CHEMISTRY LETTERS, pp. 1063-1066, 1991.

Selective Reduction of NO with Propylene on Fe-silicate Catalysts

Eiichi KIKUCHI,* Katsunori YOGO, Satoru TANAKA, and Masaki ABE
Department of Applied Chemistry, School of Science and Engineering,
Waseda University, 3-4-1 Okubo, Shinjyuku-ku, Tokyo 169

H-form Fe-silicate catalysts showed high activity and stability for the reduction of NO with propylene in the presence of a high concentration of oxygen. The catalytic activity of Fe-silicate was hardly affected by the presence of SO_2.

The removal of nitrogen oxides (NO_x) is a serious environmental problem. Iwamoto et al.1) reported that copper ion-exchanged ZSM-5 zeolites (Cu-ZSM-5) showed high catalytic activities for the direct decomposition of NO. And it was shown that these catalysts were also highly active for the reduction of NO with hydrocarbons in the presence of oxygen,2) although the role of copper in this reaction was not wholly explained. In practical use, the catalyst must be active in the exhaust stream including some hydrocarbons and SO_2. Recently, it was reported that H-form zeolites were also active for the reduction of NO with hydrocarbons.3) In our experimental studies, it was found that H-form metallosilicates showed catalytic activities for the reduction of NO with propylene, and Fe-silicate was the most active and stable for this reaction even in the presence of SO_2.

Metallosilicates (Fe-, B-, and Ga-silicates) were synthesized according to the rapid crystallization method reported by Inui et al.4) Thus synthesized metallosilicates were converted into the H-form by ion-exchange method using a 1 M NH_4NO_3 solution, followed by calcination at 540 °C. The X-ray diffraction patterns for the metallosilicates were similar to that of H-ZSM-5, indicating that these metallosilicates had a pentasil pore-opening structure. A Na-ZSM-5 having an atomic Si/Al ratio of 25 was supplied by Tosoh Corp.

The measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 1000 ppm propylene and balance nitrogen was fed on to 0.5 g catalyst at a rate of 92 cm^3(STP)•min^{-1}. Effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO.

Figure 1 shows the time-on-stream variation in catalytic activities of various metallosilicates for the reduction of NO at 300 °C. As shown here, H-Fe-silicates were active

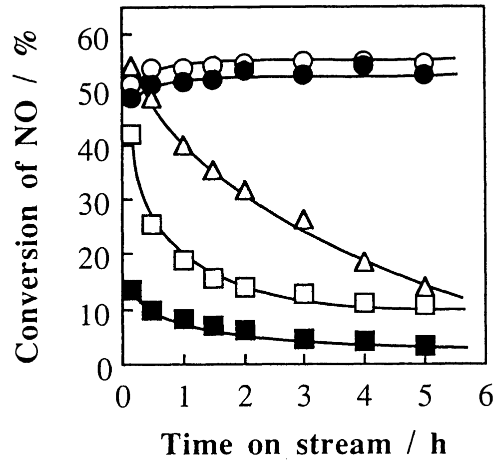

Fig. 1. Time-on-stream variation in the activities of various metallosilicates at 300 °C. Catalysts: ● , H-Fe-silicate (Si/Fe = 25); △ , H-ZSM-5 (Si/Al = 25); ○ , H-Fe-silicate (Si/Fe = 50); ■ , H-B-silicate (Si/B = 50); □ , H-Ga-silicate (Si/Ga = 50).

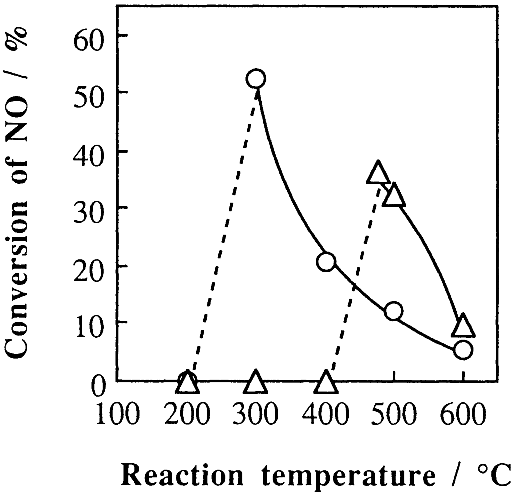

Fig. 2. Catalytic activities of H-Fe-silicate and H-ZSM-5 as a function of reaction temperature. Catalysts: ○ , H-Fe-silicate (Si/Fe = 25); △ , H-ZSM-5 (Si/Al = 25).

and stable catalysts for this reaction. The activity of either Fe-silicate initially increased slightly and reached a maximum after 1 h. The initial activities of H-ZSM-5 and Ga-silicate were comparably high, although they gradually decreased with time on stream and finally diminished under these reaction conditions.

Figure 2 compares the catalytic activities of H-Fe-silicate and H-ZSM-5 for the reduction of NO with propylene as a function of reaction temperature. The minimum temperature for the steady states activity of H-Fe-silicate was 300 °C and that for H-ZSM-5 was 475 °C. Below these temperatures, the activities of these catalysts gradually decreased and diminished finally. The steady state activities of both catalysts decreased with increasing reaction temperature. The decrease of catalytic activity at high temperatures is not attributable to catalyst deactivation, since high activities of the same level with the fresh catalysts were reproduced when the reaction temperature was decreased after the measurements of catalytic activity at these high temperatures. Probably it is due to the increased contribution of catalytic combustion of propylene at high temperatures leading to the decrease in the conversion of NO.

Figure 3 shows the effect of SO_2 on the activities of H-Fe-silicate and Cu-ZSM-5. The steady state catalytic activity of Cu-ZSM-5 was reduced to lower levels at the low temperature

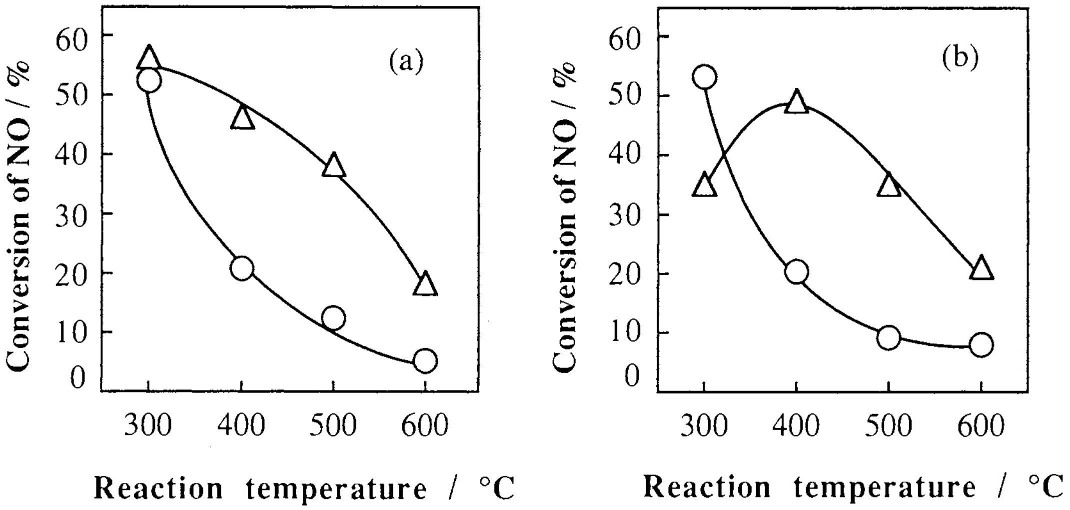

Fig. 3. The effect of SO_2 on the catalytic activities of H-Fe-silicate and Cu-ZSM-5. Reaction conditions: S.V., 12000 h^{-1}; feed concentrations, NO = 1000 ppm, O_2 = 10 %, C_3H_6 = 1000 ppm, SO_2 = 0 ppm (a), and 240 ppm (b).
Catalysts: ○ , H-Fe-silicate (Si/Fe = 25); △ , Cu-ZSM-5 (Si/Al = 25).

region by the presence of SO_2. On the contrary, SO_2 hardly gave an influence on the catalytic activity of H-Fe-silicate. Thus, it is that H-Fe-silicate is less sensitive than Cu-ZSM-5.

At reaction temperatures lower than 300 °C, the activity of H-Fe-silicate decreased with time on stream. The catalyst changed color from light brown to brown by use in reaction, and the activity of deactivated catalyst was restored by calcination in air at 500 °C for 1 h with an evolution of CO_2. At the same time, the color of the catalyst became light brown. It is, therefore, plausible that the catalyst deactivation was caused by the deposition of carbonaceous materials on the active sites.

A series of experiments were conducted at 300 °C to observe the effect of carbonaceous deposits on the activity of H-Fe-silicate. The results are shown in Fig. 4. In these runs, the catalyst bed was purged for 30 min at the same temperature after each set of reaction. After an ordinary reaction (a), the feed of propylene in the reactant stream was stopped (b), and it was found that the conversion of NO decreased gradually and completely terminated after 50 min with no more formation of CO_2. When the feed of propylene was restarted (c), the activity increased rapidly and reached the same level as that of the experiment (a). This suggests that carbonaceous deposits play an important role in this reaction. When the supply of both O_2 and propylene was stopped and only 1000 ppm NO was streamed (d), almost no reaction was observed with H-Fe-silicate. If O_2 was admitted to the reactant gas flow,

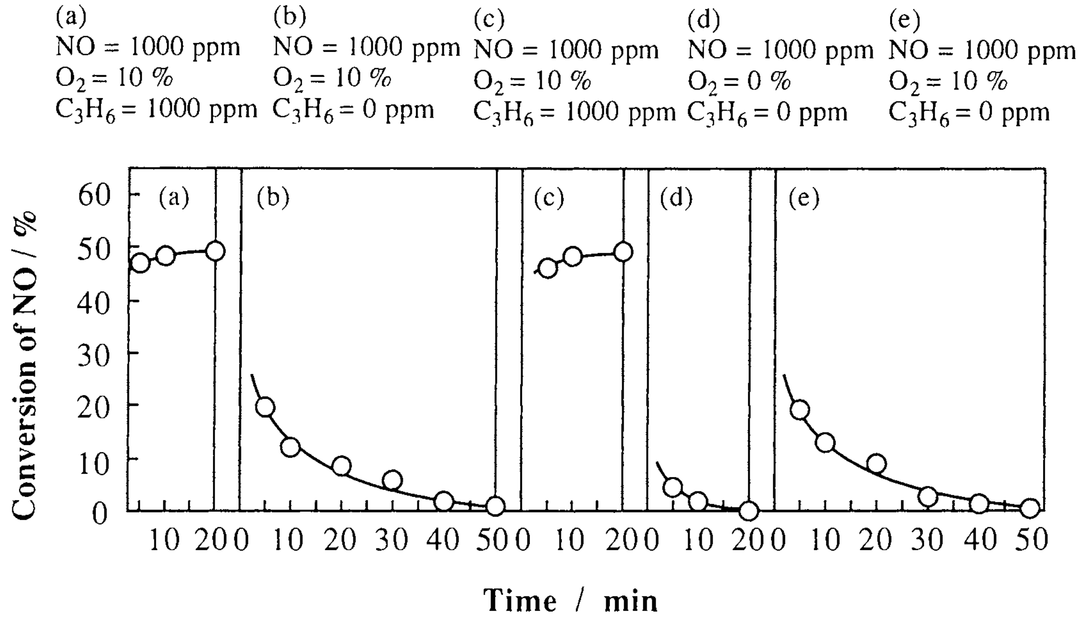

Fig. 4. Response of the conversion of NO on H-Fe-silicate when the feed composition was changed.

however, the activity manifested and it decreased with time on stream similarly to the experiment (b). Thus, oxygen is a necessary component for this reaction.

Consequently, we conclude that H-Fe-silicate is a highly active and stable catalyst for the reduction of NO with propylene, and that carbonaceous deposits on the catalyst activated by oxygen are probably concerned with this reaction.

References

1) M. Iwamoto, H. Yahiro, Y.Mine, and S. Kagawa, *Chem. Lett.*, **1989**, 213.
2) M. Iwamoto, H.Yahiro, Y. Yuu, S. Shundo, and N. Mizuno, *Shokubai,* 1990, **32**, 430.
3) H. Hamada, Y. Kintaichi, M. Sasaki, and T. Itoh, *Applied Catal.*, 1990, **64**, L1.
4) T. Inui, O. Yamase, K. Fukuda, A. Itoh, J. Tarumoto, N. Morinaga, T. Hagiwara, and Y. Takegami, Proc. 8th Intern. Cong. Catal., Berlin, 1984, III-569.

(Received March 26, 1991)