

Catalytic and adsorptive properties of a Cu-ZSM-5 catalyst synthesized by solid-phase method

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**CATALYTIC AND ADSORPTIVE PROPERTIES
OF A Cu-ZSM-5 CATALYST
SYNTHESIZED BY SOLID-PHASE METHOD**

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Abstract

A Cu-exchanged catalyst Cu-ZSM-5 has been obtained *via* an environmentally friendly solid-phase synthesis. Its catalytic activity and adsorptive properties are compared with those of a catalyst prepared by the ion exchange from solution. The properties of the catalysts were found to be similar.

Keywords: Cu-exchanged zeolite, solid-phase synthesis, DeNO_x, ammonia oxidation

INTRODUCTION

Zeolite catalysts including Cu-zeolite attract great attention as they efficiently detoxify gas emissions from nitrogen oxides and other dangerous compounds [1,2]. The catalysts are most promising if prepared as honeycomb monoliths since they are more universal and efficient in this form.

At present, ion exchange from salt solutions [3] is commonly used to obtain Cu-zeolite catalysts. However, the procedure is tedious and unattractive for industry as it wastes huge amounts of water. There is another method for introducing Cu into the zeolite – its sintering with a copper salt. Slinkin *et al.* [4,5] studied how copper ions interact with the zeolite under such thermal

treatment. They found that copper migrated into the zeolite and stabilized in it in the same state as it does in the samples ion-exchanged from solution [4,5].

Solid-phase synthesis was used in Ref. [6] to obtain Cu-Y-zeolites. The samples produced were highly active in selective catalytic reduction (SCR) of NO with ammonia.

The aim of the present work was to study the catalytic and adsorptive properties of Cu-ZSM catalysts synthesized by the solid-phase method.

EXPERIMENTAL

In order to prepare a Cu-ZSM-5 sample, we used H- and (NH₄)-ZSM-5 zeolites with Si/Al=19.5 and $S_{\text{BET}} = 293 \text{ m}^2/\text{g}$. H-ZSM-5 was obtained by calcination of NH₄-ZSM-5 at 500°C for 2 h.

Cu-ZSM-5(EX) was obtained *via* the H-ZSM-5 ion exchange with a Cu(Ac)₂ solution [3]. Then the sample was washed with water, dried and calcined in air at 500°C for 4 h. Cu content was 1.18 wt.%, $S_{\text{BET}} = 412 \text{ m}^2/\text{g}$. Before testing, the sample was repeatedly treated in an oxygen flow followed by propane flow at 500°C.

Cu-ZSM-5(S1) and Cu-ZSM-5(S2) samples were prepared *via* solid-phase synthesis. Zeolite mixture with (CuOH)₂CO₃ was pounded with a pestle. We used NH₄-ZSM-5 to obtain Cu-ZSM-5(S1) and H-ZSM-5 to obtain Cu-ZSM-5(S2). The mixtures were tabletted and calcined in air at 750°C for 2 h in the case of Cu-ZSM-5(S1) and at 700°C for 2.5 h in the case of Cu-ZSM-5(S2). Cu-ZSM-5(S1) contained 2.12 wt.% Cu, Cu-ZSM-5(S2) - 1.06 wt.% Cu, $S_{\text{BET}} = 350 \text{ m}^2/\text{g}$.

Cu-ZSM-5(M) monolith with a channel size of 0.8x0.8 mm and wall thickness of 0.2 mm was prepared from Cu-ZSM-5(S1) (83 wt.%) by extrusion with a binder and plasticizer added.

CuO was obtained by calcination of (CuOH)₂CO₃ in air at 750°C for 2 h.

A flow procedure was used to measure the catalytic activity of the samples in the selective reduction of NO by propane and ammonia. A flow-circulation procedure was used in the selective oxidation of ammonia to nitrogen. Experimental conditions of the selective NO reduction by propane were as follows: 500 ppm NO, 500 ppm C₃H₈, 2% O₂, He balance; temperature 150-500°C; reaction mixture volume rate 7500 h⁻¹; reactor of complete mixing with a vibrofluidized catalyst bed. Reaction progress was estimated as NO conversion. Nitrogen oxide was analyzed with a "Radas-1" gas analyzer, propane concentration was measured chromatographically ("Tsvet-530" chromatograph with a flame-ionization detector). Experimental conditions for the nitrogen oxide SCR with ammonia were reported in Ref. [7]. The procedure used in the study of

the catalytic activity in selective ammonia oxidation has been described elsewhere [8].

In order to consider the interaction of copper with the zeolite, we used temperature-programmed reduction (TPR) with hydrogen. Experimental conditions were as follows: 10% H₂ in argon was passed over the catalysts at the rate of 40 mL/min; the reactor was heated from room temperature to 600°C at the rate of 10°C/min; quartz (with the same particle size as the catalyst) was added to 250 mg of the weighed sample to give a total volume of 1 mL.

We studied the adsorptive properties of the catalysts by temperature-programmed desorption (TPD) of nitrogen oxide and propane from the surface of the samples. First, the catalyst was pretreated in helium at 500°C for 1 h, then fed at 50°C with mixtures of 150 ppm NO + 2.2% O₂ in helium, or 150 ppm NO + He, or 400 ppm C₃H₈ + He. After reaching the adsorption equilibrium, the reactor was blown with helium and heated at a rate of 20°C/min. Helium flow rate was 300 mL/min during NO desorption and 100 mL/min during propane desorption. Desorbed NO and propane were registered by the gas analyzer and the flame-ionization detector, respectively. In order to analyze CO and CO₂, we used a methanator (*i.e.* a reactor with a Ni-Cr catalyst to convert CO and CO₂ to methane).

RESULTS AND DISCUSSION

Figure 1 shows TPR-spectra of the sample obtained by solid-phase synthesis (Cu-ZSM-5(S1)), monolith catalyst Cu-ZSM-5(M) and the sample prepared by ion-exchange from solution (Cu-ZSM-5(EX)). The observed TPR spectra of the ion-exchanged zeolite are similar to those described in Ref. [9]. Different temperatures of the peak maxima can be attributed to some deviations in the experimental conditions. As the sample heating rate used in Ref. [9] is significantly lower, the temperature of the TPR maxima should shift towards lower temperatures and the peaks should resolve better. The data presented demonstrate that the joint calcination of copper carbonate with the zeolite substantially changes the state of copper (see TPR spectra of CuO and Cu-ZSM-5(S1)). The TPR spectra of the solid-phase and ion-exchanged samples reveal the same copper forms that reduce at 150-200°C. Hence, the sintering of copper salt with the zeolite results in ion exchange and produces copper forms similar to those formed during ion exchange from solution.

Note the interesting fact that the amount of copper reduced at 150-200°C is similar in both samples (0.00014 and 0.00016 mol/g), whereas their copper content differs (2.12% Cu for the solid-phase sample and 1.18% for the ion-exchanged one). The TPR spectrum of the solid-phase sample obviously differs

in the fact that the reduction does not end above 250°C as the spectrum line does not attain zero. This is possibly due to the reduction of other copper compounds comprising the Cu-ZSM-5(S1) sample.

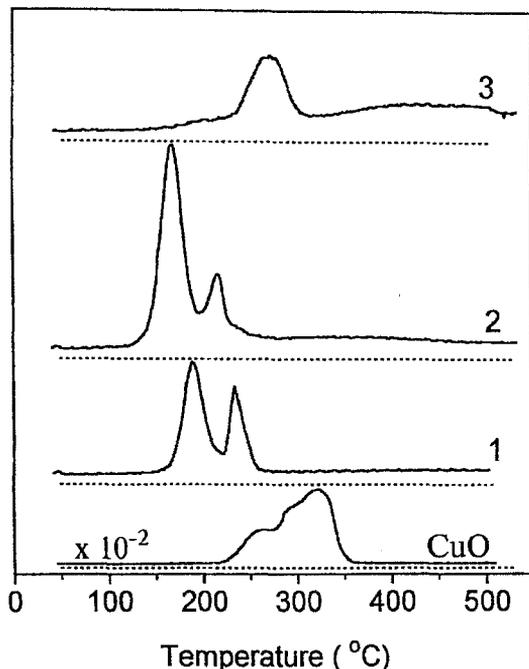


Fig. 1. TPR spectra of the catalysts:
1 - Cu-ZSM-5(EX); 2 - Cu-ZSM-5(S1); 3 - Cu-ZSM-5(M)

So, in the solid-phase synthesis of Cu-ZSM-5 a part of copper is localized in the zeolite matrix in the same way as it is in the ion-exchanged sample while another part is stabilized as other compounds.

The TPR spectrum of the monolith catalysts differs both from the ion-exchanged and solid-phase ones. Partial redistribution of copper between the zeolite and the binder and plasticizer (for example, clay) seems to occur during the monolith manufacturing.

Figure 2B shows the temperature dependence of NO conversion in the NO SCR with ammonia over the catalysts studied. Cu-ZSM-5(S1) and Cu-ZSM-5(M) are obviously highly active, their activity is close to that of the ion-exchanged sample Cu-ZSM-5(EX).

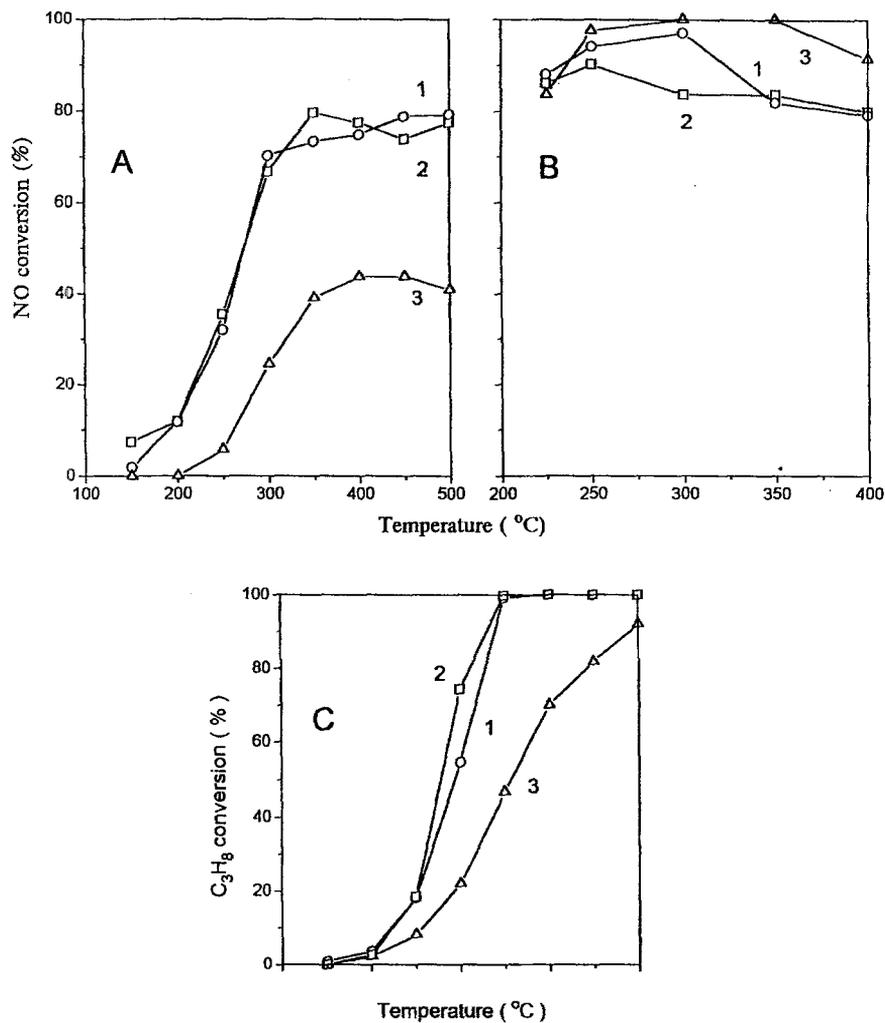


Fig. 2. NO conversion during the SCR of NO by propane (A), NO SCR by ammonia (B); propane conversion vs. reaction temperature during NO SCR by propane (C). 1 - Cu-ZSM-5(EX); 2 - Cu-ZSM-5(S1); 3 - Cu-ZSM-5(M)

Cu-substituted catalysts obtained by solid-phase synthesis show high activities in nitrogen oxide SCR with propane as well. Figures 2A and 2C demonstrate the temperature dependence of NO and C₃H₈ conversion. For reference, the figures show also the Cu-ZSM-5(EX) activity. One can see that Cu-ZSM-5(S1) and Cu-ZSM-5(EX) have similar activity in the SCR of NO by propane and in propane oxidation. Cu-ZSM-5(M) is less active in both reactions. Most likely the difference in the activity results from the different character of the reagent interaction with the catalyst surface.

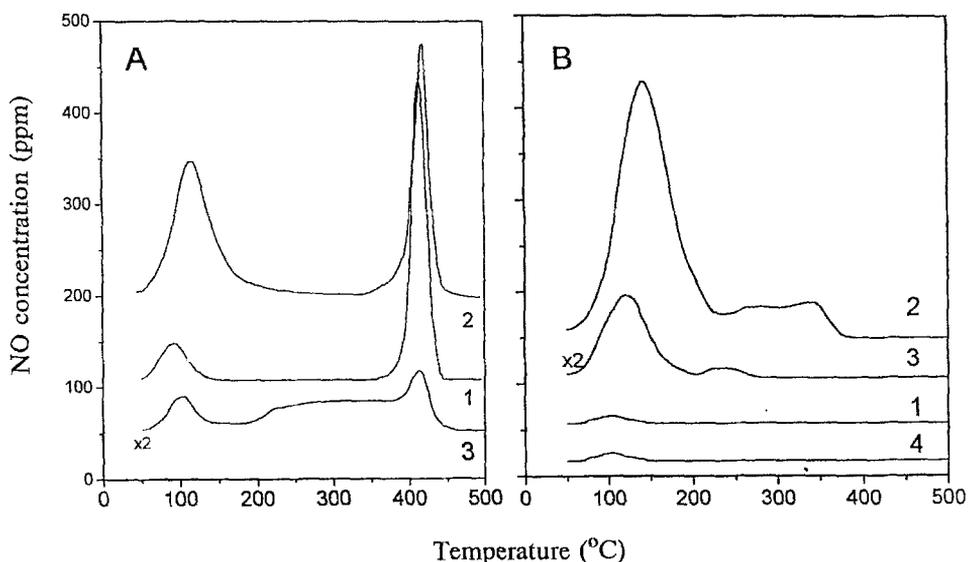


Fig. 3. NO TPD spectra after NO (A) and NO+NO₂ (B) adsorption. The spectra are normalized to the sample weight. 1 - Cu-ZSM-5(EX); 2 - Cu-ZSM-5(S1); 3 - Cu-ZSM-5(M)

The data on NO, NO+O₂ and C₃H₈ interaction with the catalyst surface are shown in Fig. 3(A, B) and Fig. 4. TPD spectra of NO and NO+O₂ are obviously similar. Adsorption centers that characterize the ion-exchanged catalysts exist on the solid-phase catalyst too. However, the NO TPD spectra of Cu-ZSM-5(S1) and Cu-ZSM-5(M) reveal new forms of NO desorption at moderate temperatures (300°C). This proves that other copper forms are present in the solid-phase and monolith samples. The TPD-spectra of propane are more complex (Fig. 4). At temperatures below 250°C, it desorbs as propane, while at higher temperatures - as products of its complete oxidation. Introduction of copper results in a change

in propane adsorption of on initial zeolite. Propane TPD spectra of Cu-ZSM-5(M) show a low content of complete oxidation products. On the contrary, mainly CO and CO₂ evolve during propane TPD from Cu-ZSM-5(S1). The propane TPD spectra of Cu-ZSM-5(EX) reveal both desorption forms. The differences observed correlate with the ability of the samples to oxidize propane (Fig. 2C).

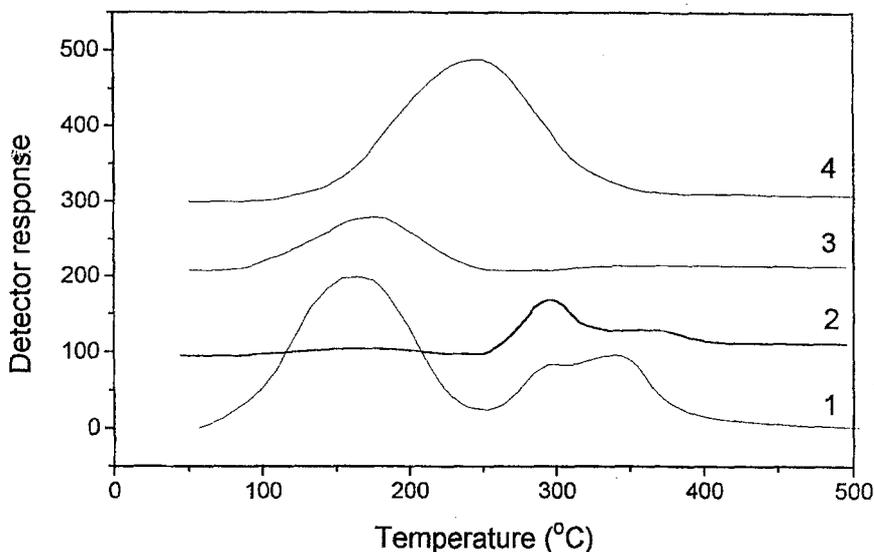


Fig. 4. Propane TPD spectra. The spectra are normalized to the sample weight. 1 - Cu-ZSM-5(EX); 2 - Cu-ZSM-5(S1); 3 - Cu-ZSM-5(M); 4 - initial zeolite

Compared to the SCR of NO by propane, that by ammonia is possibly less sensitive to the surface properties of Cu-substituted zeolite catalysts. Indeed, NO conversions in the NO SCR by ammonia almost do not differ over the catalysts studied in contrast to the that by propane (Fig. 2A and 2B). This can possibly explain the data of Ref. [6], where similar activities of Cu-Y-zeolites in the NO SCR by ammonia were observed, notwithstanding a dramatic difference of their TPR-spectra.

We tested Cu-ZSM-5(S2) catalysts prepared from H-ZSM-5 in the selective oxidation of ammonia (Fig.5). Obviously, the activity of these catalysts is comparable with that of Cu-ZSM-5(EX).

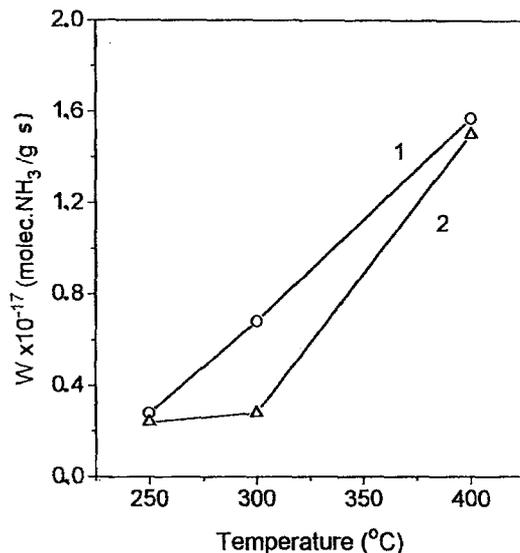


Fig. 5. Catalytic activity in ammonia oxidation to nitrogen. W is the rate of nitrogen formation. 1 - Cu-ZSM-5(EX); 2 - Cu-ZSM-5(S2)

The activity and adsorptive properties of Cu-substituted zeolite catalysts prepared by solid-phase synthesis have been studied. The high activity of the catalysts in the SCR of NO by ammonia and propane, and in the selective oxidation of ammonia is comparable with that of catalysts obtained *via* ion-exchange from solution. Solid-phase synthesis is a promising method to produce efficient honeycomb monolithic copper-substituted catalysts.

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