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Novel Preparation Method of Highly Copper Ion-exchanged ZSM-5 Zeolites and Their Catalytic Activities for NO Decomposition

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Copper(II) ion-exchanged ZSM-5 zeolites with 100% or more exchange levels were readily prepared by addition of basic compounds such as ammonia and $Mg(OH)_2$ to the mother solution. The catalytic activities of the resulting zeolites for decomposition of nitrogen monoxide are dependent on pH of the solution and the additive.

The removal of nitrogen monoxide (NO) from exhaust gas is one of serious problems in the air pollution.1) We have recently reported that the copper ion-exchanged ZSM-5 zeolites (denoted as Cu-ZSM-5), of which copper ion-exchange levels were above 100%, showed high catalytic activity for the direct decomposition of NO.2) The activity of Cu-ZSM-5 is the highest among the catalysts previously reported,3) and therefore the Cu-ZSM-5 would be the most suitable for practical use. However, at present one problem remains to be solved; that is, it is impossible to prepare excessively copper ion-exchanged ZSM-5 zeolites with copper(II) nitrate or sulfate solution and a lot of repetition of ion-exchange process is necessary to prepare them with copper acetate solution.2,4) We wish here to report that the ZSM-5 zeolites with excess loading of copper ions were readily prepared in a single step through addition of basic compounds such as NH_4OH and $Mg(OH)_2$ into the solution. The catalytic performance of the Cu-ZSM-5 zeolites obtained was comparable to or higher than those of the previously reported catalysts.2) Although it has been already known that the ion exchange with a metal ion-amine complex can be carried out,5) the present results will clarify that the basic additives have an effect on the ion exchange different from the amine complexes.

ZSM-5 zeolite, of which silica/alumina molar ratio was 23.3, was used. The catalysts were prepared as follows. About 15 g of ZSM-5 zeolite was washed in 2 dm^3 of dilute $NaNO_3$ solution, and stirred for 24 h in 1 dm^3 of aqueous copper(II) nitrate solution (12 $mmol{\cdot}dm^{-3}$). Subsequently, an aqueous basic solution (concentration were summarized in Table 1) was gradually added to the ion-exchange solution until pH of the solution increased to a desired value. After filtration, the resulting cake was dried for 24 h at room temperature in vacuo. The exchange level was calculated on the assumption that one Cu^{2+} is exchanged with two Na^+ ions.

Table 1 shows the effect of addition of basic compounds. Clearly the addition of basic compounds to the mother solution increased the amount of copper ions exchanged in a single

Table 1. Effect of addition of base on the ion-exchange level and catalytic activities of the resulting Cu-ZSM-5 zeolites

Copper salt used[a)]	Additive	Concentration / mol dm^{-3}	pH after addition[b)]	Ion-exchange level[c)] / %	Catalytic activity[d)] / %
$Cu(CH_3COO)_2 \cdot H_2O$	None		5.9	90	n.m.[e)]
	NH_4OH	3.0	7.5	148	n.m.[e)]
$Cu(NO_3)_2 \cdot 3H_2O$	None		4.2	84	20.9
	NH_4OH	3.0	7.5	140, 144, 146[f)]	48.4[g)]
	KOH	3.0	7.9	122	2.1
	NaOH	3.0	7.5	125	2.0
	$Mg(OH)_2$	S[h)]	5.8	101	32.4
	$Ca(OH)_2$	S[h)]	7.5	131	8.1
	$Ba(OH)_2$	S[h)]	7.6	137	10.9
	Pyridine	1.2	6.4	103	9.3
	en[i)]	3.0	7.5	96	4.5

a) The initial amount of Cu^{2+} in the solution was 1.50 equiv. to that of Na^+ in zeolites. b) After 24 h. c) The degree of ion-exchange was measured by atomic absorption spectroscopy after the zeolite obtained was dissolved in HF solution. d) The value is the conversion into N_2 under the following conditions; P_{NO}=4950 ppm, catalyst weight=0.5 g, flow rate=60 cm^{3}min^{-1}, temp=773 K. e) Not measured. f) In this case three experiments were performed. g) Catalytic activity of the 146% exchanged Cu-ZSM-5 zeolite. h) Saturated solution. i) Ethylenediamine.

step. In the respective procedures, no precipitate was observed, although it was confirmed in a separate experiment that without zeolites the addition of ammonia to the Cu^{2+} solution resulted in the formation of $Cu(OH)_2$ precipitate at pH=7.5.[6)] Thus, it follows that the rapid preparation of excessively metal ion-exchanged zeolites can be achieved by the addition of basic compounds into the mother solution of Cu^{2+}. It is noteworthy that no essential difference between copper salts used was observed with regard to the degree of ion-exchange levels. Concerning this phenomenon there are two points which should be clarified. One is which of the pH value and the kind of basic additive is the more important factor to determine the ion exchange level. The second point is to measure the catalytic activities of the resulting Cu zeolites and reveal the influence of the present preparation method on the activity.

The first point will be discussed here. The exchange levels were varied with basic additives and were as follows: $NH_4OH > Ba(OH)_2 > Ca(OH)_2 > NaOH \approx KOH >$ pyridine $\approx Mg(OH)_2 \approx$ ethylenediamine. Table 1 revealed that the addition of basic compounds except ethylendiamine led the exchange level to 120-150% around pH=7.5 while 100% around pH=6.0, suggesting that pH is probably more important factor to determine ion exchange

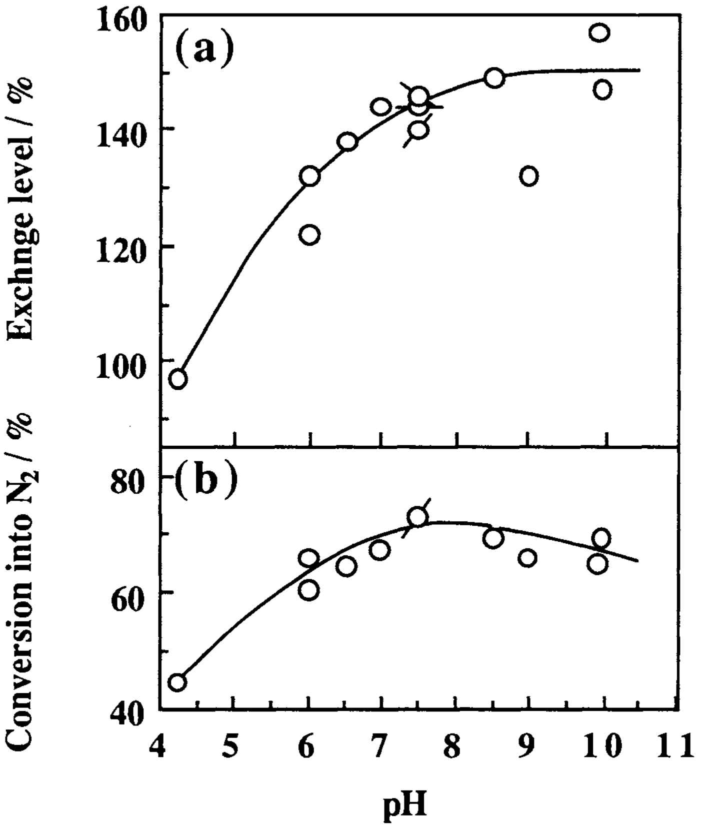

Fig. 1. Exchange level of Cu-ZSM-5 (a) and its catalytic activity (b) as a function of pH of aqueous copper(II) nitrate solution. The pH was varied by the addition of ammonia. The conditions for ion-exchange were the same as Table 1 except pH. The catalytic activities were measured at P_{NO}=2.05%, catalyst weight=0.5 g, flow rate=60 cm^3min^{-1}, and temp=823 K. Flags attached indicate different lots of catalysts.

level than the kind of basic compounds. The smaller effect of ethylenediamine would be due to the larger size of copper(II) complex coordinated by ethylenediamine than pore diameter of ZSM-5.

To confirm the dependency of exchange level on pH the effect of the ammonia addition into the solution has been studied in more detail and is summarized in Figure 1a. The exchange level increased with the increase of pH from 4 to 9 and reached nearly constant above pH 9. Above pH 9 all of Cu^{2+} ions were loaded into the zeolite. This correlation and the tendency observed in Table 1 could suggest that the exchange between Na^+ and $Cu_2(OH)^{3+}$, $Cu(OH)^+$, $Cu_2(OH)_2{}^{2+}$, or $Cu_3(OH)_2{}^{4+}$ formed at specific pH[7)] probably proceeds in zeolite.

Next, the second point was studied. The catalytic activity of the resulting zeolites for the direct decomposition of NO were shown in Table 1 and Fig. 1b. The extent of conversion of NO increased with increasing pH, attained to a maximum at pH 7.5, and then slightly decreased at higher pH region. No destruction of the zeolite lattice itself was observed by X-ray diffraction patterns after the ion exchange or the catalytic run. The observed by X-ray diffraction patterns after the ion exchange or the catalytic run. The decrement of the catalytic activity of the Cu-ZSM-5 prepared at higher pH region may be due to the change of the state of copper ions in the zeolite. The conversions of NO and into N_2 and O_2 at 823 K over the Cu-ZSM-5 catalyst prepared at pH 7.5 were 80, 72, and 60%, respectively. These values indicate that this catalyst is very active for the catalytic decomposition of NO and comparable to the Cu-ZSM-5 prepared by the repeated ion exchange method.2)

The other catalysts prepared with the addition of alkaline or alkaline earth hydroxide, except $Mg(OH)_2$, showed lower activities than that without additives as shown in Table 1. Ammonia adsorbed on the zeolites is well known to be desorbed at 573-773 K;8) therefore, in the Cu-ZSM-5 zeolites prepared with the ammonia addition there would be no ammonia at such high reaction temperatures. In contrast, alkaline or alkaline earth ions would remain on the surface. Therefore, it follows that not only pH but also the kind of basic additive is very important factor determining the catalytic activity. The present work has revealed that the copper ion exchange with ammonia addition is one of the useful method for excess loading of copper ions and that the resultant Cu-ZSM-5 is active for the catalytic reaction. The method would be applicable to another transition metal ion-exchanged zeolites.

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