

Short communication

# A novel one-pot synthesized CuCe-SAPO-34 catalyst with high NH<sub>3</sub>-SCR activity and H<sub>2</sub>O 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<sup>2+</sup>, resulting in better NH<sub>3</sub>-SCR activity than Cu-SAPO-34. Ce greatly improved the H<sub>2</sub>O resistance during the SCR process by stabilizing the zeolite structure and obstructing the transformation of active Cu<sup>2+</sup> into inactive forms.

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## 1. Introduction

Copper-containing small-pore zeolites such as Cu-SAPO-34 and Cu-SSZ-13 have been attracting increasing attention as superior NH<sub>3</sub>-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<sub>2</sub>O at 70 °C for 9 h, the NO<sub>x</sub> 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<sub>2</sub>O is detrimental to the Cu-SAPO-34 catalyst, and restricts its potential application. Since H<sub>2</sub>O 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<sub>x</sub> 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<sub>3</sub>-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<sub>2</sub>O resistance by the one-pot hydrothermal synthesis method. The effect of Ce on the structural stability, Cu species distribution, NH<sub>3</sub>-SCR performance and H<sub>2</sub>O resistance of Cu-SAPO-34 was investigated.

## 2. Experimental

### 2.1. Catalyst preparation

CuCe-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<sub>3</sub>)<sub>3</sub>:1.6PA:40H<sub>2</sub>O. 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<sub>2</sub>O were designated as used samples. Table S1

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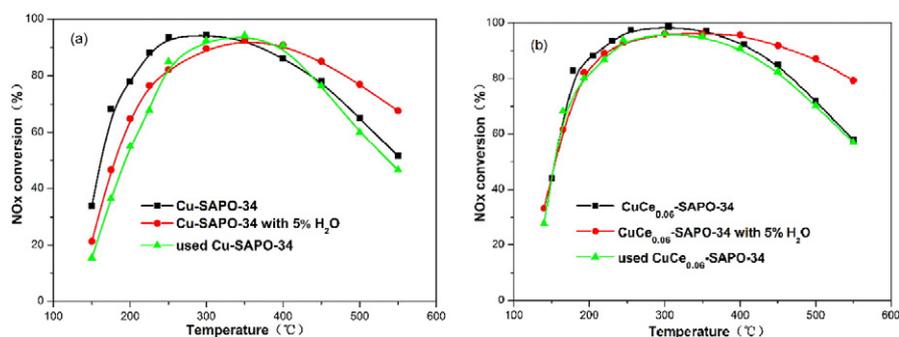


Fig. 1. The NO<sub>x</sub> conversion over (a) Cu-SAPO-34 (b) CuCe<sub>0.06</sub>-SAPO-34 in the absence and presence of H<sub>2</sub>O during the SCR process.

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<sub>3</sub>, 5 vol.% O<sub>2</sub>, 5% H<sub>2</sub>O (when used), balance N<sub>2</sub> 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<sup>-1</sup>. The effluent gas, including NO, NH<sub>3</sub>, NO<sub>2</sub>, and N<sub>2</sub>O, 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 (λ = 0.15406 nm) radiation. N<sub>2</sub> adsorption/desorption isotherms were measured at -196 °C using a Quantachrome Quadrasorb SI-MP. Prior to the N<sub>2</sub> 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<sub>2</sub>-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).

## 3. Results and discussion

### 3.1. Catalytic activity

As shown in Fig. S1(a), the NO<sub>x</sub> conversion of CuCe<sub>x</sub>-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<sub>0.06</sub>-SAPO-34 showed the best SCR activity among the prepared CuCe<sub>x</sub>-SAPO-34 samples. Hence, we chose CuCe<sub>0.06</sub>-SAPO-34 to compare with Cu-SAPO-34. As shown in Fig. 1(a), the presence of 5% H<sub>2</sub>O decreased the NO<sub>x</sub> conversion of Cu-SAPO-34 below 350 °C, and increased the NO<sub>x</sub> conversion above 350 °C which was speculated that H<sub>2</sub>O could inhibit NH<sub>3</sub> oxidation and side-products during the NH<sub>3</sub> 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<sub>2</sub>O on Cu-SAPO-34 was irreversible. As shown in Fig. 1(b), there was negligible influence of H<sub>2</sub>O on the SCR activity of CuCe<sub>0.06</sub>-SAPO-34 below 350 °C, and the NO<sub>x</sub> conversion of this sample increased above 350 °C. As with Cu-SAPO-34, the activity of used CuCe<sub>0.06</sub>-SAPO-34 was retested in dry flue gas. Only a slight loss of SCR activity was observed for the used CuCe<sub>0.06</sub>-SAPO-34 sample. To examine the low temperature hydrothermal stability of Cu-SAPO-34 and CuCe<sub>0.06</sub>-SAPO-34, these two catalysts were treated at 70 °C and 150 °C in 10% H<sub>2</sub>O/air for 12 h. As shown in Fig. S2, CuCe<sub>0.06</sub>-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<sub>0.06</sub>-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<sub>0.06</sub>-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<sub>2</sub>O [11,19]. However, there was no evident decline of crystallinity for the used CuCe<sub>0.06</sub>-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<sub>2</sub>O with other framework atoms appeared to be much weaker and was reversible, improving the stability of the zeolite

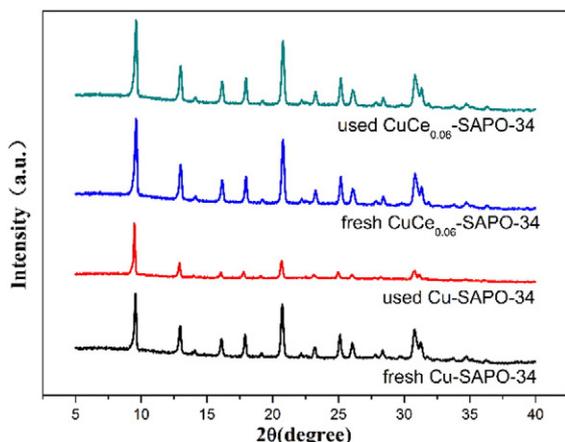


Fig. 2. The XRD results of the fresh and used Cu-SAPO-34 and CuCe<sub>0.06</sub>-SAPO-34.

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