferred to a 50-ml stainless steel autoclave and two cordierite modules were added to it. The autoclave was placed in an air-heated oven for 48 h, and operated under stirring. The selected crystallization temperature was $170 \pm 3°C$. Once the reaction was produced, the autoclave was cooled down and the samples washed and dried at 110°C. The nature of the composites so obtained were confirmed by X-ray diffraction (XRD) and absorption infrared spectrometry. The diffraction diagrams were recorded using a Philips PW 1732/10 equipment and CuKα radiation and a Ni filter, at a rate of 2°/min. Infrared spectra were recorded in a Bruker IFS66 spectrometer, using the KBr technique. The zeolite film was examined by scanning electron microscopy (SEM) using a Philips SEM 505 microscope. The chemical analyses for estimating the Si/Al ratio were carried out using energy-dispersive X-ray analysis (EDX) on a DXPRIME 10 system connected to the scanning electron microscope.

The composites prepared here were calcined in air at 540°C to eliminate the template. The copper exchange was done in an aqueous solution (solid/liquid ratio = 10 gl^{-1}) containing Cu $(CH_3COO)_2$ in the concentration required to obtain the desired amount of copper on the zeolite. This stage was done at room temperature for 24 h without stirring. The copper exchange level was determined by EDX.

2.2. Catalytic test

The activities of zeolite-coated monolith in the SCR of NO with propane were carried out in a fixed bed reactor. The catalyst was placed into a 1/3 in. OD quartz tube. Quartz wool was packed between the monolith and the tube so as to position the monolith cross-section facing the inlet gas flow. The reactant gas contained 1000 ppm of C_3H_8, 750 ppm of NO and 0–2% of O_2, balanced with He. The reactor was fed at a flow rate of 50 cm^3 min^{-1} (GHSV = 25,000 h^{-1}). The temperature range studied was 200–700°C.
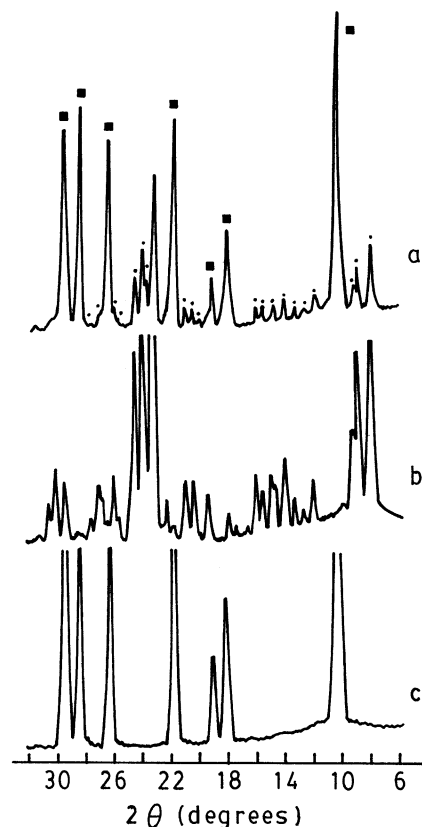

Fig. 1. XRD patterns for: (a) ■ cordierite + ● zeolite (substrate + film); (b) pure zeolite (film); (c) cordierite (substrate).
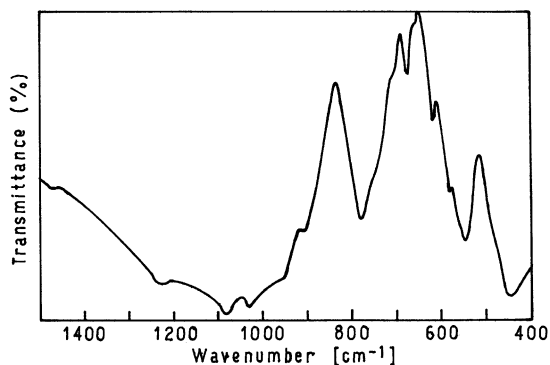
Fig. 2. IR pattern corresponding to the composite (cordierite + zeolite).

The inlet and outlet reactor gases were analyzed in a Shimadzu GC-8 gas chromatograph fitted with a thermal conductivity detector. Gas chromatographic analyses were done at 40°C, using a CTR1 (Alltech) column packed with Porapack mixture and 5A molecular sieve. Helium gas (20 cm^3 min^{-1}) was used as carrier.

3. Results and discussion

Fig. 1 shows XRD powder patterns of the coated monolith obtained after 48 h of hydrothermal treatment as well as those of the uncoated sustrate. It can be seen that ZSM-5 is the only crystalline phase grown during the hydrothermal reaction. Moreover, absorption FTIR spectrum of the crystals deposited onto the cordierite module (Fig. 2) shows the charac-
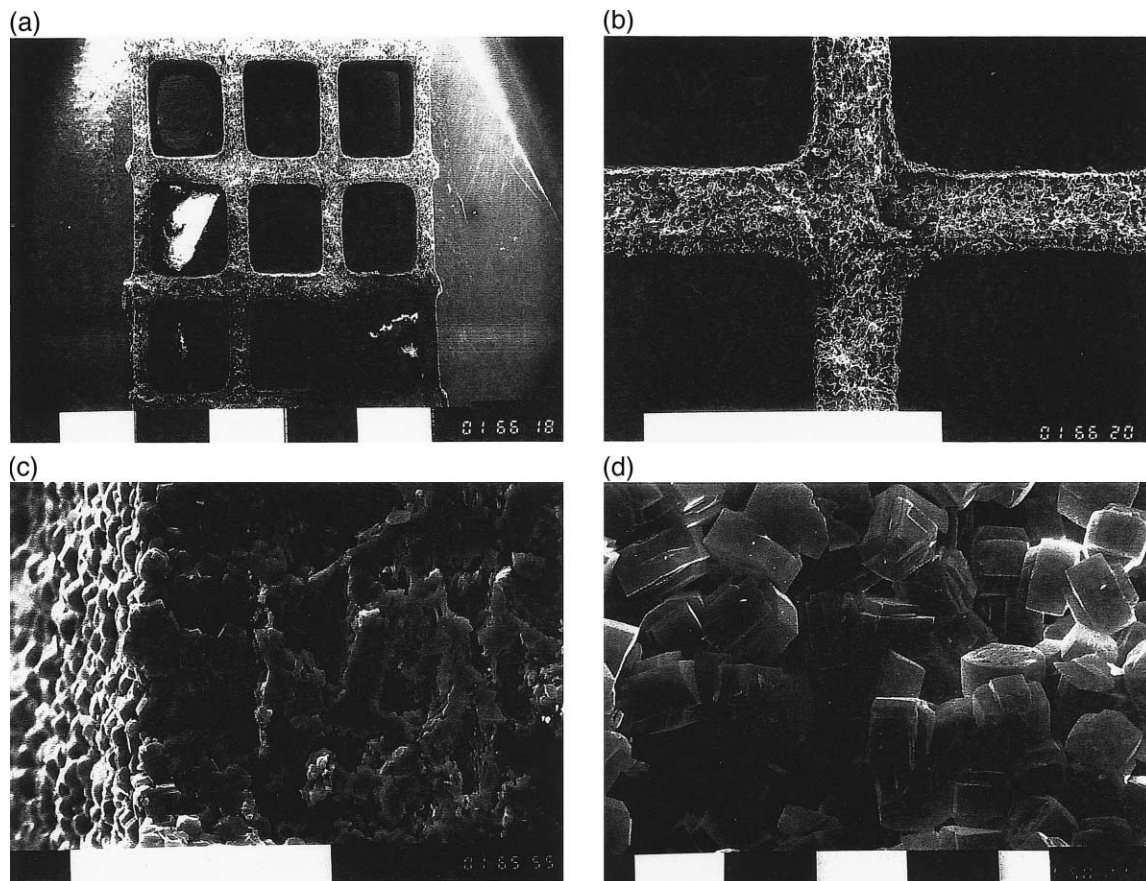

Fig. 3. SEM micrographs of a coated monolith after 48 h reaction time. (a, b and c) Cross-sections; (d) top-view of the coated surface.

teristic absorption bands [7] of ZSM-5 at 1220 and 540 cm^{-1}.

For coated monolith samples obtained during the course of the hydrothermal treatment, the SEM analysis showed the development of a continuous film adhered to the substrate surface. Film thickness was determined by studying monolith cross-sections (Fig. 3a, b and c). After hydrothermal synthesis of 48 h the film was 50 μ thick (Fig. 3b), made up by an arrangement of 8–10 μm particles, presenting one of the morphologies usually described for ZSM-5 zeolite crystals (Fig. 3d). EDX analyses of these crystals yielded Si/Al ratios in the range of 17–23 and an average Cu/Al ratio of 0.46. According to these results, Al leached from the support is incorporated in the zeolite crystals.

The temperature and O_2 partial pressure effects on the conversions of NO and hydrocarbon are shown in Figs. 4 and 5, respectively. Fig. 4 exhibits the increase in the conversion of NO, obtained when the reaction temperature was increased from 250°C to 500°C, and this behavior is similar to that of powder Cu/ZSM-5 catalyst [6]. The temperature range for maximum activity of coated Cu/ZSM-5 catalyst was 400–550°C. Experimental data at higher temperature showed a decrease in the conversion of the NO-SCR reaction owing to increasing competition with hydrocarbon combustion.

The conversion of NO-SCR-HC reaction was accelerated by oxygen added to the reaction mixture (Fig. 4a). The reduction of NO to N_2 was not observed in the absence of O_2 and the maximum conversion of NO was obtained for an O_2 content of 0.3%, $R_{ox/red} = 0.675$, as is shown in Fig. 4b. Further O_2 addition reduced the activity but to a somehow stable value at higher partial pressures.

In order to compare our catalyst with that prepared by conventional methods, we analyzed results reported by Cho [8]. In view that in the experimental conditions some differences are present, the comparison is not easy. Our catalyst reached lower NO conversion although it has the advantage of showing a wider temperature window of maximum activity (350–500°C) than those of catalyst reported by Cho for the reduction of NO by propane.

Fig. 5 allows us to observe that hydrocarbon combustion is more important at higher O_2 partial pressure, where almost all the propane was converted
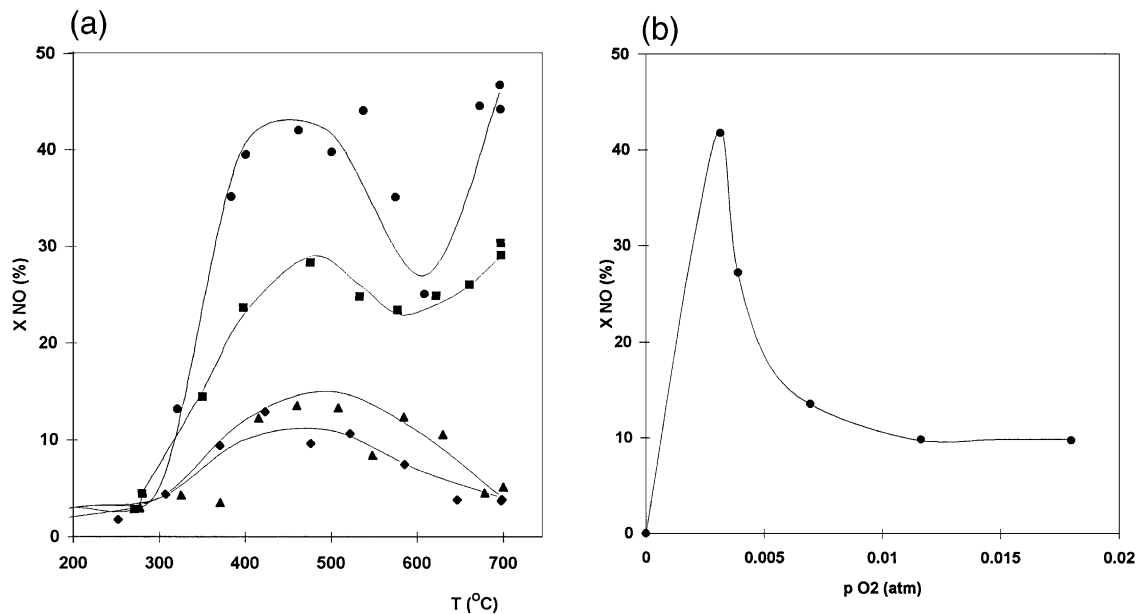

Fig. 4. Selective catalytic reduction of NO with C_3H_8. Effect of temperature (a) and O_2 (b) content on the NO conversion. [●] = 0.3%, [■] = 0.4%, [▲] = 0.8%, [◆] = 2% (v/v).
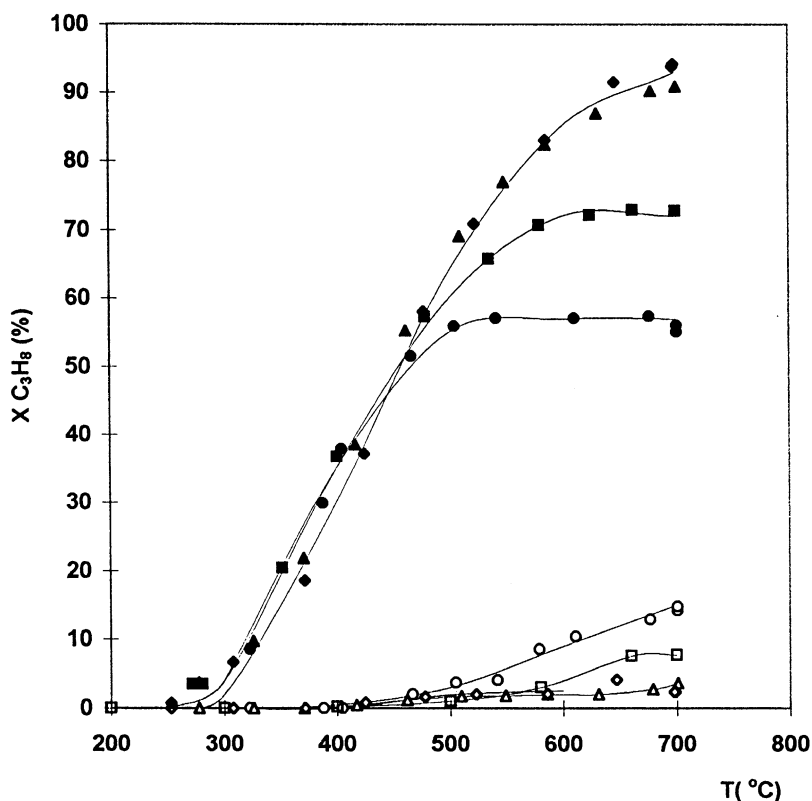
Fig. 5. Selective catalytic Reduction of NO with C_3H_8. Effect of temperature and O_2 content on the propane conversion. Symbols: closed, total combustion reaction (CO_2 formation); open, partial oxidation (CO formation) $[\bullet, \circ] = 0.3\%$, $[\blacksquare, \square] = 0.4\%$, $[\blacktriangle, \triangle] = 0.8\%$, $[\blacklozenge, \lozenge] = 2\%$.

to CO_2 and H_2O (closed symbols). Furthermore, temperatures above 600°C produce partial oxidation of propane to CO.

At the temperature corresponding to CO formation, it is also observed that a second increase of conversion of NO starts, suggesting that the NO + HC reaction is more favored than propane combustion.

4. Conclusions

These studies demonstrated that micron sized ZSM-5 films can be obtained on cordierite modules by direct crystallization at 170°C in the presence of aluminosilicate gels. Appropriate molar ratios were used in order to produce a continuous film that left no support areas uncovered.

It was shown that the Cu/ZSM-5 coated module so obtained leads to a promising material for the SCR-HC process. It was proved to be an active catalyst for the selective reduction of NO with propane at temperatures below 600°C. Besides the catalytic performance was found to be strongly affected by the presence of oxygen in the reactor feed.

References

[1] J.L. d'Itri, W.M.H. Sachtler, Catal. Lett. 15 (1992) 289.
[2] M. Iwamoto, N. Mizuno, H. Yahiro, in: L. Guczi (Ed.), Proc.

10th Int. Congress Catal., Budapest, 1992. Elsevier, 1993, p. 1285.

[3] J.C. Jansen, W. Nugroho, H. van Bekkum et al., in: R. Von Ballmoos (Ed.), Proc. 9th Int. Zeol. Conf., Montreal, 1992. Butterworth-Heineman, USA, 1993, p. 247.

[4] M.J. Den Exter, H. van Bekkum et al., Zeolites 19 (1997) 13.

[5] J.N. Armor, Appl. Catal. 78 (1991) 141.

[6] C. Quincoces, A. Kikot, E.I. Basaldella, M. Erben, M.G. González, Ind. Eng. Chem. Res. 38 (1999) 4236.

[7] G. Coudurier, C. Nacache, J.C. Vedrine, J. Chem. Soc., Chem. Commun. (1982) 1413.

[8] B.K. Cho, J. Catal. 142 (1993) 418.