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In situ Synthesis of Cu-SAPO-34/Cordierite for the Catalytic Removal of NO$_x$ from Diesel Vehicles by C$_3$H$_8$

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Abstract: A Cu-SAPO-34/cordierite catalyst was prepared by in situ hydrothermal synthesis. The morphology and structure of the Cu-SAPO-34/cordierite samples were characterized by X-ray diffraction, scanning electron microscopy, and physical adsorption-desorption analyzer. The removal of NO$_x$ from simulated diesel vehicle exhaust gas was carried out using a fixed-bed reactor. The effects of C$_3$H$_8$, O$_2$ concentrations, and water vapor on the activity of the catalyst were studied. The results indicate that the Cu-SAPO-34 coatings obtained by the in situ synthesis are firm and compact, and the loading amount was found to be more than 20% after one synthesis operation. The surface areas of the Cu-SAPO-34/cordierite catalysts increase greatly compared with that of cordierite. The active Cu component prepared through in situ synthesis can significantly improve the activity of selective catalytic reduction of NO$_x$ by C$_3$H$_8$. NO$_x$ reduction over the Cu-SAPO-34/cordierite catalyst is more than 60% between 500 and 650 °C. The NO$_x$ conversion decreases after the addition of 10% water vapor to the feed gas but the deactivation caused by water vapor is not permanent.

Key words: copper; SAPO-34 zeolite; cordierite; NO$_x$; propane; in situ synthesis; selectivity catalytic reduction; diesel engines

Along with the rapid development of the global automotive industry and the increase in automobile ownership, pollution by carbon monoxide, hydrocarbons, NO$_x$, and particulate matter in the exhaust gases of cars has become more serious. Pollution by NO$_x$ has especially received plenty of attention. However, the removal of NO$_x$ is difficult using the conventional three-way catalyst because of the high oxygen content in diesel engine exhaust gas. The selective catalytic reduction (SCR) of NO$_x$ under an oxidizing atmosphere by hydrogen, hydrocarbons or NH$_3$ has been used for the catalytic removal of NO$_x$ in diesel engine exhaust gases [1]. The catalyst can generally be divided into four categories: metal oxide catalysts, noble metal catalysts [2], molecular sieve catalysts [3], and bifunctional catalysts [4]. The metal-SAPO-34 has been reported to be highly active for the selective reduction of NO$_x$ with high thermal stability [5,6].

The carrier properties greatly affect the supported catalyst's activity and service-life. Cordierite (2MgO·2Al$_2$O$_3$·5SiO$_2$) monoliths are widely used because of their superior hydro-thermal stability, low thermal expansivity, plasticity and low price [7]. Honeycomb catalysts are generally composed of a carrier, a coating and active components. Catalysts prepared by traditional coating technology such as the γ-Al$_2$O$_3$ coating honeycomb cordierite easily lose active components resulting in the reduction of catalytic efficiency [8]. The impregnation method for the loading of active components is simple but their distribution on the carrier is inhomogeneous and the pores of the molecular sieve are easily blocked. Furthermore, the loss of active components leads to secondary pollution [9]. However, the molecular sieve coatings of the honeycomb cordierite catalysts that were prepared by in situ synthesis have a larger surface area and the internal and external surfaces of the molecular sieve may be fully used. These direct methods provide materials with good metal dispersion in the structure and the metal of the skeleton are good activity centers for oxidation or reduction [10].

In this paper, we report on the preparation of a Cu-SAPO-34/cordierite catalyst by a one-step hydrothermal procedure. The

characteristics of the Cu-SAPO-34/cordierite samples were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and physical adsorption-desorption analyzer. The removal of NO_x from simulated diesel vehicle exhaust gas was carried out. The effects of C_3H_8, oxygen concentration, and water vapor on catalyst activity were investigated.

1　Experimental

1.1　Catalyst preparation

Cordierite honeycomb was cut into square-shaped samples with dimensions of 17 mm × 17 mm × 17 mm. The samples were treated with a 15% nitric acid solution at 80 °C for 2 h, washed with deionized water, dried at 110 °C for 2 h , calcined at 700 °C for 2 h and then stored in a drier for future use.

We used morpholine as a template, copper oxide as the source of the active metal, phosphoric acid, aluminum hydroxide and silica gel as the phosphorus source, aluminum source and silicon source, respectively. The molar ratio used was 0.08 CuO:0.2 SiO_2:0.46 Al_2O_3:0.45 P_2O_5:1.25 C_4H_9NO:50 H_2O in the crystallization solution. The Cu-SAPO-34/ cordierite sample was synthesized as follows: CuO was added to the dilute solution of orthophosphoric acid. The mixture was stirred at 80 °C until the CuO was completely dissolved. $Al(OH)_3$ was then added at room temperature to form a homogeneous gel by stirring. Subsequently, SiO_2 and morpholine were added to the gel under stirring. A piece of cordierite was placed in the bottom of the PTFE liner of a 50 ml autoclave and the certain amount initial gel was put into, sealed. At 190 °C and under an autogenous pressure, the gel was statically crystallized for 7 d. The crystalline product was washed with distilled water and dried in air for 3 h. The synthesized samples were calcined under an oxygen atmosphere at 700 °C for 5 h to remove the template [11]. For comparison, SAPO-34/cordierite was also prepared according to the above-mentioned methods.

1.2　Catalyst characterization

The loading mass was calculated by weighing the cordierite before and after the loading. The mechanical intensity of the Cu-SAPO-34/cordierite and the degree of adhesion of Cu-SAPO-34 onto cordierite was evaluated using an ultrasonic generator (power 200 W, frequency 20 kHz). Cu-SAPO-34/cordierite monoliths were treated for 60 min by ultrasonic vibration. The samples were dried at 120 °C and then the mass losses were calculated based on the formulae $\omega = (m_1-m_0)/m_1 \times 100\%$ and $\Delta\omega = (m_1-m_2)/(m_1-m_0) \times 100\%$, where ω is the amount of Cu-SAPO-34 loading, $\Delta\omega$ is the mass loss of the monolithic catalyst, m_0 is the weight of raw cordierite, m_1 and m_2 are the weights of Cu-SAPO-34/cordierite before and after ultrasonic treatment, respectively.

The catalyst phase structures were examined by (Rigaku

D/max2500 diffractometer) with a graphite monochromator and Cu K_α radiation sources (λ = 0.154056 nm), a tube voltage of 40 kV and a tube current of 100 mA. The scan rate was 8°/min and the 2θ value ranged from 5° to 35°. The morphology of the samples was examined by SEM (JEOL Jsm-6700F). The samples were covered with a thin gold layer and the accelerating voltage was 10 kV. The surface area of the samples was determined by BET analysis (TriStar 3000, Micromeritics Instrument Corporation) using liquid nitrogen adsorption.

1.3　Catalyst evaluation

The activities of the Cu-SAPO-34/cordierite catalyst for the SCR reaction of NO_x by C_3H_8 at atmospheric pressure were determined using a fixed-bed flow microreactor. The devices were composed of a gas-way equipped with a flow controller, fixed bed quartz reactors (inner radii 20 mm), a temperature controller, and a detection system. A total flow rate of 420 ml/min was used for the catalytic activity runs. The feed gas consisted of 0.05% NO_x, 0.05% C_3H_8, 0–10% O_2, with or without 10% H_2O, and N_2 was used as the balance gas. The water was gasified by heating and the amount was controlled using a trace pump. Four pieces of Cu-SAPO-34/cordierite (cylindrical shape with an average diameter of 18 mm and an average length of 17 mm) were put into the quartz reactor for each run except for the evaluation of the influence of space velocity. NO, NO_2, O_2, and C_3H_8 in the gases before and after the catalytic reaction were analyzed simultaneously on-line by flue gas analysis (British, Kane-9106).

To identify the influence of H_2O in the feed gas on NO_x removal, H_2O-response experiments were performed using the fixed bed reactor and the above-mentioned typical feed gas. These experiments were carried out at 450 °C with four pieces of catalyst and a total flow of 420 ml/min. The NO_x concentration of the feed and effluent gases was also measured on-line by the flue gas analyzer.

NO_x (NO and NO_2) conversion was calculated using the following equation $X = (c_1-c_0)/c_1 \times 100\%$, where X is the conversion of NO_x, c_1 and c_0 are the concentration of NO_x before and after the reaction, respectively.

2　Results and discussion

2.1　Cu-SAPO-34 loading

The amount of loading and the degree of active component adhesion are important factors for the activity of the monolithic catalyst. The amount of Cu-SAPO-34 loading and the mass losses after ultrasonic treatment are shown in Table 1.

The loading of Cu-SAPO-34 from the three different autoclaves under the same conditions were 23.28%, 21.78%, 21.28%, respectively. Cu-SAPO-34 loading was found to be more than 20% after one synthesis operation and the repeat-

Table 1 Cu-SAPO-34 loading and the mass loss of the samples

Sample	ω/%	$\Delta\omega$/%
1	23.28	0.14
2	21.78	0.34
3	21.28	0.51

ω—the amount of Cu-SAPO-34 loading; $\Delta\omega$—the mass loss of the monolithic catalyst.

ability of the experiment was very good. The mass losses after 60 min of ultrasonic oscillations were found to be 0.14%, 0.34%, and 0.51%, respectively. These results indicate that Cu-SAPO-34/cordierite has a good degree of adhesion and that it can be used under complex conditions for the reduction of NO_x.

2.2 XRD and SEM results

The XRD patterns of blank cordierite, Cu-SAPO-34, and Cu-SAPO-34/cordierite are shown in Fig. 1. The characteristic diffraction peaks at 2θ = 9.5°, 15.96°, 17.92°, 20.05°, 25.82°, 30.92°, and 31.2° for Cu-SAPO-34/cordierite correspond to the characteristic peaks of SAPO-34, which suggests that the SAPO-34 crystallites are loaded onto the cordierite substrate. Meanwhile, a few diffraction peaks are also present in Fig. 1. It should be noted that no characteristic peaks of Cu species are present in the Cu-SAPO-34/cordierite spectrum. This is attributed to a very even Cu distribution on the surface or to the transfer of a majority of the Cu to the skeleton of the catalyst during the synthesis process [12].

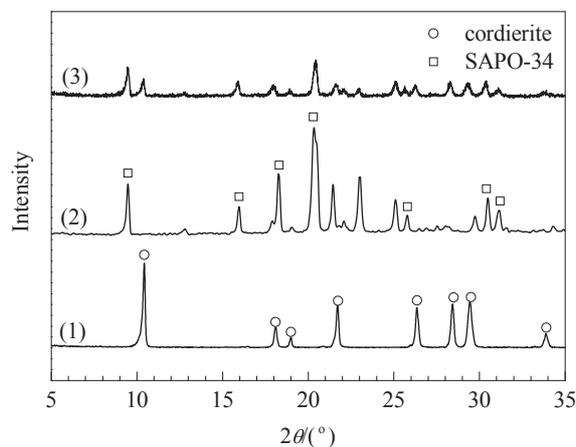The SEM images of the cordierite and Cu-SAPO-34/cordi-

Fig. 1. XRD patterns of black cordierite (1), Cu-SAPO-34 (2), and Cu-SAPO-34/ cordierite (3).

erite samples are given in Fig. 2. It is shown that the cordierite supports have an irregular structure, however, there are many grains with a regular structure and some amorphous material in Cu-SAPO-34/cordierite samples. The results from SEM are consistent with the XRD spectra of the samples. However, it is interesting that some differences exist in the feature of the component loaded on the internal and external surfaces of the carriers [13], as shown in Fig. 2. We conclude that Cu-SAPO-34 tends to form smaller crystalloids on the external surfaces than on the internal surfaces of the support, moreover, the Cu-SAPO-34 crystalloids that are loaded onto the external surface of cordierite appear to be blocked crystalloids and cracks are present on the outer surface; however, the Cu-SAPO-34 loaded on the inner surface of cordierite show
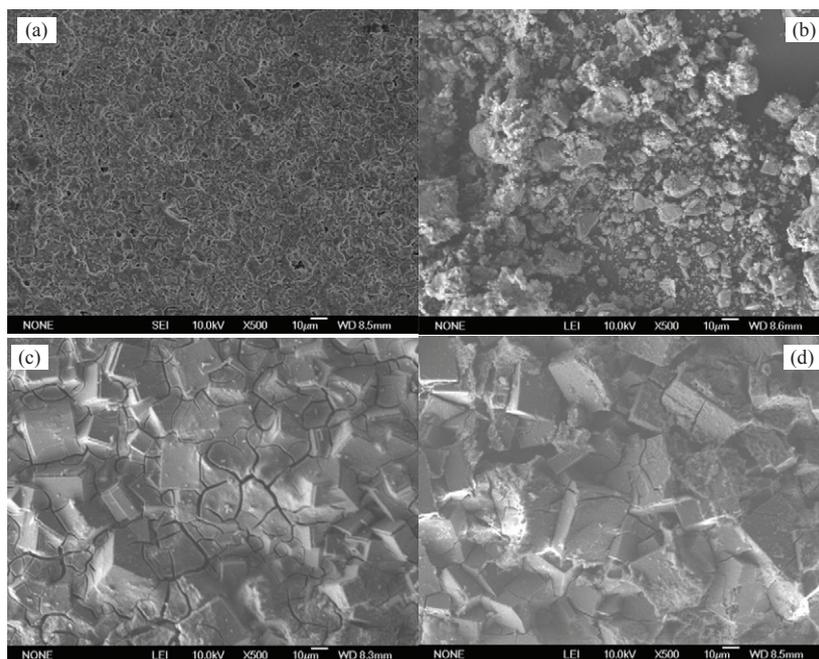

Fig. 2. SEM images of the surface of blank cordierite (a), Cu-SAPO-34/cordierite powder (b), external surface (c), and internal surface (d) of Cu-SAPO-34/cordierite.

uniform rectangles crystalloids of about 20 μm in length.

The cordierite substrate has an irregular macroporous structure and its specific surface area was only 1 m^2/g. The specific surface areas of the monolithic catalyst after loading Cu-SAPO-34 increase greatly to 30 m^2/g. This increase in specific surface area is essential for the catalytic reaction and it provides more sites for chemical adsorption and catalytic reactions so that it is good for the reactions [14].

2.3 NO$_x$-SCR activity of the monolithic catalysts

The NO$_x$-SCR activity of SAPO-34/cordierite and Cu-SAPO-34/cordierite under dry conditions (0.05% NO$_x$, 7% O$_2$, SV = 6000 h^{-1}) from 200 to 650 °C was investigated and the results are shown in Fig. 3. The highest conversion rate of NO$_x$ on the SAPO-34/cordierite was around 10% between 560 and 585 °C. The conversion rate of NO$_x$ on the Cu-SAPO-34/cordierite was 30% between 500 and 650 °C. This result suggests that the addition of copper significantly improves the monolithic catalyst activity, which is the same as the results of Iwamoto et al. [15]. Figure 3 also shows that NO$_2$ selectivity over both the catalysts was high from 300 to 400 °C. However, from 560 to 585 °C where NO$_x$ conversions were high, the NO$_2$ selectivities were only about 5.6% and 3.9% for SAPO-34/cordierite and Cu-SAPO-34/cordierite, respectively.

2.4 Effect of reaction conditions on NO$_x$-SCR activity

The diesel engine, as a true lean-burn engine, works under excess oxygen conditions. Moreover, the SCR activity of NO$_x$ over C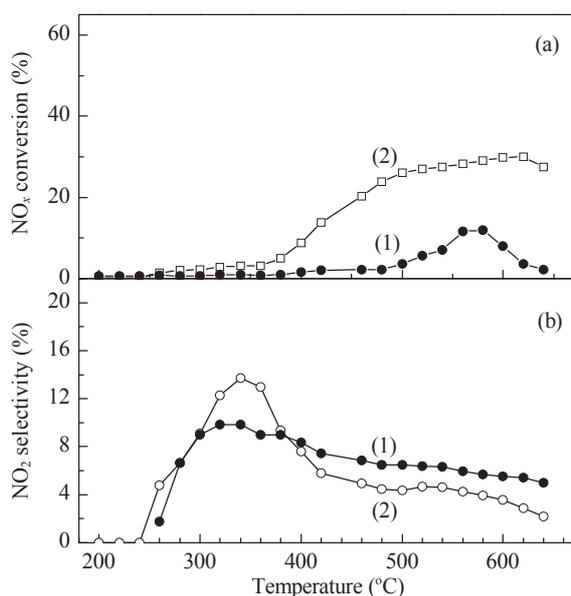u-SAPO-34/cordierite in lean mixture environments was investigated. The factors that influence the SCR activity of NO$_x$ are mainly the space velocity, the reducing agent, and the O$_2$ concentration.

The concentration of hydrocarbon in a diesel engine changes greatly under different conditions so that the SCR activity of NO$_x$ is greatly influenced by the reducing agent's concentration. Figure 4 shows the effect of the reducing agent C$_3$H$_8$ concentration on the NO$_x$-SCR over the monolithic catalyst at 0.05% NO$_x$, 7% O$_2$, and a SV of 3000 h^{-1}. The NO$_x$ conversion rate increases from 50.2% to 80.2% when the C$_3$H$_8$/NO$_x$ ratio increases from 1:2 to 2:1. At a C$_3$H$_8$/NO$_x$ ratio of 2, the conversion rate of NO$_x$ is more than 60% between 480 and 680 °C. This suggests that a moderate increase in hydrocarbon favors NO$_x$-SCR activity.

Figure 4(b) shows that C$_3$H$_8$ was completely oxidized at a reaction temperature of 600 °C and the results show that C$_3$H$_8$ is activated with difficulty on the catalyst. An increase in the hydrocarbon concentration does not affect the C$_3$H$_8$ oxidation process.

The NO$_x$-SCR activity of the catalysts was investigated using different O$_2$ concentrations and the results are shown in Fig. 5. The NO$_x$ conversion decreases gradually with an increase in the O$_2$ concentration. At an O$_2$ concentration of 2%, NO$_x$ conversion is 78.0% between 500 and 650 °C, however, at an O$_2$ concentration of 10%, NO$_x$ conversion lower than 50%. This means that the SCR process of NO$_x$ will be inhibited because of the oxidative reaction at the high O$_2$ concentration.

The catalysts used in exhaust gas purification operate under complex conditions such as fast changes in gas flow. There-
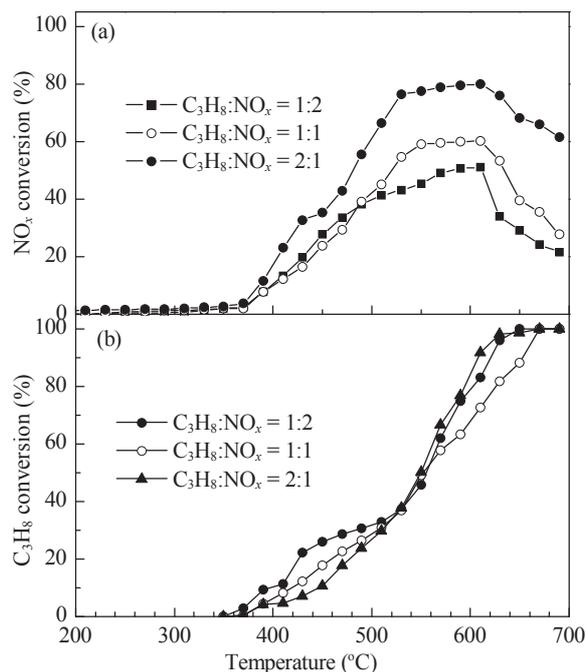

Fig. 3. NO$_x$ conversion (a) and NO$_2$ selectivity (b) of SAPO-34/cordierite (1) and Cu-SAPO-34/cordierite (2). Experimental conditions: 0.05% NO$_x$, 0.05% C$_3$H$_8$, 7% O$_2$, and SV = 6000 h^{-1}.

Fig. 4. Effect of C$_3$H$_8$/NO$_x$ ratio on the NO$_x$-SCR activity of Cu-SAPO-34/cordierite. Experimental conditions: 0.05% NO$_x$, 7% O$_2$, C$_3$H$_8$/NO$_x$ = 1:2, 1:1 or 2:1, and SV = 3000 h^{-1}.
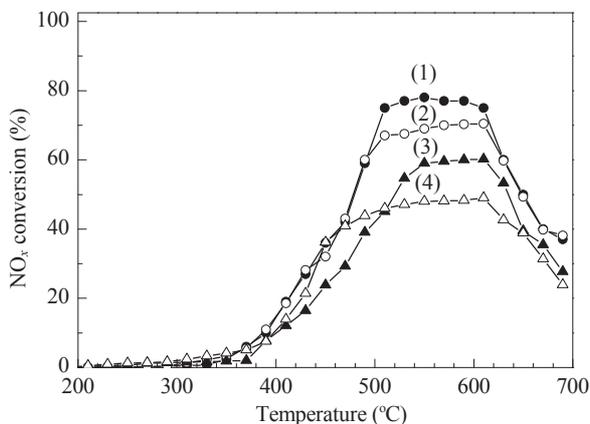
Fig. 5. Effect of O_2 concentration on the NO_x-SCR activity of Cu-SAPO-34/cordierite. O_2 concentration: (1) 2%; (2) 5%; (3) 7%; (4) 10%. Experimental conditions: 0.05% NO_x, 0.05% C_3H_8, and SV = 3000 h^{-1}.

Fig. 7. Effect of water vapor on the NO_x-SCR activity of Cu-SAPO-34/cordierite. (1) Before adding water; (2) Adding water; (3) Stop adding water. Experimental conditions: 0.05% NO_x, 0.05% C_3H_8, 7% O_2, and SV = 3000 h^{-1}.

fore, the effect of space velocity on the NO_x-SCR activity of Cu- SAPO-34/cordierite was investigated and the results are shown in Figure 6. We found that NO_x conversion remains high over a broader range of space velocity and it decreases with an increase in space velocity. When the space velocity is 3000 h^{-1}, NO_x conversion reaches 60%. The contact time of the reaction gas is long at a low space velocity, which leads to high NO_x-SCR activity [16].

The effect of 10% water vapor on the NO_x-SCR activity of Cu-SAPO-34/cordierite is shown in Figure 7. NO_x conversion decreases obviously from 60.2% without water to 38.8% with water. When water addition was stopped the highest NO_x conversion was still 45%.

To differentiate the effect of H_2O on the NO_x-SCR activity, H_2O-response experiments were carried out. In this experiment, H_2O was added to the feed gas at specific times and then removed when the NO_x concentration in the effluent did not
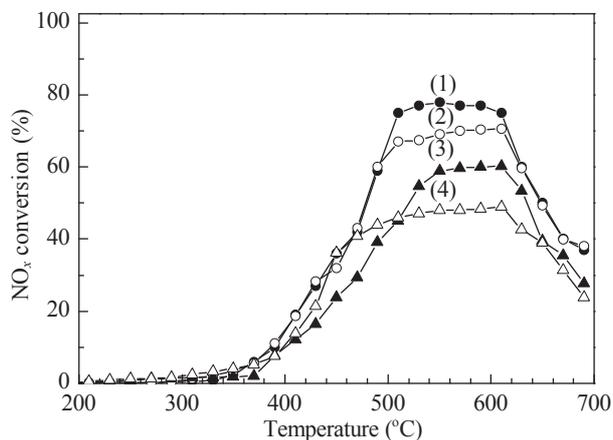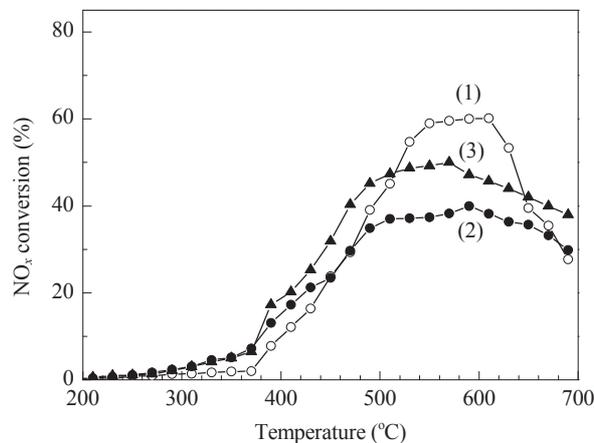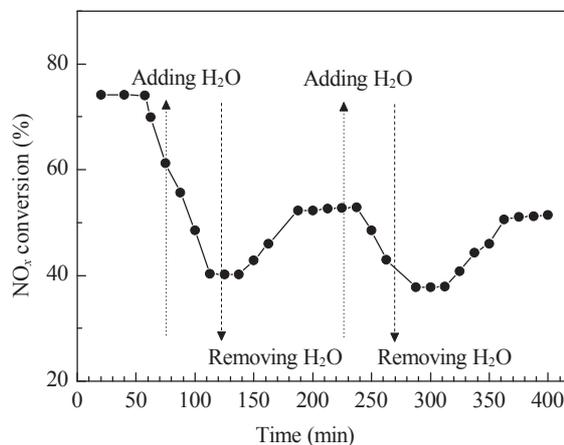

Fig. 8. Effect of H_2O on the NO_x concentration of the effluent in Cu-SAPO-34/cordierite. Reaction conditions: 0.05% NO_x, 0.05% C_3H_8, 7% O_2, 10% H_2O (when used), SV = 3000 h^{-1}, and 500 °C.

change. The results are shown in Figure 8. It can be seen that the NO_x concentration of the exhaust decreased obviously after H_2O addition, and the NO_x concentration rose to a stable value after H_2O removal. The deactivation caused by water vapor is not permanent. Shelef [17] found that the formation of NO_2 on the catalyst surface is rate controlled during the SCR reaction. Competitive adsorption between H_2O molecules and NO_2 molecules on the surface of the catalyst resulted in a decrease in catalyst activity.

3 Conclusions

The Cu-SAPO-34/cordierite monolithic catalyst was prepared by in situ hydrothermal synthesis. The amount of Cu-SAPO-34 loading on cordierite is more than 20% after one synthesis operation and its degree of adhesion is high. The specific surface area of the monolithic catalyst significantly

Fig. 6. Effect of space velocity on the NO_x-SCR activity of Cu-SAPO-34/cordierite. Space velocity: (1) 3000 h^{-1}; (2) 4000 h^{-1}; (3) 6000 h^{-1}; (4) 12000 h^{-1}. Reaction conditions: 0.05% NO_x, 0.05% C_3H_8, and 7% O_2.

increases to 30 m^2/g. The prepared monolithic catalyst shows high activity for the de-NO$_x$ reaction with more than 60% conversion between 500 and 650 °C. A higher amount of C$_3$H$_8$, a lower oxygen concentration or a lower space velocity favors NO$_x$-SCR activity. NO$_x$ conversion decreases after the addition of 10% water to the feed gas and the deactivation trend caused by water vapor is abated when it is removed.

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