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Short communication

A novel one-pot synthesized CuCe-SAPO-34 catalyst with high NH_3-SCR activity and H_2O resistance

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ABSTRACT

CuCe-SAPO-34 catalysts based on the one-pot hydrothermal synthesis method were prepared for the first time. The addition of Ce suppressed the formation of CuO and increased the amount of active Cu^{2+}, resulting in better NH_3-SCR activity than Cu-SAPO-34. Ce greatly improved the H_2O resistance during the SCR process by stabilizing the zeolite structure and obstructing the transformation of active Cu^{2+} into inactive forms.

1. Introduction

Copper-containing small-pore zeolites such as Cu-SAPO-34 and Cu-SSZ-13 have been attracting increasing attention as superior NH_3-SCR catalysts [1–6]. The Cu-SAPO-34 catalyst showed excellent SCR activity over a wide range of temperature and quite outstanding hydrothermal stability at high temperatures [7–9].

However, it was reported that deactivation of Cu-SAPO-34 can take place in the presence of water at low temperatures. K. Leistner et al. [10] reported that after exposure to H_2O at 70 °C for 9 h, the NO*x* conversion over Cu-SAPO-34 decreased from 87% to 6% at 200 °C. J. Wang et al. [11] found that hydrothermal treatment at 70 °C could lead to the collapse of the Cu-SAPO-34 structure. Therefore, the presence of H_2O is detrimental to the Cu-SAPO-34 catalyst, and restricts its potential application. Since H_2O cannot be avoided during the SCR process due to the presence of a certain amount of water in diesel exhaust, there is an urgent need to improve the water resistance of this catalyst.

Recently, Z. Ma [12] and W. Shan [13] found that ceria exhibited superior redox ability, facilitating the SCR performance. X. Dong et al. [14] showed that incorporating CeO*x* into a Cu-SAPO-34 catalyst by the incipient wetness impregnation method could improve the SCR activity and suppress the nonselective side reactions. Y. Cao et al. [15,16] reported that CuCe-SAPO-34, which was prepared by wet impregnation of Ce-SAPO-34, showed higher SCR activity, and exhibited better high temperature hydrothermal stability and hydrocarbon resistance than Cu-SAPO-34. Hence, Ce is a promising candidate for improving the NH_3-SCR performance of catalysts, especially under severe conditions.

Lately, copper-tetraethylenepentamine (Cu-TEPA) has been designed to fit the CHA structure [4], and used in the one-pot hydrothermal synthesis method to prepare Cu-SAPO-34 directly [5] which showed high SCR activity and hydrothermal stability [17]. The method is easy to perform, with facile control of Cu loading, and might be applicable at industrial scale. Therefore, in this study, we attempted to prepare a novel CuCe-SAPO-34 catalyst with excellent H_2O resistance by the one-pot hydrothermal synthesis method. The effect of Ce on the structural stability, Cu species distribution, NH_3-SCR performance and H_2O resistance of Cu-SAPO-34 was investigated.

2. Experimental

2.1. Catalyst preparation

CuCex-SAPO-34 catalysts, with x representing the Ce/Al molar ratio in the gel, were prepared by the one-pot hydrothermal synthesis method using Cu-TEPA as the Cu source, cerous nitrate as the Ce source, propylamine (PA) as a co-template, pseudoboehmite as the Al source, 85% phosphoric acid as the P source, and fumed silica as the Si source. The molar composition of the synthesis gel was: 1Al:1P:0.25Si:0.06Cu-TEPA:(0.01/0.04/0.06/0.08)$Ce(NO_3)_3$:1.6PA:40H_2O. The resulting gel was crystallized for 72 h at 180 °C, and calcined in air at 700 °C for 5 h to remove the organic templates. The Cu-SAPO-34 catalyst was prepared by the above method without Ce addition. The catalysts after SCR reaction with 5% H_2O were designated as used samples. Table S1

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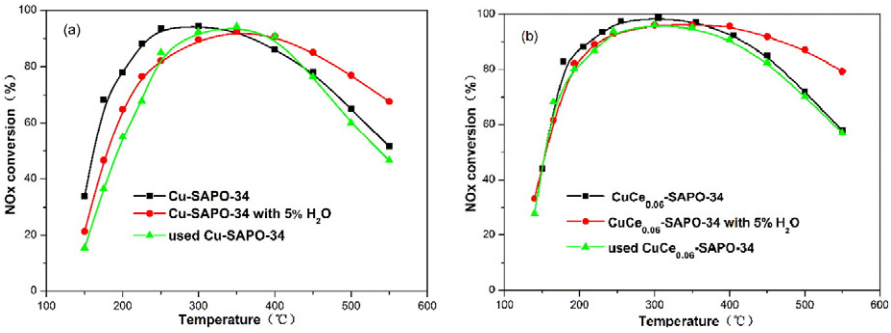

Fig. 1. The NO*x* conversion over (a) Cu-SAPO-34 (b) $CuCe_{0.06}$-SAPO-34 in the absence and presence of H_2O during the SCR process.

shows that the Cu loading and Si:P:Al molar ratio of all samples were quite close.

2.2. Activity measurement

SCR activity tests of the sieved powder catalysts were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, 5% H_2O (when used), balance N_2 and 500 mL/min total flow rate. During the performance tests, about 60 mg catalyst was used, yielding a rather high GHSV of 400,000 h^{-1}. The effluent gas, including NO, NH_3, NO_2, and N_2O, was continuously analyzed by an online NEXUS 670-FTIR spectrometer.

2.3. Characterization

The component contents of catalysts were analyzed using an inductively coupled plasma instrument (ICP, OPTMIA 2000DV) with a radial view of the plasma. Powder X-ray diffraction (XRD) measurements were carried out on a computerized PANalytical X'Pert Pro diffractometer with CuKα ($\lambda = 0.15406$ nm) radiation. N_2 adsorption/desorption isotherms were measured at −196 °C using a Quantachrome Quadrasorb SI-MP. Prior to the N_2 physical adsorption, the samples were degassed at 300 °C for 5 h. Micropore surface areas and micropore volumes were determined by the t-plot method. The surface morphology of the samples was studied using a Field-Emission Scanning Electron Microscope (FE-SEM, SU-8020). Temperature-programmed reduction with hydrogen (H_2-TPR) experiment was carried out on a Micromeritics AutoChem 2920 chemisorption analyzer. X-ray photoelectron spectroscopy (XPS) with Al Kα radiation (1486.7 eV) was used to analyze the oxidation state of copper species on the catalysts' surface (Axis Ultra, Kratos Analytical Ltd).

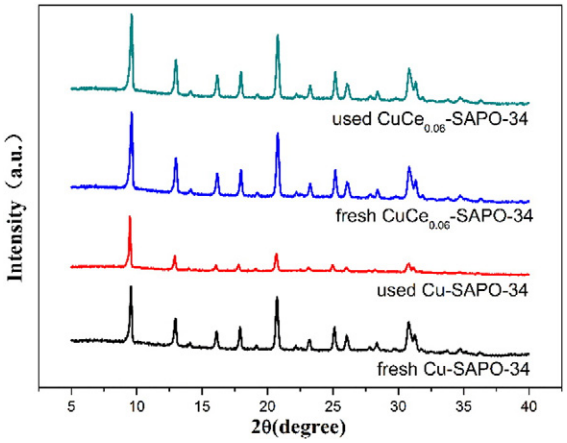

Fig. 2. The XRD results of the fresh and used Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34.

3. Results and discussion

3.1. Catalytic activity

As shown in Fig. S1(a), the NO*x* conversion of CuCex-SAPO-34 increased with increasing Ce loading when the Ce/Al molar ratio was less than 0.06 and then decreased for higher Ce loading. The $CuCe_{0.06}$-SAPO-34 showed the best SCR activity among the prepared CuCex-SAPO-34 samples. Hence, we chose $CuCe_{0.06}$-SAPO-34 to compare with Cu-SAPO-34. As shown in Fig. 1(a), the presence of 5% H_2O decreased the NO*x* conversion of Cu-SAPO-34 below 350 °C, and increased the NO*x* conversion above 350 °C which was speculated that H_2O could inhibit NH_3 oxidation and side-products during the NH_3 oxidation process at high temperatures [18]. The activity of a used Cu-SAPO-34 sample was tested in dry flue gas. The results showed that the effect of H_2O on Cu-SAPO-34 was irreversible. As shown in Fig. 1(b), there was negligible influence of H_2O on the SCR activity of $CuCe_{0.06}$-SAPO-34 below 350 °C, and the NO*x* conversion of this sample increased above 350 °C. As with Cu-SAPO-34, the activity of used $CuCe_{0.06}$-SAPO-34 was retested in dry flue gas. Only a slight loss of SCR activity was observed for the used $CuCe_{0.06}$-SAPO-34 sample. To examine the low temperature hydrothermal stability of Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34, these two catalysts were treated at 70 °C and 150 °C in 10% H_2O/air for 12 h. As shown in Fig. S2, $CuCe_{0.06}$-SAPO-34 showed higher stability than Cu-SAPO-34 after the low-temperature hydrothermal aging. This indicated that the addition of Ce into Cu-SAPO-34 might improve the stability of the sample in moist conditions. Furthermore, the high temperature hydrothermal stability of Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34 were compared as shown in Fig.S1(b), indicating that introducing 0.10 wt.% Ce into Cu-SAPO-34 by the one-pot hydrothermal synthesis method could not significantly affect the hydrothermal stability of Cu-SAPO-34.

3.2. XRD

Fig. 2 shows the XRD patterns of fresh and used Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34 samples. The addition of Ce did not affect the framework or crystallinity of fresh Cu-SAPO-34 as shown in Fig. S3(a). For used Cu-SAPO-34, the intensity of all diffraction peaks decreased significantly. The XRD patterns showed that the crystalline structure was changed by the action of H_2O [11,19]. However, there was no evident decline of crystallinity for the used $CuCe_{0.06}$-SAPO-34 sample compared to the fresh one. This indicated that Ce ions may replace the proton of the Si—O(H)—Al bond to decrease the concentration of Si—O(H)—Al bonds, preventing the hydrolysis reactions at the acid sites [11,20]. The interaction of H_2O with other framework atoms appeared to be much weaker and was reversible, improving the stability of the zeolite

Table 1
Micropore surface area, micropore volume, Cu species distribution and H_2/Cu (mol/mol) ratio of the fresh and used Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34 samples.

Samples	Micropore surface area, m^2/g	Micropore volume, cm^3/g	Proportion of total copper species, %			H_2/Cu, mol/mol
			Cu^{2+}	CuO	Cu^{+}	
Fresh Cu-SAPO-34	533.6	0.28	52	23	25	0.62
Used Cu-SAPO-34	480.2	0.24	35	61	4	0.81
Fresh $CuCe_{0.06}$-SAPO-34	519.7	0.28	64	3	33	0.52
Used $CuCe_{0.06}$-SAPO-34	513.6	0.28	69	3	28	0.52

[19]. The higher stability of the CHA structure in $CuCe_{0.06}$-SAPO-34 contributed to its higher water resistance in comparison with Cu-SAPO-34.

3.3. N_2 adsorption/desorption

According to the N_2 adsorption/desorption results as shown in Table 1, the micropore surface area of Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34 were 533.6 and 519.7 m^2/g respectively, and the micropore volume of those two samples were same. It indicated that the addition of Ce did not result in the significantly decrease of the micropore surface area and micropore volume of Cu-SAPO-34. Therefore, the possibility of blockage Ce due to its large kinetic diameter can be ignored. Furthermore, the used $CuCe_{0.06}$-SAPO-34 contained almost all of the micropore surface area and micropore volume, revealing that the addition of Ce can stabilize the framework structure in consistent with the results of XRD and SEM (Fig. S4).

3.4. H_2-TPR

H_2-TPR was used to identify and quantify the copper species distribution in the catalysts, and the results are shown in Fig. 3. The ratio of Cu species to total copper species were calculated from the results of H_2-TPR, and shown in Table 1. It showed that the ratio of Cu^{2+} to total copper loadings increased from 52 to 64% for the fresh $CuCe_{0.06}$-SAPO-34 and Cu-SAPO-34 sample. This suggested that the addition of Ce to Cu-SAPO-34 could increase the amount of isolated Cu^{2+} ions which are active sites for SCR reaction at low temperatures [21,22], resulting in the observed increase of SCR activity below 350 °C. Similar results were reported by Y. Cao et al. [15], that the interaction between cerium and copper could improve the dispersion of copper species and increase the amount of isolated Cu^{2+} ions. Meanwhile, the addition of Ce decreased the amount of CuO, which could lead to non-selective oxidation of NH_3 at high temperatures [23,24]. $CuCe_{0.06}$-SAPO-34 showed lower NH_3 oxidation at high temperatures (Fig. S5), leading to better SCR activity than Cu-SAPO-34 above 350 °C.

The ratio of Cu^{2+}/Cu loading was 0.64 for fresh and 0.69 for used $CuCe_{0.06}$-SAPO-34, however, in the case of Cu-SAPO-34, the Cu^{2+}/Cu loading decreased from 0.52 to 0.35, with obviously CuO formation. The Cu loadings of Cu-SAPO-34 (3.29%) and CuCe-SAPO-34 (3.28%) was quite same (Table S1). The data indicated that the migration of copper species and formation of CuO occurred for the used Cu-SAPO-34 sample, in accordance with a previous report [10], resulting in the deactivation of Cu-SAPO-34 after the SCR reaction with H_2O and the failure of the catalyst's ability to recover SCR activity in the absence of H_2O (Fig. 1a). In contrast, little change in the copper species distribution was observed on the used $CuCe_{0.06}$-SAPO-34 sample. This result further

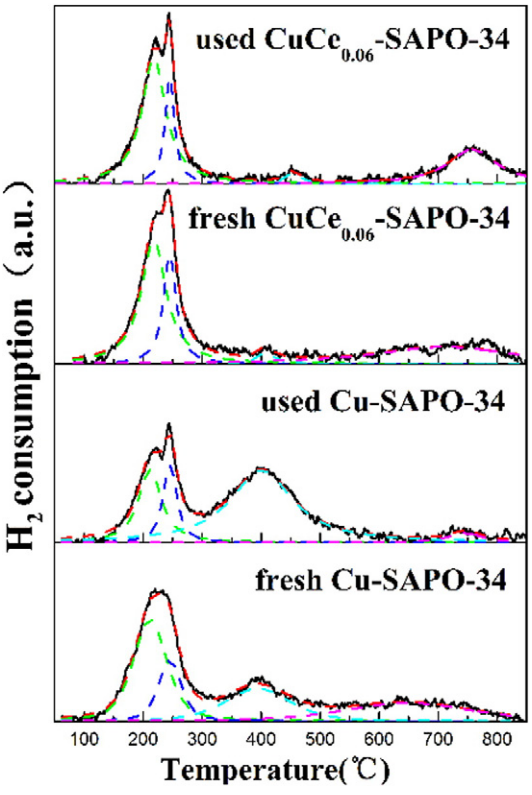

Fig. 3. The H_2-TPR results of the fresh and used Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34.

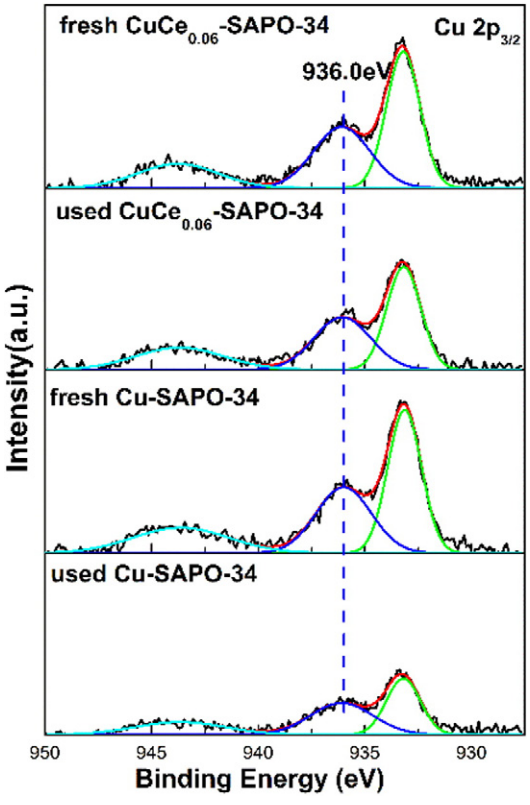

Fig. 4. Cu $2p_{3/2}$ XPS spectra of fresh and used Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34.

confirmed the higher stability of Cu^{2+} ions on $CuCe_{0.06}$-SAPO-34 than on Cu-SAPO-34, leading to the excellent water resistance of the $CuCe_{0.06}$-SAPO-34 catalyst during the SCR reaction (Fig. 1b).

3.5. XPS

The XPS results of the fresh and used Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34 samples are shown in Fig. 4. Cu $2p_{3/2}$ peaks were observed in the ranges of 930.0–940.0 eV. The Cu $2p_{3/2}$ peak around 936.0 eV as well as the satellite peak around 940.0–948.0 eV is used as a characteristic to determine Cu^{2+} [25,26]. The peaks of Cu $2p_{3/2}$ are further discussed in the terms of the effect of water on Cu valence state on the surface of the catalysts. It was found that the relative concentration of isolated Cu^{2+} on the surface of used Cu-SAPO-34 decreased significantly after SCR process involved with water which may be associated with the agglomeration of CuO [26]. Less Cu^{2+} on the surface of used Cu-SAPO-34 sample led to the performance decline for NO*x* removal in a certain degree. However, the change of isolated Cu^{2+} concentration on used $CuCe_{0.06}$-SAPO-34 was not very obvious, indicating that the copper species was not affected by water evidently in accordance with the H_2-TPR results.

4. Conclusions

The effects of H_2O during the SCR process on Cu-SAPO-34 and $CuCe_{0.06}$-SAPO-34 catalysts were investigated by ICP, BET, SEM, XRD, H_2-TPR and XPS. The results indicated that the introduction of Ce could improve the NH_3-SCR performance and H_2O resistance of Cu-SAPO-34. Modification by Ce could decrease the amount of CuO and increase Cu^{2+} ions in Cu-SAPO-34. The addition of Ce could stabilize the framework structure and active Cu^{2+} ions in the presence of H_2O during the SCR process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.04.007.

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