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Research Article

Catalytic Properties of Pd Modified Cu/SAPO-34 for NO_x Removal from Diesel Engine

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The Cu/SAPO-34 catalysts with different Cu contents were prepared by in situ hydrothermal synthesis. The selected Cu/SAPO-34 was modified by impregnating 1 wt% $Pd(NO_3)_3$. The morphology and structure of the samples were characterized via XRD and SEM techniques. The effects of Cu contents and the Pd modification on the de-NO_x activity of the samples were investigated through the selective catalytic reduction by C_3H_6 and NH_3. The Cu contents do not change the skeleton structure of the SAPO-34 crystalline and the Cu/SAPO-34 catalysts with Cu/Si ratios of 0.05, 0.1, and 0.2 have better de-NO_x activity than other catalysts. The addition of Pd can improve the de-NO_x activity of the Cu/SAPO-34 catalysts. The maximum of NO conversion of samples with Pd could reach 90%. Besides, the effect of aging treatment for Cu/SAPO-34 catalysts with and without Pd on the de-NO_x activity was also investigated. The results indicated that the Cu/SAPO-34 catalysts modified by Pd have better antiaging performance than raw samples.

1. Introduction

NO_x can react with hydrocarbons (HC) and produce photochemical smog, which is increasingly highlighted and to be concerned about [1–3]. Selective catalytic reduction (SCR) is an effective method for controlling the emission of NO_x, which has already been used in industry [4–6]. The development of high efficiency catalyst, as the key technology of SCR, has received more and more concerns [7]. Depending on high thermal and hydrothermal stability [8–11], metal-SAPO-34 has a broad application prospect. The proper pore structure makes it exhibit excellent properties in the region of diesel engine exhaust purification [12]. As is known to all, the dispersion of the active sites is closely related to the metal loading for the supported catalysts. When the loading amount of metal is much too high, it could aggregate easily during the calcination process. Therefore, there should be a suitable amount of active components, neither too much nor too little, loading on the support. Meunier et al. [13] found that a maximum NO_x conversion could be available on Ag/Al_2O_3 when the Ag loading was 1%; however, the conversion decreased obviously when Ag loading was 2%. Horiuchi et al. [14] reported that the highest activity could be achieved over Co/Al_2O_3 when Co loading was 0.5%. These results indicate that the active metal content of the catalysts is very important for the catalytic activity.

As a kind of low-cost active constituent for the SCR of NO, Cu has drawn the attentions of many researchers [15, 16], but diesel exhaust is often at high temperatures (>650°C) and the antiaging capacity is required [17, 18]. Morever, as one of the noble metals, Pd is a promising candidate for HC-SCR in excess oxygen [19–21]. In this paper, a series of Cu/SAPO-34 catalysts were prepared by hydrothermal synthesis. The effect of Cu content and Pd modifying on the de-NO_x activity were investigated. The morphology and structure of the samples were characterized using XRD and SEM. In addition, the influence of the aging treatment of the prepared catalysts was studied.

2. Experimental

2.1. Preparation of Catalysts. The Cu/SAPO-34 catalysts with different Cu contents were prepared by insitu hydrothermal synthesis, and the details were as follows: CuO, H_3PO_4, $Al(OH)_3$, and silica gel were used as the sources of Cu, P, Al, and Si, respectively. Morpholine (C_4H_9NO) was selected as the template. The crystallization gel was prepared according to the mole ratio of n CuO : 0.2 SiO_2 : 0.92 $Al(OH)_3$: 0.9 H_3PO_4 : 1.25 C_4H_9NO : 50 H_2O : 0.01 HF (n = 0, 0.005, 0.01, 0.02, 0.04, and 0.08). Firstly, H_3PO_4 was added to deionized water, followed by CuO at 80°C while stirring until dissolved completely. And then, $Al(OH)_3$, silica gel, morpholine, and HF were added. The initial gel was loaded into the stainless reaction kettles equipped with a polytetrafluorethylene liner of 200 mL and crystallized for 72 h at 190°C. The product was washed and then calcined. Finally, the Cu/SAPO-34 catalysts were obtained. And the preparation method had been described in our previous paper [22].

The Pd modified Cu/SAPO-34 catalysts were prepared with pore volume impregnation. The details were as follows: the Cu/SAPO-34 catalysts were impregnated by $Pd(NO_3)_2$ solution(1 mol/L) overnight to give a 0.5% Pd loading, and then dried at 120°C and calcined at 600°C for 3 h.

2.2. Characterization. The XRD patterns of powder samples were obtained on a Japanese Rigaku D/MAX2500 diffractometer at 45 kV and 100 mA with CuKα radiation (λ = 0.154 nm). The scanning rate and range were 8°/min and 5°–85°, respectively.

The SEM images were obtained by a Japanese Jeol Jsm-6700 F at 10 kV. The samples were covered with a thin gold layer before scanning.

The Cu content was measured using an atomic absorption spectroscopy (AAS; Varian AA240FS, USA) with a 324.7 nm Cu testing wavelength, operating at 3.0 mA lamp current and a fuel gas of C_2H_2 (1700 mL/min).

2.3. Activity and Antiaging Capacity Test. The activities of the Cu/SAPO-34 catalysts for the selective catalytic reduction (SCR) of NO_x by C_3H_6 or NH_3 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 reactor (Φ = 8.5 mm), a temperature controller, and a detection system. A total flow rate of 100 mL/min was used for the catalytic activity runs. The feed gas consisted of 0.6% NO, 0.6% C_3H_6 or 0.6% NH_3, and 5% O_2 with He as the balance gas. The catalyst powder (40–60 mesh) was placed into the center of the quartz reactor.

Firstly, He gas flow of 100 mL/min was used to sweep off for 2 h in order to eliminate the N_2 residue in the reactor and then switched to the simulated exhaust. The reactor was heated up to 50°C, holden for 0.5 h, and then risen to 600°C at a rate of 7°C/min. NO, NO_2, O_2, and C_3H_6 in the gases before and after the catalytic reaction were analyzed simultaneously online by gas chromatograph (GC-9890A, Shanghai Linghua Instrument Company Limited) equipped with column Porapak Q for separating N_2O and CO_2 and column molecular sieve 5A for separating N_2, O_2 and CO.

The aging treatment is also carried out using the above-mentioned fixed-bed flow microreactor. Catalyst samples were exposed to a stream of gases containing 0.03% SO_2 and 10% vapor balanced with Ar with the total rate of 400 mL/min at the temperature of 720°C for 10 h. Then, the same way as described above was used to test the aged catalyst activity.

NO conversion was calculated using the following equation:

$$X = \frac{(c_1 - c_0)}{c_1} \times 100\%, \quad (1)$$

where X is the conversion of NO and c_1 and c_0 are the concentrations of NO_x (NO, NO_2, and N_2O) before and after the reaction, respectively.

3. Results and Discussion

3.1. Effect of Cu Content on NO Conversion. The NO conversions over the Cu/SAPO-34 catalysts with different Cu contents were investigated using C_3H_6 and NH_3 as the reductant. The Cu content can be represented by the Cu/Si atom ratio of the crystallization gel. In this paper, the Cu/Si atom ratios included 0 (without Cu), 0.025, 0.05, 0.1, 0.2, and 0.4.

The NO conversions of the Cu/SAPO-34 catalysts with different Cu/Si atom ratios are shown in Figure 1 ((a): C_3H_6-SCR and (b): NH_3-SCR). When the reductant was C_3H_6, the NO conversions of all catalysts were below 70% in the temperature range of 100–600°C; Particulary, that of the catalyst without Cu was below 20%. It can be also seen that the NO conversions of the catalysts with Cu/Si atom ratios 0.05, 0.1 of and 0.2 were higher than these with Cu/Si atom ratios of 0.025 and 0.4. The NO conversions of all Cu/SAPO-34 catalysts increased as the temperature increases from 100°C to 600°C. Moreover, the NO conversions of all Cu/SAPO-34 catalysts increased sharply at low temperature, while it increased slowly at high temperature.

When the reductant was NH_3, the NO conversions of all catalysts were much higher than using C_3H_6 as the reductant in the temperature range of 100–600°C. Particulary, at 600°C, the NO conversions of the Cu/SAPO-34 catalysts can reach to about 96% using NH_3 as the reductant, while it only reached 65% using C_3H_6 as the reductant. In addition, like C_3H_6, the NO conversions of the catalysts with Cu/Si atom ratios from 0.05 to 0.2 were higher than these with Cu/Si atom ratios of 0.025 and 0.4.

On the basis of the above results, it can be concluded that as the Cu/Si atom ratios of the crystallization gel were in the range of 0.05–0.2, the de-NO_x activity of the Cu/SAPO-34 catalysts was better than others.

The XRD patterns of the Cu/SAPO-34 catalysts with different Cu contents are shown in Figure 2. It can be obviously found that all samples have SAPO-34 characteristic peaks around 2θ = 9.45°~9.65°, 16.0°~16.2°, 17.85°~18.15°, 20.55°~20.9°, 24.95°~25.4°, and 30.5°~30.7°, indicating that SAPO-34 was successfully formed using in-situ hydrothermal synthesis. As the Cu content increases, the peaks position of all the samples do not change. It indicates that the amount of

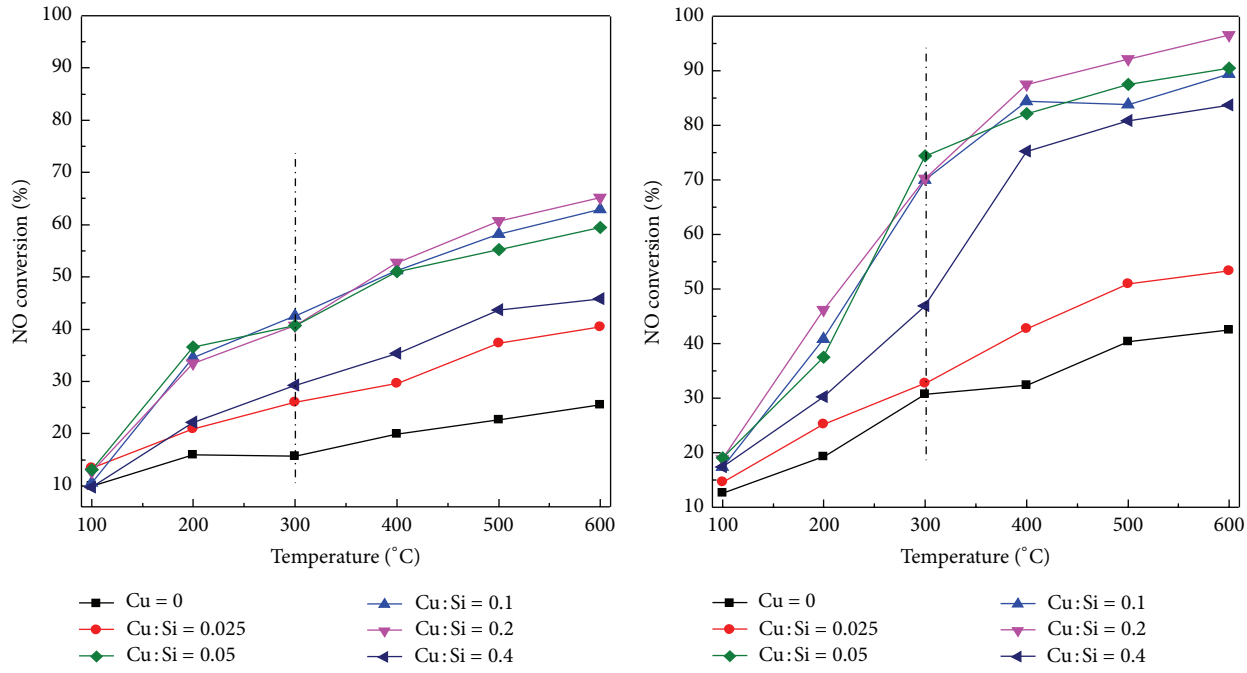

Figure 1: Effect of the Cu contents of crystallization gel of Cu/SAPO-34 on NO conversion (GHSV: 10,000 h^{-1}).

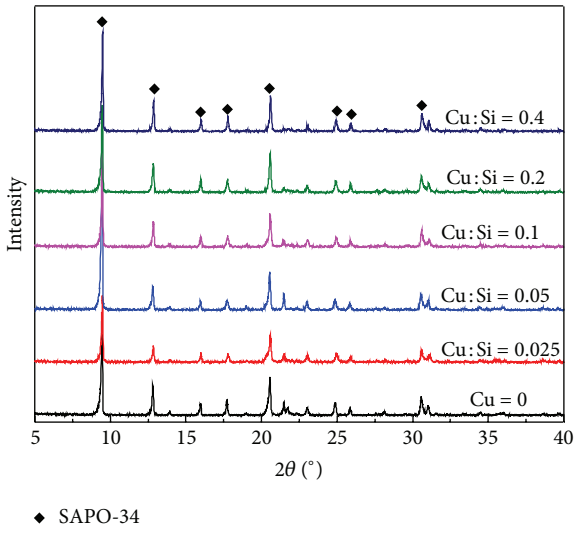

Figure 2: XRD patterns of SAPO-34 catalysts with different Cu contents in the crystallization gel.

Cu content has no effect on the CHA structure of SAPO-34. Besides, it should be noted that the peaks became higher and sharper as the SAPO-34 was modified by Cu because the introduction of Cu into the framework could reduce the crystal defects and increase the crystallinity [23–26]. It is also found that no peaks related to CuO and Cu_2O species appeared in the XRD spectrum of catalyst, indicating that the Cu loadings were low or the Cu species were not big enough to be detected [27, 28].

The SEM images of the Cu/SAPO-34 catalysts with different Cu contents are displayed in Figure 3. The morphology features of the Cu/SAPO-34 catalysts with different Cu contents were compared with those without Cu. It can be found that all the samples were cubic crystals with similar averaged sizes (0.6–2 μm), which suggested that the addition of Cu did not change the CHA structure and crystal morphology of SAPO-34. It is consistent with the XRD results. When the Cu/Si atom ratios were 0 and 0.025, there was no random-shaped material around the cubic crystals. Some random-shaped materials appeared as the Cu content in Cu/SAPO-34 catalysts increased. When the Cu/Si atom ratio was 0.2, the surface of the crystals was nearly covered with the random-shaped material. When the Cu/Si atom ratio was 0.4, big cubic SAPO-34 crystals were formed with the random-shaped material. It should be noted that the relative crystallinity of all the samples was above 92% (Table 1). It means that the random-shaped material was not copper oxide and they could be SAPO-34 crystals with different crystal morphologies. Thus, it can be deduced that the high Cu content could change the morphology of SAPO-34 crystal.

For clarifying the effect of different Cu contents in Cu/SAPO-34 explicitly, the physical properties of samples are summarized in Table 1. It is notable that the Cu/Si atom ratios of Cu/SAPO-34 catalysts were quite different from these of precursor solution, but the trend was inconsistent. It indicated that only a part of Cu could enter into the pore and the skeleton of SAPO-34. In addition, it can be seen from Table 1 that the range of grain sizes of the Cu/SAPO-34 catalysts became smaller as the Cu/Si ratio increases from 0 to 0.2. The smaller grain sizes may be beneficial to the catalytic activity. The sample *e* (Cu/Si = 0.2) has the highest crystallinity and the smallest grain sizes among the six samples, which is consistent with its high de-NO_x activity.

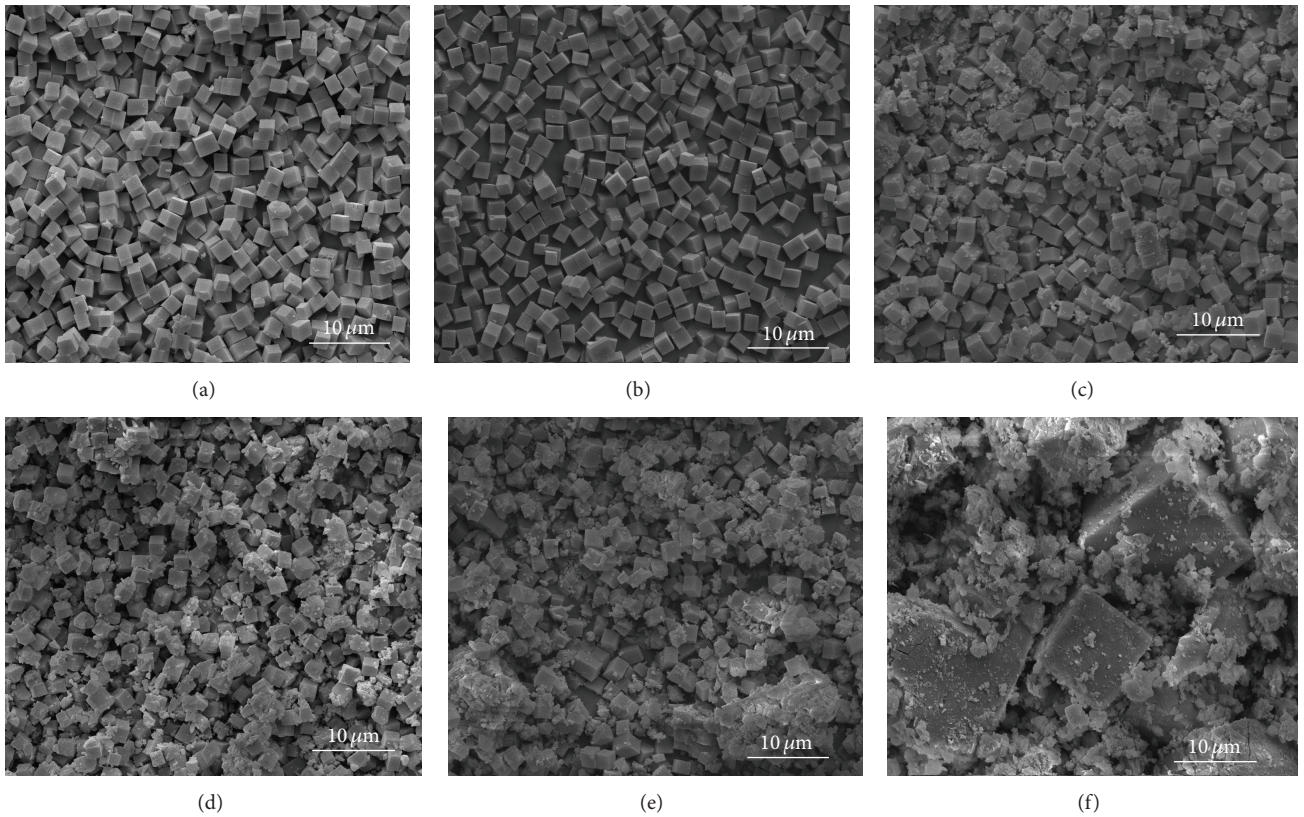

Figure 3: SEM images of Cu/SAPO-34 catalysts with different Cu contents ((a): Cu/Si = 0, (b): Cu/Si: = 0.025, (c): Cu/Si = 0.05, (d): Cu/Si = 0.1, (e): Cu/Si = 0.2, and (f): Cu/Si = 0.4).

Table 1: Physical properties of the Cu/SAPO-34 catalysts with different Cu contents.

Physical properties	Samples					
	a	b	c	d	e	f
Cu/Si atom ratio of initial gel	0	0.025	0.05	0.1	0.2	0.4
Cu/Si atom ratio of Cu/SAPO-34	0	0.023	0.038	0.065	0.120	0.171
Relative crystallinity %	98.36	94.21	93.81	94.83	99.65	92.18
Grain size/μm	0.6–2.0	1.5–2.0	1.2–2.0	0.8–2.0	1.0–1.5	0.6–18

3.2. Activity Test of Pd Modified Cu/SAPO-34. For further improving the de-NO_x activity of the Cu/SAPO-34 catalysts, the noble metal Pd was introduced into the Cu/SAPO-34 catalysts with Cu/Si = 0.05 and 0.2 by impregnated using $Pd(NO_3)_2$ as precursor. The Pd loading on catalyst was 0.5% (denoted as PdCu/SAPO-34). Figure 4 illustrates the NO conversions of the PdCu/SAPO-34 catalysts. The experimental GHSV is 40,000 h^{-1}, which is close to the real diesel engine exhaust.

When C_3H_6 was used as reducing agent and the temperature was below 300°C, the NO conversions of the PdCu/SAPO-34 catalysts were similar to the samples without Pd. However, when the temperature rises from 300°C to 600°C, the advantage of Pd became significant. The NO conversions of PdCu/SAPO-34 catalysts were much higher than these of Cu/SAPO-34 catalysts and it can reach to around 70%. It is also found that the de-NO_x activities of the PdCu/SAPO-34 catalysts with Cu/Si = 0.2 were superior to these of Cu/Si = 0.05, especially, at the higher temperature.

When NH_3 was used as reducing agent, the NO conversions of the PdCu/SAPO-34 catalysts were similar to those of the Cu/SAPO-34 catalysts, especially, at the low temperature. The de-NO_x activities of the PdCu/SAPO-34 catalysts with Cu/Si = 0.2 were higher than these with Cu/Si = 0.05, and the maximum of the NO conversion can reach to 90%. That is because the reaction between NH_3 and NO with low activation energy is quite easy [29]. According to the previous reports [30], the ammonium ion would react with the NO-Pd^{2+} species to give N_2. Similarly, the activity of the Pd modified Cu/SAPO-34 samples was superior to those without Pd, especially, at the high temperature.

3.3. Antiaging Performance of Catalysts

3.3.1. Cu/SAPO-34 Catalysts. The effects of aging on the de-NO_x activity of the Cu/SAPO-34 catalysts with Cu/Si = 0.2 and Cu/Si = 0.05 were shown in Figures 4(a) and 4(c). The NO conversion of the two kinds of the Cu/SAPO-34 catalysts

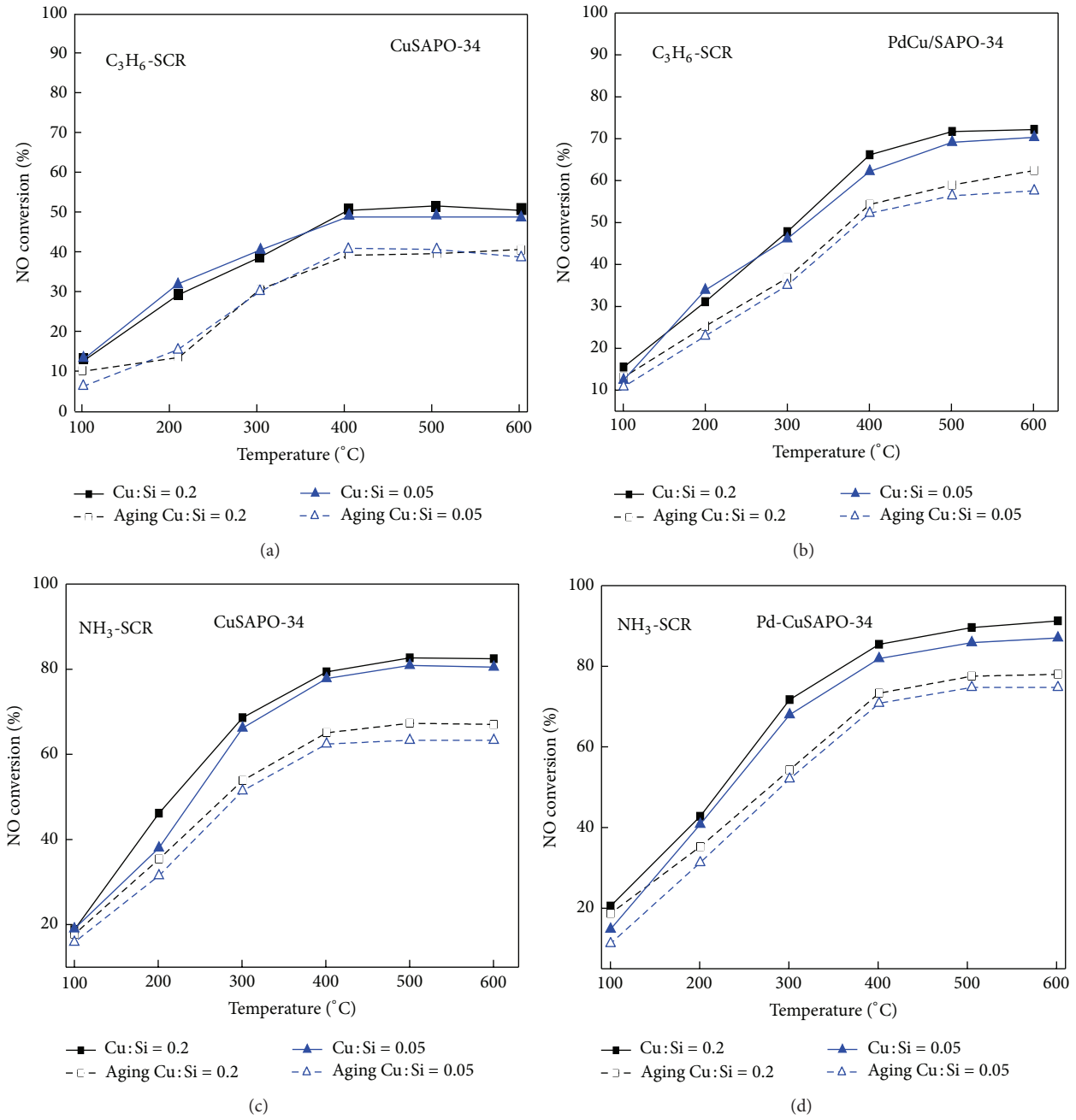

Figure 4: NO conversion of PdCu/SAPO-34 and Cu/SAPO-34 catalysts (GHSV: 40,000 h^{-1}).

decreased sharply after aging for C_3H_6-SCR, especially, when the temperature is in the range of 200–600°C. For NH_3-SCR, the NO conversions of the two kinds of Cu/SAPO-34 catalysts decreased slightly at low temperature, but it decreased significantly as the temperature was above 200°C, particularly, for the sample with Cu/Si = 0.05.

Figure 5 illustrates the XRD patterns of the Cu/SAPO-34 catalysts before and after aging. The intensities of the characteristic peaks weakened after aging compared with the fresh samples, which indicated that the aging process had a negative effect on the crystallinity. It may be the reason for the decrease of the de-NO_x activity.

In order to investigate the effect of aging on the morphology and structure of the Cu/SAPO-34 catalysts, the samples before and after aging were characterized by SEM and the results are shown in Figure 6. Comparing with the fresh samples, more random-shaped materials were found around the crystal particles; the smooth and regular crystal grains were partly destroyed, which leads to the decrease of the NO conversion of the Cu/SAPO-34 catalysts.

3.3.2. PdCu/SAPO-34 Catalysts. The activity test of the PdCu/SAPO-34 catalysts before and after aging in C_3H_6 and NH_3 is also shown in Figures 4(b) and 4(d). The NO

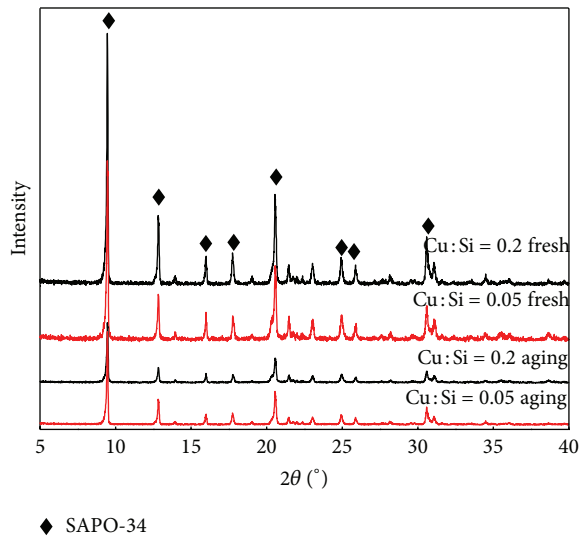

Figure 5: XRD patterns of Cu/SAPO-34 samples before and after aging.

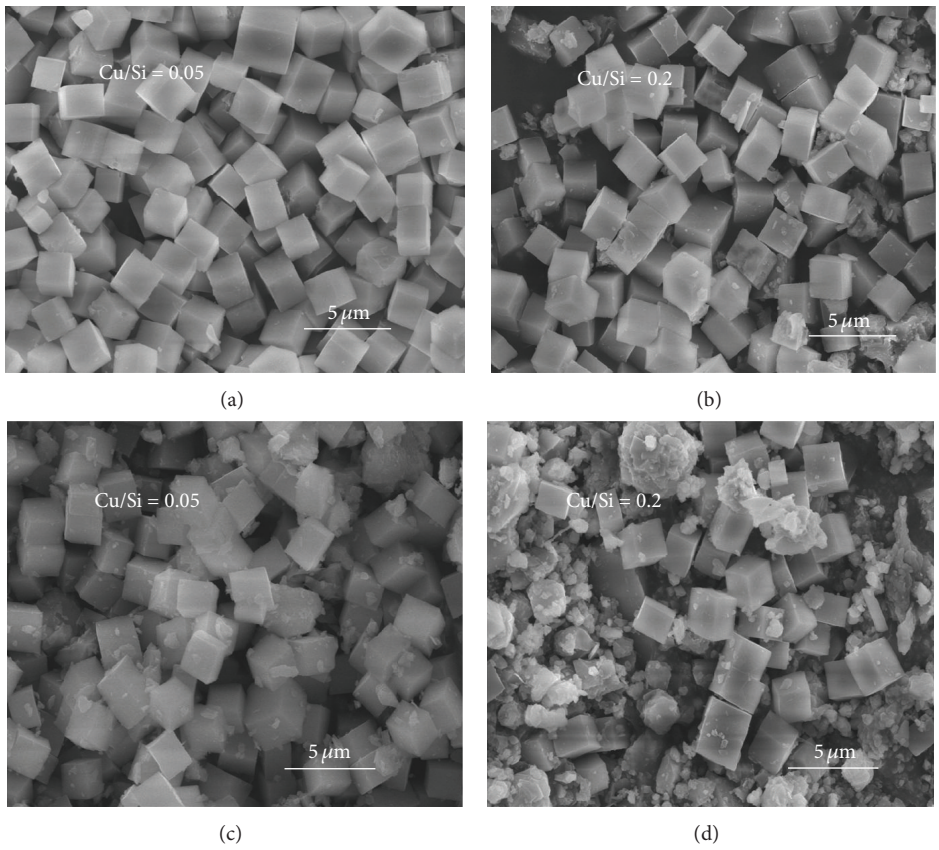

Figure 6: SEM images of Cu/SAPO-34 before ((a) and (b)) and after aging ((c) and (d)).

conversion of the two PdCu/SAPO-34 samples decreased less than the samples without Pd after aging. Besides, the de-NO_x activities of the aged PdCu/SAPO-34 catalysts were superior to that of the aged Cu/SAPO-34 catalysts. It indicated that the addition of Pd can improve the antiaging performance of the Cu/SAPO-34 catalysts.

The XRD patterns of the PdCu/SAPO-34 catalysts are shown in Figure 7. Compared with Figure 1, it can be found that the peaks positions are not remarkably changed by the addition of Pd. No characteristic peak for Pd was visible, which should be related to the low Pd addition amount. The crystal type was still mainly occupied by the SAPO-34 catalyst. The XRD patterns of the PdCu/SAPO-34 samples after aging treatment are also displayed in Figure 7. The crystalline types of samples before and after aging treatment had no obvious changes and also mainly composed of the SAPO-34

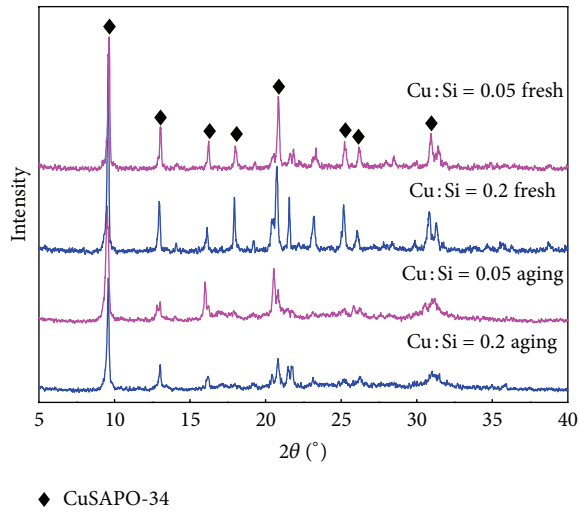

Figure 7: XRD patterns of PdCu/SAPO-34 before and after aging treatment.

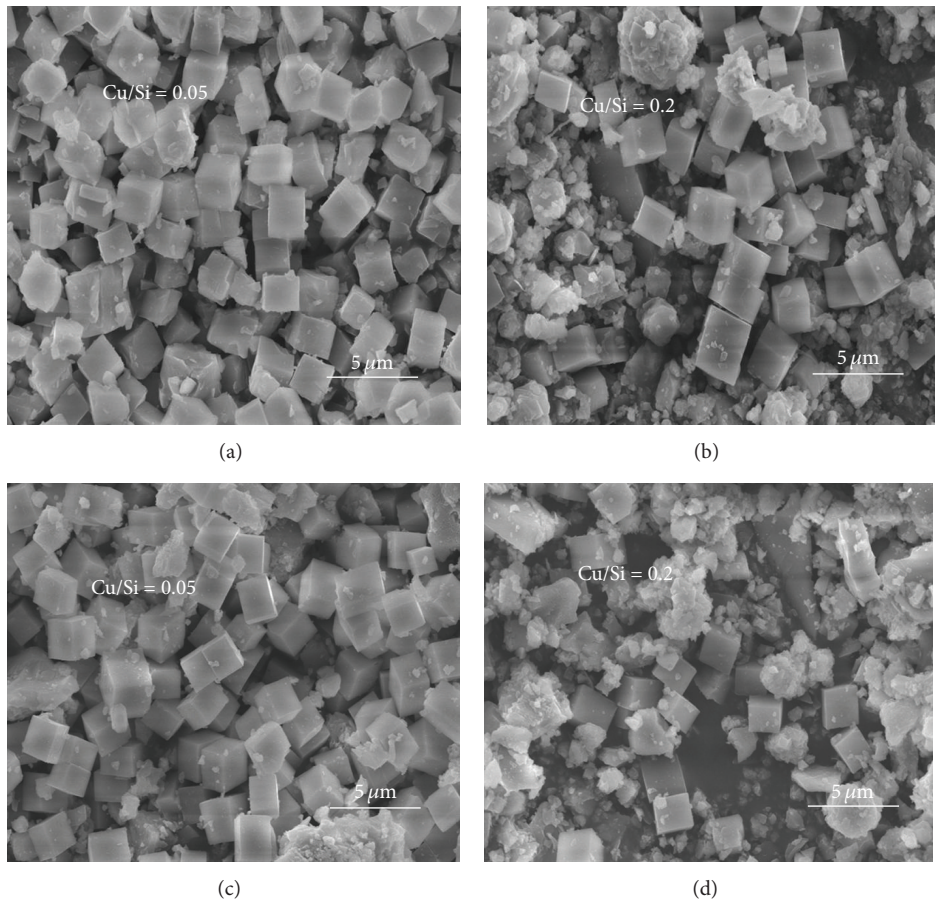

Figure 8: SEM images of PdCu/SAPO-34 before ((a) and (b)) and after aging ((c) and (d)).

catalyst. However, the peaks intensity of the SAPO-34 catalyst corresponding to 2θ = 16.0°~16.2°, 17.85°~18.15°, 20.55°~20.9°, 24.95°~25.4°, and 30.5°~30.7° was weakened obviously, indicating that the aging treatment partially destroyed the regularity and crystallinity of SAPO-34.

The SEM images of the PdCu/SAPO-34 catalyst with Cu/Si = 0.05 and 0.2 are given in Figure 8. All of the samples were mainly composed of the cubic crystal grains, which were the SAPO-34 crystals surrounded by some random-shaped materials. Comparing with the fresh samples, the

aged samples had more random-shaped materials which were the fragment of SAPO-34 crystals. It suggested that more SAPO-34 crystals had been broken after aging treatment, which resulted in the decrease of the NO conversion of the PdCu/SAPO-34 catalysts.

It can be concluded that the de-NO_x activity of the Cu/SAPO-34 and PdCu/SAPO-34 catalysts had a decrease due to the rupture of SAPO-34 crystals resulted by the aging treatment. But the antiaging performance of PdCu/SAPO-34 catalysts was better than Cu/SAPO-34 catalysts.

4. Conclusions

The Cu/SAPO-34 catalysts were successfully prepared by in-situ hydrothermal synthesis. The results of XRD and SEM analysis indicated that the addition of Cu does not change the CHA structure of SAPO-34 crystal and the prepared Cu/SAPO-34 catalysts were cubic crystals with similar averaged sizes (0.6–2 μm). But the high Cu content could change the morphology of the SAPO-34 crystals. The Cu/SAPO-34 catalysts with Cu/Si = 0.05, 0.1, and 0.2 had better de-NO_x activities than other Cu/SAPO-34 and SAPO-34 catalysts.

The antiaging performance of the Cu/SAPO-34 and PdCu/SAPO-34 catalysts was studied and the experiment results suggested that the de-NO_x activity of the Cu/SAPO-34 and PdCu/SAPO-34 catalysts had a decrease due to the rupture of SAPO-34 crystals resulted by the aging treatment. However, the addition of Pd could improve the de-NO_x activity and antiaging performance of the catalysts.

Acknowledgments

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