

Short communication

A novel one-pot synthesized CuCe-SAPO-34 catalyst with high NH₃-SCR activity and H₂O resistance



Can Niu^{a,b}, Xiaoyan Shi^{a,b,*}, Kuo Liu^a, Yan You^a, Shaoxin Wang^a, Hong He^a

^a State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

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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 Cu²⁺, resulting in better NH₃-SCR activity than Cu-SAPO-34. Ce greatly improved the H₂O resistance during the SCR process by stabilizing the zeolite structure and obstructing the transformation of active Cu²⁺ 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 NH₃-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 H₂O 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 H₂O is detrimental to the Cu-SAPO-34 catalyst, and restricts its potential application. Since H₂O 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 NH₃-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 H₂O resistance by the one-pot hydrothermal synthesis method. The effect of Ce on the structural stability, Cu species distribution, NH₃-SCR performance and H₂O 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(NO₃)₃:1.6PA:40H₂O. 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% H₂O were designated as used samples. Table S1

* Corresponding author.

E-mail address: xyshi@rcees.ac.cn (X. Shi).

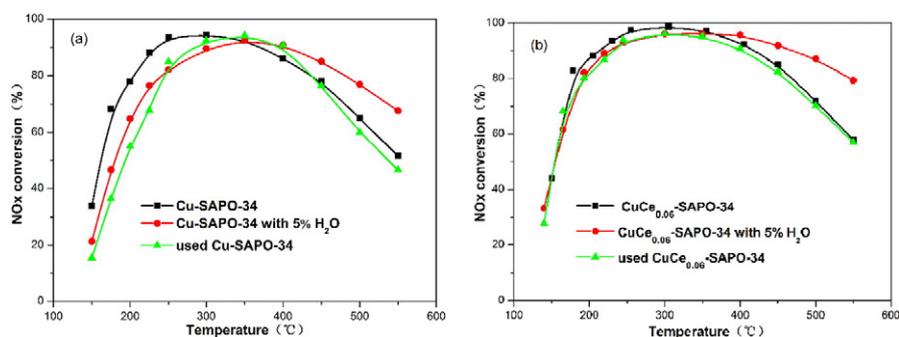


Fig. 1. The NO_x conversion over (a) Cu-SAPO-34 (b) CuCe_{0.06}-SAPO-34 in the absence and presence of H₂O during the SCR process.

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 NH₃, 5 vol.% O₂, 5% H₂O (when used), balance N₂ 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, NH₃, NO₂, and N₂O, 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 CuK α ($\lambda = 0.15406$ nm) radiation. N₂ adsorption/desorption isotherms were measured at -196 °C using a Quantachrome Quadrasorb SI-MP. Prior to the N₂ 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 (H₂-TPR) experiment was carried out on a Micromeritics AutoChem 2920 chemisorption analyzer. X-ray photoelectron spectroscopy (XPS) with Al K α 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_x conversion of CuCe_x-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 CuCe_x-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% H₂O 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 H₂O could inhibit NH₃ oxidation and side-products during the NH₃ 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 H₂O on Cu-SAPO-34 was irreversible. As shown in Fig. 1(b), there was negligible influence of H₂O 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% H₂O/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 H₂O [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 H₂O with other framework atoms appeared to be much weaker and was reversible, improving the stability of the zeolite

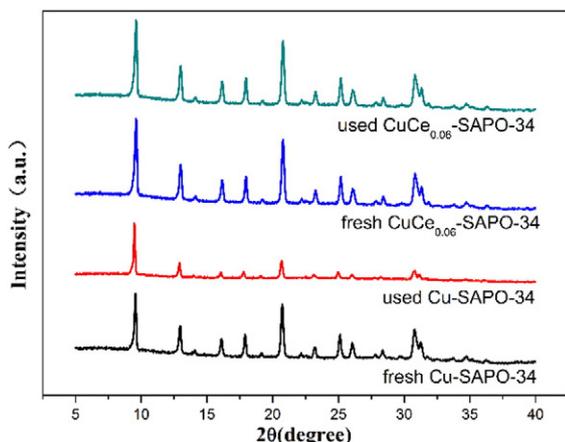


Fig. 2. The XRD results of the fresh and used Cu-SAPO-34 and CuCe_{0.06}-SAPO-34.

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