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Improvement of low-temperature hydrothermal stability of Cu/SAPO-34 catalysts by Cu^{2+} species

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ABSTRACT

The destructive effect of H_2O on SAPO-34 framework and Cu^{2+} species protection mechanism at low temperature were studied in this research. A series of Cu/SAPO-34 samples with varying Cu loadings (0–6.78 wt%) were hydrothermally treated at 70 °C with 80% humidity. Textural characterization results showed that this treatment led to the collapse of SAPO-34 framework at zero or low Cu loadings, which was caused by the breakage of Si–O–Al bonds proved by *ex-situ* DRIFTS and NMR results. The copper content increase enhanced SAPO-34 stabilization. Selective catalytic reduction (SCR) reaction rates were severely reduced after the treatment, while this decrease was gradually suppressed with increasing Cu loading up to 6.78 wt%. NH_3-TPD and EPR results revealed that both the number of Brønsted acid sites and Cu^{2+} species decreased after the treatment, which likely contributed to the reduced SCR reaction rates. Our study indicated that the isolated Cu^{2+} ions were both SCR active site and structure protective agent.

1. Introduction

Recently, Cu/Chabazite catalysts have received widespread attention as ammonia-selective catalytic reduction (NH_3-SCR) catalysts with excellent activity and N_2 selectivity. Also, they demonstrated superior hydrothermal stability at high temperature [1,2]. However, it was reported that the structure and acidity of SAPO-34 molecular sieves deteriorated rapidly and irreversibly when exposed to moisture at low temperatures (<100 °C) after removing the template [3]. This rapid loss of structural integrity and acidity has become a major drawback for the practical application of SAPO-34. Several research groups have investigated this deactivation phenomenon and proposed potential deactivation mechanisms, such as Si–O–Al bonds opening [3–5] and P–O–Al bonds opening [6,7]. In addition, Janssen et al. [8] proposed methods to inhibit the skeleton collapse of SAPO molecular sieve by using templates and carbonaceous material to shield the catalytic sites from contacting with H_2O molecules. Mees et al. [9] found that the hydrothermal stability of SAPO-34 was greatly improved by replacing the hydroxyl groups by amino species. These modification methods may be applied for the process of methanol to olefins (MTO); however, they are not practical for Cu/SAPO-34 catalysts during SCR process as hydrothermal exposure cannot be avoided in vehicle exhaust. In this context, it is important to explore an efficient resolution to improve the durability of SAPO-34 in the presence of water at low temperatures.

This work examines the effect of Cu species introduction on the low-temperature hydrothermal stability of Cu/SAPO-34 catalysts. Cu/SAPO-34 samples were characterized by XRD, N_2 adsorption–desorption measurements, *ex-situ* DRIFTS, and NMR to elaborate deactivation and Cu^{2+} protection mechanism. Furthermore, the variation of acid sites and Cu^{2+} sites caused by the low-temperature hydrothermal treatment (LTH treatment) was examined to understand its effects on the SCR reaction rates.

2. Experimental

2.1. Catalyst preparation

Cu/SAPO-34 catalysts were synthesized using a modified "one-pot" method similar to procedures reported by Prakash and

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Unnikrishnan [10] and others [11–14]. Synthesis gel composition was the following: 1 Al_2O_3: 0.9 P_2O_5:0.7 SiO_2: (0–0.2) CuO: 2 Morpholine (MOR): (0–0.2) Tetraethylenepentamine (TEPA): 5.69 H_2O. The Si, P, Al, and Cu sources were silica sol (40 wt% SiO_2, Qingdao Jiyida Silica Reagent Factory, China), orthophosphoric acid (85 wt% H_3PO_4, Tianjin Kemiou Chemical Reagent Co., Ltd., China), pseudoboehmite (68 wt% Al_2O_3, Shandong Aluminium Industry Co., Ltd., China), and Copper (II) sulfate pentahydrate (purity above 99 wt%, Tianjin Kemiou Chemical Reagent Co., Ltd., China), respectively. MOR (purity above 99 wt%, Tianjin Kemiou Chemical Reagent Co., Ltd., China) was used as the template agent and TEPA (purity above 90 wt%, Tianjin Kemiou Chemical Reagent Co., Ltd., China) as complexing agent of copper (II). The detailed synthesis procedure was as follows: Firstly, the orthophosphoric acid and the pseudoboehmite were mixed with distilled water, and the mixture was marked as Mix 1. The silica sol, MOR, TEPA, $CuSO_4 \cdot 5H_2O$, and distilled water were mixed together, and the mixture was marked as Mix 2. Then, Mix 2 was slowly added into Mix 1, and the two mixtures were well mixed. Secondly, the resulting gel mixture was sealed in a 200-mL Teflon-lined stainless steel pressure vessel and heated in an oven at 200 °C under autogenic pressure for 48 h. After the crystallization process, the sediment was separated from the mother liquid via centrifugation, washed by distilled water, and then filtrated. Finally, the zeolite powder was dried at 120 °C in oven for 12 h and calcined in muffle furnace with air at 650 °C for 6 h.

To examine the stability of Cu/SAPO-34 catalysts, all the catalysts were treated in a humidity chamber for 60 h. The temperature and relative humidity were held at 70 °C and 80%, respectively. Then the catalysts were placed into an oven at 150 °C for 1 h to remove excess water. These samples are named as "F-CuX" and "LH-CuX", where X stands for the Cu loading measured by ICP analysis, and "F" and "LH" stand for fresh samples and samples after LTH treatment, respectively.

2.2. Characterization

Cu contents in Cu/SAPO-34 samples were determined by inductively coupled plasma and atomic emission spectrometry (ICP–AES).

X-ray diffraction (XRD, Bruker D8 Advance TXS, Cu Kα radiation, $\lambda = 1.5418$ Å) was utilized to determine the phase compositions and samples' structures. The XRD patterns were collected with a step size of 0.02° in the 2θ range from 15° to 45°. The relative crystallinity of the samples was expressed as the normalized total area of five peaks (201, 003, 211, 104, and 220) relative to that of the F-Cu0.00 sample (SAPO-34) which was used as a reference with 100% crystallinity [3].

The textural properties such as surface area (BET method) and micropore volume (t-plot method) of the samples were measured by N_2 adsorption–desorption carried out at −196 °C using an automatic micropore physisorption analyzer (Micromeritics ASAP 2020) after the samples were degassed at 300 °C for at least 10 h under 0.133 Pa pressure.

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were measured on Nicolet 6700 spectrometer equipped with a MCT detector and a high-temperature reaction chamber with ZnSe windows. The chamber was connected to a gas-dosing system. In order to exclude the interference of water, Cu/SAPO-34 samples were dried in infrared drying oven for 0.5 h to remove adsorbed water before each measurement. DRIFTS were recorded in the range of 4000–650 cm^{-1} with a resolution of 4 cm^{-1}. *Ex-situ* spectra were recorded at 200 °C, and the KBr spectrum under the same condition was used as the background.

^{27}Al, ^{29}Si, and ^{31}P MAS NMR measurements were performed on a Varian Infinity plus 300WB spectrometer at resonance frequencies of 78.13, 59.57, and 121.37 MHz, respectively, with samples spinning rates of 4 kHz for ^{29}Si, 8 kHz for ^{27}Al, and ^{31}P MAS NMR spectroscopy. Tetramethylsilane (TMS) was used as a chemical reference for ^{29}Si NMR spectroscopy, and H_3PO_4 aqueous solution was used as a chemical reference for ^{31}P NMR spectroscopy, whereas $Al(NO_3)_3$ aqueous solution was used for ^{27}Al NMR spectroscopy. Before MAS NMR measurements, the samples were dried at 150 °C for 1 h to obtain dehydrated Cu/SAPO-34 samples. NMR experiments were conducted on the Cu0.35, Cu1.70, and Cu6.78 samples.

Temperature-programmed desorption using NH_3 (NH_3-TPD) experiments was performed to evaluate the acidity over samples. Prior to the experiments, Cu/SAPO-34 catalysts were pre-treated at 500 °C for 30 min in 10% O_2/N_2, and then cooled to 80 °C in N_2. NH_3 adsorption was performed in 500 ppm NH_3/N_2 until the outlet NH_3 concentration was stable. Then, Cu/SAPO-34 catalysts were purged with N_2 to remove any weakly absorbed NH_3 at 80 °C. Finally, the catalysts were heated from 80 °C to 600 °C at a heating rate of 10 °C/min.

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ESP320 spectrometer. Bruker ESP320E software was used for data analysis. Each spectrum was obtained by multiple scans in order to achieve a satisfactory signal to noise ratio. Prior to the EPR analysis, Cu/SAPO-34 samples were pre-treated in 20% O_2/N_2 at 500 °C for 2 h. Then, X-band ($\upsilon = 9.78$ GHz) was recorded at room temperature, and the magnetic field was swept from 2000 Gauss to 4000 Gauss. Quantification of isolated Cu^{2+} amount was done by using standard solutions of copper (II) sulfate pentahydrate (at −150 °C). All the EPR spectra of Cu/SAPO-34 catalysts were also obtained at −150 °C.

2.3. Kinetics measurement

NH_3-SCR reaction rates of Cu/SAPO-34 catalysts were measured at atmospheric pressure in a quartz reactor (4 mm inner diameter). 25 mg catalysts (80–100 mesh) mixed with 75 mg quartz sand were packed in the plug flow reactor, and the temperature was controlled by a type K thermocouple inserted into the center of the catalysts bed. The gas composition was controlled by mass flow controllers, and the outlet concentrations (NO, NO_2, N_2O, and NH_3) were analyzed by a Fourier transform infrared (FTIR) spectrometer (MKS-2030) equipped with a 5.11-m gas cell. The SCR reaction was kinetically controlled, and no mass transfer limited under this condition (Fig. S1). The differential regime (NO conversions ⩽20%) was highlighted in Fig. S2. Before kinetic experiments, the samples were pre-treated in 5% O_2/N_2 at 500 °C for 30 min. The reaction gas consisted of 500 ppm NO, 500 ppm NH_3, 5% O_2 with N_2 as the balance. Kinetic steady state measurements were obtained at 25 °C intervals, and at each temperature the system kept stable for at least 1 h.

By assuming plug flow reactor and free of diffusion limitations, the NH_3-SCR reaction rates can be calculated from the NO_x conversion by

$$\mathrm{rate}\left[\mathrm{mol\,NO}_x\cdot \mathrm{g_{cata}}\cdot \mathrm{s}^{-1}\right]=\frac{\mathrm{X}_{\mathrm{NO}_x}\,[\%]\times \mathrm{F}_{\mathrm{NO}_x}\left[\mathrm{L}_{(\mathrm{NO}_x)}\cdot \mathrm{min}^{-1}\right]}{\mathrm{m_{catal}}\,[\mathrm{g}]\times 60\left[\mathrm{s}\cdot \overset{-1}{\mathrm{min}}\right]\times 22.4\left[\mathrm{L}\cdot \mathrm{mol}^{-1}\right]}\times\left[\mathrm{mol\,NO}_x\cdot \mathrm{g_{catal}}\cdot \mathrm{s}^{-1}\right] \quad (1)$$

Turnover frequency (TOF), defined as the number of NO molecules converted per second on each isolated Cu^{2+} species in Cu/SAPO-34, was calculated by the following equation:

$$\mathrm{TOF}=\frac{\mathrm{X}_{\mathrm{NO}_x}\,[\%]\times \mathrm{F}_{\mathrm{NO}_x}\left[\mathrm{L}_{(\mathrm{NO}_x)}\cdot \mathrm{min}^{-1}\right]\times 63.5\left[\mathrm{g}\cdot \mathrm{mol}^{-1}\right]}{\mathrm{m_{catal}}\,[\mathrm{g}]\times \mathrm{M}_{\mathrm{Cu}^{2+}}\,[\%]\times 60\left[\mathrm{s}\cdot \mathrm{min}^{-1}\right]\times 22.4\left[\mathrm{L}\cdot \mathrm{mol}^{-1}\right]}\left[\mathrm{s}^{-1}\right] \quad (2)$$