



# Nitrous oxide decomposition over transition metal exchanged ZSM-5 zeolites prepared by the solid-state ion-exchange method

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## ABSTRACT

This paper studied nitrous oxide decomposition over a series of transition metal exchanged ZSM-5 zeolites prepared by solid-state ion-exchange method. Crystallographic structure of the catalysts has been investigated with the aid of XRD analysis. The texture of the prepared catalysts was investigated using nitrogen sorption. FTIR measurements applying pyridine as a probe molecule have been carried out in order to investigate the nature of the acid sites of the different catalysts. In situ electrical conductivity measurements were carried out in order to relate the activity of this series of catalysts to their electrical conductivity variation in the presence of N<sub>2</sub>O. The obtained results revealed that the N<sub>2</sub>O decomposition activity is related to the relative conductivity decrease upon the admission of N<sub>2</sub>O over metal exchanged ZSM-5 zeolites. Further studies have been performed over Co-, Cu- and Fe-ZSM-5 catalysts since they showed the highest activity patterns among all the tested catalysts. Such studies included the effect of changing Si/Al ratio, the exchange level, the calcination temperature and the milling time.

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## 1. Introduction

The study of the catalytic decomposition of nitrous oxide has gained more attention because N<sub>2</sub>O was cited according to the Kyoto Protocol as a non-CO<sub>2</sub> greenhouse gas. Nitrous oxide is also known to participate in the destruction of the stratospheric ozone layer [1–4]. In this context, it was reported that a doubling in the atmospheric laughing gas concentration could result in 12% decrease in the total stratospheric ozone [4]. In the recent years an increased number of articles was published aiming to suggest routes for the reduction of nitrous oxide emission (see for example refs. [3–57]). The suggested solutions include, (i) utilization of N<sub>2</sub>O in the selective oxidation of methane to methanol [5,6] and benzene to phenol [6–18], (ii) direct catalytic decomposition of N<sub>2</sub>O into its elements [3,19–41], and (iii) selective catalytic reduction (SCR) of N<sub>2</sub>O with ammonia [41–43], carbon monoxide [44–49] and hydrocarbons [4,50–57]. Among the catalysts tested for N<sub>2</sub>O conversion metal exchanged ZSM-5 zeolites exhibited

promising activity features. This is not only true for the direct decomposition [3,19–26,35–41] and the SCR of N<sub>2</sub>O [4,41–45,50–57], but also for the SCR of NO [58–60]. Moreover, enhancement effect of NO for the direct N<sub>2</sub>O decomposition was reported over Fe-ZSM-5 catalysts [61,62].

Different preparation methods have been utilized for the preparation of transition metal exchange ZSM-5 catalysts. These include conventional ion exchange in aqueous solution, solid-state ion-exchange (SSIE), sublimation or chemical vapour deposition and the ex-framework method, i.e. M-ZSM-5 which contains extra-framework metal species prepared by calcinations and steam treatment of M-ZSM-5. In this context, it was reported that Fe-ZSM-5 prepared by the SSIE method is more active towards direct N<sub>2</sub>O decomposition than that obtained via aqueous ion exchange [20,41]. The same authors [20] also showed that ex-frame Fe-ZSM-5 is more active than Fe-ZSM-5 prepared by the SSIE methods towards the same reaction. Meanwhile, approximately similar activity features were reported for Fe-ZSM-5 prepared by the SSIE and the chemical vapour deposition [63]. Kögel et al. [50] revealed that Fe-ZSM-5 prepared via the SSIE method has a high activity in N<sub>2</sub>O reduction with propane in the presence of NO. The same catalyst exhibited also high activity during NO reduction with isobutane [64]. SSIE method was applied also for the preparation of active Co-ZSM-5 in the ammoxidation of ethane to acetonitrile [65].

In the preparation of transition metal exchanged ZSM-5 catalysts H- or NH<sub>4</sub>-forms of the zeolite powder are mixed with

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a metal salt (usually chloride). Uniform mixtures are obtained by using ball milling [65]. However, mixing with agate mortar was also reported [66]. The obtained mixture is then heated in air, inert atmosphere or vacuum. During the thermal treatment, the solid-state interaction occurs which is accompanied by evolution of HCl or  $\text{NH}_4\text{Cl}$  gases, respectively. Generally, solid-state ion-exchange method has the following advantages: (i) it allows the control of the metal loading, (ii) it allows the exchange of multivalent cations into zeolite site which is normally very difficult because of the large size of the hydrated metal complex [65], (iii) it is reproducible even in the presence of air atmosphere, (iv) it can create some active sites that are different from those obtained by aqueous exchange [65], and (v) it allows the control of the crystallite size. Such properties facilitate the solid-state ion-exchange method to be applied in the large-scale manufacture of metal exchanged zeolite catalysts. The present investigation was undertaken to shed some light on the activity of a series of transition metal exchanged ZSM-5 catalysts, prepared via the SSIE method, towards direct  $\text{N}_2\text{O}$  decomposition. Further experiments were carried out on the most active catalysts, namely Co-, Cu- and Fe-ZSM-5 catalysts. This includes the influence of Si/Al ratio, exchange level, calcination temperature and milling time.

## 2. Experimental

### 2.1. Catalysts preparation

The zeolite ZSM-5 materials with different Si/Al ratios (25, 40, 50, 100, 150, and 200) were synthesized in a 2 L stirring autoclave through hydrothermal crystallization of a reaction mixture starting from sodium aluminate as the  $\text{Al}_2\text{O}_3$  source, colloidal silicic acid as the  $\text{SiO}_2$  source, and tetrapropylammonium-bromide (TPABr) as the template according to the procedure reported recently [18]. The chemical composition determined by ICP yields iron content less than 0.01 wt.% for all samples. The ammonium form of the Na-ZSM-5 zeolites was prepared by the conventional ion exchange with ammonium nitrate solution (2 M) at 95 °C under stirring. The working procedure was done for three times, 15 min stirring at 95 °C for the first two exchanges and 3 h stirring for the last one. The obtained  $\text{NH}_4$ -ZSM-5 zeolites were, then, dried at 110 °C for 16 h.

Transition metal-exchanged ZSM-5 zeolites were obtained by solid-state ion-exchange (SSIE) of its ammonium form as reported previously [50,62]. Briefly, 5 g of the parent zeolite was mechanically mixed with the transition metal chlorides or nitrates in case of silver and cerium ions (adjusted to achieve 100% exchange level taking into account the metal oxidation state, for example in case of silver; Ag/Al = 1.0, for copper; Cu/Al = 0.5) for 1 h in a ball mill (type Fritsch, which contains 5 balls). Subsequently, the mixture was heated to 550 °C within 3 h in chamber furnace and kept at this temperature for 6 h under static air conditions. During this thermal treatment the ion exchange between the  $\text{NH}_4^+$  ions of the zeolite and the metal cations of the salt takes place. Afterwards the product was cooled down to ambient temperature, washed intensively with de-ionized water to remove the adsorbed chloride ions and then dried at 110 °C for 16 h. Finally, the obtained catalysts were pressed to tablets, crushed and sieved to obtain fractions of 630–800  $\mu\text{m}$ . The obtained samples were denoted as M-ZSM-5, where M denotes the metal cation used.

### 2.2. Characterization of the catalysts

Chemical composition of the different catalysts was determined by using inductively coupled plasma atomic emission spectroscopy (ICPAES) using a PerkinElmer Plasma 400 emission spectro-

meter. The samples were dissolved in a mixture of concentrated HCl,  $\text{HNO}_3$ , and HF. Powder X-ray diffractograms were obtained in the  $2\theta$  range 5–80° with the aid of Philips X-Pert-Pro using the Ni-filtered  $\text{CuK}\alpha$  radiation. Adsorption-desorption isotherms of nitrogen (at –196 °C) were conducted with the aid of ASAP 2010, Micromeritics gas sorption apparatus. The catalysts were evacuated at 250 °C for 4 h before the nitrogen adsorption measurements. Micropore-surface area as well as micropore-volume of some catalysts was evaluated using Dubinin-Astakhov method. Pyridine adsorption was used to investigate the nature of the acid sites. Approximately 10 mg were pressed into thin wafers using a 13 mm diameter die and applying 10 ton pressure. The obtained wafers were mounted on a quartz holder and installed in a quartz glass vacuum chamber. Prior to pyridine adsorption, the wafers were activated by heating them under vacuum at 350 °C for 2 h. Following activation the samples were allowed to cool to 200 °C and pyridine vapour was admitted for 45 min. A second pyridine step was done by admitting pyridine vapour for 30 min at 160 °C. This is to be sure that enough pyridine is adsorbed on the zeolites. The wafers were, then, cooled to 140 °C and evacuated for 2 h. Finally, the wafers were allowed to cool down to room temperature and, then, the glass chamber was transferred to FTIR spectrophotometer. FTIR spectra were recorded using PerkinElmer VX170 spectrophotometer.

### 2.3. Activity and in situ electrical conductivity measurements

The catalytic measurements were carried out in an electrically heated quartz tube reactor. The temperature in the reactor was measured using a thermocouple on the catalyst bed. Prior to each experiment 500 mg catalyst were treated in He at 550 °C for 1 h and then cooled to the desired temperature. The concentration of reactant gas, 500 ppm  $\text{N}_2\text{O}$ , was added with the aid of Bronkhorst thermal mass flow controllers using He as a balance gas, the volumetric flow rate was 125  $\text{cm}^3 \text{min}^{-1}$  (NTP). The gases used were all of >99% purity and He was >99.999% purity, and they were used without further purification. The exit concentrations were monitored by means of non-dispersive infrared analyzer for the  $\text{N}_2\text{O}$  (Hartmann and Braun, Uras 10E). The steady state was reached after 30 min to 1 h for the different catalysts tested. In situ electrical conductivity measurements were carried out using a conductivity cell similar to that described by Chapman et al. [67]. The resistance measurements were carried out using a Keithley 610 C solid-state electrometer. In each run 500 mg of the catalyst were placed between two electrodes (1.0 cm diameter) and pressed by the upper electrode in order to ensure a good contact between the particles. The cell was heated to 500 °C and the electrical conductivity was monitored till a steady value was reached ( $\sigma_0$ ). Then, 500 ppm  $\text{N}_2\text{O}$  in nitrogen was introduced to the cell with the aid of Aalborg thermal mass flow controllers, in a flow rate of 200  $\text{cm}^3 \text{min}^{-1}$  (NTP) and the values of the electrical conductivity were recorded with time ( $\sigma$ ).

## 3. Results and discussion

### 3.1. Chemical composition and X-ray diffraction

Table 1 shows the chemical composition of the H-ZSM-5 as well as the different transition metal containing ZSM-5 zeolites. The Si/Al ratio in all the solids agreed well with the nominal value and, as expected, did not experience significant changes upon SSIE treatment. The transition metals content; approximately similar values to the nominal ones were observed for the most of the catalysts. This in turn confirms that the washing step in the working procedure applied did not lead to a significant metal loss.

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