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Silicalite-1@Cu-ZSM-5 core-shell catalyst for N_2O decomposition

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ABSTRACT

Silicalite-1 particles with an average size of 260 nm were used as seeds to prepare Silicalite-1@ZSM-5 core-shell crystals with sizes on the order of 500 nm. A Silicalite-1@Cu-ZSM-5 catalyst was then prepared by ion exchange with copper acetate. Upon appropriate pretreatment in He at 500 °C, the core-shell catalyst showed much higher activity in N_2O decomposition than Cu-ZSM-5 prepared using commercial ZSM-5 as the precursor. Characterization of relevant samples was conducted employing N_2 adsorption-desorption, XRD, ICP, XRF, SEM, TEM, XPS, CO-IR, H_2-TPR, and O_2-TPR. It was found that Silicalite-1@Cu-ZSM-5 has more dimetric Cu^+ upon thermal pretreatment in He. In addition, less O_2 can be adsorbed on Silicalite-1@Cu-ZSM-5. Both factors contribute to the much higher activity of Silicalite-1@Cu-ZSM-5. The effect of co-fed O_2 and H_2O vapor on the catalytic performance was also studied.

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1. Introduction

Zeolites are aluminosilicates with well defined crystalline structures/topologies and micropores. They have thermal stability, acid properties, as well as adsorption and ion-exchange capacities. Therefore, they have been frequently used as catalysts, adsorbents, and ion-exchangers in practical applications. In particular, ZSM-5 (a zeolite with MFI framework topology) and its derived catalysts have found wide applications in fine-chemical synthesis [1–4], conversion of hydrocarbons [5–7], and environmental catalysis including NO decomposition [8,9], selective reduction of NO [10–12], N_2O decomposition [13–17], Fenton's reaction [18,19], and photo-degradation of dyes [20].

The catalytic performance of ZSM-5 is certainly related to its morphological, structural, and chemical properties. Because different types of catalytic reactions have different requirements of detailed location/distribution of active sites, the synthesis of ZSM-5 with controlled structures/morphologies has become an important task.

Seed-induced crystallization has been employed in the synthesis of ZSM-5 with controllable sizes and morphologies [21–23]. However, less attention has been paid to the seed-induced synthesis of "core-shell" structures with ZSM-5 shells. Recently, a seed-induced crystallization method was adopted to prepare Silicalite-1@ZSM-5 core-shell structure, in which Silicalite-1 is the core, and ZSM-5 is the shell [24–26]. It would be interesting to explore the catalytic applications of this type of materials.

N_2O is a green-house gas and may contribute to the ozone-layer depletion [27]. It can be decomposed at elevated temperatures in the presence of a catalyst such as Cu-ZSM-5 [13–16]. Since catalytic reactions take place on the surface region of heterogeneous catalysts, it would be desirable that the active sites are enriched on the surface region of catalyst particles. In this study, Silicalite-1@Cu-ZSM-5 core-shell particles were prepared by ion exchanging Silicalite-1@ZSM-5 with Cu^{2+}, and the catalytic performance in N_2O decomposition was evaluated. Upon appropriate pretreatment in He at 400 °C, the catalyst showed higher activity than Cu-ZSM-5 prepared using commercial ZSM-5 as the precursor. The correlation between physicochemical properties and catalytic performance of these catalysts are discussed.

2. Experimental

2.1. Synthesis of Silicalite-1 seeds

Silicalite-1 seeds with an average crystal size of 260 nm were synthesized according to a previous work [24]. NaOH was dissolved in an aqueous solution (40 wt.%) of tetrapropylammonium hydroxide (TPAOH), and tetraethyl orthosilicate (TEOS) was added. The composition of the mixture was 2.2 $(TPA)_2O$:0.1

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Na_2O:25 SiO_2:1050H_2O:100 EtOH. The mixture was stirred at room temperature for 24 h to ensure the complete hydrolysis of TEOS. Afterwards, it was transferred to a polypropylene bottle and hydrothermally treated at 100 °C for 3 days, and used directly in the following synthesis without any centrifugation or washing process.

2.2. Seeded synthesis of ZSM-5

$Al_2(SO_4)_3{\cdot}18H_2O$ was dissolved in an aqueous solution of NaOH, and a colloidal SiO_2 solution (40 wt.%) was added under stirring. The composition was 1.0Al_2O_3:100SiO_2:28Na_2O:4000H_2O. After the mixture was stirred for 15 min, a calculated amount of Silicalite-1 seed suspension was added. The amount (16 wt.% adopted here) was calculated by (SiO_2 weight in seed sol)/(total SiO_2 weight in starting gel) × 100%. The mixture was stirred at room temperature for 3 h, poured into an autoclave, and the autoclave was rotated (30 rpm) in an oven at 210 °C for 2 h. After cooling the autoclave, the final product was separated by filtration and washed with water for 3 times, dried at 80 °C for 1 day and then calcinated at 550 °C for 6 h. The sample synthesized is denoted as ZM-16, where 16 represents the weight percentage (wt.%) of the seed used in the synthesis.

2.3. Cu exchange procedure

ZM-16 (1 g) was added into 150 mL 0.01 mol/L $Cu(CH_3COO)_2$ solution and stirred at ambient temperature for 24 h. Then, the sample was filtrated and washed with water for 3 times and dried at 80 °C for 1 day. The ion exchanging procedure was repeated 3 times. After that, the sample was calcinated at 550 °C for 6 h in flowing air. The obtained sample is denoted as CZM-16.

For comparison, NH_4-ZSM-5 (Si/Al = 30) from Zeolyst was ion-exchanged to Na-ZSM-5 (denoted as ZM-C) by 0.1 mol/L $NaNO_3$ solution at room temperature with a solid/liquid ratio of 1:150 for three times, and further exchanged with Cu^{2+} and calcined. The obtained sample is denoted as CZM-C.

2.4. Characterization

Scanning electron microscopy (SEM) experiments were conducted using a Philips XL30 D6716 instrument at an operating voltage of 25 kV. Transmission electron microscopy (TEM) experiments were carried out with a JEOL JEM-2010 instrument at an operating voltage of 200 kV. Additional TEM-EDS and TEM-mapping experiments were conducted on an FEI Tecani G^2 F20 S-Twin instrument. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-rB 12 kW diffractometer with Cu Kα radiation. The Cu contents of catalysts were measured by Inductive Coupled Plasma (ICP) Emission Spectrometer (Themo-6300). The actual Si/Al ratios in the prepared samples were determined by X-ray fluorescence (XRF, ZSX Primus II, Rigaku).

Temperature programmed reduction (TPR) with H_2 was carried out in a FINETEC FINESORB-3010 apparatus. A 0.12 g sample (40–60 mesh) was placed in a U-type quartz tube, pretreated in 50 mL/min of He flow at 500 °C for 2 h and then cooled down to 60 °C. The sample was heated to 800 °C (ramping rate 10 °C/min) under 30 mL/min of 10 vol.% H_2 (balance Ar). The H_2 consumption was continuously monitored with a thermal conductivity detector (TCD). A cold trap was used to trap water vapor before the gas stream entered the TCD detector.

In situ DRIFTS experiments were performed with a FTIR spectrometer (Nicolet 6700) equipped with an MCT detector cooled by liquid N_2. A sample was placed in an IR cell fitted with CaF_2 windows and heating cartridge. Prior to recording spectra, individual samples from the same batch of catalyst were pretreated in flowing He (50 mL/min) at room temperature, 150, 250, or 400 °C for 2 h and cooled to room temperature. Then 0.2 vol.% CO (balance He) was passed continuously over the samples at room temperature for 1 h. Finally, IR spectra with 100 scans at a resolution of 4 cm^{-1} were recorded after the samples were swept under flowing He at room temperature for 1 h.

X-ray photoelectron spectroscopy (XPS) data were obtained on a Perkin-Elmer PHI 5000C spectrometer with MgKα radiation as the excitation source.

Temperature-programmed desorption (TPD) of O_2 was also performed on the FINETEC FINESORB-3010 apparatus equipped with a TCD detector. 0.15 g sample was pre-treated in flowing He (50 mL/min) for 2 h at 500 °C with a heating rate of 10 °C/min and then cooled down to room temperature. Afterwards, the sample was treated by flowing O_2 (30 mL/min) for 1 h, and swept with He (30 mL/min) to remove physically adsorbed O_2. Finally, the sample was heated up to 690 °C at a heating rate of 10 °C/min under flowing He (30 mL/min), and O_2 desorbed during the heating was monitored by TCD.

2.5. Catalytic evaluation

N_2O decomposition was carried out in a U-shape quartz fixed-bed reactor loaded with 0.2 g of catalyst. Prior to the reaction testing, the catalyst was pretreated at 500 °C in a flow of pure He (50 mL/min) for 2 h. A gas mixture containing 0.5% N_2O in He with a total flow rate of 60 mL/min was fed immediately after the catalyst was cooled down to room temperature. After 1 h, the reaction temperature was ramped to 100 °C, and then the temperature was varied from 100 to 500 °C stepwise. At each step, the reaction was stabilized for 0.5 h, and the reactor effluent was con-

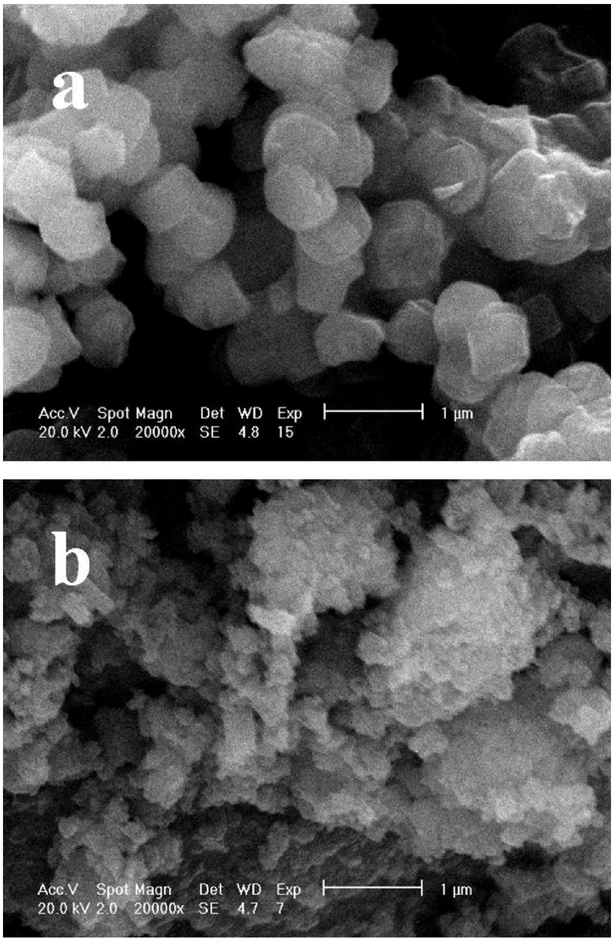

Fig. 1. SEM images of ZM-16 (a) and ZM-C (b).

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