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The Stability of Monolith CuZSM-5 Catalysts for the Selective Reduction of Nitrogen Oxides with Hydrocarbons: II. Synthesis and Characterization of Bulk Cu(80% ZSM-5 + 20% Al_2O_3) Catalysts

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Abstract—The effects of ion-exchange conditions and the zeolite Si/Al atomic ratio on the copper contents of Cu(80% ZSM-5 + 20%Al_2O_3) catalysts and on the catalytic activity in the selective reduction of NO with propane were studied. It was found that the synthesis of these catalysts exhibited the same behavior as in the case of bulk CuZSM-5 catalysts containing no Al_2O_3. The copper contents of the catalysts depend on the pH and concentration of copper solutions used for ion exchange, and the maximum activity (NO conversion) is attained even at an exchange level (Cu/Al) close to 100% regardless of pH and the zeolite Si/Al atomic ratio. At 300–400°C, the activity of the test catalysts is 10–20% lower than the activity of CuZSM-5 catalysts containing no Al_2O_3 at equal exchange levels. This difference in the activity almost disappeared as the reaction temperature was increased. It was also found that in the Cu(80% ZSM-5 + 20%Al_2O_3) catalysts, an exchange level close to that in CuZSM-5 catalysts is attained by ion exchange from more concentrated solutions. An increase in the exchange level to $\geqslant$100% (by an increase in the pH of a copper solution from ~6 to ~10, as in the case of CuZSM-5 catalysts), had no effect on the activity.

INTRODUCTION

This work is a continuation of previously reported studies [1], and it is devoted to the synthesis and characterization of bulk (unsupported) copper-substituted zeolite catalysts prepared using 80% HZSM-5 + 20% γ-Al_2O_3 compositions. The properties of these catalysts were examined because, as noted previously [1], the final goal of these studies is to prepare and characterize monolith catalysts containing zeolite in a washcoating. It is well known that a washcoating can be formed only with a binding agent; a pseudoboehmite aluminum hydroxide gel is commonly used as such a binding agent [2–4]. The calcination of the hydroxide at ~600°C results in the formation of γ-Al_2O_3. As noted previously [3], the adhesive strength between the washcoating and the monolith support was reasonably high at a ~20% concentration (on an Al_2O_3 base) of the binding agent in a suspension. Because of this, we decided on 80% HZSM-5 + 20% γ-Al_2O_3 as the starting composition.

Previously [1], it was found that the exchange level (the Cu/Al atomic ratio or 2Cu/Al $\times$ 100%) in CuZSM-5 catalysts prepared on the basis of HZSM-5 can be changed over a wide range by varying the conditions of ion exchange, and this level can be much higher than 100%. However, even at an exchange level of ~100%, the activity in selective NO reduction with propane was maximum regardless of the pH of solution and the Si/Al atomic ratio of zeolite, and only the reaction temperature was responsible for the absolute value of this activity. The amount and state of copper in these catalysts was responsible for the stability of catalysts in time. The amount and state of copper depended on the pH and concentration of the solution in which ion exchange was performed.

In this work, we studied the effect of ion-exchange conditions on the activity and stability of bulk catalysts prepared on the basis of the 80% HZSM-5 + 20% γ-Al_2O_3 composition.

EXPERIMENTAL

The HZSM-5 zeolite samples whose properties were described in [1] were used for preparing catalysts. Commercial aluminum hydroxide with the pseudoboehmite structure was used as a binding agent, the properties of which were examined and described previously [5].

The preparation of the initial 80% HZSM-5 + 20% γ-Al_2O_3 composition involved the following stages:

(i) preparation of a sol by the treatment of aluminum hydroxide with a mineral acid;

Table 1. Copper concentrations in CuO/Al_2O_3 samples prepared under conditions similar to ion exchange

Preparation conditions		Cu content, wt % (chemical analysis)
pH	copper concentration in the solution (on a CuO basis), mg/ml	
6	10	1.57
6	2	0.96
10	8	2.29
10	2	1.07

(ii) preparation of a suspension of the 80% HZSM-5 + 20% γ-Al_2O_3 composition by the addition of a zeolite powder to the sol;

(iii) drying and thermal treatment of the resulting composition at 600°C and the preparation of a fraction with a particle size of 1 to 2 mm.

The ion exchange was performed using copper acetate solutions (pH ~6) and an ammonia solution of copper acetate (pH ~10) by varying copper concentration in these solutions (on a CuO basis) as described in [1]. To evaluate the Cu/Al ratio that corresponds to only zeolite, Cu/Al_2O_3 samples were prepared under conditions that were analogous to ion exchange. In all of the experiments, the solution-to-zeolite volume ratio was 10/1. Table 1 summarizes data on the copper content of aluminum oxide.

The catalyst activity was characterized by NO conversion measured in the reaction of selective nitrogen oxide reduction with propane. This reaction was conducted in a flow reactor at 300–600°C under conditions specified previously [1].

RESULTS AND DISCUSSION

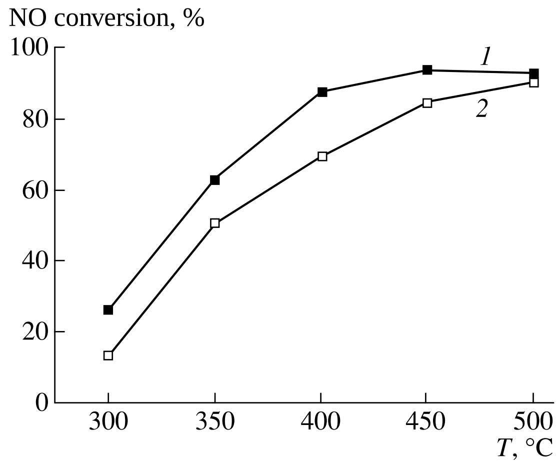
Table 2 summarizes data on the effects of the conditions of ion exchange and of the zeolite Si/Al atomic ratio on the exchange level (Cu/Al) in the zeolite and on the activity of Cu(80% ZSM-5 + 20% Al_2O_3) catalysts. The Cu/Al values in the zeolite were calculated taking into account the copper content of Al_2O_3 (Table 1) and the ratio between HZSM-5 and Al_2O_3 in the starting composition. It can be seen that, both at pH ~6 and at pH ~10, the copper contents of both the zeolite and the catalyst as a whole clearly depend on the copper concentration in the initial solution. At similar copper concentrations in solution, the copper contents of samples prepared at pH ~10 were higher than that at pH ~6. Therefore, as in the case of CuZSM-5 [1], the exchange level increased with copper concentration and pH of the solution in use. Note that, regardless of the pH of solution and the zeolite Si/Al atomic ratio, more concentrated copper solutions are required for preparing Cu(80% ZSM-5 + 20% Al_2O_3) samples with the same exchange level as that in CuZSM-5.

The catalytic activity (NO conversion) of Cu(80% ZSM-5 + 20% γ-Al_2O_3) catalysts is independent of the pH of the solution and of the zeolite Si/Al

Table 2. Properties of bulk Cu(80% ZSM-5 + 20% Al_2O_3) catalysts as functions of the conditions of ion exchange and of the zeolite Si/Al atomic ratio

Zeolite Si/Al atomic ratio	Cu concentration in the solution, mg/ml (on a CuO basis)	[Cu], wt %		Cu/Al, atom/atom	NO conversion, %, at temperatures, °C				
		in the sample (chemical analysis)	in the zeolite (calculation)		300	350	400	450	500
Ion exchange from copper acetate (pH ~6)									
73	10	1.09	0.78	0.59	13	51	70	85	91
	5	0.89	0.58*	0.44	15	54	85	92	93
	2	0.73	0.54	0.41	15	50	72	86	90
34	10	1.19	0.88	0.42	22	58	72	81	89
	5	1.11	0.85*	0.38	19	57	77	86	88
	2	0.88	0.69	0.33	17	47	73	86	90
Ion exchange from copper ammoniate (pH ~10)									
73	8	2.30	1.84	1.40	14	51	81	90	92
	4	2.13	1.67*	1.27	16	59	83	95	93
	2	1.14	0.93	0.71	19	47	79	91	93
34	8	2.14	1.68	0.79	23	56	78	84	88
	4	1.84	1.54*	0.71	25	54	78	89	95
	2	1.43	1.18	0.57	22	50	73	85	86

* The amount of copper bound to aluminum oxide was determined by calibration curves plotted with the use of data given in Table 1.



Temperature dependence of NO conversion for (*1*) a CuZSM-5 catalysts [1] and (*2*) a Cu(80% ZSM-5 + 20% Al_2O_3) catalyst prepared by ion exchange at pH ~6 (Si/Al = 73; Cu/Al = 0.59).

atomic ratio over a wide range of Cu/Al values (Table 2). The absolute value of this activity depends only on the reaction temperature, as is also the case with CuZSM-5 catalysts [1]. However, as can be seen in the figure, the conversion of NO on a Cu(80% ZSM-5 + 20% γ-Al_2O_3) sample at 300–450°C is 10–20% lower than that on a catalysts free of Al_2O_3 at the same exchange level. At 500°C, the activities of samples from both of these series are almost the same.

Thus, an exchange level close to 100% suffices to provide a maximum activity in the test catalysts, which either contain Al_2O_3 or are free of Al_2O_3.

The results allow us to soundly decide on preparation conditions for monolith catalysts containing copper-substituted zeolite in a secondary layer.

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