



Catalytic decomposition of N₂O over Cu-ZSM-5 nanosheets

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ABSTRACT

ZSM-5 nanosheets were prepared using [C₁₈H₃₇-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₆H₁₃]Br₂ as a template and then ion-exchanged with Cu cations. The catalytic performance of the obtained Cu-ZSM-5 nanosheets in N₂O decomposition was investigated and compared with that of conventional Cu-ZSM-5. Higher activity as well as better stability was observed for Cu-ZSM-5 nanosheets although the Cu contents of the catalysts were identical. Relevant characterization was conducted using XRF, ICP, XRD, N₂ adsorption–desorption, SEM, TEM, CO-IR, H₂-TPR and O₂-TPD. The data show that the better catalytic performance of Cu-ZSM-5 nanosheets is probably due to better accessibility of active sites, better reducibility of active Cu⁺ species, and the weakened interaction between oxygen and Cu⁺ sites.

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1. Introduction

Zeolites are an important family of aluminosilicates with ordered pore structures, high thermal stability, and diversified types. These properties make them useful in separation and catalysis. However, the crystallite sizes of zeolites are usually on the order of micrometers. The diffusion of molecules in and out of zeolites as well as the accessibility of active sites is constrained by the large crystallite size. To address this limitation, a lot of hierarchical zeolites with both micropores and mesopores (or macropores) have been synthesized [1–9]. Enhanced activities were obtained by the introduction of mesopores/macropores, due to the better accessibility of active sites.

The problem can also be overcome by reducing the thickness of the zeolites crystals, which reduces diffusion path lengths and thus improves molecular diffusion. This has been realized by synthesizing nanosheet zeolites. ZSM-5 nanosheets with high surface areas and short diffusion paths were synthesized using some specially designed surfactants [10–12]. These zeolites can be used directly as catalysts for the cracking of branched polyethylene [10], decalin [13], *n*-heptane [14], and *n*-octane [15], the conversion of methanol to hydrocarbons/gasoline [16–18], gas-phase Beckmann rearrangement [19], gas-phase isomerization and disproportionation of 1,2,4-trimethylbenzene [20], isomerization and

hydrocracking of *n*-decane [21], and catalytic pyrolysis of cellulose, hemicelluloses, and lignin [22]. In addition, ZSM-5 nanosheets were also used as supports to make Pt/ZSM-5 nanosheets for the hydroisomerization of *n*-heptane [23] and MoO_x/ZSM-5 nanosheets for direct methane conversion [24].

Heteroatoms can be incorporated into ZSM-5 nanosheets to design new catalysts. For instance, Fe-ZSM-5 nanosheets were tested in the selective oxidation of benzene with N₂O [25] and the selective catalytic reduction of NO by ammonia [26]. Ti-ZSM-5 nanosheets were used in the epoxidation of olefins [27,28]. Sn-ZSM-5 nanosheets were used in the Baeyer–Villiger oxidation of cyclic ketones [29]. The presence of heteroatoms and the short diffusion path of the ZSM-5 nanosheets are both important factors for these reactions.

In view of the interesting structure and properties of ZSM-5 nanosheets, it would be of great interest to further explore their catalytic applications. Here we report a case on the catalytic decomposition of N₂O on Cu-ZSM-5 nanosheets. N₂O is a potent greenhouse gas and contributes to ozone layer depletion. N₂O is usually eliminated by direct catalytic decomposition [30,31]. Metal cation-exchanged zeolites have been frequently used for catalytic decomposition of N₂O [32–39]. In particular, Cu-ZSM-5 shows higher activity than Cu-FER, Cu-MOR, Cu-BEA, and Cu-Y [32].

In the present work, Cu-ZSM-5 nanosheets were prepared by cation-exchange method, and their catalytic performance for decomposition of N₂O was investigated and compared with that of conventional Cu-ZSM-5. Possible reasons for the better performance of Cu-ZSM-5 nanosheets are discussed.

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2. Experimental

2.1. Catalyst preparation

ZSM-5 nanosheets were prepared following the procedures in the literature [10], using $[C_{18}H_{37}N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}]Br_2$ (denoted as $C_{18-6-6}Br_2$) as a template. Typically, 0.36 g NaOH was dissolved in 20 ml deionized water, then 1.5 g $C_{18-6-6}Br_2$ and 0.37 g $Al_2(SO_4)_3 \cdot 18H_2O$ were added, and the mixture was agitated continuously at 60 °C for 1 h. Then 6.73 g silica gel (25 wt%) was added dropwise at room temperature, and the mixture was stirred at 60 °C for 1 h to obtain a gel with composition of 50 $SiO_2:Al_2O_3:8 Na_2O:4 C_{18-6-6}Br_2:2000 H_2O$. The gel was transferred into a Teflon-lined stainless-steel autoclave and heated at 150 °C for 7 d. The product was filtered, washed with deionized water, dried at 120 °C, and calcined at 550 °C for 4 h in air to remove the template. The obtained sample was exchanged with 1 mol/l $NaNO_3$ solution (with a solution/zeolite ratio of 10 ml/g) at 80 °C for 4 h. The Si/Al ratio of the obtained Na-ZSM-5 nanosheets was determined by XRF as 39.

2 g Na-ZSM-5 nanosheets were ion-exchanged in 41 ml aqueous Cu(II) acetate (0.01 mol/l). The ion-exchange procedure was repeated three times to ensure a full exchange (*i.e.*, Cu/Al ratio = 0.5) [40]. The sample was dried at 100 °C, and denoted as Cu-ZSM-5 nanosheets. For comparison, conventional Cu-ZSM-5 with Si/Al molar ratio of 36 was prepared as follows. NH_4 -ZSM-5 from Zeolyst (CBV8040, Si/Al = 36 measured by XRF) was calcined in static air at 450 °C for 4 h. The resulting H-ZSM-5 was ion-exchanged in 1 mol/l $NaNO_3$ solution with a solution/zeolite ratio of 10 ml/g at 80 °C for 4 h. The ion-exchange procedure was repeated three times, and the obtained Na-ZSM-5 was exchanged by aqueous Cu(II) acetate as described above.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) was carried out on a Bruker D8 Advance X-ray diffractometer with nickel-filtered $Cu K\alpha$ radiation. The bulk Si/Al ratios of Na-ZSM-5 sheets and conventional Na-ZSM-5 were measured by XRF on a Bruker-AXS S4 Explorer. The Cu content was determined by inductively coupled plasma (ICP) atomic emission spectroscopy using a Thermo Electron IRIS Intrepid II XSP spectrometer after dissolving the samples in HF. The BET surface areas and micropore volumes of samples were analyzed by N_2 adsorption at –196 °C using a Micromeritics ASAP 2010 instrument. Scanning electron micrograph (SEM) images were taken on Nova NanoSEM450 instruments. Transmission electron microscope (TEM) images were taken with a JEOL JEM-3010 with an accelerating voltage of 300 kV.

DRIFTS data were recorded on an FTIR (Nicolet 6700) equipped with an MCT detector cooled by liquid N_2 . The DRIFTS cell was fitted with CaF_2 windows and a heating cartridge. Samples were activated in He at 150, 250 or 400 °C for 2 h, cooled to room temperature under flowing He (50 ml/min), and treated in flowing 0.2 vol.% CO–He mixture for 60 min, then swept under the He flow for 60 min. Spectra were collected at room temperature under flowing He, with a resolution of $4 cm^{-1}$ and accumulation of 100 scans.

Temperature-programmed reduction (TPR) profiles were obtained on a Micromeritics AutoChem II apparatus. The sample (100 mg) was pretreated in He at 500 °C for 2 h, cooled to 50 °C in He, and subsequently contacted with a H_2/Ar mixture (10 vol.% H_2 , 30 ml/min). The temperature was ramped to 800 °C at a rate of 10 °C/min. The H_2 consumption was monitored using a thermal conductivity detector (TCD).

O_2 temperature-programmed desorption (O_2 -TPD) was carried out in a quartz reactor. The loaded sample (100 mg) was pretreated with pure He (50 ml/min) at 200 °C for 2 h, then cooled to room

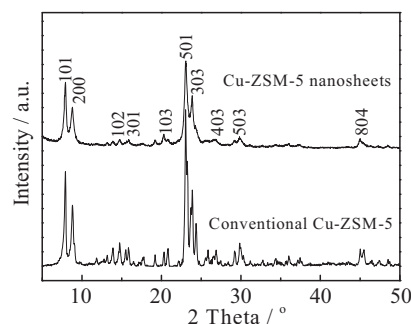


Fig. 1. XRD patterns of Cu-ZSM-5 samples.

temperature. The ambient was switched to 5% O_2/He (flow rate: 50 ml/min), the catalyst was heated to 500 °C at a rate of 10 °C/min, and then kept at 500 °C for 2 h. After cooling down to room temperature, the ambient was switched to pure He (50 ml/min) to remove physisorbed oxygen during the He purging for 1 h. Finally, the catalyst was heated in He (50 ml/min) to 550 °C at a rate of 10 °C/min and kept at 500 °C for 20 min. The desorbed oxygen was monitored by a TCD detector.

2.3. Catalytic testing

The catalytic measurements for N_2O decomposition were carried out in a fixed-bed flow reactor at atmospheric pressure [39]. Briefly, 0.2 g catalyst (40–60 mesh) was loaded into a U-shaped glass tube (7 mm i.d.), heated to 500 °C at a rate of 10 °C/min under flowing He (50 ml/min), and held at 500 °C for 2 h. After cooling down to room temperature, 0.5% N_2O/He (60 ml/min) flowed through the catalyst for 1 h, during which the concentration of N_2O were periodically measured by GC (Agilent 7890A) that can separate N_2O , N_2 , and O_2 . After reaching adsorption–desorption equilibrium, the difference in several consequent GC measurements was generally within 0.3%. The reaction temperature was then varied using a furnace and kept at various elevated temperatures for 30 min in each temperature step. The existing stream was again periodically analyzed by the GC, and the conversion of N_2O was calculated according to $X = ([N_2O]_{in} - [N_2O]_{out})/[N_2O]_{in}$, where $[N_2O]_{in}$ refers to the N_2O concentration or peak area at room temperature, and $[N_2O]_{out}$ refers to the N_2O concentration or peak area at an elevated temperature [39].

In order to study the influence of O_2 on the catalytic activity, 5% O_2 was added into the reaction mixture whereas the concentration of N_2O was still 0.5%, and the total flow rate of the reaction mixture was still 60 ml/min. To test the stability of catalysts, the N_2O conversions on Cu-ZSM-5 nanosheets and conventional Cu-ZSM-5 were measured as a function of time on stream. After pretreatment in He at 500 °C, the catalyst was cooled to 475 °C. The ambient was switched to 0.5% N_2O/He , and the exiting stream was periodically analyzed by GC for 50 h. Finally, the catalyst was cooled down while 0.5% N_2O/He was still flowing. The $[N_2O]_{in}$ was obtained when the catalyst was cooled and no N_2O decomposition took place.

3. Results

3.1. Structural, morphological and textural properties

Fig. 1 shows the XRD patterns of Cu-ZSM-5 nanosheets as well as conventional Cu-ZSM-5. Both samples exhibit diffraction peaks characteristic of MFI structure. For Cu-ZSM-5 nanosheets, only the peaks at $2\theta = 7.87^\circ$, 8.80° , 20.34° , 23.08° , 23.90° , 29.93° , and 44.95° corresponding to crystal planes (1 0 1), (2 0 0), (1 0 3), (5 0 1), (3 0 3), (5 0 3), and (8 0 4) are obvious, whereas reflections corresponding

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