represented by such a nucleation mechanism for hemispherical centers: eq 31 with instantaneous nucleation and edge growth, eq 33 with progressive nucleation and edge growth, and eq 37 with progressive nucleation and growth from the basal area.

Therefore, the three nucleation mechanisms have been compared by transformation of the eq 31, 33, and 37 into a linear relationship and fitting the experimental data. The theoretical curves in Figures 3 and 4 were calculated by using these data. Details of this procedure are given in part II.

As can be convincingly seen, the measurements of Figures 3 and 4 coincide excellently with a particular nucleation mechanism, whereas the others deviate considerably. The given examples follow different nucleation mechanisms:

(i) Relaxation of octadecanoic acid monolayers at 30 mN m^{-1} and T = 30 °C is described by instantaneous nucleation with hemispherical edge growth.

(ii) Relaxation of octadecanoic acid monolayers at 34 mN m^{-1} and T = 20 °C is described by progressive nucleation with hemispherical edge growth.

Summing up, this investigation provides clear evidence that the relaxation experiments giving apparent molecular areas as a function of time at constant surface pressure can be explained by a nucleation process for transforming of monolayer material to 3D centers. The nucleation model presented above is based on homogeneous nucleation and growth of centers with assumed geometrical shape. The theoretical calculation is characterized by two main features: (i) the overall rate of the process is described by convolution of nucleation rate and growth rate and (ii) the overlap of the growing centers is taken into consideration. The theoretical model allows to distinguish between different nucleation mechanisms. Two experimental examples of octadecanoic acid monolayers have been given for different nucleation mechanisms.

Conclusions

The nucleation–growth model introduced for apparent area relaxation of insoluble monolayers at constant surface pressure has the potential to quantitatively describe experimental measurements. The derived model possesses general validity for the theoretical description of the transformation of monolayer material to overgrown 3D phase. As a result of the experimental examination, evidence has been given that different nucleation mechanisms occur. Excellent accordance of calculated and experimental relaxation kinetics has been obtained. Based on this nucleation model, work is in progress to characterize relaxation of insoluble monolayers at constant surface pressure in more detail.

Registry No. Octadecanoic acid, 57-11-4.

Removal of Nitrogen Monoxide through a Novel Catalytic Process. 1. Decomposition on Excessively Copper Ion Exchanged ZSM-5 Zeolites

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Repeated ion exchange of the ZSM-5 zeolite using aqueous copper(II) acetate solution was found to bring about excess loading of copper ions above an exchange level of 100%. The high activity of the resulting catalyst for NO decomposition was consistent for at least 30 h even at short contact time and low NO pressure. The number of copper ions that can adsorb NO molecules has been determined by a temperature-programmed desorption technique combined with IR measurement; 94% of Cu^{2+} ions in ZSM-5 were active for the adsorption. The activity of excessively copper ion exchanged ZSM-5 zeolite was slightly reduced by the oxygen in the feed gas while that of the zeolite, of which the loading amount of copper was less than 100%, was greatly diminished under the same condition. SO$_2$ completely poisons the activity at 673–923 K, but the activity can be regenerated at the higher temperature treatment.

Introduction

Air pollution and acid rain seriously affect the terrestrial and aquatic ecosystems and therefore are very important problems that must be solved as soon as possible.[1] The exhaust gases from vehicles' engines and industrial boilers contain mainly carbon oxides (CO and CO$_2$), nitrogen oxides (NO$_x$), hydrocarbons, sulfur dioxide, particles, and soot. At present, one of the most significant problems is removal of NO$_x$, which is produced during high-temperature combustion. In particular, the decomposition or reduction of nitrogen monoxide (NO) is a dominant target to be achieved because NO is an inert and the major component of NO$_x$ in exhaust gases.

It is well-known that NO is thermodynamically unstable relative to N$_2$ and O$_2$ at temperature below 1200 K,[2] and its catalytic decomposition is the simplest and most desirable method for NO removal. To date, however, no suitable catalyst, of which the activity continues to be high, has been found. This is due to the fact that oxygen contained in the feed or produced in the decomposition of NO competes with NO for the adsorption sites.[2] Thus, high reaction temperature and/or gaseous reductants are required to remove surface oxygen and regenerate the catalytic activity. At present catalytic reduction processes using NH$_3$, CO, or hydrocarbons on V$_2$O$_5$–TiO$_2$ or Pt–Pd–Rh catalysts have been practically applied.[1,3] On the other hand, copper ion exchanged zeolites,[4-9] Pt/Al$_2$O$_3$, YBa$_2$Cu$_3$O$_y$ supported on MgO,[10] Sr^{2+}-

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(1) Crucq, A.; Frennet, A. In *Catalysis and Automotive Pollution Control*; Elsevier: Amsterdam, 1987; p 1. Bosch, H.; Janssen, F. *Catal. Today* **1987**, *2*, 369.

(2) Hightower, J. W.; Van Leirsbung, D. A. In *The Catalytic Chemistry of Nitrogen Oxides*; Klimish, R. L., Larson, J. G., Eds.; Plenum: London, 1975; p 63.

(3) Harrison, B.; Wyatt, M.; Gough, K. G. In *Catalysis*; Royal Society of Chemistry: London, 1982; Vol. 5, p 127.

(4) Iwamoto, M.; Yokoo, S.; Sakai, K.; Kagawa, S. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1629.

(5) Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.; Kagawa, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1273.

(6) Iwamoto, M.; Furukawa, H.; Kagawa, S. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Elsevier: Amsterdam, 1986; p 943.

(7) Iwamoto, M.; Yahiro, H.; Tanda, K. In *Successful Design of Catalysts*; Inui, T., Ed.; Elservier: Amsterdam, 1988; p 219.

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substituted perovskite,[11-13] and Ag–Co_3O_4[14] have recently been reported as the candidates for the catalyst of the direct decomposition of NO. Among the catalysts, the copper ion exchanged zeolites first reported by Iwamoto and co-workers are the most suitable for the reaction. It must be very desirable to enhance the catalytic activity of the Cu zeolites to develop a new process for the removal of NO from the exhaust streams. In addition, the correlation between the exchange level and catalytic activity should be clarified to characterize the active sites for the reaction.

In the present work, we have found that repeated ion exchange of the ZSM-5 zeolite with Cu^{2+} solution resulted in excess loading of copper ions above 100% exchange level, and catalytic activities of the resulting Cu–ZSM-5 zeolites were very high for the decomposition of NO. Furthermore, physicochemical characterization of the zeolites and temperature-programmed desorption (TPD) experiments of NO have elucidated that copper ions exist as Cu^{2+} and Cu^+ after evacuation at elevated temperature, and most of the copper ions in the ZSM-5 zeolite are available for NO adsorption. These findings would serve as further progress in the chemistry of ion exchange and NO decomposition.

Experimental Section

The parent zeolite of ZSM-5 (silica/alumina = 23.3) was supplied by Tosoh Corp. The sample was termed MFI. The zeolite was ion-exchanged with the usual procedure; it was washed with dilute $NaNO_3$ solution, ion-exchanged in an aqueous copper acetate solution of an adequate concentration, washed with water, and dried at 383 K overnight. The typical conditions of ion exchange were as follows. Approximately 15 g of MFI zeolite was ion-exchanged in 1 dm^3 of the copper(II) acetate solution with 10–11 mmol dm^{-3} overnight and filtered. The obtained wet cake was again ion-exchanged in new copper(II) acetate solution. After the desired repetition of the ion-exchange treatment, the sample was washed and dried under vacuum. The amount of copper ions in the zeolite was determined by atomic absorption spectroscopy after the zeolite sample obtained was dissolved in HF solution. The degree of ion exchange was calculated by 2·(amount of Cu)/(amount of Al), where the amount of Al was measured by a Si MAS NMR method. Hereafter the sample was abbreviated as Cu–MFI–100 (cation–zeolite structure–degree of exchange).

The NO decomposition reaction was carried out in a flow reactor made of stainless tube. The zeolite catalyst (1.0 g) placed in the reactor was heated at 773 K for 5 h under a He stream (30 cm^3 cm^{-1}) in order to remove such impurities on the zeolite surface as water, caron dioxide, and oxygen. The catalytic reaction was then started. A gas mixture of NO (0.2–2.0 vol %) and He (balance) was fed at a flow rate (F) of 30 cm^3 min^{-1} ($W/F = 2.0$ g s cm^{-3}, W = catalyst weight) unless otherwise stated. The reaction temperature was increased stepwise from 373 to 973 K, and the reaction was carried out at each temperature until the conversion reached constant. The gas composition was analyzed by gas chromatography using Porapak Q (N_2O) and Molecular Sieve 5A (O_2, N_2, and NO) columns.

The TPD technique was applied here to the NO–zeolite system to determine the amount of NO adsorbed and the catalyst state. The TPD profiles were measured with the same apparatus as was used for the flow reaction. After the catalyst was used in the steady-state catalytic decomposition of NO, zeolite was cooled to 323 K from 773 K in He and then exposed to the gas mixture of NO (2.05%) and He for 60 min. Subsequently, the gas was again changed to pure helium (30 cm^3 min^{-1}). The sample was heated to 773 K at a heating rate of 4.17 K min^{-1}, and desorbed gases were analyzed by gas chromatography.

Results and Discussion

Characterization of the Resulting Copper Ion Exchanged ZSM-5 Zeolites. Repeating the ion-exchange procedure three or more times resulted in the excess loading of copper ions above 100% of exchange level. The degree of ion exchange of the copper ranged from 30% to 143%. In contrast, it was confirmed in a separate experiment that it is impossible to prepare excessively copper ion exchanged ZSM-5 zeolites with copper(II) nitrate or sulfate solution. The excess loading has been reported in the ion-exchange system of $CuCl_2$ + acetic acid solution and Y-type zeolite by Schoonheydt et al.[15] The findings suggest that the excess loading of copper ions on zeolites commonly takes place in the presence of acetate buffer. The state of copper was here investigated on a Cu–MFI–116 catalyst after various treatments by ESR, phosphorescence, and CO adsorption techniques.

After Cu–MFI–116 was evacuated at room temperature, the ESR signal attributed to hydrated Cu^{2+} ions[16] was observed while no phosphorescence spectrum due to Cu^+ ions[17] was detected. The sample was evacuated at 773 K for 30 min, exposed to oxygen of 13 kPa at the same temperature for 30 min, reevacuated for 30 min, and then cooled to room temperature under vacuum. After this treatment the sample gave the intense ESR signals similar to those attributable to Cu^{2+} ions located on the zeolite lattice.[18] The comparison of double integration of the ESR spectrum with that of the standard sample ($CuSO_4 \cdot 5H_2O$) concluded that approximately 50% of Cu in Cu–MFI–116 exists as Cu^{2+}, which can be detected by ESR.

After the above pretreatment phosphorescence signals were observed at 480 and 540 nm. The spectra are clearly due to Cu^+ ions located in the zeolite framework.[17,19] The presence of the Cu^+ ions in the pretreated Cu–MFI–116 was further confirmed by the IR measurements. The admission of CO onto the zeolite resulted in the appearance of a strong IR adsorption band at 2154 cm^{-1} assigned to Cu^+–CO species.[20] These observations clarified that the high-temperature treatment brought about the generation of Cu^+ ions. As it was widely accepted that only Cu^+ can irreversibly adsorb CO at room temperature while Cu^{2+} and Cu^0 cannot,[20] the quantitative analysis of CO irreversibly adsorbed makes it possible to measure the amount of Cu^+ active for CO adsorption. The results obtained by the volumetric method suggested that the amount of Cu^+ after the pretreatment was about 40% of Cu in the zeolite. The proportion is larger than those reported on copper ion exchanged Y-type zeolites;[21] however, it would be reasonable because in the present zeolite the degree of the ion exchange exceeds 100%.

The physicochemical analyses clarified that the copper atoms exchanged into the Cu–MFI–116 zeolite exist as Cu^{2+} (50%), Cu^+ (40%), and unknown species (10%) after the pretreatment. Naccache et al.[22] and Jacobs et al.[21] have reported that during the ion-exchange procedure of Y-type zeolite the water molecules coordinated near Cu^{2+} ions are easily ionized and dissociated because of the strong electrostatic fields, and then $Cu(OH)^+$ and Brönsted acid site (proton) were formed. Therefore, in the present work, the excess loading of copper ions (above 100%) would be explained as follows: $Cu(OH)^+$ and Brönsted acid site, together with Cu^{2+}, are formed on Cu–MFI–116 during the copper ion exchange, and the as-formed proton can take part in ion exchange with $Cu(OH)^+$. The appearance of Cu^+ at elevated temperatures is probably due to the dimerization or polymerization of $Cu(OH)^+$

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(8) Iwamoto, M.; Yahiro, H.; Kutsuno, T.; Bunyu, S.; Kagawa, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 583.

(9) Iwamoto, M.; Yahiro, H.; Mine, Y.; Kagawa, S. *Chem. Lett.* **1989**, 213.

(10) Shimada, H.; Miyama, S.; Kuroda, H. *Chem. Lett.* **1988**, 1797.

(11) Uchijima, T. *Hyomen* **1980**, *18*, 132.

(12) Teraoka, Y.; Fukuda, H.; Kagawa, S. *Chem. Lett.* **1990**, 1.

(13) Yasuda, H.; Mizuno, N.; Misono, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1094.

(14) Hamada, H.; Kintaichi, Y.; Sasaki, M.; Ito, T. *Chem. Lett.* **1990**, 1069.

(15) Schoonheydt, R. A.; Vandamme, L. J.; Jacobs, P. A.; Uytterhoeven, J. B. *J. Catal.* **1976**, *43*, 292.

(16) Richardson, J. T. *J. Catal.* **1967**, *9*, 178.

(17) Texter, J.; Strome, D. H.; Herman, R. G.; Klier, K. *J. Phys. Chem.* **1977**, *81*, 333.

(18) Sendoda, Y.; Ono, Y. *Zeolites* **1986**, *6*, 209.

(19) Barrie, J. D.; Dunn, B.; Hollingsworth, G.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 3958.

(20) Huang, Y. Y. *J. Catal.* **1973**, *30*, 187.

(21) Jacobs, P. A.; Wilde, W.; Schoonheydt, R. A.; Uytterhoeven, J. B.; Beyer, H. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1221.

(22) Naccache, C. M.; Taarit, Y. B. *J. Catal.* **1971**, *22*, 171.

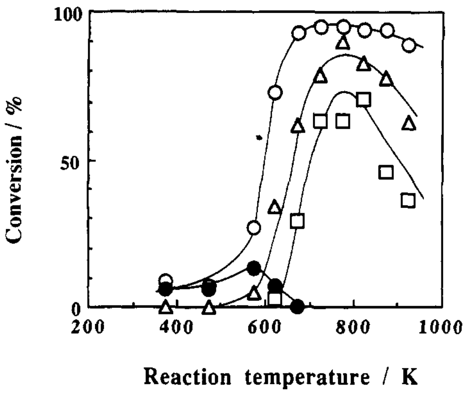

Figure 1. Temperature dependence of decomposition of NO over Cu-MFI-143 at 4.0 g s cm^{-3} and P_{NO} = 1.0%. △, □, and ● correspond to conversions of NO (○) into N_2, O_2, and N_2O, respectively.

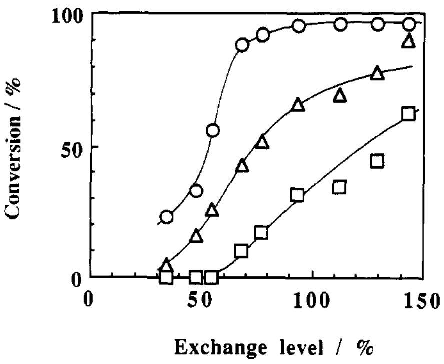

Figure 2. Correlation between exchange level of copper ions and the conversions of NO (○) into N_2 (△) and O_2 (□). Temperature = 723 K, W/F = 4.0 g s cm^{-3}, P_{NO} = 1.0%.

species by dehydration to form Cu^{2+}–O^{2-}–Cu^{2+} species and subsequent reduction of Cu^{2+} by the $^1/_2O_2$ evolution.[23] In fact, the desorption of water and oxygen was observed by a mass spectrometer when the evacuation temperature for the fresh sample was elevated.

As will be shown in the next section, the resulting Cu–MFI zeolites are active for the direct decomposition of NO; therefore, the number of copper ions active for the adsorption of NO molecules has been determined. In the IR experiments,[6] it was confirmed at room temperature that NO could be adsorbed as NO^+, NO^-, and $(NO)_2^-$ species on the Cu zeolite, and the anionic species decreased with adsorption time to yield N_2 and N_2O in the gas phase whereas NO^+ increased. After adsorption of NO for about 1 h, the anionic species almost disappeared and the intensity of NO^+ species became approximately constant. These results indicate that all Cu^+ ions generated through pretreatment at elevated temperature were oxidized to Cu^{2+} ions by oxygen or NO_2 produced in the reaction of NO at ambient temperature,[24] and a part of the resulting Cu^{2+} ions acts as adsorption sites for NO^+ (Cu^{2+} + NO = Cu^+–NO^+). This NO^+ species could not be desorbed by evacuation at room temperature. The IR spectra indicated the presence of a large amount of NO^+ and small amounts of NO_2 and NO_3 adsorbates and the absence of weakly adsorbed or physisorbed NO molecules. The phenomena were further confirmed by ESR experiments; that is, the adsorption–desorption cycles of NO resulted in a decrease–increase in the intensity of Cu^{2+} ESR signals.[25] The IR and ESR experiments suggest that quantitative measurement of the adsorbed NO^+ species makes it possible to determine the amount of Cu^{2+} ions active for NO adsorption. The TPD technique was employed to determine the amount.

The thermal desorption profile of NO adsorbed on the Cu–MFI zeolites consisted of two peaks at 373–473 K and around 653 K. Oxygen desorption was also observed around 653 K. Part of the NO desorbed at higher temperature would be due to the decomposition of NO_2 or NO_3 adsorbate, as the corresponding IR bands disappeared around 653 K. The amount of the lower NO peak revealed that 94% of Cu^{2+} ions exchanged into the Cu–MFI–122 were active for NO adsorption, indicating that most of copper ions loaded in the ZSM-5 structure are useful for adsorption of NO even at the excess exchange level.

Direct Decomposition of NO over Excessively Copper Ion Exchanged ZSM-5 Zeolite Catalysts. The respective catalytic activities of Cu–MFI samples with various exchange levels for the NO decomposition were measured as a function of reaction temperatures. The results of Cu–MFI–143 are shown in Figure 1 as an example. No deterioration of the catalyst was observed even after 30 h of continuous service; in the present work an experiment was not carried out after 30 h. The decrease in the amount of NO (conversion of NO) was larger than the amounts of N_2 and O_2 produced. As reported previously,[6] the discrepancy is due to the formation of NO_2, which cannot be detected by usual gas chromatography. In fact, in a separate experiment the formation of NO_2 was detected by infrared and mass spectroscopies. Very recently, the stoichiometry of the NO decomposition over the Cu–ZSM-5 zeolites was strictly confirmed by Li and Hall.[26]

A small amount of N_2O appeared below 623 K, indicating that the decomposition of N_2O, which is one of the intermediate products during the NO decomposition, proceeds faster than that of NO at high temperatures. The same result was observed in the direct decomposition of NO on Cu–Y zeolites.[4] The catalyst has predominant activity around 573–673 K, and the conversion leveled off at 723–773 K. Then the conversion decreased slightly at higher temperatures. The temperature dependence shown in Figure 1 is in good agreement with that reported previously for the Cu–MFI–73 zeolite.[5] The slight decrement of the catalytic activity at higher temperatures is not attributable to the deactivation of the catalyst, since the conversion did not change when the reaction temperature was raised and lowered stepwise between 773 and 923 K. The decrement of the conversion above 773 K therefore may be due to reversible change of the structure of active site and/or adsorbability of NO. It should be noted that first the decrease of the activity above ca. 773 K was much improved when the copper ion exchange level increased, and secondly the maximum conversion on each catalysts was mostly observed around 723 K.

The correlation between the catalytic activity at 723 K and the exchange level of copper ion is depicted in Figure 2. In the present experiments, 80–85% conversion into N_2 was the best result, indicating that the copper zeolite with the exchange level of 100% or above shows steady activity which is evidently higher than those reported previously.[6,10–14] In the figure, two noticeable facts were observed. One is the fact that the conversions of NO and into N_2 and O_2 showed an S-shaped dependence on the exchange level; the decomposition rate gradually increased on lower exchange level and increased sharply above the exchange level of 40%. The phenomena may be explained by the following two possible reasons: (1) ZSM-5 has two or more cation-exchangeable sites,[27] one of which is most readily exchanged with a copper ion and is inactive site for the decomposition of NO. The other sites are active for the decomposition of NO and are not readily ion-exchanged below the ion-exchange level of 40%. (2) The decomposition of NO proceeds only under cooperation of two adjacent active sites which could be formed at high extents of ion exchange. The decomposition rate was proportional to the 1.2–1.5 order with

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(23) The formation of Cu^+ by evacuation at high temperatures was also estimated in the TPD experiments of oxygen from Y zeolites. Iwamoto, M.; Maruyama, K.; Yamazoe, N.; Seiyama, T. *J. Phys. Chem.* **1977**, *81*, 622. Jacobs, P. A.; Beyer, H. K. *J. Phys. Chem.* **1979**, *83*, 1174.

(24) The increase of Cu^{2+} ESR signals was indeed observed upon the addition of O_2 on the pretreated Cu zeolite. It should be made sure, however, which of O_2 generated through the decomposition and NO_2 formed by disproportionation reaction of NO is an effective oxidant for Cu^+.

(25) Similar results have already been reported on Cu–Y zeolites. Kasai, P. H.; Bishop, R. J., Jr. *J. Phys. Chem.* **1973**, *77*, 2308.

(26) Li, Y.; Hall, W. K. *J. Phys. Chem.* **1990**, *94*, 6145.

(27) Mortier, W. J. In *Compilation of Extra Framework Sites in Zeolite*; Butterworth: London, 1982; p 53.

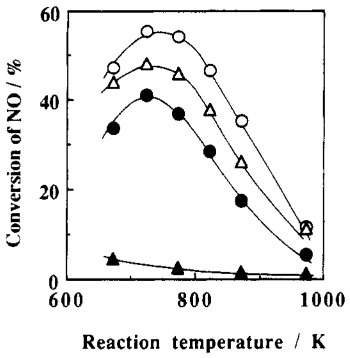

Figure 3. Influence of oxygen on the decomposition activities of Cu-MFI-122 (●, ○) and 89 (▲, △) catalysts at 1.0 g s cm^{-3}. (●) P_{O_2} = 8%, P_{NO} = 0.47%. (▲) P_{O_2} = 3%, P_{NO} = 0.50%. (○, △) P_{O_2} = 0%, P_{NO} = 0.51%.

respect to P_{NO} as is described in the next section, suggesting that the latter is correct, though further study is necessary to make clear the correlation.

Another interesting point is the catalytic activities of Cu-MFI above the exchange level of 100%; the rate of decomposition to N_2 and O_2 monotonically increased with increment of exchange levels even above 100%. This means that the amount of NO_2 produced decreased with the increase of copper ion exchange levels. Therefore, the copper ions excessively loaded into the ZSM-5 zeolite framework are also effective for the direct decomposition of NO. This result agreed well with the fact that most of the copper ions exchanged into ZSM-5 are useful for the NO adsorption and suggests that excess loading of copper ions is one possible way to develop more active catalyst for the direct decomposition of NO.

Effects of NO Pressure, Contact Time, and Coexisting Gases on NO Decomposition. The pressure dependence of the NO decomposition was examined over Cu-MFI-122 at 753 K. The conversion of NO increased from 27% to 75% with increment of NO pressure from 0.18% to 2.05%. We could obtain linear correlation lines in log-log plots of partial pressure of NO (P_{NO}) vs the reaction rate of NO, and the rate was proportional to the 1.2-1.5 order with respect to P_{NO}, where the values were changed with the contact time or GHSV. Clearly, the present results cannot be treated as a differential reaction system owing to too great conversion levels of NO, and therefore the above values are not accurate; however, the values would be useful guides for discussing the reaction mechanism and/or for comparison with the other catalytic systems.

The conversion of NO increased with the contact time; the conversions of NO on Cu-MFI-122 at 753 K reached 40-60% at 0.2 g s cm^{-3} (GHSV = 7500 h^{-1}) and 13-25% even at 0.025 g s cm^{-3} (GHSV = 60000 h^{-1}). The NO conversion reached ca. 100% above the contact time of 4.0 g s cm^{-3}. These results demonstrate that the present catalyst has excellent activity for the catalytic decomposition of NO even at such large GHSV, which is important for the practical use.

The effect of addition of carbon dioxide, water vapor, oxygen, or sulfur dioxide on the catalytic activity of the Cu zeolites was examined. When CO_2 was added to the reactant gas flow, no reduction in the catalytic activity was observed. The addition of H_2O resulted in the decrease of the catalytic activity. The effect, however, is fully reversible; that is, the activity was reduced in the presence of H_2O but regenerated by its absence.

The effect of addition of oxygen was dependent on the zeolite structure, the degree of exchange of Cu^{2+} ions, and the relative pressure of oxygen to that of NO. The typical results of copper ion exchanged ZSM-5 are shown in Figure 3. For example, when oxygen (8 vol %) was added to a mixture of 0.47% NO and 91.53% He, the conversion of NO decreased from 55% (without oxygen) to 40% at 753 K on Cu-MFI-122. On the other hand, over Cu-MFI-89 the conversion of NO decreased to 5% from 47% on addition of 3% oxygen to the NO-He (NO = 0.5 vol %) stream. It should be noted that the catalytic activity of Cu-MFI-122 is little influenced by the presence of oxygen in the feed. An excess loading of copper ions brings about an increase not only in the catalytic activity but also in the tolerance to oxygen poisoning. When the partial pressure of NO was only 1000 ppm, the extent of the conversion into N_2 was diminished from 23% (without oxygen) to 5% by the addition of 0.5% O_2 on Cu-MFI-152 at 773 K and 0.3 g s cm^{-3}. This indicates that the conversion level was also a function of ratio of P_{O_2}/P_{NO}.

SO_2 completely poisons the activity at 673-923 K. With ZSM-5, the desorption treatment of adsorbed SO_2 at higher temperature resulted in regeneration of the decomposition activity. SO_2 would compete with NO for the adsorption sites and prevent the catalytic reaction.

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