Carbonaceous Deposit as a Preferential Reductant in the Reduction of NO with C_2H_4 in Excess Oxygen over Alumina

Ryuta Fujii, Sayaka Kitagawa, Kou Takahashi, Noriyasu Okazaki, and Akio Tada*
Department of Applied and Environmental Chemistry, Kitami Institute of Technology, Koencho, Kitami 090-8507

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Carbonaceous deposit (denoted as C(d)) which was formed on alumina by C_2H_4 pyrolysis at 550 °C reacted selectively and preferentially with a mixture of NO and O_2 in the presence of C_2H_4, suggesting that the C(d) acts as an effective intermediate during the selective reduction of NO with C_2H_4 too.

The selective catalytic reduction of nitrogen oxides (NO_x) by hydrocarbons (HC) in excess oxygen (denoted as HC-SCR) has been regarded as a promising process for removing NO_x in exhaust gases, and many catalysts were proposed such as zeolites, metal oxides, and supported noble metals.[1,2] On alumina, one of such oxides, carbonaceous deposit (denoted as C(d)) was formed as an intermediate during C_3H_6-SCR, and found to act as an effective reductant of NO.[3,4] On the other hand, there has been reported another intermediate such as isocyanate (–NCO)[5,6] for HC-SCR over alumina or doped alumina. Thus, there are at least two reaction pathways for HC-SCR; one is via C(d) and the other is via another intermediate. Which pathway is more predominant? There has, however, been no answer so far, because there is very few report on HC-SCR over alumina covered with a considerable amount of C(d).[3,4] Therefore, the present paper deals with C_2H_4-SCR, C(d)-SCR, and C(d)-C_2H_4-SCR over alumina catalyst, and discusses the reactivity of the C(d) by comparing with that of C_2H_4 gas.

Alumina was produced by heating its precursor at 600 °C for 24 h, which was prepared by the controlled hydrolysis of aluminum triisopropoxide. It was then pressed into a disc under 200 $kg \cdot m^{-2}$, followed by crushing, sieving (355–500 µm) and again heating at 800 °C for 4 h in air. Every reaction including C_2H_4-SCR was performed using a fixed-bed flow tubular reactor under conditions as follows: W/F was 0.18 $g \cdot s \cdot cm^{-3}$ (catalyst, 0.40 g; total flow rate, 130 $mL \cdot min^{-1}$) and the composition of the typical reactant gas was NO (1000 or 0 ppm), O_2 (2%), C_2H_4 (500 ppm), and helium as a balance. The accumulation of C(d) on alumina was carried out by the pyrolysis of C_2H_4 (1000 ppm) at 550 or 800 °C for 3 h in the above reactor. The outflow gas was analyzed by gas chromatography with a Molecular Sieve 5A (separation of H_2, N_2, O_2, CO, CH_4, and NO) and Porapak Q (separation of CO_2, C_2H_4, N_2O, and H_2O). The length of Molecular Sieve 5A and Porapak Q columns was 3 m. Helium was used as the carrier gas (30 $mL \cdot min^{-1}$).

The ethene pyrolysis was carried out at 550 °C, followed by C(d)-SCR or C(d)-C_2H_4-SCR at 550 °C at which NO conversion was known to reach a maximum in C_2H_4-SCR over alumina.[7] For comparison, C_2H_4-SCR was also conducted. As can be seen in Figure 1, the NO conversion in the C_2H_4-SCR reached the plateau immediately after the start, while the NO conversion in the C(d)-C_2H_4-SCR was higher from the start, and then decreased to the plateau; the latter surpassed the plateau for 20 min. Such excess N_2-yield is apparently caused by the C(d), because the integrated excess N_2-yield is almost equal to the integrated N_2-yield in the C(d)-SCR. Figure 1 also shows the concentration ratios (denoted as r) of $N_2/(CO + CO_2)$ in the outlet gases. Interestingly, the r for the C(d)-C_2H_4-SCR was higher than the r for the C_2H_4-SCR at the early stage, while the r for the C(d)-SCR was very low.

In order to investigate in detail what happens in an excess N_2-yield period, a great deal of C(d) needs be accumulated, and so the ethene pyrolysis was carried out at 800 °C. In the

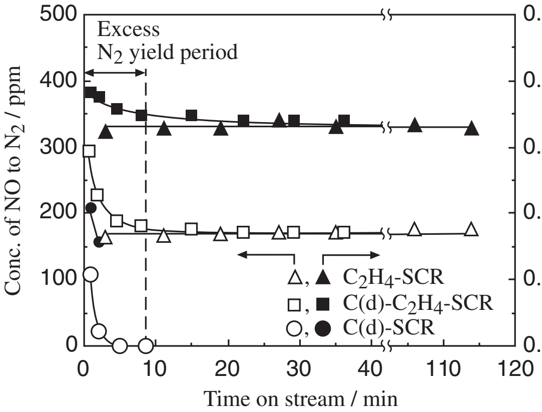

Figure 1. Conversion (open points) of NO to N_2 during C(d)-SCR, C_2H_4-SCR, and C(d)-C_2H_4-SCR over alumina and concentration ratio (filled points) of $N_2/(CO + CO_2)$ in the outlet gases. Ethene pyrolysis temp. = 550 °C, reac. temp. = 550 °C.

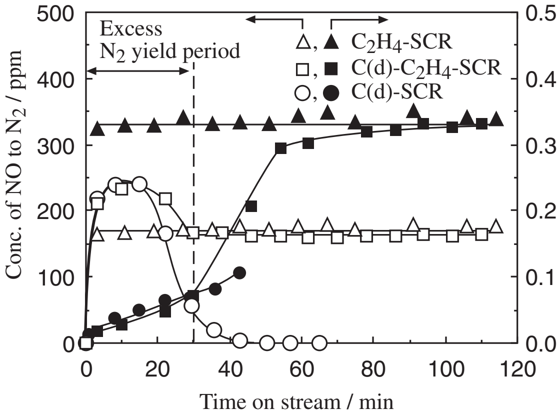

Figure 2. Conversion (open points) of NO to N_2 during C(d)-SCR, C_2H_4-SCR, and C(d)-C_2H_4-SCR over alumina and concentration ratio (filled points) of $N_2/(CO + CO_2)$ in the outlet gases. Ethene pyrolysis temp. = 800 °C, reac. temp. = 550 °C.

$C(d)$-C_2H_4-SCR, the maximum NO conversion appeared after an induction period, and the integrated excess N_2-yield became larger (Figure 2). Unexpectedly, the r for the $C(d)$-C_2H_4-SCR was markedly lower than the r for the C_2H_4-SCR, indicating that the C(d) reduced NO less selectively than C_2H_4 gas. The r for the C(d)-SCR increased gradually, indicating that the reactivity of the C(d) during the C(d)-SCR was improved by interacting with a mixture of NO and O_2. Interestingly, the r for the C(d)-SCR nearly synchronized with that for the $C(d)$-C_2H_4-SCR at the early stage.

When the ethene pyrolysis was carried out at 550 °C, the catalyst bed became gray, indicating that it was partly covered with C(d). The r for the C(d)-SCR was lower than the r for the $C(d)$-C_2H_4-SCR. This will be explained as follows: The C(d) interacts with C_2H_4 molecules to form a new reactive C(d), and it reacts with NO_x over alumina to result in C(d)-NCO-like species. The r for the C(d)-SCR in which the C(d) was formed at 550 °C was higher than the r for the C(d)-SCR in which the C(d) was formed at 800 °C. This is probably due to difference in reactivity which reflects difference in crystallinity of carbon in the C(d); the higher the temperature of the ethene pyrolysis, the higher the content of graphite in the C(d). In this connection, active charcoal and graphite were used instead of the C(d) in C(d)-SCR and it was found that graphite was inactive, while active charcoal was somewhat active but its reactivity (1.3×10^3 ppm N_2/g-carbon) was much lower than C(d) formed at 800 °C (1.7×10^4 ppm N_2/g-carbon) and the r for active-charcoal-SCR under the same reaction conditions as the C(d)-SCR shown in Figure 2 was 0.01 (not shown). In addition, a mechanical mixture of active charcoal (0.014 g, equal to the amount of C(d) formed at 800 °C) and γ-alumina (0.40 g) was used instead of the C(d) in the C(d)-SCR in Figure 2, resulting in 70 ppm of N_2 with the r of 0.03 (not shown), while the N_2 concentration in the C(d)-SCR was 170 ppm (Figure 2).

When the ethene pyrolysis was carried out at 800 °C, the catalyst bed became black, indicating that it was completely covered with C(d). In order to understand the time course of the r for the $C(d)$-C_2H_4-SCR, concentrations of C_2H_4 and H_2O at the outlet of the reactor were studied (Figures 3 and 4). In the presence of alumina, the outlet C_2H_4 concentration during the C_2H_4-SCR was 220 ppm, while in the absence of alumina, the outlet C_2H_4 concentration was 500 ppm, indicating no reaction occurred. These results clearly indicate that C(d) was formed during the C_2H_4-SCR. Interestingly, the outlet C_2H_4 concentration (315 ppm) at the early stage during the $C(d)$-C_2H_4-SCR was higher than that during the C_2H_4-SCR over alumina, although the NO conversion during the $C(d)$-C_2H_4-SCR was higher than that during the C_2H_4-SCR for a period of 30 min (Figure 2). This suggests that not C_2H_4 but the C(d) reduced NO, and this situation is likely to have took place for 40 min. Then the outlet C_2H_4 concentration decreased to 220 ppm, which is equal to that during the C_2H_4-SCR. In this period, the contribution of the C(d) as a NO reductant seems to diminish gradually. The time course of the outlet C_2H_4 concentration during the $C(d)$-C_2H_4-SCR is consistent with that of the corresponding H_2O concentration; the H_2O concentration was initially zero, increased, and finally reached that during the C_2H_4-SCR (370 ppm) through the plateau (170 ppm). No formation of H_2O is ascribed to the C(d) which completely covered alumina surface. The H_2O concentrations, 370 and 170 ppm, almost correspond to the respective H_2O concentrations which were estimated from the outlet C_2H_4-shortages. The H_2O concentrations for the C_2H_4-SCR (at NO conversion = ca. 32%) and the $C(d)$-C_2H_4-SCR (at NO conversion = ca. 47%) are defined as [the inlet C_2H_4 conc. (500 ppm) − the outlet C_2H_4 conc. (220 ppm)] $\times 2 = H_2O$ conc. (560 ppm) and [the inlet C_2H_4 conc. (500 ppm) − the outlet C_2H_4 conc. (320 ppm)] $\times 2 = H_2O$ conc. (360 ppm), respectively.

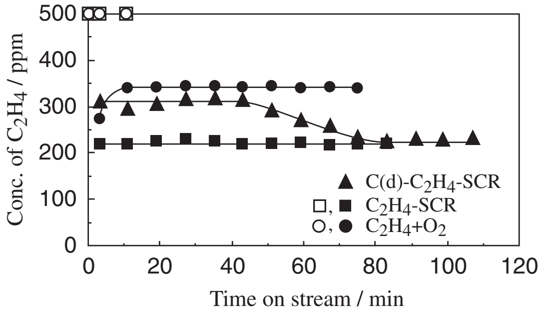

Figure 3. Outlet C_2H_4 concentrations during various reactions in the presence of alumina (filled points) and in the absence of alumina (open points). Ethene pyrolysis temp. = 800 °C, reac. temp. = 550 °C.

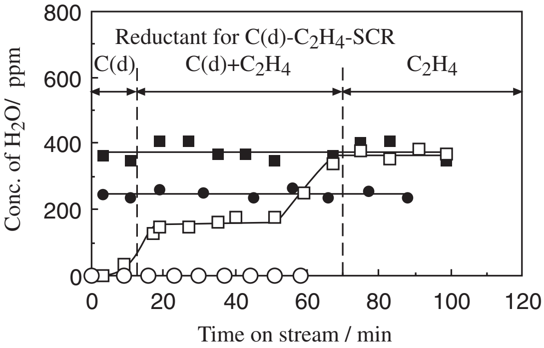

Figure 4. Water concentration during C_2H_4-SCR(■), $C(d)$-C_2H_4-SCR(□), C(d)-SCR(○), and $C_2H_4 + O_2$(●) over alumina. Ethene pyrolysis temp. = 800 °C, reac. temp. = 550 °C.

In brief, the reactivity of C(d) depended on its preparative temperature and its reaction atmosphere (existence of ethene); during $C(d)$-C_2H_4-SCR, C(d) formed from C_2H_4 at 550 °C reacted selectively and preferentially with a mixture of NO and O_2, while C(d) formed from C_2H_4 at 800 °C reacted not selectively but preferentially with the reactants, namely, its excess N_2-yield reflected not qualitative but quantitative effect of the C(d).

References

1 M. Iwamoto and H. Yahiro, *Catal. Today*, **22**, 5 (1994).
2 H. Hamada, *Catal. Today*, **22**, 21 (1994).
3 A. Obuchi, A. Ogata, K. Mizuno, A. Ohi, M. Nakamura, and H. Obuchi, *J. Chem. Soc., Chem. Commun.*, **1992**, 247.
4 A. Obuchi, M. Nakamura, A. Ogata, K. Mizuno, A. Ohi, and H. Obuchi, *J. Chem. Soc., Chem. Commun.*, **1992**, 1150.
5 G. R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno, and J. Skrzypek, *Appl. Catal., B*, **6**, 311 (1995).
6 K. Shimizu, H. Kawabata, H. Maeshima, A. Satsuma, and T. Hattori, *J. Phys. Chem. B*, **104**, 2885 (2000).
7 N. Okazaki, Y. Shiina, H. Itoh, A. Tada, and M. Iwamoto, *Catal. Lett.*, **49**, 167 (1997).

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