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Reaction Mechanism of NO Reduction by CH_4 over Rare Earth Oxides in Oxidizing Atmosphere

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Rare earth oxides have been examined as catalysts for the catalytic reduction of NO by CH_4 in the presence of oxygen. Among the rare earth oxides examined, Sc_2O_3 and Sm_2O_3 were found to be active for this reaction. For the Sm_2O_3 catalyst, ZrO_2 was the most effective support. The mechanism of the reaction was studied over the Sm_2O_3/ZrO_2. Kinetic studies indicated that CH_4 oxidation is initiated by O_2, and NO can react only with CH_3 radicals formed from the reaction of CH_4 with O_2. Ab-initio MO calculations also suggested that CH_3 radical is a more favorable reducing species for selective reduction of NO than CH_4. It is thus proposed that NO is reduced into N_2 by the CH_3 radical formed from the activation of methane by oxygen.

The gasoline lean burn engine and Diesel engine are promising technologies for suppressing carbon dioxide emissions, a major factor behind global warming, and for improving fuel economy. Those engines, however, are having the difficulties of controlling the NO_x emissions, because the existing three-way catalysts cannot work under such oxidizing conditions. In this connection, many researchers and institutes have been studying selective reduction of NO_x by hydrocarbons in an oxygen-rich atmosphere. A wide variety of catalysts have been reported to be active, and zeolite-related catalysts have been recognized to show the highest catalytic activity among them. However, the oxide catalysts have several advantages with regard to the durability in use and the simplicity for preparation in spite of having a lower activity than that of zeolite.

Rare earth oxides, which have been recognized to show high heat resistance, have been reported as active catalysts for selective reduction of NO by methane by Vannice et al.,[1,2] and a basic reaction mechanism has been suggested. The detailed reaction mechanism, however, has not been confirmed. In this paper the performances of rare earth oxides are examined for NO reduction using CH_4 as a reductant and the effective supports are investigated to improve the activities of rare earth oxides. Then kinetic studies are carried out and the detailed reaction mechanism of NO reduction by CH_4 in the presence of O_2 will be discussed. Some theoretical considerations based on ab-initio molecular orbital theory are also presented.

Experimental

The reactions were carried out using a conventional fixed-bed flow system with a quartz tubular reactor (i.d.=8 mm) under atmospheric pressure. The standard reaction conditions were as follows: weight of catalyst, 0.5 g; temperature, 873—973 K; NO concentration, 9200 ppm; CH_4, 8500 ppm; O_2, 5%; flow rate, 58 $cm^3\ min^{-1}$. The effluent gases were analyzed by gas-chromatography.

Sm_2O_3 (5 wt%)/ZrO_2 was prepared by the impregnation method using ZrO_2 powder and aqueous solution of $Sm(NO_3)_3$. The appropriate amount of $Sm(NO_3)_3$-impregnated ZrO_2 was dried and calcined at 573 K for 30 min and at 973 K for an additional 2 h. The other supported Sm_2O_3 catalysts were prepared by an impregnation method similar to that of Sm_2O_3/ZrO_2. The yields of N-compound (N_2, N_2O) and CO_x (CO, CO_2) were calculated on the basis of nitrogen and carbon number respectively.

Ab-initio molecular orbital calculations were performed using the Gaussian92 program package. Unrestricted MP2 method was used for geometry optimization with 6-31G** basis set and its energy calculation including zero-point vibration energy was obtained by using spin projection MP2 method. Each optimized structure was verified by a frequency calculation, and then IRC calculation was performed to verify that the obtained transition state connect to the minimum state.

Results and Discussion

Catalytic Performance over a Series of Rare Earth Oxides. Figure 1 shows the N_2 yield of NO decomposition, NO reduction by CH_4 (NO+CH_4) and NO reduction by CH_4 in the presence of O_2 (NO+CH_4+O_2) for a series of rare earth oxides without supports at 873 and 973 K.

NO decomposition activities were measured between 573 and 973 K. NO decomposition did not proceed for any oxide tested at these conditions except for Pr and Sc oxides. Pr_6O_{11} catalyzed NO decomposition above 700 K, and the N_2 yield at 973 K was 7%.

Most of the catalysts shown in Fig. 1 were active for NO

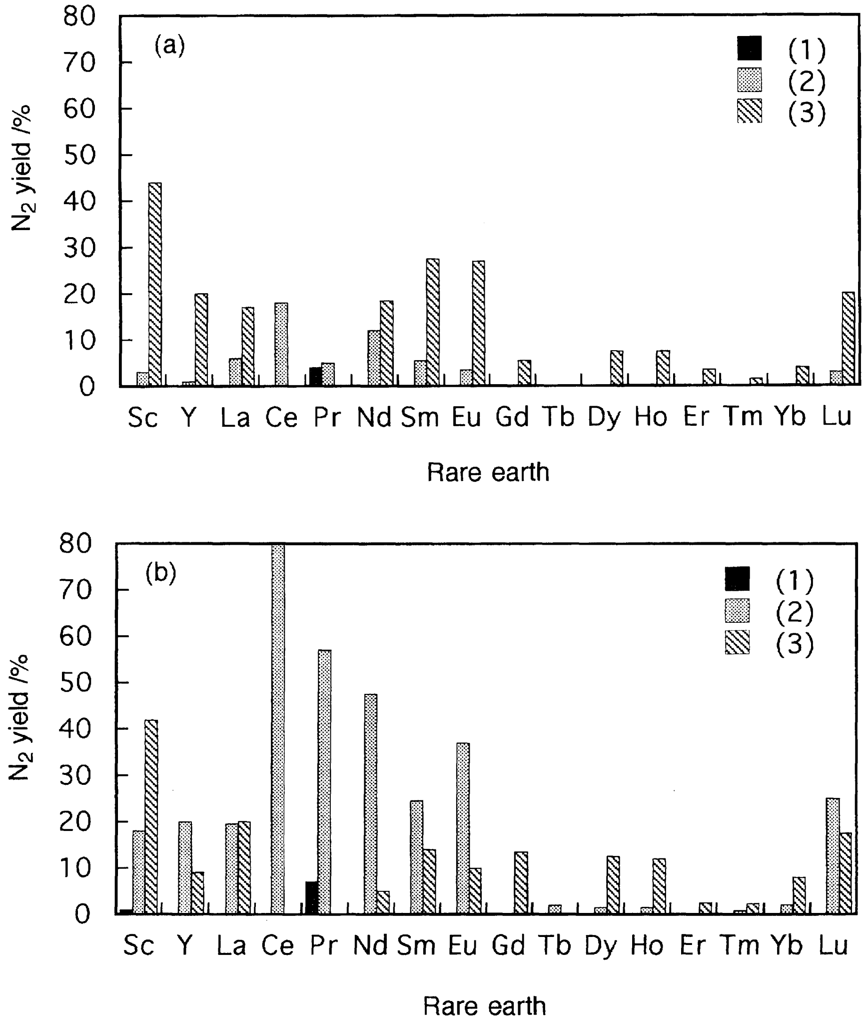


Fig. 1. N_2 yield over rare earth oxides for (1) NO decomposition, (2) $NO+CH_4$ reaction, and (3) $NO+CH_4+O_2$ reaction at (a) 873 and (b) 973 K under standard reaction conditions: NO, 9200 ppm; CH_4, 8500 ppm; O_2, 5%; weight of catalyst, 0.5 g; flow rate, 58 $cm^3\ min^{-1}$.

reduction by CH_4 in the absence of O_2 in contrast to the direct NO decomposition. The oxides of Ce, Pr, Nd, and Eu showed higher activity than others. Among the catalysts tested, CeO_2 was the most active catalyst for NO reduction by CH_4, and the N_2 yield at 973 K reached 80%.

O_2 addition increased the N_2 yield for all the catalysts at 873 K except for Ce, Pr, and Tb oxides as shown in Fig. 1. The order of N_2 yield at 873 K was as follows; $Sc_2O_3 > Sm_2O_3 \fallingdotseq Eu_2O_3 > Lu_2O_3 \fallingdotseq Y_2O_3 > Nd_2O_3 \fallingdotseq La_2O_3 > Dy_2O_3 \fallingdotseq Ho_2O_3 > Gd_2O_3 > Yb_2O_3 > Er_2O_3 > Tm_2O_3$. The correlation between activity and catalyst was quite different from that of NO reduction by CH_4 in the absence of O_2. As shown above, Sc, Sm, and Eu oxides showed high catalytic activities for the selective reduction of NO with CH_4 and O_2. Therefore, we have chosen Sm_2O_3 as a representative catalyst of these rare earth oxides for further studies.

Catalytic Activity of Sm_2O_3. The catalytic activity of Sm_2O_3 was measured as a function of reaction temperature between 500 and 973 K as illustrated in Fig. 2. NO reduction by CH_4 in the absence and presence of O_2 was observed above 700 K, while the direct decomposition of NO did not proceed at any temperatures. N_2O was detected below 873 K, but the amount of N_2O was negligible compared with the amount of N_2 formed. In the case of NO reduction in the absence of O_2, N_2 yield increased with increasing reaction temperature up to 973 K. In the presence of O_2, on the contrary, the maximum N_2 yield was observed at 873 K, and it decreased at higher temperature. This temperature dependence, which was typically observed in other catalytic systems, can be accounted for by the preferential reaction between O_2 and CH_4 at higher temperature. CO_2 yield increased with increasing temperature for both reactions as shown in Fig. 2. CO_2 yield for NO reduction in the presence of O_2 was much higher than in the absence of O_2. Detailed reaction mechanism will be discussed later on the bases of kinetic studies and computational chemistry.

Catalytic Activity of Supported Sm_2O_3. We looked for effective supports for the Sm oxide in order to improve the catalytic activity. Figure 3 shows the N_2 and CO_2 yield of selective reduction of NO over Sm oxide catalysts supported on various supports at 873 K. The content of Sm_2O_3 (0.025

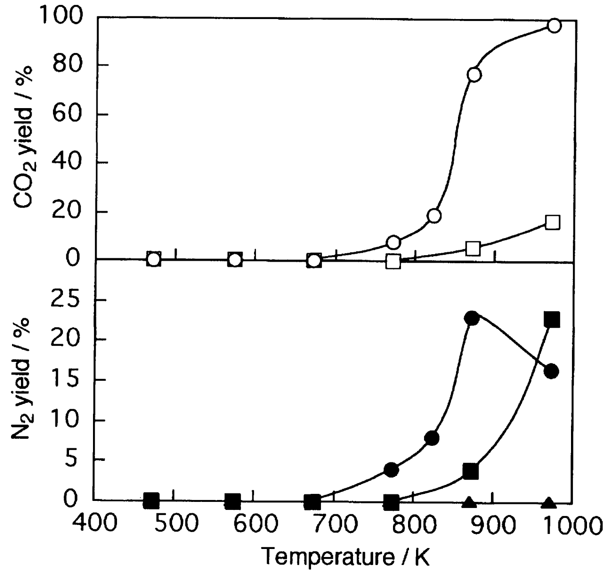


Fig. 2. Temperature dependencies of N_2 yield and CO_2 yield over Sm_2O_3 for NO decomposition (N_2: ▲), NO+CH_4 reaction (N_2: ■, CO_2: □), and NO+CH_4+O_2 reaction (N_2: ●, CO_2; ○) under standard reaction conditions.

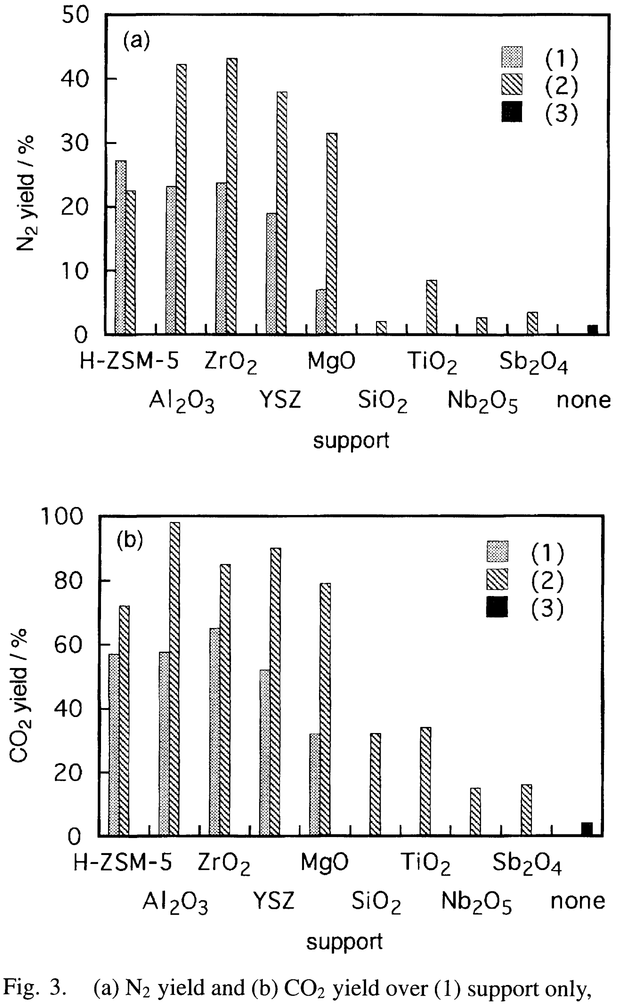


Fig. 3. (a) N_2 yield and (b) CO_2 yield over (1) support only, (2) Sm_2O_3 (5 wt%)/support, and (3) Sm_2O_3 (0.025 g) at 873 K under standard reaction conditions.

g) was adjusted to 5 wt% for the supported catalysts. SiO_2, TiO_2, Nb_2O_5, and Sb_2O_4 were not effective supports from the standpoint of N_2 yield. H-ZSM-5 itself is a good catalyst for selective NO reduction as reported by Hamada et al.[3] and Kikuchi and Yogo,[4] and it also showed good performance at the conditions in this study. However, N_2 yield was decreased by Sm_2O_3 loading, while CO_2 yield was increased. On the other hand, Al_2O_3, ZrO_2, YSZ (yittria stabilized zirconia), and MgO were found to be the effective supports. Among the supports tested, Al_2O_3 and ZrO_2 showed the highest enhancing effect on the basis of the N_2 yield, which exceeded 40%. However, the CO_2 yield was more than 97% for Sm_2O_3/Al_2O_3, and it was 84% for Sm_2O_3/ZrO_2. This result indicates that the selectivity of CH_4–NO reaction is higher for Sm_2O_3/ZrO_2 than Sm_2O_3/Al_2O_3. Based on the results above, it was found that ZrO_2 was the most effective support for Sm_2O_3. Therefore, more detailed studies will be carried out on Sm_2O_3/ZrO_2.

The dependence of the loading of Sm_2O_3 for Sm_2O_3/ZrO_2 at short contact time and low concentration of NO and CH_4 (catalyst weight, 0.5 g; flow rate, 580 ml min^{-1}; NO, 5000 ppm; CH_4, 5000 ppm) on the catalytic activity is shown in Fig. 4. The effect on N_2O yield and CO yield was not so appreciable, but maximum N_2 and CO_2 yield were observed at 10% loading. Furthermore, the profiles of loading effects on N_2 and CO_2 yields were very similar. These results suggested that N_2 formation is closely related to CH_4 oxidation.

Kinetic Studies on Selective Reduction of NO by CH_4 over Sm_2O_3/ZrO_2. The effect of reaction temperature on catalytic activity of Sm_2O_3 (5 wt%)/ZrO_2 was examined. N_2, N_2O, CO_2, and CO yields as a function of reaction temperature are shown in Fig. 5. Main products were N_2 and CO_2, and small amounts of N_2O and CO were produced, of which maxima were 3 and 8% respectively. The reaction proceeded above 773 K, and the conversions of NO and

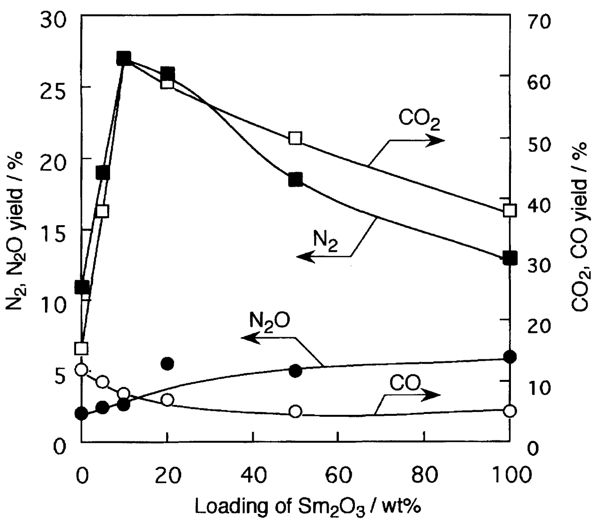


Fig. 4. Effect of Sm_2O_3 loading on (■) N_2 yield, (●) N_2O yield, (□) CO_2 yield, and (○) CO yield: NO, 5000 ppm; CH_4 5000 ppm; O_2, 5%; catalyst, weight, 0.5 g; flow rate, 580 cm^3 min^{-1}; temperature, 866 K.

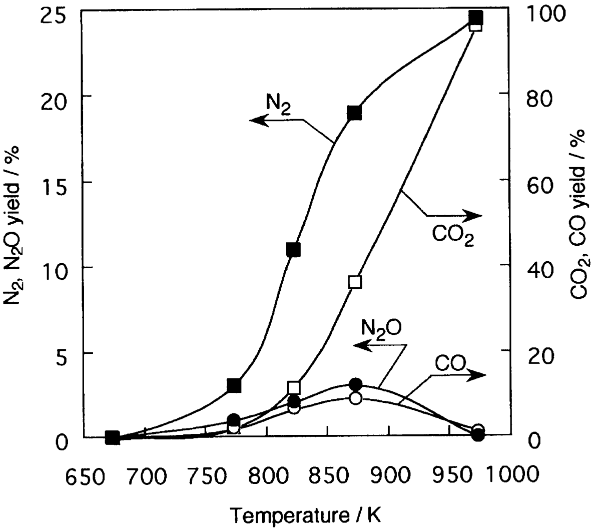


Fig. 5. Temperature dependencies of (■) N_2 yield, (●) N_2O yield, (□) CO_2 yield, and (○) CO yield over Sm_2O_3/ZrO_2: NO, 5000 ppm; CH_4, 5000 ppm; O_2, 5%; catalyst weight, 0.5 g; flow rate, 580 cm^3 min^{-1}.

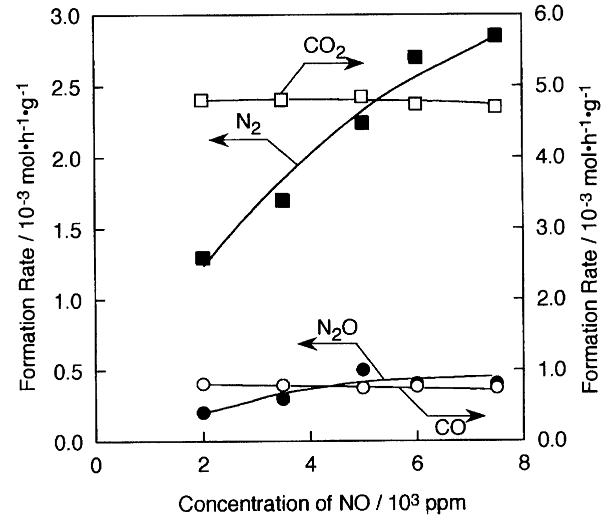


Fig. 7. NO concentration effect on (■) N_2, (●) N_2O, (□) CO_2, and (○) CO formation rate over Sm_2O_3/ZrO_2: Temperature, 866 K; CH_4, 5000 ppm; O_2, 5%; catalyst weight, 0.5 g; flow rate, 580 cm^3 min^{-1}.

CH_4 increased with increasing temperature. CH_4 conversion constantly increased with temperature, and it exceeded 90% above 950 K. The increase in NO conversion at temperatures above 850 K, on the contrary, was not as marked as that of CH_4 conversion. Thus, the selectivity of CH_4 used for NO reduction decrease at high reaction temperatures.

Figure 6 shows the effect of CH_4 concentration on the formation rate of N_2, N_2O, CO_2, and CO at 866 K. The conversion rates of both NO and CH_4 increased monotonously with increasing the concentration of CH_4.

Figure 7 shows the effect of NO concentration on the formation rate of products at 866 K. The formation rate of N_2 and N_2O increased with increasing concentration of NO, but the formation rates of CO_2 and CO were not affected by the NO concentration. Because the rate-determining step of methane oxidation over rare earth oxides is believed to be hydrogen atom abstraction from CH_4, independence of NO concentration on CH_4 conversion indicates that NO does not directly react with CH_4. Therefore, it is suggested that NO can react only with a reaction intermediate generated from CH_4, but cannot activate CH_4 itself.

Figure 8 shows the effect of O_2 concentration on the formation rate of products at 866 K. N_2 formation was accelerated by O_2 at low O_2 concentration (< 2%), but decreased above 2% concentration of O_2. This volcano-shape dependence of O_2 concentration has been observed in many other catalytic systems. The acceleration effect of O_2 at low concentration has been ascribed to the formation of active intermediates

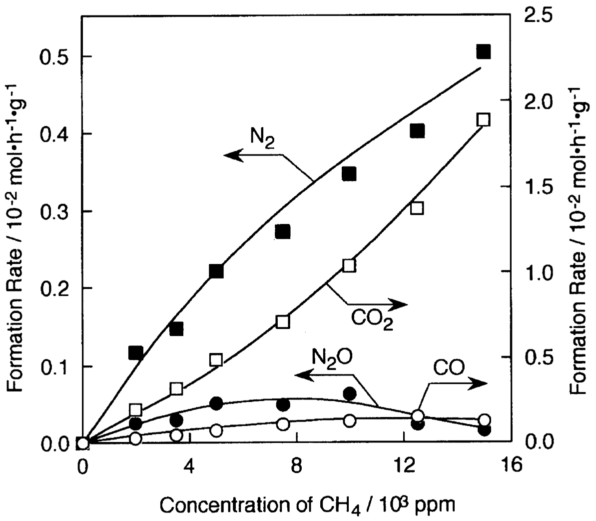


Fig. 6. CH_4 concentration effect on (■) N_2, (●) N_2O, (□) CO_2, and (○) CO formation rate over Sm_2O_3/ZrO_2: Temperature, 866 K; NO, 5000 ppm; O_2, 5%; catalyst weight, 0.5 g; flow rate, 580 cm^3 min^{-1}.

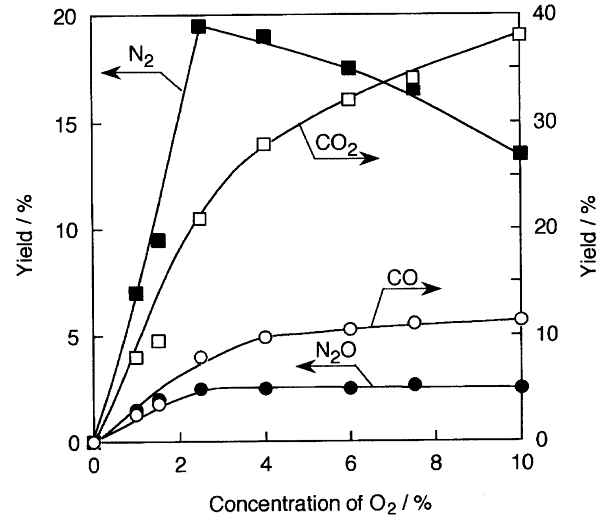


Fig. 8. O_2 concentration effect on (■) N_2 yield, (●) N_2O yield, (□) CO_2 yield, and (○) CO yield over Sm_2O_3/ZrO_2: Temperature, 866 K; CH_4, 5000 ppm; NO, 5000 ppm; catalyst weight, 0.5 g; flow rate, 580 cm^3 min^{-1}.

generated by the reaction of hydrocarbons with oxygen as described with regard to the results of Fig. 7. However, the deceleration effect at high O_2 concentration in Fig. 8 can be explained in terms of the decrease in the steady-state concentration of the active intermediate due to their further conversion into CO_2 at high O_2 concentration.

Kinetic Studies on CH_4 Oxidation by O_2 without NO over Sm_2O_3/ZrO_2. CH_4 oxidation by O_2 in the absence of NO was carried out in order to get information about the role of NO in the reaction mechanism. The major products were CO_2 and CO, and no oxidative coupling products such as C_2H_6 and C_2H_4, which are the major products at CH_4 rich condition, was detected under any conditions of this work. Figure 9 shows the effect of temperature on CH_4 conversion. The reaction proceeded above 773 K, and conversion of CH_4 reached 91% at 973 K. If we compare the results of Fig. 9 with those of CO_2 and CO formations in Fig. 5, it is obvious that the presence of NO does not affect the conversion rates of CO_2 and CO formations appreciably at any temperatures.

Figure 10 shows the effect of O_2 concentration on the yields of products at 866 K. The results in this figure show that the yield of CO_2 was lower for the CH_4 oxidation without NO than that with NO in Fig. 8, while total conversions of CH_4 (viz. CO_2+CO) were almost the same for both reactions.

Reaction Mechanism of Selective Reduction of NO by CH_4 over Sm_2O_3/ZrO_2. As described earlier, the reaction intermediate generated from the reaction between CH_4 and O_2 may play an important role in the selective NO reduction by CH_4 in the presence of O_2. Rare earth oxides are also well-known to be active catalysts for the oxidative coupling of methane,[5,6] and a methyl radical generated by the reaction between CH_4 and O_2 may be a reaction intermediate resulting in the formation of a coupled product, i.e., C_2H_6. Figure 11

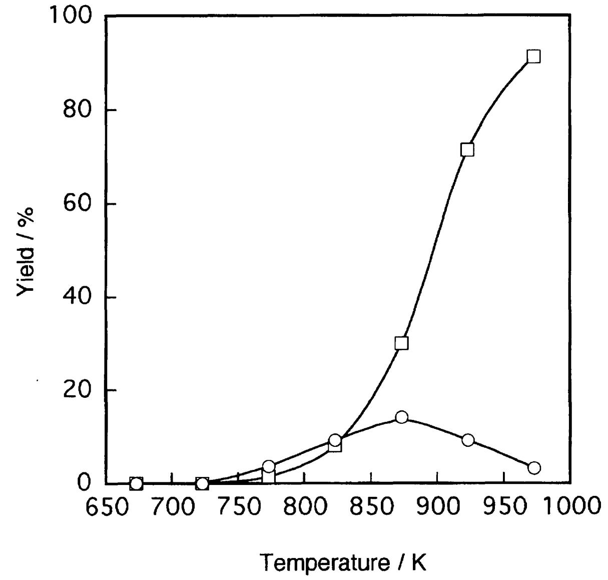


Fig. 9. (□) CO_2 yield and (○) CO yield for CH_4+O_2 (without NO) reaction at different temperatures: CH_4, 5000 ppm; O_2, 5%; catalyst weight, 0.5 g; flow rate, 580 cm^3 min^{-1}.

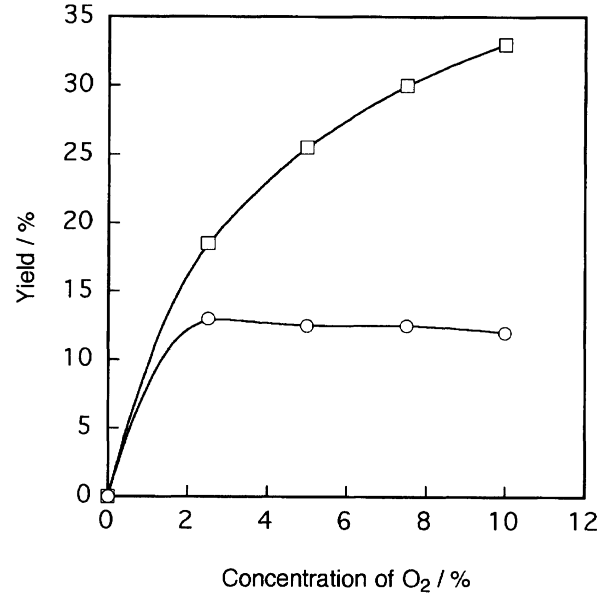


Fig. 10. O_2 concentration effect on (□) CO_2 yield and (○) CO yield for CH_4+O_2 (without NO) reaction: Temperature, 866 K; CH_4, 5000 ppm; catalyst weight, 0.5 g; flow rate, 580 cm^3 min^{-1}.

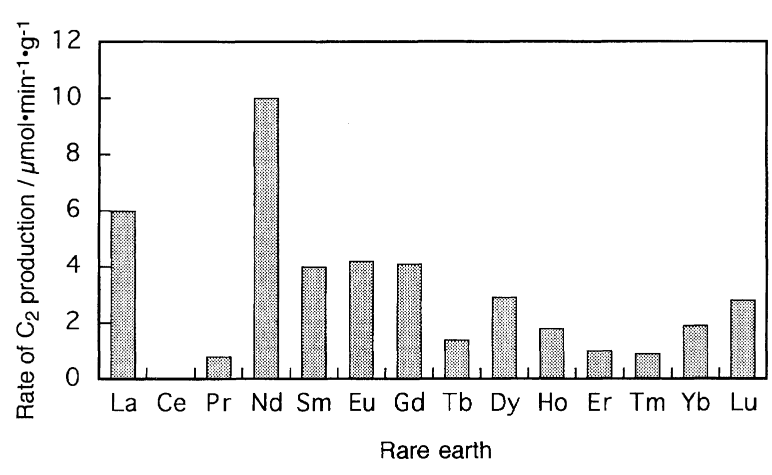


Fig. 11. Rate of C_2 production for CH_4 oxidative coupling reaction over rare earth oxides reported by Otsuka et al.[5] The specific rates were normalized per gram of catalysts.

shows the C_2 compound production rate measured for various rare earth oxides reported by Otsuka et al.[5] Figure 12 shows methyl radical formation rate measured by using MIESR technique in CH_4 oxidation by O_2 for the series of rare earth oxides reported by Lunsford et al.[6] The correlation of methyl radical formation rates was in good agreement with that of C_2 coupling activities (Fig. 11) and NO selective reduction activities (see the results of (3) in Fig. 1). For comparison of the results of Fig. 1, Fig. 11, and Fig. 12, it is suggested that the activity of NO selective reduction is closely related to the methyl radical formation as well as to oxidative coupling of methane.

The reactivities of CH_3 radical and CH_4 were investigated by computational chemical studies on the basis of ab-initio molecular orbital theory. In order to get information about the reactivity, activation energies were estimated by calculating potential energy surface of the reactions. Figure 13 illustrates the structures obtained from energy optimized calculation. Their corresponding optimized parameters are summarized in Table 1. Table 2 summarizes the Mulliken charge population on NO and O_2 at transition state and product state. Negative value of charge population stands for electron transfer from reductant (CH_3•, CH_4) to oxidant (NO, O_2). The optimized structures indicate that N–O and O–O bond are weakened by the interaction with both of CH_3 radical and CH_4. It is also indicated from the data of charge population that electrons transfer to NO and O_2 from reductant in all reactions. These results indicate that the reactions of NO and O_2 with CH_3 radical and CH_4 can be interpreted as an electron donation to π^* orbital of NO and O_2 from reductnat (CH_3•, CH_4).

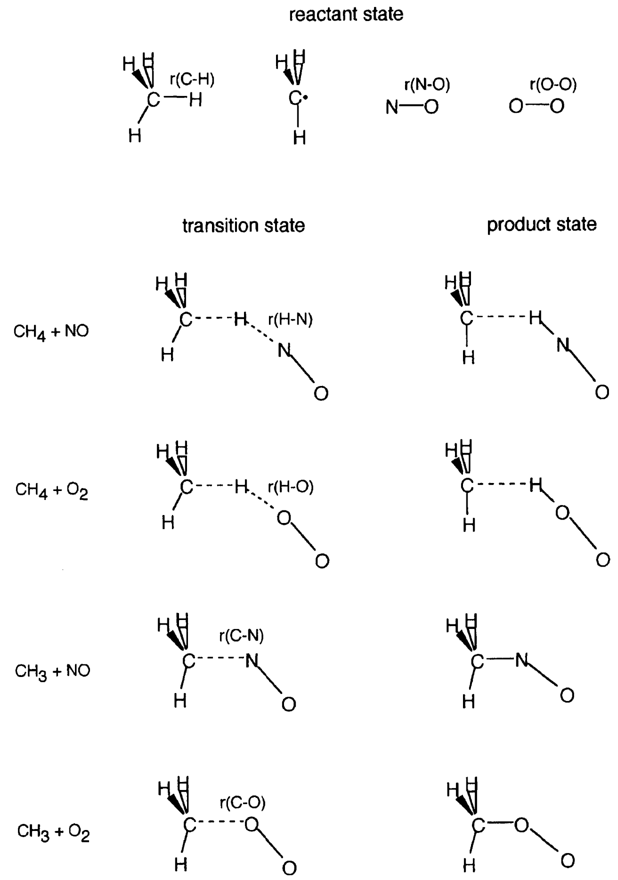


Fig. 13. Illustration of optimized geometries for reactions of CH_4+NO, CH_4+O_2, CH_3•+NO, and CH_3•+O_2.

The total energy of reactant state and transition states are listed in Table 3. Activation energy is estimated from the energy difference between the total energy of reactant state and transition state. In the case of reaction with CH_3 radical, the energy barrier for NO is much lower than O_2, while they are nearly equal for the reaction with CH_4. This result suggests that the activated intermediate such as CH_3 radical is a better reducing species for selective reduction of NO than a saturated hydrocarbon such as CH_4.

Many groups have suggested that NO_2 formed from reaction of NO with O_2 initiated the selective NO reduction in various catalytic systems.[4,7—11] Kikuchi and Yogo[4] proposed that the reaction proceeded via the reaction between NO_2 and CH_4 on the grounds that the presence of NO enhances the CH_4 conversion. Such enhancement of CH_4 conversion by NO, however, was not observed for the reaction over rare earth oxide in our experiment. This result suggests that se-

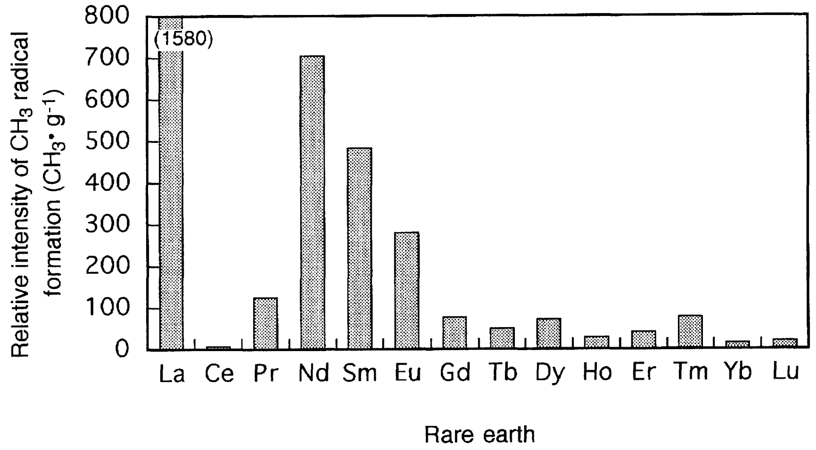


Fig. 12. Relative intensities for methyl radical formation over rare earth oxides reported by Lunsford et al.[6] The specific rates were normalized per gram of catalysts.

Table 1. Optimized Bond Length at Reactant, Transition, and Product States (in Ångstrom)

Reactant	Bond length	Reactant state	Transition state	Product state
CH_4+NO	r(C–H)	1.09	1.64	2.29
	r(N–O)	1.14	1.15	1.24
	r(H–N)	—	1.14	1.05
CH_4+O_2	r(C–H)	1.09	1.45	2.21
	r(O–O)	1.25	1.29	1.32
	r(H–O)	—	1.10	0.98
CH_3+NO	r(N–O)	1.14	1.23	1.24
	r(C–N)	—	1.49	1.48
CH_3+O_2	r(O–O)	1.25	1.21	1.31
	r(C–O)	—	2.01	1.45

Table 2. Mulliken Charge Population on NO and O_2

Reactant	Transition state	Product state
CH_4+NO	−0.256	−0.291
CH_3+O_2	−0.403	−0.404
CH_3+NO	−0.266	−0.256
CH_3+O_2	−0.114	−0.396

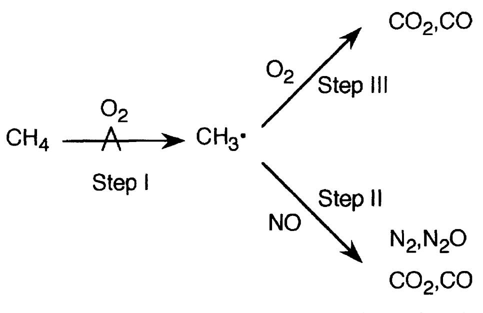
Table 3. Total Energies and Activation energies for the Reaction of NO and O_2 with CH_4 and CH_3

Reaction	Reactant state	Transition state	Activation energy
	a.u.	a.u.	kcal mol^{-1}
CH_4+NO	−169.8723697	−169.770807	63.7
CH_4+O_2	−190.2706370	−190.159610	69.7
CH_3+NO	−169.2181942	−169.2754007	−35.9
CH_3+O_2	−189.6164615	−189.6055867	6.8

lective reduction of NO over rare earth oxides proceed by a different mechanism from that of Ga/ZSM-5.

We propose the following reaction mechanism (Scheme 1) from the observations described above. The reaction proceeds through a CH_3 radical as a reaction intermediate formed from the activation of CH_4 by O_2 (Step I). NO is reduced by the CH_3 radical producing N_2, N_2O, CO_2, and CO (Step II). The CH_3 radical also easily reacts with O_2 producing CO and CO_2 (Step III).

Assuming Step I is the rate-determining step, CH_4 conversion is dependent on O_2 concentration but independent on NO concentration. Since CH_3 radical concentration is dependent on the concentration of CH_4, conversion rate of NO is influenced by CH_4 concentration. Because O_2 is indispensable for CH_3 radical formation, the presence of O_2 induces NO reduction. However, high concentration of O_2 is unfavorable for selective reduction of NO, because O_2 also consumes CH_3 radical by successive oxidation; thus the NO conversion decreases at high O_2 concentration (Fig. 8). The relative rates of CH_3 radical reactions (Step II or III) are changed by reaction temperature because of the difference of activation energies in the reaction with NO and that with O_2. At higher temperature the reaction of CH_3 radical with O_2 is more favorable than with NO due to the higher activation energy for the reaction with O_2 than with NO as suggested by theoretical calculation described above. Therefore, the selectivity of CH_4 reacting with NO decreases at temperatures higher than 873 K (Fig. 5).



Scheme 1. Reaction mechanism of selective NO reduction over Sm_2O_3/ZrO_2.

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