# Catalytic decomposition of $N_2O$ over Cu-ZSM-11 catalysts

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## ARTICLE INFO

## ABSTRACT

The catalytic decomposition of $N_2O$ was investigated over a series of Cu-ZSM-11 catalysts with different Si/Al ratios. The physicochemical properties of the catalysts were characterized by XRD, $N_2$ adsorption, SEM, $^{27}Al$ MAS NMR, DRIFTS, XPS, and $H_2$-TPR. These catalysts were found to be effective for $N_2O$ decomposition. The catalytic activity in terms of conversion decreases when the Si/Al ratio increases, due to the decreased amount of active $Cu^+$ species and the weakened reducibility of active sites. A comparison of Cu-ZSM-11 and Cu-ZSM-5 with the same Si/Al ratio demonstrates that Cu-ZSM-11 is apparently more active than Cu-ZSM-5, due to the enhanced reducibility of active $Cu^+$ species and better accessibility of active sites in Cu-ZSM-11.

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## 1. Introduction

Nitrous oxide ($N_2O$), commonly known as laughing gas, is a potent greenhouse gas with a global warming potential 310 times that of $CO_2$, and it also contributes to ozone layer depletion. Anthropogenic $N_2O$ comes from the combustion of fossil fuels and biomass, the production of nitric and adipic acids, the use of nitrogen-fertilizers and so on. Considering that the concentration of atmospheric $N_2O$ is increasing at an annual rate of 0.2–0.3% [1], it is necessary to reduce the emission of $N_2O$. $N_2O$ can be eliminated by thermal decomposition [2], non-selective catalytic reduction [1], selective catalytic reduction [3,4] and direct catalytic decomposition [5–8]. Among these techniques, direct catalytic decomposition of $N_2O$ ($N_2O = N_2 + 1/2O_2$) is considered to be the most efficient and economic.

Catalysts that have been explored in the decomposition of $N_2O$ include supported noble metals [8–10], pure and mixed oxides [7,11–14], and zeolite-based catalysts [15–18]. Since Iwamoto and co-workers [19] discovered the superior activity of Cu-ZSM-5 in NO decomposition, attempts have been made to demonstrate the application of copper-containing and other transition metal-containing zeolites in $N_2O$ decomposition. Smeets et al. [17] found that among $Cu^{2+}$-exchanged zeolites with different topologies, Cu-

ZSM-5 performed best for $N_2O$ decomposition. Thus, it is a common notion that ZSM-5 has some special properties that makes it particularly useful in $N_2O$ decomposition after being exchanged with $Cu^{2+}$.

Both ZSM-11 and ZSM-5 belong to the Pentasil family. Nevertheless, ZSM-11 only has straight micropores whereas ZSM-5 has both straight and sinusoidal micropores. The catalytic performance of ZSM-11 has been studied in the aromatization and isomerization of 1-hexene [20], the cracking of pentenes to $C_2-C_4$ olefins [21], and the conversion of methanol to hydrocarbons [22]. In most cases, ZSM-11 showed better catalytic performance than ZSM-5. Therefore, it would be interesting to study whether Cu-ZSM-11 outperforms Cu-ZSM-5 in $N_2O$ decomposition. In the present work, we report the development of a new Cu-ZSM-11 catalyst system exhibiting remarkable activity in $N_2O$ decomposition. The effect of Si/Al ratio and impact of the zeolite structure (ZSM-11 vs. ZSM-5) on the performance of the $Cu^{2+}$-exchanged materials are discussed based on the characterization results.

## 2. Experimental

### 2.1. Catalyst preparation

Na-ZSM-11 samples with different Si/Al molar ratios were hydrothermally prepared according to Ref. [23] with minor modification of the procedure. Sodium aluminate and sodium hydroxide were dissolved in an aqueous solution of tetrabuthylammonium

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hydroxide (TBAOH), and tetraethylorthosilicate was then added. The mixture was stirred till uniform. The molar composition of the resulting gel was $4Na_2O:Al_2O_3:xSiO_2:20TBAOH:200H_2O$, where $x$ was 30, 50 and 70, respectively. The gel was transferred into a Teflon lined autoclave and crystallized at 150 °C for 3 days. The product was filtered, washed, dried at 100 °C overnight and then calcined in air at 550 °C for 4 h to remove the template. The obtained samples were exchanged in 1 M $NaNO_3$ solution with a solution/zeolite ratio of 10 mL $g^{-1}$ at 80 °C for 4 h.

The copper-containing catalysts were prepared by ion exchange [24]. The Na-ZSM-11 samples were exchanged in 0.01 M copper acetate solution at room temperature for 24 h. The amount of $Cu^{2+}$ solution added depended on the Si/Al ratio to ensure a full exchange (i.e., Cu/Al ratio = 0.5). The exchange procedure was repeated three times for each zeolite sample. After the third exchange process, the zeolites were filtered, washed and dried at 100 °C overnight. The as-prepared samples were denoted as Cu-ZSM-11($Y$), where $Y$ represents the Si/Al molar ratio measured by X-ray fluorescence (XRF).

For comparison, Cu-ZSM-5(36) 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 exchanged in 1 M $NaNO_3$ solution with a solution/zeolite ratio of 10 mL $g^{-1}$ at 80 °C for 4 h. The exchange procedure was repeated three times. Cu-ZSM-5(36) was prepared in the same way as Cu-ZSM-11 using the Na-ZSM-5 as the starting material.

## 2.2. Catalyst characterization

X-ray powder diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer with nickel-filtered Cu Kα radiation with a voltage and current of 40 kV and 40 mA, respectively. The bulk Si/Al ratios of the prepared ZSM-11 zeolites and a reference sample ZSM-5 from Zeolyst were measured by XRF on a Bruker-AXS S4 Explorer. The Cu and Al contents were determined by inductively coupled plasma (ICP) atomic emission spectroscopy using a Thermo Electron IRIS Intrepid II XSP spectrometer after dissolution of the samples in HF. BET surface areas and micropore volumes of the catalysts were analyzed by $N_2$ adsorption at −196 °C using a Micromeritics ASAP 2010 instrument. Scanning electron microscopy (SEM) images were recorded digitally on a Philips XL 30 microscope operating at 30 kV. $^{27}Al$ magic-angle spinning nuclear magnetic resonance ($^{27}Al$ MAS NMR) measurements were performed on a Bruker DSX-300 spectrometer at a resonance frequency of 104.3 MHz. The spectra were recorded at a spinning rate of 12 kHz. The samples were hydrated in a desiccator over a saturated NaCl solution for 3 days prior to the measurements.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization of the catalysts was performed using a Nicolet 6700 spectrometer equipped with a high-sensitive MCT detector. The DRIFTS cell was fitted with $CaF_2$ windows and a heating cartridge. The dry samples were activated in He at 25, 100, 200, 400, or 500 °C for 2 h, respectively, and then cooled to 25 °C to adsorb CO. After the samples were treated in flowing 0.5 vol.% CO–He mixture for 0.5 h, and then swept under the He flow for 0.5 h, IR spectra were recorded 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 loaded with 100 mg of sample. The samples were pretreated in He at 500 °C for 2 h, then cooled to 60 °C in He. The samples were subsequently contacted with a $H_2$/Ar mixture (10 vol.% $H_2$) flowing at 30 mL $min^{-1}$, and heated with a ramping rate of 10 °C $min^{-1}$ to a final temperature of 800 °C. The $H_2$ consumption was monitored using a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a

Perkin–Elmer PHI 5000C spectrometer with MgKα radiation as the excitation source. The adventitious carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energy (BE). Before the measurements, the samples were pretreated ex-situ in He at 500 °C for 2 h.

## 2.3. Catalytic tests

The catalytic measurements for $N_2O$ decomposition were carried out in a fixed-bed flow reactor at atmospheric pressure. The catalysts (0.2 g, 40–60 mesh) were packed into the isothermal part of the quartz tubular reactor. Prior to the reaction, the catalysts were pretreated in situ in He at 500 °C for 2 h. The gas reactant contained 0.5% $N_2O$ and balancing He. The total flow rate of the gas reactant was 60 mL $min^{-1}$. The reaction temperature was from 275 to 500 °C. At each temperature the reactions were stabilized for 0.5 h. The feed and the reaction products were analyzed on-line by a gas chromatograph (Agilent 7890A) equipped with a TCD.

## 3. Results

### 3.1. Structural, morphological and textural properties

The XRD patterns of Cu-ZSM-11 samples with different Si/Al ratios (15, 25, 36) are shown in Fig. 1. It is evident that these samples exhibit the characteristic reflections of the MEL topology [25]. Cu-ZSM-5(36) with Si/Al molar ratio of 36 is also given in Fig. 1 for comparison. It has a typical MFI structure [25]. The differences between two kinds of zeolites can be found clearly in the $2\theta$ range of 22.5–25.0° and 44.5–46.0°, respectively [20,25].

$^{27}Al$ MAS NMR is a powerful technique to characterize the local coordination environment of aluminum atoms in zeolites [26,27]. Fig. 2 depicts the $^{27}Al$ MAS NMR spectra of Cu-ZSM-11 and Cu-ZSM-5(36). Only an intense signal at 56 ppm (assigned to framework aluminum atoms in tetrahedral coordination) is observed for Cu-ZSM-11 samples with different Si/Al ratios (15, 25, 36), implying that all of the Al atoms are located in the framework of ZSM-11. In addition to the intense signal at 56 ppm, a very weak signal at 0 ppm attributed to extra-framework aluminum atoms in octahedral coordination can be found for Cu-ZSM-5(36).

Fig. 3 displays the SEM images of Cu-ZSM-11 and Cu-ZSM-5(36). For Cu-ZSM-11 samples with different Si/Al ratios, the particles exhibit rectangular parallelepiped shapes with the length of 1–1.5 μm, and the width of 200–500 nm. For Cu-ZSM-5(36), most of the particles are approximately sphere-shaped with diameters in the range of 250–500 nm. Some bigger granules about 1 μm can also be identified.

Table 1 collects additional data on the physicochemical properties of the samples. As shown in Table 1, the bulk Si/Al ratio of ZSM-11 measured by XRF is close to that of the initial gel. The
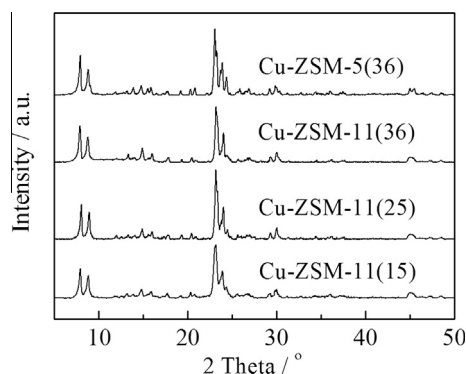


**Fig. 1.** XRD patterns of different samples.