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Selective catalytic reduction of N_2O by C_3H_6 over Fe-MFI

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The catalytic activities of Fe-MFI (88% exchange) and Cu-MFI (122% exchange) zeolite catalysts for the decomposition and mainly the selective reduction of nitrous oxide by propene have been studied in the temperature range from 523 to 773 K. In the presence of oxygen and water vapor, both materials reveal strong retardation of their activity. When propene is added as reductant, Fe-MFI showed very high activity even in the low-temperature region and at low propene concentrations, whereas Cu-MFI is strongly deactivated.

Keywords: nitrous oxide, propene, selective reduction, Fe-MFI, Cu-MFI

1. Introduction

Nitrous oxide (N_2O) is known to contribute to the catalytic destruction of ozone in the stratosphere and to be a greenhouse gas component. The concentration of N_2O in the atmosphere increases by 0.2–0.3% per year. This increase is mainly caused by anthropogenic activities [1,2]. Furthermore, N_2O arises as a co-product in the production of adipic acid for Nylon 66 [3], as a component of the exhausts of automobiles and of the emission of various chemical processes. N_2O is very stable in air and the atmospheric lifetime is about 150 years. Thus, the removal of N_2O by suitable catalytic methods is a very urgent subject in order to protect our global environment.

Recently, many studies have been focused on the direct decomposition of nitrous oxide. Li and Armor [4] reported the catalytic activity of Cu-MFI and Co-MFI to be higher than those of noble metal-exchanged catalysts, such as Rh-MFI and Ru-MFI. Nevertheless, the activity of Rh-MFI and Ru-MFI is high, compared to Al_2O_3-supported forms. Furthermore, it has been stated by Chang et al. [5], that Ru–Na-MFI materials with high ion-exchange levels are not deactivated in the presence of excess oxygen, and show high activity for the direct N_2O decomposition. According to Kannan and Swamy [6], the activity of hydrotalcite catalysts for the direct decomposition is higher than those of Co-MFI and Cu-MFI. Rh/ZnO catalysts which have been calcined in air have higher reaction rates than Rh-MFI and hydrotalcites [7]. Recent work by Kapteijn et al. [8] has focused on comparative kinetic and DRIFT studies of the direct nitrous oxide decomposition over Co-, Fe- and Cu-MFI. The catalytic behavior of RhO_x/CeO_2, Rh_2O_3 and CeO_2 materials has been elucidated by Cunningham et al. [9]. However, these studies have been carried out in the absence of hydrocarbons which are components of various exhausts. Therefore, high catalytic activities in the presence of hydrocarbons are an essential precondition for a suitable catalyst.

In a previous work we already reported about the high activity of Fe-MFI for the selective reduction of NO by propene in the low-temperature region [10]. The high catalytic activity is not significantly affected, even in the presence of water vapor. In the present research, we focused on the catalytic activity of Fe-MFI for the direct decomposition of N_2O, but mainly on the activity for the selective reduction of N_2O in the presence of propene.

2. Experimental

2.1. Preparation of Fe-MFI and Cu-MFI

MFI was supplied by Tosoh Co. in the sodium form (Si/Al = 11.7). Fe-MFI was prepared by ion-exchange with a dilute solution of $Fe(SO_4)$ at 323 K under nitrogen atmosphere. The exchange was carried out in a refluxing flask with stirring. After 20 h, the ion-exchanged product was filtered, washed with distilled water and dried at 353 K in vacuum. Finally, the sample was calcined for 12 h at 773 K in air. Cu-MFI was prepared under the same conditions, using $[Cu(NO_3)_2]$ as source for copper. The loading of Fe-MFI and Cu-MFI was determined by X-ray fluorescence analysis (XRF).

2.2. Reaction conditions

The reaction was carried out in the temperature range from 523 to 773 K, using a standard flow reactor, SV = 50000 h^{-1}, a mixture of N_2O (500 ppm), C_3H_6 (0–1000 ppm), O_2 (0 and 5%) and H_2O (0 and 10%) diluted

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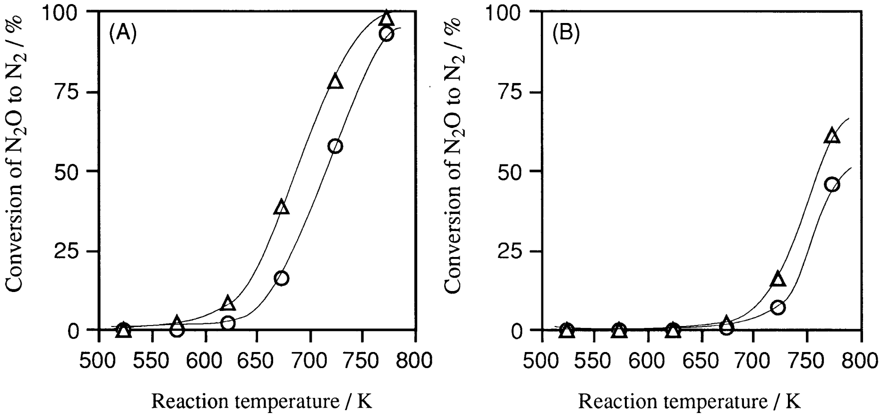

Figure 1. Decomposition of N_2O over (○) Fe-MFI (88%) and (△) Cu-MFI (122%) as a function of the reaction temperature, SV = 50 000 h^{-1}. (A) N_2O (500 ppm) + O_2 (5%) + He (balance gas); (B) N_2O (500 ppm) + O_2 (5%) + H_2O (10%) + He (balance gas).

with He (weight of catalyst: 0.09 g, total flow: 150 $cm^3\,min^{-1}$). NO and NO_2 were analyzed by a chemoluminescence NO_x analyzer, and a gas chromatograph was used to detect N_2, N_2O, CO, CO_2 and H_2O. However, NO and NO_2 were not detected in this experiment at all. The catalytic activity was estimated by the conversion of N_2O to N_2.

3. Results and discussion

Figure 1 shows the conversion of N_2O, obtained with Fe-MFI (88% exchange) and Cu-MFI (122% exchange) in the presence of excess oxygen. In the absence of water vapor (figure 1A), both catalysts exhibit appreciable conversions at 623 K, whereas Cu-MFI shows the higher activity. However, the results cannot be directly compared due to the different ion-exchange levels. When water vapor is added, both catalysts showed strong deactivation (figure 1B). At 773 K the conversion rate is decreased to about 45% of the values obtained in the absence of water. Nevertheless, considering these experimental conditions, Cu-MFI still reveals a higher catalytic activity.

The results obtained when adding propene (1000 ppm) are most remarkable. They are illustrated in figure 2. They are in strong contrast to the data displayed in figure 1. It is obvious that Cu-MFI is very strongly deactivated, while the catalytic activity of Fe-MFI is significantly increased (figure 2A). These effects result in a higher conversion rate over Fe-MFI, compared to Cu-MFI. Considering these reaction conditions, the addition of water vapor leads to a retardation of both materials (figure 2B). Nevertheless, Fe-MFI possesses a much higher activity. Judged by the results shown in figures 1 and 2, propene promotes the catalytic activity of Fe-MFI, whereas the catalytic activity of Cu-MFI is unambiguously strongly decreased.

Figure 3 exhibits the transient responses for the N_2O reduction over Cu-MFI and Fe-MFI. At stage I, only

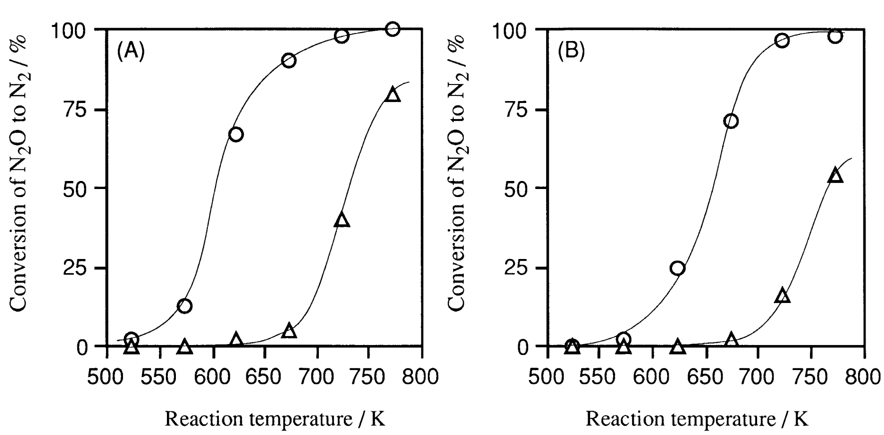

Figure 2. Selective reduction of N_2O by propene over (○) Fe-MFI (88%) and (△) Cu-MFI (122%) as a function of the reaction temperature, SV = 50 000 h^{-1}. (A) N_2O (500 ppm) + C_3H_6 (1000 ppm) + O_2 (5%) + He (balance gas); (B) N_2O (500 ppm) + C_3H_6 (1000 ppm) + O_2 (5%) + H_2O (10%) + He (balance gas).

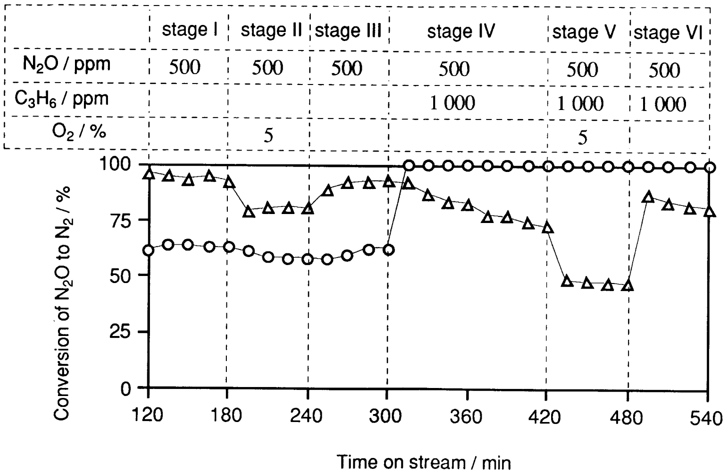

Figure 3. Transient responses for N_2O reduction over (○) Fe-MFI (88%) and (△) Cu-MFI (122%) at 723 K, SV = 50 000 h^{-1}.

N_2O (500 ppm) was supplied. After steady-state activity was achieved at stage I, 5% O_2 were added at stage II. The conversion over Cu-MFI was significantly reduced, while the conversion over Fe-MFI remained mainly unchanged. When the oxygen supply was cut down at stage III, both materials revealed about the same activities as obtained at stage I. Propene (1000 ppm) was added at stage IV, leading to a gradual deactivation of Cu-MFI to about 20% lower conversion rates than reached at stage I. The conversion over Fe-MFI was very strongly increased, reaching 100%. At stage V, oxygen (5%) was added to the feeding gas. This results in a decrease of the N_2O conversion over Cu-MFI for about 25%, whereas the catalytic activity of Fe-MFI was not affected. The activity of Cu-MFI was recovered while cutting down the oxygen supply at stage VI, and the conversion reached about the same value as obtained at stage IV. The very high activity of Fe-MFI was not affected at all.

The dependence of the N_2O conversion over Cu-MFI and Fe-MFI on the propene concentration at a reaction temperature of 723 K is displayed in figure 4. Figure 4A shows the results obtained in the absence of water vapor and a feeding gas composition of 500 ppm N_2O, 5% O_2. The concentration of C_3H_6 was varied from 0 to 1000 ppm. Even low concentrations of propene (100 ppm) caused a strong retardation for Cu-MFI, whereas the catalytic activity of Fe-MFI is rapidly increased. At C_3H_6 concentrations of about 250 ppm, the conversion over Cu-MFI is only about 50%, while the N_2O conversion over Fe-MFI reaches nearly 100%. The further increase of the propene concentration up to 1000 ppm leads to a gradual decrease of the catalytic activity of Cu-MFI. Above concentrations of 250 ppm propene, the conversion over Fe-MFI is 100%. In the presence of water vapor (10%) and in the absence of propene, both catalysts reveal only very low activities (figure 4B). The conversions are about 17% (Cu-MFI) and 7% (Fe-MFI), respectively. When propene is supplied, the activity of Fe-MFI is very strongly increased

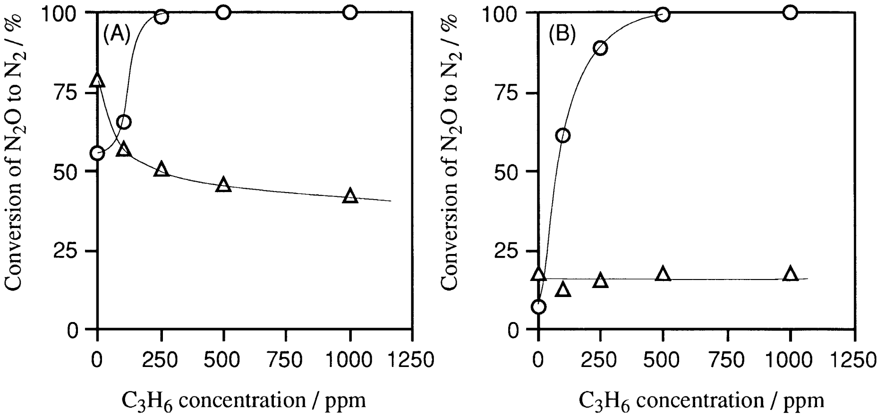

Figure 4. Selective reduction of N_2O over (○) Fe-MFI (88%) and (△) Cu-MFI (122%) at 723 K as a function of the propene concentration, SV = 50 000 h^{-1}.

and at propene concentrations of 500 ppm, N_2O conversions of 100% are achieved. The activity of Cu-MFI is, in contrast to that of Fe-MFI, not significantly affected by the addition of propene, and the conversion stays around 20%.

As our studies unambiguously reveal, Fe-MFI is a highly active catalyst for the selective reduction of nitrous oxide by propene. This is true, even in the low-temperature region and in the presence of water vapor. In contrast to the results obtained on Fe-MFI, the presence of propene even at low concentrations leads to a very strong deactivation of Cu-MFI. Possible reasons could be differences in the interactions between adsorbed propene molecules and the two different metal-ions. Further studies will be carried out, in order to elucidate the nature of these interactions and their influence on the catalytic activity of both materials.

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