

# A Novel Method for Synthesis of ZSM-5 Coatings on Monolithic Cordierite Substrate

WANG, Ai-Qin\*(王爱琴) LIANG, Dong-Bai(梁东白) ZHANG, Tao(张涛)

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, China

ZSM-5 coatings have been synthesized onto a monolithic cordierite substrate by an environmental friendly and high coating selectivity method—Vapor Phase Transport (VPT). With this method, an aluminosilicate gel coated onto the monolithic cordierite substrate has been transformed into a ZSM-5 layer under vapors of *n*-butylamine and water. *n*-Butylamine played a key role in the forming of ZSM-5 layer on the cordierite substrate. The ZSM-5/cordierite monolith composites prepared by this method were ion-exchanged with  $\text{Cu}^{2+}$  and tested for the selective catalytic reduction of NO by propane. The  $\text{deNO}_x$  activities of Cu/ZSM-5 monolith catalysts were not only dependent on the ion-exchange methods, but also on the ZSM-5 loading of the monolith catalysts. The best result was obtained over the Cu(B3)/ZSM-5 monolith catalyst, which had a ZSM-5 loading of about 13% and was prepared by a pressure exchange procedure. At a temperature of 723 K and a space velocity of 10,000  $\text{h}^{-1}$  (based on the monolith volume), 85% of NO conversion and 93% of  $\text{C}_3\text{H}_8$  conversion were achieved over the Cu(B3)/ZSM-5 monolith catalyst.

**Keywords** ZSM-5 coating, *in-situ* synthesis, VPT, monolith, HC-SCR

## Introduction

Ever since the selective catalytic reduction of NO by various hydrocarbons in the presence of excess  $\text{O}_2$  (HC-SCR) was first reported,<sup>1-3</sup> numerous studies have been conducted using various metal-exchanged zeolites.<sup>4</sup> However, among those reports, most tests were conducted on pellets or granular catalysts, few were over monolith catalysts.

Monolith reactors are widely used in automotive catalytic converters (TWCs).<sup>5</sup> It generally consists of a monolithic cordierite substrate, a washcoat of alumina or zeolites, and the active metals supported on it. Zeolites can be supported onto the cordierite substrate either by dip-coating<sup>6</sup> or by *in-situ* hydrothermal synthesis.<sup>7-10</sup> For the dip-coating technique, the zeolites must be wash-coated onto the cordierite substrate together with some binders to make it strongly adhered to the substrate. However, this procedure usually results in a lowering of the zeolite activity, and the washcoat procedure often requires many repetitions so as to acquire an enough thickness of zeolite layers. The *in-situ* hydrothermal synthesis technique has been widely used in preparing zeolite composite membranes, and this method can generally give a stronger adherence between zeolite layer and the substrate.<sup>11-15</sup> However, during the hydrothermal synthesis procedure, alongside with the forming of a zeolite coating on the substrate surface, zeolite powders will also be inevitably produced at the autoclave bottom, and this will decrease the coating selectivity to some extent.

In our previous paper, we have reported the *in-situ* synthesis of ZSM-5 and Analcime on the monolithic cordierite substrate by hydrothermal technique.<sup>16</sup> In the present paper, we use VPT (Vapor Phase Transport) method, which was first developed by Dong *et al.*<sup>17,18</sup> to the synthesis of ZSM-5 onto monolithic cordierite substrates. And, to show the feasibility of the synthesized zeolite/cordierite monoliths for  $\text{deNO}_x$  applications, the preparation of copper ion exchanged catalysts on the as-synthesized zeolite/cordierite monoliths, and the HC-

\* E-mail: aqwang@dicp.ac.cn

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SCR performance of the catalysts, have also been investigated.

## Experimental

### *Synthesis procedure*

The cordierite monoliths (62 cells/cm<sup>2</sup>) were first cut into cylindrical pieces with a diameter of 16 mm and a length of 25 mm. Before coating, they were calcined at a temperature of 823 K for 3 h. For the preparation of a precursor gel, an aqueous solution of NaOH was added to a given amount of silica sol (25% SiO<sub>2</sub>, provided by Fusun Petrochemical Co., China), and stirred for 2 h at room temperature. Then Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution was added dropwise and stirred for another 2 h. The resulting aluminosilicate gel had a molar composition of 60SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:12.5Na<sub>2</sub>O:5000H<sub>2</sub>O. A monolith substrate piece was then dipped into the gel for 20 min, and after this, it was suspended in the upper part of an autoclave, into which 6 mL of *n*-butylamine (NBA) and 6 mL of H<sub>2</sub>O were added. The autoclave was then transferred into a preheated oven and crystallization was carried out at 443–453 K for 3–7 days. After crystallization, the monolith was washed with hot distilled water and dried at room temperature.

### *Catalyst preparation*

The as-synthesized NaZSM-5/cordierite monoliths were ion-exchanged with the following two different exchange procedures:

A. Conventional exchange procedure: NaZSM-5/cordierite monoliths were ion-exchanged with a 0.01 M copper acetate solution at 353 K for 1 h. The exchange procedure was repeated for 4 or 6 times, and the monolith catalyst prepared by this method was designated as Cu(A1)/ZSM-5 and Cu(A2)/ZSM-5, respectively.

B. Pressure exchange procedure: the exchange was carried out with a 0.01 M copper acetate solution in an autoclave at 423 K for 1 h at autogenous pressure, and this procedure was repeated for twice. The catalyst prepared by this new exchange procedure was designated as Cu(B0)/ZSM-5, Cu(B1)/ZSM-5, Cu(B2)/ZSM-5, and Cu(B3)/ZSM-5, respectively.

Then these catalysts were thoroughly washed with distilled water, dried at 393 K overnight, and calcined at 773 K for 3 h.

### *Characterization of the monolith catalysts*

The mass of the zeolite coating on a cordierite substrate was determined from the difference in the mass of the substrate before and after the synthesis. The crystal structure and the morphology of the zeolite coatings on the cordierite substrate were characterized by XRD (Rigaku Rotaflex Ru-200B) and SEM (Hitachi S-3200N). Cu contents of the monolith catalysts were measured with XRF (Model SRS 3400X).

### *Catalyst test*

Catalytic tests were performed in a single-pass flow reactor at a space velocity of 10,000 h<sup>-1</sup> (based on the monolith volume). The fixed catalyst bed in the reactor was made by inserting the monolithic catalyst sample inside a 17 mm I. D. quartz tube, and the gap between them was filled with quartz wool. The reacting gases were mixed and preheated prior to entering the reactor. The gas flow rate through the reactor was measured and controlled by a mass flowmeter. The composition of the feed gas was as follows: NO 1,000 ppm, C<sub>3</sub>H<sub>8</sub> 1,000 ppm, O<sub>2</sub> 2.0% and the balance of N<sub>2</sub>. Two thermocouples were used to monitor the temperature in the preheating zone and the catalyst bed. The concentrations of the various components of the feed and the effluent gases were analyzed on-line by an analyzer specially designed for automobile gas analysis (FGA 4005, produced by the Fushan Xinyu Instrument Co., China), which is capable of measuring 5 kinds of gaseous concentrations continuously and simultaneously, including NO, O<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>x</sub>H<sub>y</sub>. NO and C<sub>3</sub>H<sub>8</sub> conversions were defined as (inlet NO-outlet NO)/(inlet NO) and (inlet C<sub>3</sub>H<sub>8</sub>-outlet C<sub>3</sub>H<sub>8</sub>)/(inlet C<sub>3</sub>H<sub>8</sub>), respectively.

## Results and discussion

### *Zeolite coating identification*

Fig. 1 shows the XRD patterns of the ZSM-5 coating on the cordierite substrate prepared by the VPT method. Comparing Fig. 1a with Fig. 1b, it can be clearly seen that the five peaks at  $2\theta = 7.92, 8.8, 23.12, 23.8$  and  $24.36$  degree represent the five most strong peaks of ZSM-5 crystals, indicating that after treating with the vapor mixture of NBA (*n*-butylamine) and water, the alu-

minosilicate gel on the cordierite substrate has transformed into ZSM-5 layer. Furthermore, a destruction test by scraping with a sharp tool showed that the ZSM-5 coating was strongly adhered to the cordierite substrate. Compared with the cordierite peaks, the ZSM-5 peaks are very small, since for this sample, the ZSM-5 coating accounts only for about 4.3% of the substrate weight. Fig. 2 is the SEM photographs of different parts on the same ZSM-5/cordierite monolith surface. It can be seen from Fig. 2 that the ZSM-5 crystals are hexagonal or square and have an average size of about  $3 \times 2 \times 10 \mu\text{m}$ . Compared Fig. 2A with Fig. 2B, it can also be seen that although a certain amount of ZSM-5 crystals had grown onto the cordierite substrate, the substrate surface was not completely covered by the ZSM-5 crystals after one synthesis operation. Further experiments showed that after 2 repeated syntheses, the cordierite surface was almost covered by ZSM-5 crystals.

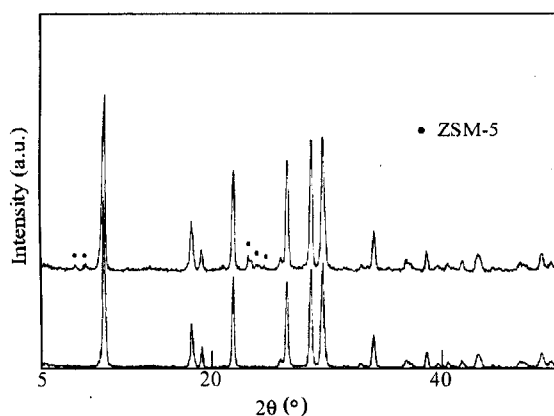


Fig. 1 XRD patterns of (a) cordierite; (b) ZSM-5/cordierite composite.

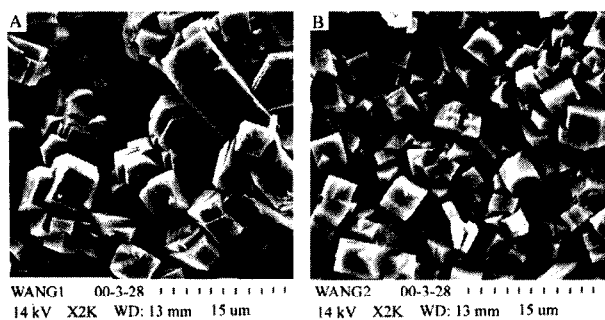


Fig. 2 SEM photographs of different parts on the same ZSM-5/cordierite monolith surface.

#### Effect of vapor phase composition on the zeolite coating

Table 1 lists the products formed on the cordierite substrate when different vapor-phase compositions were employed, and Fig. 3 shows the XRD patterns of the monoliths when different types of templates were used. It can be seen from Fig. 3 that only when NBA or a mixture of  $\text{Et}_3\text{N}$  (triethylamine) and EDA (ethylenediamine) was used as the template, ZSM-5 peaks appeared in the XRD patterns of the honeycomb monoliths. The other templates used in our work such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , ethanol or  $\text{Pr}_3\text{N}$  (tripropylamine), were not valid in directing the transformation of aluminosilicate gel to the ZSM-5 layer. From Table 1 it is concluded that when the vapor phase was comprised of NBA and water, no matter what the molar composition was, ZSM-5 coatings of good quality were formed on the substrate. Furthermore, the vapor phase composed of NBA and  $\text{H}_2\text{O}$  can be repeatedly used without any side effect on the quality of zeolite coating. This result implied that VPT method is an environmentally friendly synthesis technique.

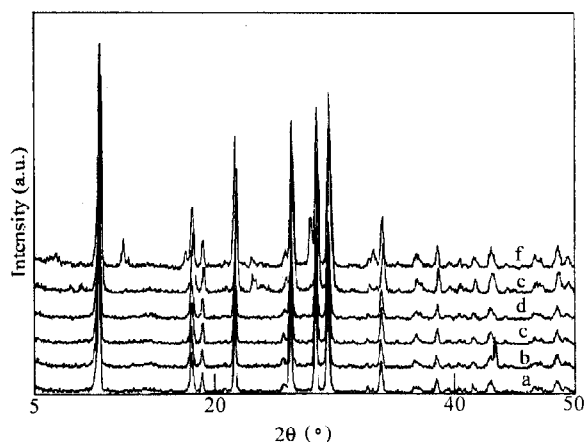


Fig. 3 XRD patterns of monolith honeycombs after VPT synthesis of ZSM-5 using (a)  $\text{H}_2\text{O}$ ; (b) ethanol; (c)  $\text{NH}_3 \cdot \text{H}_2\text{O}$ ; (d)  $\text{Pr}_3\text{N}$ ; (e) NBA; (f)  $\text{Et}_3\text{N}$  + EDA as template.

It is very interesting that when a mixture of  $\text{Et}_3\text{N}$  and EDA, together with water, was employed as the vapor phase, which was similar to the situation of Dong *et al.*,<sup>17,18</sup> a large amount of impurity crystals, with only a little amount of ZSM-5 crystals, was simultaneously formed on the substrate (see Fig. 3f). This is very different from the results reported in the literature,<sup>17-20</sup> in which pure ZSM-5 was produced with  $\text{Et}_3\text{N}$  and EDA as templates by the VPT method. These different results are considered as due to the different substrate systems

used. In their experiments,  $\alpha$ - $\text{Al}_2\text{O}_3$  was used as the substrate, while cordierite was employed in our work. Therefore, in our investigations, NBA may be a more

suitable template for the formation of ZSM-5 coatings on cordierite substrates.

**Table 1** Effect of vapor phase composition on the products formed on the cordierite monolith substrate

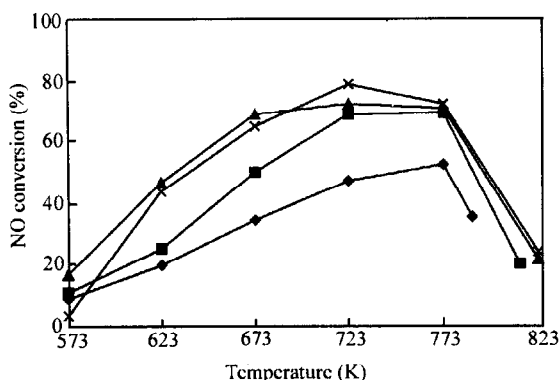
Vapor phase composition (mol)	Product formed on the substrate
0.06 <i>n</i> -butylamine:0.33 $\text{H}_2\text{O}$	ZSM-5 coating
0.01 <i>n</i> -butylamine:0.67 $\text{H}_2\text{O}$	ZSM-5 coating
0.06 <i>n</i> -butylamine:0.33 $\text{H}_2\text{O}$ (reused)	ZSM-5 coating
0.25 $\text{NH}_3$ :0.25 $\text{H}_2\text{O}$	Amorphous aluminosilicate gel
0.25 ethanol:0.25 $\text{H}_2\text{O}$	Amorphous aluminosilicate gel
0.25 $\text{Pr}_3\text{N}$ :0.25 $\text{H}_2\text{O}$	Amorphous aluminosilicate gel
0.10 EDA:0.43 $\text{Et}_3\text{N}$ :0.28 $\text{H}_2\text{O}$	Major impurity crystals + minor ZSM-5 crystals

Gel composition:  $60\text{SiO}_2:\text{Al}_2\text{O}_3:12.5\text{Na}_2\text{O}:5000\text{H}_2\text{O}$ ; Crystallization conditions: 453 K, 7 days.

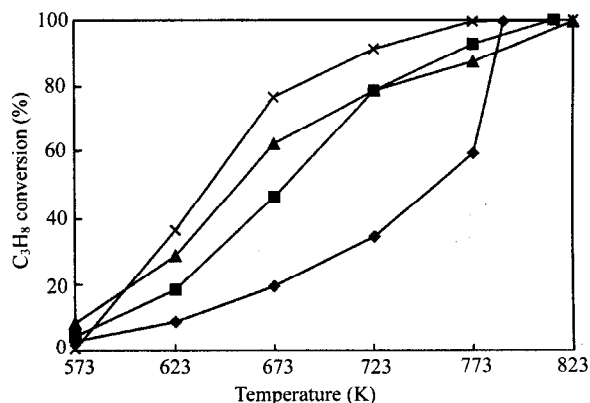
#### Catalytic activity for the reaction of $\text{C}_3\text{H}_8 + \text{NO} + \text{O}_2$

Fig. 4 and Fig. 5 illustrate the conversion of NO and  $\text{C}_3\text{H}_8$  as a function of temperature over the four monolith catalysts that were prepared by different exchange methods. Table 2 lists some preparation parameters of the tested monolith catalysts. Among these four monolith catalysts, Cu(A1)/ZSM-5 and Cu(A2)/ZSM-5 were prepared by the conventional exchange method, while Cu(B1)/ZSM-5 and Cu(B2)/ZSM-5 were prepared by the pressure exchange method. From Fig. 4 and Fig. 5, it can be seen that the NO conversions have the similar dependence upon temperature over the four Cu/ZSM-5 monolith catalysts. Namely, with an increase of the temperature, NO conversion increased and

reached the maximum value at an optimum temperature. After that point, it began to decrease due to the oxidation of  $\text{C}_3\text{H}_8$  with  $\text{O}_2$ . The  $\text{deNO}_x$  activities of the four catalysts followed the order: Cu(B2)/ZSM-5 > Cu(B1)/ZSM-5 > Cu(A2)/ZSM-5 > Cu(A1)/ZSM-5. From Table 2 we know that although the above four monolith catalysts have almost the same zeolite loading, the Cu content of them is very different. The much higher Cu content of the Cu(B1)/ZSM-5 and Cu(B2)/ZSM-5 monolith catalysts than that of Cu(A1)/ZSM-5 and Cu(A2)/ZSM-5 indicated that the pressure exchange procedure dramatically increased the exchange level of  $\text{Cu}^{2+}$ , so resulted in an enhancement of the  $\text{deNO}_x$  activity.



**Fig. 4** NO conversion as a function of temperature over Cu(A1)/ZSM-5 ( $\blacklozenge$ ), Cu(A2)/ZSM-5 ( $\blacksquare$ ), Cu(B1)/ZSM-5 ( $\blacktriangle$ ), and Cu(B2)/ZSM-5 ( $\times$ ). Reaction conditions; NO = 1000 ppm,  $\text{C}_3\text{H}_8$  = 1000 ppm,  $\text{O}_2$  = 2.0%; SV = 10,000  $\text{h}^{-1}$ .



**Fig. 5**  $\text{C}_3\text{H}_8$  conversion as a function of temperature over Cu(A1)/ZSM-5 ( $\blacklozenge$ ), Cu(A2)/ZSM-5 ( $\blacksquare$ ), Cu(B1)/ZSM-5 ( $\blacktriangle$ ), and Cu(B2)/ZSM-5 ( $\times$ ). Reaction conditions; NO = 1000 ppm,  $\text{C}_3\text{H}_8$  = 1000 ppm,  $\text{O}_2$  = 2.0%; SV = 10,000  $\text{h}^{-1}$ .

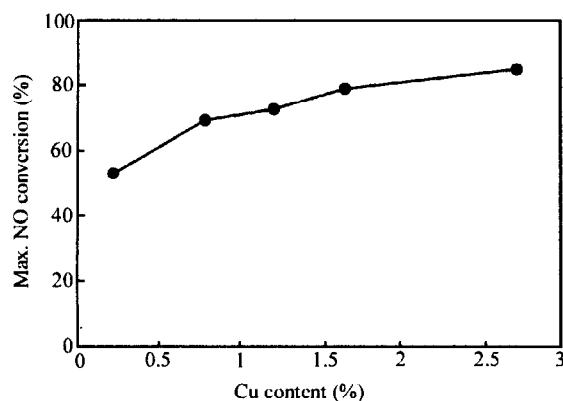
In order to further elucidate the effect of Cu contents on the deNO<sub>x</sub> activities of the tested Cu/ZSM-5 monolith catalysts, the dependence of maximum NO conversion on the Cu contents of the monolith catalysts

was illustrated in Fig. 6. Apparently, with an increase of the Cu content of the monoliths, the Max. NO conversion increased. This result is in accordance with the literature reported.<sup>21</sup>

**Table 2** Some preparation parameters of the four monolith samples

Monolith sample	Monolith volume (mL)	Substrate weight (g)	Zeolite coating weight (g)	Zeolite loading (%)	Cu <sup>2+</sup> exchange condition	Cu content (%)
Cu(A1)/ZSM-5	4.00	2.15	0.08	3.7	353 K, atmospheric pressure, 4 times	0.22
Cu(A2)/ZSM-5	4.48	2.59	0.12	4.6	353 K, atmospheric pressure, 6 times	0.79
Cu(B0)/ZSM-5	5.56	2.87	0	0	423 K, autogenous pressure, twice	-
Cu(B1)/ZSM-5	4.38	2.45	0.08	3.3	423 K, autogenous pressure, twice	1.22
Cu(B2)/ZSM-5	4.09	2.28	0.10	4.3	423 K, autogenous pressure, twice	1.67
Cu(B3)/ZSM-5	3.52	2.00	0.26	13.0 <sup>a</sup>	423 K, autogenous pressure, twice	2.73

<sup>a</sup> this value was obtained after 2 synthesis procedure.



**Fig. 6** Max. NO conversion as a function of Cu content of the monolith catalysts. Reaction conditions; NO = 1000 ppm, C<sub>3</sub>H<sub>8</sub> = 1000 ppm, O<sub>2</sub> = 2.0%; SV = 10,000 h<sup>-1</sup>.

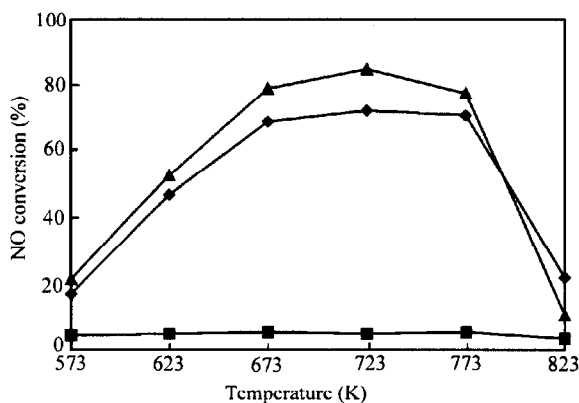
Fig. 7 and Fig 8 show the deNO<sub>x</sub> activities of the three monolith catalysts that had different ZSM-5 loading. Clearly, compared with Cu(B1)/ZSM-5 and Cu(B3)/ZSM-5 monolith catalysts, Cu(B0)/cordierite which did not contain any ZSM-5 crystals showed very low activities. Over the whole temperature range investigated, NO conversion was lower than 5%, and C<sub>3</sub>H<sub>8</sub> conversion was only 21.9% at 773 K. On the other hand, the other two Cu(B)/ZSM-5 monolith catalysts exhibited high deNO<sub>x</sub> activities, indicating that ZSM-5

layer is an indispensable component for the catalytic reduction of NO with C<sub>3</sub>H<sub>8</sub>. Especially over Cu(B3)/ZSM-5, which has ZSM-5 loading of about 13%, the maximum NO conversion achieved 85% at 723 K and the corresponding C<sub>3</sub>H<sub>8</sub> conversion was about 92.8% at that temperature, nearly 13% higher than that over Cu(B1)/ZSM-5. This activity level is also higher than that reported in the literature.<sup>22-24</sup> Although many factors affected the catalytic activity of monolith catalysts, such as cell density, length/diameter ratio, zeolite loading and metal loading of the monolith substrate, as well as the reaction conditions, we believe that the higher deNO<sub>x</sub> activity of Cu(B3)/ZSM-5 should be attributed to its higher ZSM-5 loading. The high ZSM-5 loading not only provided more exchangeable sites for metal ions (indicated by the high Cu content of the Cu(B3)/ZSM-5 monolith catalyst), but also decreased the real space velocity through the zeolite layer, thus increasing the catalytic activity. Therefore, a ZSM-5 layer with an enough thickness on the cordierite substrate was necessary for the catalytic reduction of NO with C<sub>3</sub>H<sub>8</sub>.

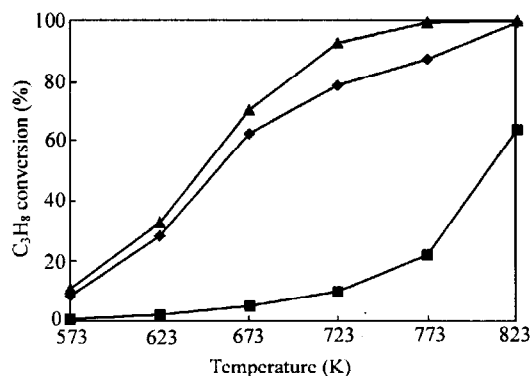
## Conclusions

Under a vapor mixture of *n*-butylamine and water, an amorphous aluminosilicate gel coated onto the

cordierite monolith has been transformed into a strongly adhered ZSM-5 layer on the substrate. Among various types of organic amines, *n*-butylamine has been proved to be a suitable template for the vapor phase synthesis of ZSM-5 on monolith cordierite substrate.



**Fig. 7** NO conversion as a function of reaction temperature over Cu(B0)/ZSM-5 (■), Cu(B1)/ZSM-5 (◆), and Cu(B3)/ZSM-5 (▲). Reaction conditions; NO = 1000 ppm, C<sub>3</sub>H<sub>8</sub> = 1000 ppm, O<sub>2</sub> = 2.0%; SV = 10,000 h<sup>-1</sup>.



**Fig. 8** C<sub>3</sub>H<sub>8</sub> conversion as a function of reaction temperature over Cu(B0)/ZSM-5 (■), Cu(B1)/ZSM-5 (◆), and Cu(B3)/ZSM-5 (▲). Reaction conditions; NO = 1000 ppm, C<sub>3</sub>H<sub>8</sub> = 1000 ppm, O<sub>2</sub> = 2.0%; SV = 10,000 h<sup>-1</sup>.

The as-synthesized ZSM-5/cordierite monoliths were ion exchanged with Cu<sup>2+</sup> and tested for the catalytic reduction of NO with C<sub>3</sub>H<sub>8</sub>. The deNO<sub>x</sub> activities were not only dependent on the ion-exchange procedures, but also on the ZSM-5 loading of the monoliths. Both the pressure exchange procedure and the high ZSM-5 loading can lead to the high Cu content, thus resulted in a high deNO<sub>x</sub> activity of the Cu/ZSM-5 monolith catalysts.

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