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Q1 Effects of Na^+ on Cu/SAPO-34 for ammonia selective catalytic reduction

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ABSTRACT

Copper-exchanged chabazite (Cu/CHA) catalysts have been found to be affected by alkali metal and alkaline earth ions. However, the effects of Na^+ ions on Cu/SAPO-34 for ammonia selective catalytic reduction (NH_3-SCR) are still unclear. In order to investigate the mechanism, five samples with various Na contents were synthesized and characterized. It was observed that the introduced Na^+ ion-exchanges with H^+ and Cu^{2+} of Cu/SAPO-34. The exchange of H^+ is easier than that of isolated Cu^{2+}. The exchanged Cu^{2+} ions aggregate and form "$CuAl_2O_4$-like" species. The NH_3-SCR activity of Cu/SAPO-34 decreases with increasing Na content, and the loss of isolated Cu^{2+} and acid sites is responsible for the activity loss.

Introduction

Ammonia selective catalytic reduction (NH_3-SCR) has been considered to be one of the most promising techniques to reduce NO_x emissions due to its high efficiency and broad operating temperature window (Koebel et al., 2000). Copper chabazites (Cu/CHA, *e.g.*, Cu/SSZ-13 and Cu/SAPO-34) have been studied extensively as excellent SCR catalysts due to their outstanding catalytic activity, N_2 selectivity and hydrothermal stability (Fickel et al., 2011; Ishihara et al., 1997; Wang et al., 2012, 2013; Xue et al., 2013; Yu et al., 2013; Liu et al., 2016; Ma et al., 2016; Panahi et al., 2015). In spite of their excellent performance in NH_3-SCR, Cu/CHA catalysts face chemical deactivation problems such as sulfur poisoning (Li et al., 2014; Shen et al., 2015) and alkali metal poisoning (Jing et al., 2015; Q5 Liu et al., 2015; Xie et al., 2015).

In commercial applications, the ammonia used in NH_3-SCR is produced *via* decomposition of a urea solution that may contain trace amounts of alkali metal and alkaline earth ions (*e.g.*, K^+, Na^+, Ca^{2+}, Mg^{2+}). These ions, which have easy access to the SCR catalyst, have been reported to affect the properties of Cu/CHA catalysts (Fedeyko and Chen, 2015; Gao et al., 2015b; Ma Q6 et al., 2015; Liu et al., 2015; Xie et al., 2015). Xie et al. (2015) studied the effects of Na co-cations on the hydrothermal

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stability of Cu/SSZ-13, and the results showed that Cu/SSZ-13 with high Na contents and low Cu contents exhibited poor hydrothermal stability. Fedeyko et al. (2013) and Gao et al. (2015b) investigated the effects of alkali metal and alkaline earth co-cations (Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}) on the activity and hydrothermal stability of Cu/SSZ-13. Their results demonstrated that by removing a portion of the Brønsted acid sites, all co-cations helped to mitigate hydrolysis of the zeolite catalysts during hydrothermal aging. For Cu/SAPO-34, Liu et al. (2015) compared the potassium poisoning phenomena of Cu/SAPO-34 and V_2O_5 $(WO_3)/TiO_2$ by impregnating KOH solution into these two catalysts. The results demonstrated that potassium indeed had negative effects on the catalytic performance of Cu/SAPO-34, even though the poisoning effect of potassium on Cu/SAPO-34 was less significant compared to that of V_2O_5 $(WO_3)/TiO_2$. Ma et al. (2015) investigated the potassium poisoning mechanism for Cu/SAPO-34 by impregnating the catalyst with KNO_3 solutions, to obtain five samples with different potassium contents. Their results illustrated that the transformation of isolated Cu^{2+} to square-plane copper oxide clusters arising from the potassium poisoning was considered to be the main reason for the deactivation of the Cu-SAPO-34 catalyst, although the Brønsted acid sites were also decreased. The study only investigated the effect of K^+ on Cu/SAPO-34, but both K^+ and Na^+ co-exist in urea solutions. Thus, it is necessary to examine the Na effect on Cu/SAPO-34 and the mechanism of its effect on SCR reactions.

In this study, different Na contents were investigated (0, 0.3, 0.7, 1.0 and 1.5 wt.%). The compositions of these samples were characterized by inductively coupled plasma and atomic emission spectrometry (ICP-AES), and the effects of Na on the structure and Cu species of Cu/SAO-34 were studied through specific surface area test, X-ray diffraction (XRD), temperature programmed desorption by NH_3 (NH_3-TPD), temperature programmed reduction by hydrogen (H_2-TPR) and electron paramagnetic resonance (EPR). Na species were determined with CO_2 adsorption diffuse reflectance infrared Fourier transform spectroscopy (CO_2-DRIFTS). Catalytic performance tests and kinetic experiments were also conducted to explore the effects of Na^+ on the NH_3-SCR reaction, and to gain insights into the mechanism of its effect.

1. Materials and methods

1.1. Catalyst preparation

Cu/SAPO-34 catalysts were synthesized using a modified "one-pot" method from a gel with a molar composition of: 1.0 Al_2O_3:1.0 P_2O_5:0.6 SiO_2:0.05 CuO:0.05 tetraethylenepentamine (TEPA):2.0 morpholine (MOR):60 H_2O (Fan et al., 2013; Gao et al., 2013; Martínez-Franco et al., 2012). The sources of Al, P, Si and Cu were pseudoboehmite (83.5 wt.% Al_2O_3), orthophosphoric acid (99 wt.% H_3PO_4), LUDOX (40% SiO_2) and copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) respectively. MOR was chosen as the template agent and TEPA as the Cu^{2+} complexing agent. The detailed synthesis procedures were as follows: firstly, the H_3PO_4 and the pseudoboehmite were mixed with distilled water and stirred for 2 hr at room temperature, and the mixture was named Mix1. Silica sol, MOR, TEPA and $CuSO_4{\cdot}5H_2O$ were mixed with distilled water and stirred for 1 hr at room temperature, named Mix2. Mix2 was slowly added into Mix1, stirred for more than 3 hr at room temperature, and then sealed in a 200 mL Teflon-lined stainless-steel pressure vessel and heated at 200°C for 44 hr for crystallization in an oven under autogenic pressure. Subsequently, the sediment was separated from the mother liquid by centrifuging, then successively washed with distilled water and centrifuged more than 3 times. Finally, the zeolite powder was dried at 120°C in an oven for 12 hr.

The Na-containing samples were synthesized by wetness impregnation with sodium nitrate solutions. The impregnated samples were firstly dried at 100°C for 12 hr, calcined in a muffle furnace with air at 650°C for 5 hr, and finally treated at 750°C for 24 hr in 10 vol.% H_2O/air to imitate the interaction environment of Na^+ and Cu/SAPO-34. The Na-free sample was impregnated with pure water and treated like the Na-containing samples. The fresh sample is designated Cu-F, and others are named Cu-NaX, where "X" represents the nominal weight percentage of sodium. The compositions of the samples from ICP measurements are listed in Table 1 and all catalysts contain similar Cu contents with varying amounts of Na.

1.2. Characterization of catalysts

The compositions (Cu and Na contents) of Cu/SAPO-34 catalysts were determined by ICP-AES.

XRD patterns (Cu *K*α radiation, wavelength (λ) = 1.5418 Å) (Bruker D8 Advance TXS, Bruker, USA) were used to characterize the structure and phase compositions of catalysts, measured in the range of $5° < 2\theta < 50°$ with a step size of 0.01°. Brunauer–Emmett–Teller (BET) surface area was calculated from the linear portion of the BET plot through measuring the N_2 isotherm of the samples at 77 K using F-Sorb 3400 volumetric adsorption–desorption apparatus (F-Sorb 3400, Jin Aipu, China). The catalysts were evacuated at 150°C for 3 hr to remove absorbed water and clean the surface of the catalysts before the measurement.

NH_3-TPD experiments were performed to evaluate the acid sites of the catalysts. 0.1 g catalyst (powder 60–80 mesh) and 0.9 g quartz sand were mixed, and then the mixture was packed in a plug flow reactor. A K type thermocouple was inserted into the center of the catalyst to control the temperature. Prior to the experiments, the catalysts were pretreated at 500°C in 5% O_2/N_2 for 30 min, and then cooled to 100°C. When the temperature had become stable, 500 ppm NH_3/N_2 was flowed through until the outlet NH_3 concentration was stable. Then the catalysts were purged with N_2 to remove weakly absorbed NH_3 until the NH_3 concentration in the outlet gas was lower than 10 ppm. Finally, the catalysts were heated from 100 to 600°C with a ramp rate of 10°C/min. A Fourier transform infrared spectrometer (FTIR) (MKS-2030,

Table 1 – Chemical composition of Cu/SAPO-34 catalysts.

Samples	Cu-F	Cu-$Na_{0.4}$	Cu-$Na_{0.8}$	Cu-$Na_{1.3}$	Cu-$Na_{1.8}$
Cu contents (wt.%)	1.95	1.95	1.93	2.02	2.04
Na contents (wt.%)	–	0.37	0.80	1.29	1.77

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