Correlation between the Cu/Al Value and Activity of Cu-ZSM-5 Catalysts and the Chemical Nature of the Starting Copper Salt

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Abstract—Cu-ZSM-5 catalysts for the selective reduction of NO with propane were obtained by ion exchange between H-ZSM-5 zeolite and an aqueous or aqueous ammonia solution of a copper salt (acetate or nitrate). Their Cu/Al values (%) defined as 2×100 (Cu : Al), where Cu : Al is the copper-to-aluminum atomic ratio, were determined as a function of ion exchange pH, which was varied by changing the copper salt and solution concentration. Cu/Al is primarily determined by the chemical nature of the starting copper salt. For a given salt, it is governed by the salt concentration in the solution. At a fixed salt concentration, Cu/Al is always larger for copper acetate than for copper nitrate. It can be raised to $\geqslant 100\%$ by using an aqueous ammonia solution of a copper salt. Furthermore, it increases with increasing Si/Al in the starting zeolite if the other ion exchange conditions are equal. Irrespective of preparation conditions, the catalytic activity of Cu-ZSM-5 grows in proportion to Cu/Al. It peaks at Cu/Al ~ 100% and then remains constant up to Cu/Al ~ 400%. In order to achieve Cu/Al ~ 100%, it is most appropriate to use a copper acetate solution.

Cu-ZSM-5 catalysts, which are prepared by ion exchange between H-ZSM-5 zeolite and an aqueous solution of a copper salt, remain a focus of researchers' attention, for they are the most effective catalysts for the selective reduction of nitrogen oxides with hydrocarbons and for other gas treatment processes [1–4]. The main characteristic of the activity of these catalysts is Cu/Al = $2 \times 100 \times$ (Cu : Al) (at %), where Cu : Al is the copper-to-aluminum atomic ratio [5–8]. This characteristic is derived from chemical analysis data under the formal condition that there must be two aluminum atoms per copper atom [9].

The theoretical limit of Cu/Al in these zeolites is 100%, which is attained at Cu : Al = 0.5. Deviations from this ion-exchange stoichiometry generally take place, resulting in the formation of small copper clusters both on the surface and in the bulk of the zeolite [5–8, 10–12]. If this is the case, the researcher deals with a so-called overexchanged Cu-ZSM-5 specimen with Cu/Al $\gg$ 100% (sometimes, >600% [8]). Obviously, the ratio of isolated copper cations to aggregated ones in Cu-ZSM-5 catalysts depends on ion exchange conditions.

Although Cu-ZSM-5 has been the subject of numerous studies, there remains an open question concerning the optimum Cu/Al value maximizing the activity of this catalyst and as to whether it is appropriate to prepare overexchanged specimens [1, 4, 6, 7, 11–16]. This vagueness is primarily due to the fact that there have been no systematic studies in this field and no unified approach to the synthesis of Cu-ZSM-5 has been devised. Each previous study dealt with its particular set of synthesis parameters: silica modulus (Si/Al atomic ratio) and form of zeolite, solution pH, copper salt concentration, temperature, and ion exchange duration. It was in no way explained why one copper salt had been preferred to the others, so it seemed that starting salts were chosen at random. There have been syntheses using copper acetate [1, 6], nitrate [4, 7, 13, 14], and sulfate [16]. Furthermore, aqueous ammonia solutions of copper nitrate have been employed to obtain overexchanged zeolite specimens [6, 7, 11–13].

Earlier, we studied the effect of ion exchange conditions in H-ZSM-5 (Si/Al = 34 or 73) zeolite–copper acetate systems on the Cu/Al value (calculated as described in [5–8]; see above), on the state of the copper ion, and on the activity of the resulting catalyst in the selective reduction of NO with propane [17]. It was demonstrated that, at room temperature and an ion exchange time of 48 h, increasing the solution-to-zeolite volume ratio from 10 to 50 has no effect on Cu/Al. For copper acetate solutions of concentration 2–10 mg/ml (in terms of CuO) at pH ~ 6, Cu/Al in Cu-ZSM-5 is 80–140% and is governed by salt concentration in the solution and by Si/Al in the zeolite. In the case of ammonia solutions of copper acetate with pH ~10, much larger Cu/Al values up to ~400% are attainable, but catalytic activity is the same. However, the data reported in [17] are limited to Cu/Al $\geq$ 100% and copper acetate solutions with pH $\geq$ 6.

In order to extend the reported correlation between the activity of Cu-ZSM-5 and Cu/Al [17] to a wider range of conditions, to optimize synthesis conditions on the basis of the new correlation, and to determine the composition at which the catalyst is most active in the selective reduction of NO with propane, we studied

Cu-ZSM-5 specimens with Cu/Al ≤ 100% obtained by ion exchange at pH <6. Solution pH was varied by using either copper acetate or copper nitrate, by varying salt concentration, or by acidifying the solution. Copper nitrate was used for the reason that its solutions have a lower pH than copper acetate solutions at a fixed solute concentration. Furthermore, comparison of data obtained with copper acetate and nitrate, including earlier data [17], is of interest from the standpoint of the effect of the nature of the starting copper salt on the properties of Cu-ZSM-5.

EXPERIMENTAL

The starting zeolite was H-ZSM-5 with Si/Al = 30 or 45 and physicochemical properties similar to the properties reported in [17].

Cu-ZSM-5 catalysts were prepared by ion exchange between H-ZSM-5 and an aqueous solution of copper acetate (series A) or copper nitrate (series N) at pH <6 and a solution-to-zeolite volume ratio of 10. Solution pH for a given series was controlled by varying salt concentration (in milligrams of CuO per milliliter). In reference experiments, the starting copper acetate or copper nitrate solution was acidified with acetic anhydride or nitric acid to a lower pH value without changing the salt concentration, or an aqueous ammonia solution of copper nitrate with pH ~10 was used. Ion exchange was performed at room temperature for 2 days. The resulting solid was washed, dried, and calcined at 500°C for 4 h. In the case of twice and thrice repeated ion exchange, all of the above procedures were repeated two and three times, respectively.

Catalyst specimens were compared in terms of Cu/Al = 2×100 (Cu : Al) derived from chemical analysis data as described in [5–8].

Catalytic activity was characterized by NO conversion (%) in the nitrogen oxide–propane reaction at 300–500°C in a flow reactor. The catalyst volume was 4 cm³, and the volumetric space velocity of the gas was 42 000 h⁻¹. The original gas mixture had the following composition: NO, ~300 ppm; C_3H_8, ~0.12 vol %; O_2, ~3.5 vol %; and N_2, balance. The original and product mixtures were analyzed using an ECOM-SG^{plus} gas analyzer with an accuracy of 1 ppm for NO, 0.01 vol % for C_3H_8, and 0.1 vol % for O_2.

RESULTS AND DISCUSSION

Synthesis, composition, and activity data for the catalysts examined are listed in the table. As is noted above, Cu/Al can be considered as a measure of the catalytic activity of Cu-ZSM-5. Therefore, the primary purpose of data analysis was to see whether it is possible to control Cu/Al. We revealed the following correlations between Cu/Al and ion exchange conditions:

At a given salt concentration in the solution, the copper content and, accordingly, the calculated Cu/Al value are ~3 times greater for series A (specimens 1–3) than for series N (specimens 4–6).

In both series, Cu/Al increases with increasing salt concentration. However, in series A, Cu/Al is close to its theoretical ion-exchange limit (84% for specimens 2 and 3) at salt concentrations as low as 5–10 mg/ml. By contrast, Cu/Al in series N does not exceed 50% even at salt concentrations of 20 and 30 mg/ml (specimens 7 and 8).

Cu/Al in series N can be raised by multiple ion exchange runs, as in the case of specimens 9 and 10. However, it will still be smaller than the Cu/Al in series A.

At fixed synthesis conditions, aqueous ammonia solutions of copper nitrate with pH ~10 (see specimens 11 and 13), as with similar solutions of copper acetate [17], afford markedly larger Cu/Al values (up to ~200%) than more acidic solutions.

As with Cu/Al in series A [17], Cu/Al in series N increases with increasing Si/Al (compare specimen 5 with specimen 12 and specimen 11 with specimen 13).

The fact that the extent of ion exchange is larger for series A than for series N at pH <6 may seem to be explicable in terms of copper acetate solutions having a higher pH than copper nitrate solutions with the same salt concentration. However, this view is in conflict with the fact that, in both series, Cu/Al increases with increasing salt concentration and, accordingly, with decreasing pH. Therefore, for pH <6, Cu/Al in Cu-ZSM-5 depends both on the chemical nature of the starting copper salt and on salt concentration. Variation of these parameters causes changes in pH, diminishing the role of pH as an independent ion exchange parameter. Moreover, it is believed that deliberately reducing the pH value that is determined by the nature and concentration of the salt will not have any effect on Cu/Al if the salt concentration is invariable.

To verify this assumption, we prepared catalysts using copper acetate and nitrate solutions acidified with nitric acid (specimens 14–16) and acetic anhydride (specimens 17 and 18). Salt concentration was 5 mg/ml in the preparation of specimens 14 and 17 from copper acetate solutions (the reference specimen was no. 2) and 2 mg/ml in the preparation of specimens 15, 16, and 18 from copper nitrate solutions (the reference specimen was no. 4).

As is clear from the data listed in the table, Cu/Al in specimens obtained from solutions acidified with either nitric acid (no. 14) or acetic anhydride (no. 17) is equal to Cu/Al in the reference specimen 2, irrespective of pH. Likewise, in specimens obtained using acidified copper nitrate solutions (nos. 15, 16, 18) is equal to Cu/Al in the reference specimen 4.

Thus, these data demonstrate that, at pH <6, Cu/Al in series A and N can be controlled by varying salt concentration. The marked difference in Cu/Al between series A and series N specimens synthesized under the same conditions indicates that ion exchange depends strongly on the nature of the starting copper salt, which

Effect of ion exchange conditions on the properties of Cu-ZSM-5 catalysts obtained from H-ZSM-5 zeolite with Si/Al = 3

Specimen no.	Salt concentration in the solution (in terms of CuO), mg/ml	Solution pH	Cu content of the specimen, wt %	Cu/Al, %	NO conversion, %*
Specimens obtained using copper acetate solutions (series A)				
1	2	5.8	0.84	64	88
2	5	5.6	1.10	84	84
3	10	5.5	1.10	84	85
Specimens obtained using copper nitrate solutions (series N)				
4	2	5.0	0.27	20	31
5	5	4.6	0.33	26	32
6	10	4.3	0.36	28	47
7	20	4.1	0.50	38	54
8	30	3.9	0.62	48	67
9	10 (twice repeated ion exchange)	4.3	0.60	46	60
10	10 (thrice repeated ion exchange)	4.3	0.96	74	77
11	5	10.2***	2.35	187	79
12**	5	4.6	0.56	68	51
13**	5	10.2***	1.96	242	72
Specimens obtained using copper acetate (A) and nitrate (N) solutions acidified with nitric acid				
14 (A)	5	4.6	1.03	79	66
15 (N)	2	4.3	0.27	20	38
16 (N)	2	3.5	0.26	20	38
Specimens obtained using copper acetate (A) and nitrate (N) solutions acidified with acetic anhydride				
17 (A)	5	4.6	1.12	86	85
18 (N)	2	4.0	0.30	22	29

 *Reaction temperature is 400°C.

 **The starting zeolite is H-ZSM-5 with Si/Al = 45.

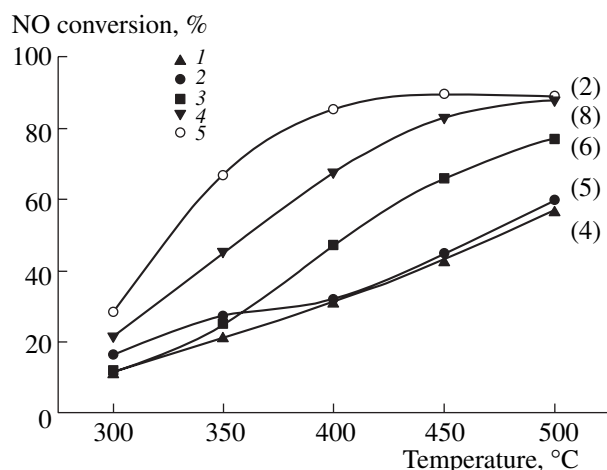 ***Obtained in an aqueous ammonia solution of copper nitrate.

determines the state of copper cations in solution. At a given pH, copper salts are hydrolyzed to different extents in their aqueous solutions. As a consequence, these solutions may differ considerably in the ratio of hydrated Cu^{2+} cations to partially hydrolyzed copper complexes.

It was demonstrated in early studies [18] that, at pH values below the pH of hydrolysis of the dissolved copper salt, the predominant state of copper in Cu-exchanged zeolites is the isolated Cu^{2+} cation. As pH is raised, the salt undergoes partial hydrolysis to form dinuclear and polynuclear oxocopper cations, resulting in deviations from ion exchange stoichiometry and in the formation of copper clusters. This process yields overexchanged copper–zeolite catalysts containing polynuclear copper complexes in ion exchange sites of the zeolite [1, 6, 7, 10–13] and tending to form CuO phase upon calcination or during reaction. Cu-ZSM-5 zeolites with Cu/Al ≫ 100% obtained in aqueous ammonia solutions of copper acetate with pH ~10, reported here and in [17], are examples of such catalysts. However, note that, at equal ion exchange conditions, ammonia solutions of copper acetate with pH ~10 afford Cu-ZSM-5 with Cu/Al ~ 400% [17], while

ammonia solutions of copper nitrate afford Cu/Al values of about 200% (specimens 11 and 13 in the table).
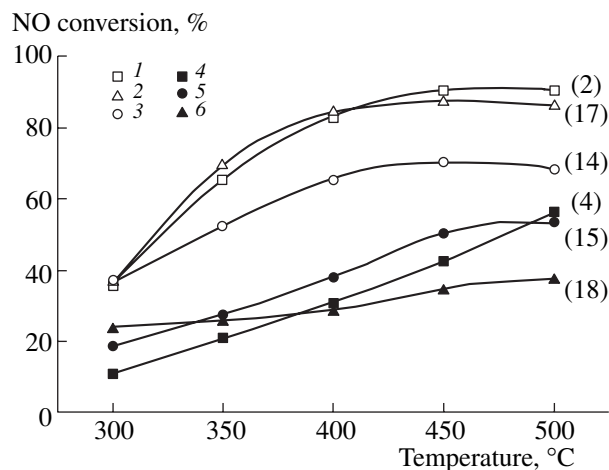
It is clear from the data listed in the table that, at 400°C, series A catalysts (specimens 1–3) are more active than series N catalysts prepared at the same copper concentration (specimens 4–6). In series N, the increase in Cu/Al achieved by raising the copper nitrate concentration enhances the activity of the catalyst (compare specimens 7 and 8), but, all the same, series N catalysts remain less active than series A catalysts. This difference is observed throughout the reaction temperature range examined (300–500°C; see Fig. 1). A more significant increase in catalytic activity in series N is attainable by thrice repeated ion exchange, as in the case of specimen 10. This effect may be due to the still larger Cu/Al value of this specimen. However, further raising Cu/Al to ~200% does not enhance catalytic activity in series N (see specimens 11 and 13, which are obtained using aqueous ammonia solutions of copper nitrate with pH ~10) (table).

As can be seen in Fig. 2, the activity of catalysts 2 (series A) and 4 (series N) is affected only slightly by adding an acidifier with the like anion to the starting solution, specifically, nitric acid to the copper nitrate

NO conversion, %

Fig. 1. Temperature dependence of the activity of (*1–4*) series N and (*5*) series A Cu-ZSM-5 catalysts. Cu/Al = (*1*) 20, (*2*) 26, (*3*) 28, (*4*) 48, and (*5*) 84%. Parenthesized numbers are specimen numbers in the table.

solution (specimen 15) and acetic anhydride to the copper acetate solution (specimen 17). Addition of nitric acid to the copper acetate solution (specimen 14) or of acetic anhydride to the copper nitrate solution (specimen 18) reduces catalytic activity, particularly in series A. This does not eliminate the difference in activity between the catalyst series, supporting the view that ion exchange depends primarily on the chemical nature of the copper salt.
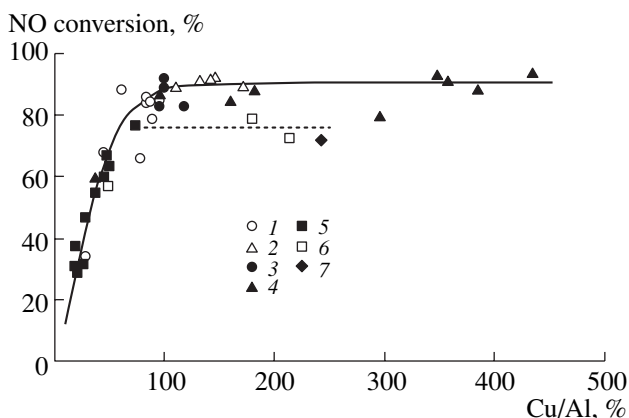
NO conversion, %

Fig. 2. Temperature dependence of the activity of Cu-ZSM-5 catalysts prepared using acidified solutions of copper salts: (*1*) the starting solution of copper acetate with pH 5.6, (*2*) the starting solution of copper acetate acidified with nitric acid to pH 4.6, (*3*) the starting solution of copper acetate acidified with acetic anhydride to pH 4.6, (*4*) the starting solution of copper nitrate with pH 5.0, (*5*) the starting solution of copper nitrate acidified with nitric acid to pH 4.3, (*6*) the starting solution of copper nitrate acidified with acetic anhydride to pH 4.0. Parenthesized numbers are specimen numbers in the table.

The above results combined with earlier data acquired under similar measurement conditions [17] demonstrate that the catalytic activity of Cu-ZSM-5 increases in proportion to Cu/Al and peaks at a Cu/Al value close to 100%, irrespective of ion exchange conditions. At larger Cu/Al values, catalytic activity remains constant up to Cu/Al ~ 400%, which is attainable only when an aqueous ammonia solution of a copper salt is used in ion exchange (Fig. 3).

The constancy of catalytic activity for Cu/Al ≥ 100% (Fig. 3) is explained by the fact that low-activity copper clusters build up as Cu/Al increases, ultimately yielding CuO phase, which was shown to be inactive by special experiments. As is noted above, the formation of these structures is due to the fact that, at pH ≥ 7 (established by adding aqueous ammonia to the copper nitrate or acetate solution), the copper salt undergoes partial hydrolysis and, as a consequence, associated copper complexes ($[CuOH]^+$ and multiply charged dinuclear and polynuclear oxo complexes [1, 6, 7, 10–13, 18]) can be involved in ion exchange along with Cu^{2+} cations.

This view is in agreement with the earlier inference that the high catalytic activity of Cu-ZSM-5 in the selective reduction of NO with propane is mainly due to Cu^+ cations [17], which are readily reducible species, whose most likely precursors are Cu^{2+} cations [19].

Evidently, in order to obtain a highly active Cu-ZSM-5 catalyst with Cu/Al ~ 100%, ion exchange should be conducted at pH ~6 in a copper acetate solution much less concentrated than the copper nitrate solutions (table). These conditions ensure a higher limiting level of catalytic activity (Fig. 3). Furthermore, copper acetate solutions are superior to copper nitrate solutions from the engineering and environmental

NO conversion, %

Fig. 3. Activity of Cu-ZSM-5 catalysts as a function of Cu/Al at 400°C (including data from [17]): (*1*) series A (pH 4.6–5.9; Si/Al = 30), (*2*) series A (pH ~10; Si/Al = 34 [17]), (*3*, *4*) series A (pH 5.6–5.9 and ~10, respectively; Si/Al = 73 [17]), (*5*, *6*) series N (pH 3.9–5.0 and ~10, respectively; Si/Al = 30), and (*7*) series N (pH ~10; Si/Al = 45).

standpoints, since they are less toxic and have pH ~6 in a rather wide concentration range.

Thus, the above results suggest that, for pH <6, the chemical nature of the starting copper salt (acetate or nitrate) determines the value of Cu/Al in Cu-ZSM-5 if the other ion exchange conditions are equal. For pH <6 and a given copper salt, Cu/Al increases with increasing salt concentration. Reducing the pH of the solution (acidification) without changing the salt concentration exerts no effect on Cu/Al. Irrespective of ion exchange conditions, the catalytic activity of Cu-ZSM-5 grows in proportion to Cu/Al. It peaks at a Cu/Al of about 100% and then remains invariable up to Cu/Al ~ 400%. Copper acetate solutions with pH ~6 are optimal for Cu-ZSM-5 synthesis.

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