Performance of a protonated Co-contained silicate catalyst for NO reduction in equivalent conditions to diesel engine exhaust

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Effects of co-existence of H_2O, CO_2, and SO_2 in the reaction gas on the catalytic performance of cobalt containing silicate having ZSM-5 (MFI) structure (Co-silicate) were studied. Water vapor retarded only the hydrocarbon conversion to CO_2 but no effect was observed on NO conversion. Addition of CO_2 or SO_2 did not affect the reaction. The stability of H-Co-silicate against H_2O, CO_2, and SO_2 was ascribed to the state of metallic active species which were stabilized by incorporation into the high siliceous MFI structure.

Keywords: Co-silicate; deNOx catalyst; diesel engine exhaust; product inhibition; catalyst stability

1. Introduction

Recently, a number of papers on the elimination of NO in the presence of excess oxygen and a low concentration of an appropriate hydrocarbon have been reported using zeolite catalysts, mainly ion-exchanged zeolites [1–5]. However, it has been recognized that ion-exchanged ZSM-5, especially Cu-ion exchanged H-ZSM-5 [6,7], are gradually deteriorated in the presence of water vapor under high temperature conditions owing to both sintering of copper atoms and dislocation of the aluminum ingredient from the framework position. These kinds of disadvantages would be extended to other transition metal ion-exchanged zeolites. In order to avoid these disadvantages, we have applied metallosilicate catalysts to this reaction [8–11]. By adding the metal sources at the stage of gel formation and synthesizing the metallosilicates according to the rapid crystallization method [12,13], the transition metal elements were incorporated in the structure and stabilized with high dispersion. The higher thermal stability of metallosilicates was confirmed through comparison between Cu-ion-exchanged H-ZSM-5 and Cu-incorporated silicate of MFI structure by the forced oscillating reaction method

[14,15]. Among various kinds of metallosilicates, it was found that H-Co-silicate exhibited the highest performance for NO removal under the excess O_2 condition with coexistence of a low concentration of cetane [9]. In order to investigate the performance of H-Co-silicate further, the effects of water vapor, carbon dioxide, and sulfur oxide on the reaction were examined, aiming at its application to the diesel exhaust treatment.

2. Experimental

Co-silicate catalysts of MFI structure were hydrothermally prepared according to the rapid crystallization method [12,13]. Cobalt nitrate was used as the cobalt source. The charged content of cobalt in the reaction gel was 20 expressed as Si/Co atomic ratio. The obtained crystals were washed, dried, and then heated in an air stream at 550°C for 3.5 h to burn off the organic template, followed by ion-exchange with 1 N NH_4NO_3 solution, and calcined at 550°C in air for 3.5 h. They were pressed with a tablet machine and crushed to 15–24 mesh to provide for the reaction. A 2.0 g (ca. 3.0 ml) portion of the catalyst was packed in a 10 mm inner diameter quartz tube. The reaction gas, containing 1000 ppm NO, 10.0% O_2, and a low concentration (330 or 3000 ppm) of cetane (n-$C_{16}H_{34}$) diluted with N_2 was allowed to flow through the catalyst bed with a space velocity of 30 000 h^{-1}. Addition of water vapor up to 10% into the reaction gas was conducted by passing N_2 through a saturator at various temperatures. According to the increase in supply of water vapor, the space velocity (SV) was increased from 30 000 to 33 000 h^{-1}. In the case of the addition of CO_2 and SO_2, N_2 was replaced by these components, so the SV was not changed. NO and CO were continuously monitored with a chemiluminescence NO analyzer (Shimadzu NOA-305A) and an infrared gas analyzer (Shimadzu URA-106), respectively. CO_2 was analyzed with a gas chromatograph (Shimadzu GC-7A with active carbon column).

3. Results and discussion

3.1. EFFECT OF H_2O ADDITION

The prepared catalysts showed XRD patterns consistent with the MFI structure. Because any peaks for cobalt oxides or other phases were not detected in the XRD, the cobalt component was incorporated in a high dispersion manner. However, a part of the cobalt was discharged during the procedures to prepare the H-form catalysts and the obtained H-Co-silicate had a Si/Co atomic ratio of ca. 100.

The influence of H_2O concentration in the feed gas on the catalytic performance of Co-silicate at 500°C is shown in fig. 1. As shown, in the curve plotted with closed

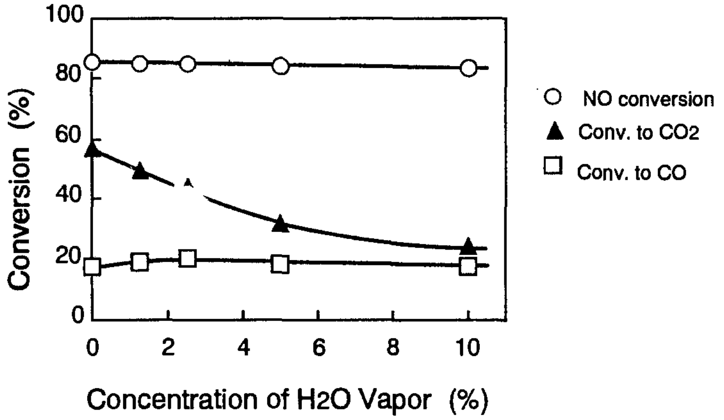

Fig. 1. Effect of H_2O addition on NO conversion on Co-silicate. 1000 ppm NO, 10.0% O_2, 3000 ppm n-$C_{16}H_{34}$, 0–10% H_2O, balance N_2, SV = 30 000–33 000 h^{-1}, reaction temperature 500°C. (○) NO conversion, (▲) HC conversion to CO_2, (□) HC conversion to CO.

triangles, the cetane conversion to CO_2 was gradually depressed with an increase in H_2O concentration, while a significant change in CO formation was not observed. It is noteworthy that a high NO conversion (85%) to N_2 was maintained almost constant irrespective of increase in H_2O concentration. This is clearly different from the result obtained for Cu-ion-exchanged H-ZSM-5 [16], in which NO conversion decreased with an increase in H_2O vapor concentration. The effect of H_2O vapor under a condition of very low concentration of cetane (330 ppm) was examined. As shown in fig. 2, NO conversion did not experience any effect although the conversion level was considerably lower (30%).

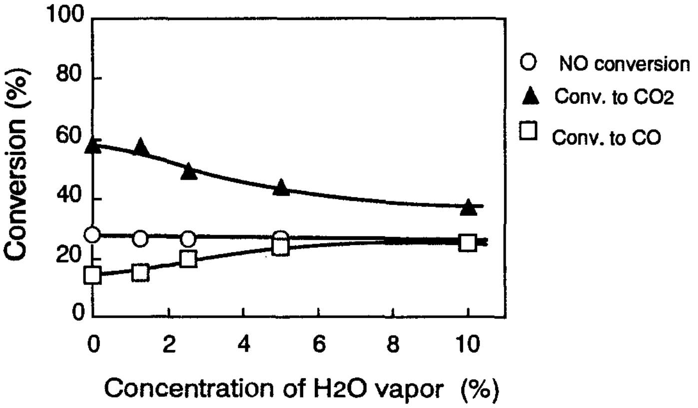

Fig. 2. Effect of H_2O addition on NO conversion reaction. 1000 ppm NO, 10.0% O_2, 330 ppm n-$C_{16}H_{34}$, 0–10% H_2O, balance N_2, SV = 30 000–33 000 h^{-1}, reaction temperature 500°C. (○) NO conversion, (▲) HC conversion to CO_2, (□) HC conversion to CO.

3.2. EFFECT OF CO_2 ADDITION

As the exhaust gases contain about 10% of CO_2, the effect of CO_2 presence was then examined. As shown in fig. 3, CO_2 addition up to 10% gave no significant effect on both NO conversion and hydrocarbon combustion. This is consistent with the case of Cu-ion-exchanged ZSM-5 [17]. The effect of co-existence of both H_2O and CO_2 was examined by varying the H_2O concentration up to 10% while maintaining the CO_2 concentration at 10%. The result was very similar to that of H_2O additions. This indicates that adsorption of CO_2 under the reaction condition is negligible. In the comparison of XRD profiles of H-Co-silicate before and after reactions with 10% CO_2 and 10% H_2O at 500°C for 5 h, not any change was observed. This result indicates that the MFI structure of H-Co-silicate catalysts was highly stable and dispersion of the cobalt species was stably maintained.

3.3. EFFECT OF SO_2 ADDITION

SO_2 poisoning has a possibility to be a crucial problem in this reaction system [18,19]. An irreversible inhibition of the catalytic activity was progressed on supported precious metal catalysts, whereas Cu-ion-exchanged ZSM-5 exhibited reversible retardation with a presence of SO_2 [20]. However, in the case of H-Co-silicate catalyst, as shown in fig. 4, the addition of SO_2 up to 200 ppm did not severely decrease the performance and only the cetane conversion to CO was retarded slightly. These results would be ascribed to the high dispersion of cobalt species, which have weak interaction with SO_2.

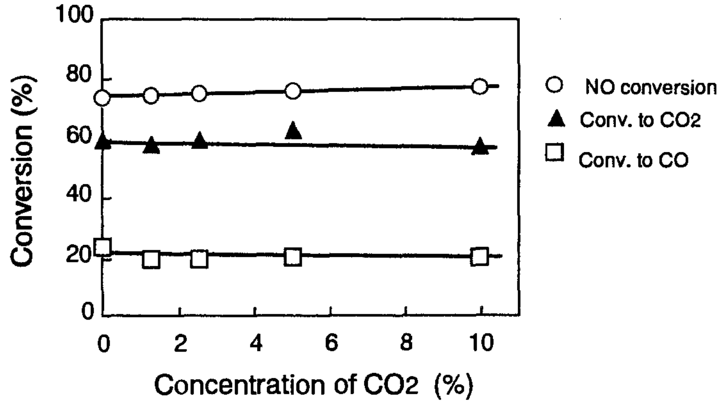

Fig. 3. Effect of CO_2 addition on NO conversion reaction. 1000 ppm NO, 10.0% O_2, 3000 ppm n-$C_{16}H_{34}$, 0–10% CO_2, balance N_2, SV = 30 000 h^{-1}, reaction temperature 500°C. (○) NO conversion, (▲) HC conversion to CO_2, (□) HC conversion to CO.

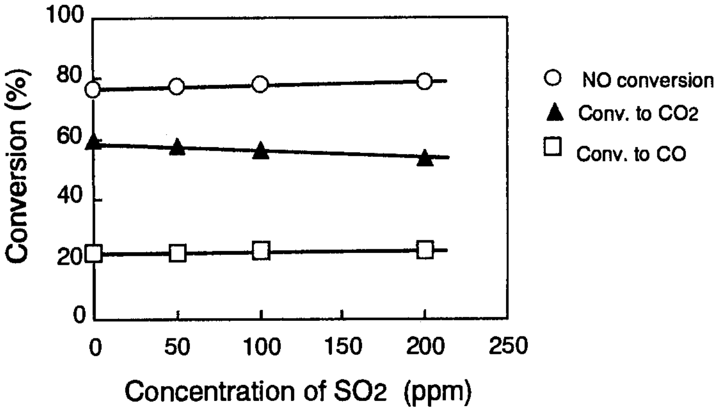

Fig. 4. Effect of SO_2 addition on NO conversion reaction. 1000 ppm NO, 10.0% O_2, 3000 ppm n-$C_{16}H_{34}$, 0–200 ppm SO_2, balance N_2, SV = 30 000 h^{-1}, reaction temperature 500°C. (○) NO conversion, (▲) HC conversion to CO_2, (□) HC conversion to CO.

4. Conclusion

Cobalt-silicate of MFI structure showed a highly active NO conversion (ca. 85%) under the condition of excess O_2 and coexistence of cetane at 500°C and with a considerably high space velocity 30 000 h^{-1}. Combustion of added cetane to CO_2 was affected with addition of water vapor; however, NO conversion did not experience any effect. CO_2 and SO_2 gave no effect on the reaction. Those stabilities of H-Co-silicate would be ascribed to the anchoring of the active metallic species by the crystal framework, which is different from the ion-exchanged metallic species in the pore of the ZSM-5 structure.

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