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PARTIAL OXIDATION OF METHANE OVER FINE PARTICLES OF VARIOUS AMORPHOUS OXIDES INCLUDING LANTHANUM

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Partial oxidation of methane was carried out over fine particles of amorphous lanthanum oxides including 3B element and amorphous yttrium aluminum oxide. At low temperatures and low methane/oxygen ratios products were CO, CO_2, C2 hydrocarbon, hydrogen and water, and no formaldehyde was detected. The discussion on the contribution of catalyst components to the reaction suggested that 3B elements substantially influenced methyl radical formation and consumption while rare earth elements sufficiently affected formaldehyde decomposition.

Keywords: Partial oxidation, methane, fine particle, amorphous lanthanum oxide, 3B element, amorphous yttrium oxide, formaldehyde.

1. Introduction

Partial oxidation of methane is one of the most important reactions in relation to the chemical utilization of natural gas. Although many studies [1–8] have been made using N_2O or O_2 as oxidants, there exist some problems such as an expensive oxidant, low yield of formaldehyde and so on. Previously in the kinetic study [9] for oxidative coupling of methane over fine particles of lanthanum boron oxide, we could explain experimental results on the basis of the reaction mechanism including reaction intermediates as formaldehyde. Moreover we revealed that these reactions occurred on the catalyst surface, and derived a following theoretical equation,

$$\frac{\mathrm{C2}}{\mathrm{CO_2}} \approx \frac{k_2^{0.5} \cdot k_3^{0.5} \cdot K_1^{0.5}}{k_6} \frac{P_\mathrm{M}^{0.5}}{P_\mathrm{O}^{0.75}}$$

where P_M and P_O are the pressures of methane and oxygen, respectively, k_2, k_3 and k_6 the rate constants of the formation of methyl radicals, the formation of ethane by coupling of methyl radicals and the formation of CH_3OO radicals by the oxidation of methyl radicals, respectively, and K_1 the equilibrium constant of adsorbed oxygen species. This expresses that the formation of CO_x via formaldehyde increases with decreasing methane/oxygen ratio, and also suggests the possibility that we can detect formaldehyde under suitable conditions (much milder conditions than that in the above study).

In the present study, we carried out the reaction over fine particles of various amorphous oxides at lower methane/oxygen ratios. We have discussed the above possibility and the contribution of each catalyst component to the elementary reaction of the proposed mechanism.

2. Experimental

The raw materials are shown as follows; $La(NO_3)_3 \cdot 6H_2O$ (Soekawa), H_3BO_3 (Wako), $Al(NO_3)_3 \cdot 9H_2O$ (Wako), $Ga(NO_3)_3 \cdot nH_2O$ (Soekawa), $In(NO_3)_3 \cdot 3H_2O$ (Soekawa), $Tl(NO_3)_3 \cdot 3H_2O$ (Aldrich), and $Y(NO_3)_3 \cdot 6H_2O$ (Soekawa). Powdered lanthanum oxide containing a 3B element was prepared by the mist decomposition method [10] with a mixed nitrate solution (5 wt%) of lanthanum and the 3B element. Powdered yttrium aluminum oxide was also prepared from a mixed nitrate solution (5 wt%) of yttrium and aluminum in the same way. The details of the preparation conditions are described elsewhere [12]. These powders had a rare earth element-to-a 3B element atomic ratio of 9.0. These were spherical and had average diameters less than 800 nm. The XRD measurements also revealed that their structures were almost amorphous. The powder was dried at 110 ° C overnight, pressed into tablets, crushed, sized (60–80 mesh) and used as a catalyst. These BET surface areas were 5–9 m^2/g after the pretreatment at 710 ° C for 16 h in a stream of dry air, and indicated the constant values before and after the reaction.

The activity was measured by an atmospheric flow method [10] with and without the catalysts. The reactants were methane and oxygen, and nitrogen was used as diluent. A special quartz reactor [11] was used in the present study. Methane and oxygen-nitrogen mixture were preheated separately in a two-fluid nozzle and mixed rapidly just before the catalyst bed in the reactor. The exit gas was rapidly cooled by an air cooler, and special care was taken to remove the homogeneous gas phase reaction before and after the catalyst bed. The catalyst (10 mg) was diluted 7-fold by weight (total mass: 70 mg) with quartz powder (60–80 mesh) and pretreated in a stream of purified air at 710 ° C for 16 h. The reactions were carried out in a temperature range between 400 and 680 ° C. The products were analysed by gas chromatography [9].

3. Results and discussion

The following mechanism was proposed on the basis of a kinetic study for oxidative coupling of methane over lanthanum boron oxide [9].

$$\begin{array}{llll}
\frac{1}{2}O_2 & \rightleftharpoons K_1 & O(ad) & (1) \\
CH_4 + O(ad) & \rightarrow k_2 & CH_3(ad) + OH(ad) & (2) \\
2CH_3(ad) & \rightarrow k_3 & C\text{-}C & (3) \\
CH_3(ad) & \rightarrow k_4 & CH_3(g) & (4) \\
2OH(ad) & \rightarrow k_5 & H_2O + O(ad) & (5) \\
CH_3(ad) + O_2 & \rightarrow k_6 & CH_3OO(ad) & (6) \\
CH_4 + CH_3OO(ad) & \rightarrow k_7 & CH_3(ad) + CH_3OOH(ad) & (7) \\
CH_3OOH(ad) & \rightarrow k_8 & HCHO(ad) + H_2O & (8) \\
HCHO(ad) & \rightarrow k_9 & CO + H_2 & (9) \\
HCHO(ad) + O(ad) & \rightarrow k_{10} & CO_2 + H_2. & (10)
\end{array}$$

The formaldehyde intermediate is formed in reactions (6)–(8) and is decomposed to CO_x and hydrogen in reactions (9) and (10). It was difficult to detect formaldehyde under the conditions used when we obtained the above mechanism. Thus to obtain formaldehyde we need to carry out the study under much milder conditions (lower temperatures and 400–680 °C and lower methane/oxygen ratios of 1). Significant homogeneous gas phase reactions, however, are expected to occur under these conditions, because the gas phase reaction increases with increasing oxygen pressure at a temperature range between 500 and 680 °C, and this makes it hard to investigate the action of the catalyst. The influence of various parameters on this reaction were studied and the effect of SV and D (dilution ratio defined as pressures of reactants divided by total pressure) on homogeneous gas phase reaction indicated that no reaction occurred in the region of high SV (> 125 min^{-1}) and low D (< 0.27). Thus this reaction was studied under the conditions ($SV = 125$ min^{-1}, $CH_4/O_2 = 1$ and $D = 0.13$).

Fig. 1 shows the dependence of the formation rates of products (per unit surface area of the catalyst) on reaction temperature over lanthanum aluminum

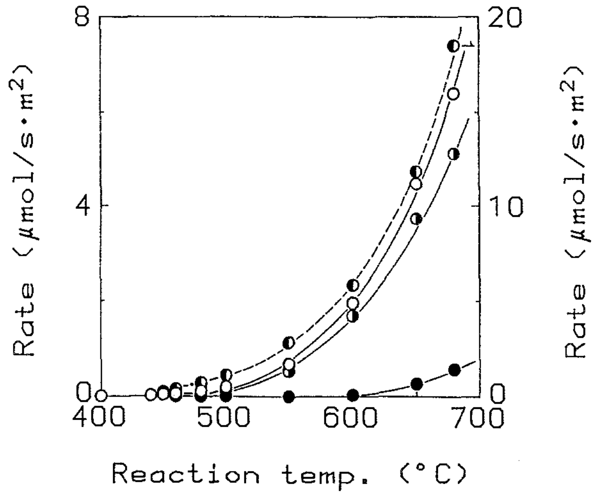

Fig. 1. The dependence of the formation rates on reaction temperature over lanthanum aluminum oxide. $W/F = 4$ g·s/l, $CH_4/O_2 = 1$, $D = 0.13$, ○: CO_x, ●: C2, ◑: H_2, ◐: H_2O.

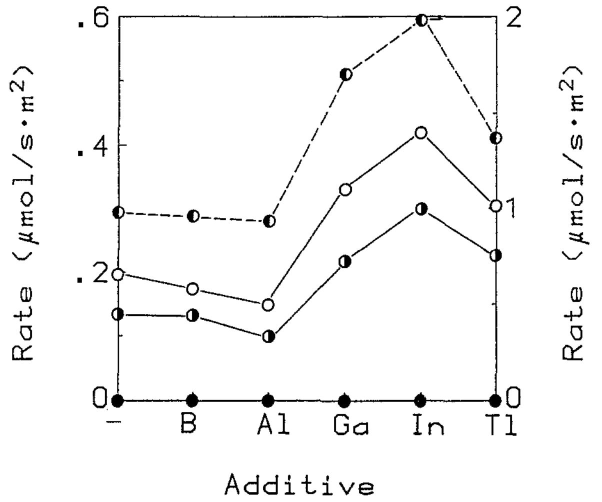

Fig. 2. The dependence of the formation rates on the added 3B element in amorphous lanthanum oxides at 500 °C. –: without additive, $W/F = 4$ g·s/l, $CH_4/O_2 = 1$, $D = 0.13$, ○: CO_x, ●: C2, ◑: H_2, ◐: H_2O.

oxide. The temperature of initial formation for CO_x, hydrogen and water (440 °C) is different from that for C2 hydrocarbon (600 °C). All rates increase with increasing reaction temperature. This tendency is similar to that observed over lanthanum oxides including other 3B elements. No formaldehyde, however, was detected in any of the catalysts. The quantitative correspondence between the formation of CO_x and hydrogen, and the agreement between the temperatures of initial formation for CO_x and hydrogen suggest that formaldehyde was really formed and immediately decomposed to CO_x and hydrogen. The possibility that CO_2, CO and hydrogen are simultaneously formed via water-gas shift reaction (WGS) was completely denied by the following fact: the reaction between methane and water over lanthanum aluminum oxide resulted in no formation of CO_x and hydrogen at a temperature less than 710 °C. This supports the validity of the above mechanism and also indicates that the decomposition rate of formaldehyde is greatly more rapid than that of formaldehyde desorption. The results were almost the same on all lanthanum oxides containing the 3B element, and also suggest that the same reaction scheme can be applied in these catalysts.

Fig. 2 shows the dependence of the formation rates of products on the added 3B element in amorphous lanthanum oxides at 500 °C. Under this condition, no C2 hydrocarbon was detected. The ratio of the formation rates of CO_x, hydrogen and water on each catalyst, $CO_x/H_2/H_2O$, is almost the same despite the difference of the added 3B element. This suggests that the ratios of the rate constants for CO_x, hydrogen and water formation are all the same over these catalysts.

The activity of the most active lanthanum indium oxide was about 2.1 times higher than that of the least active lanthanum aluminum oxide, but these

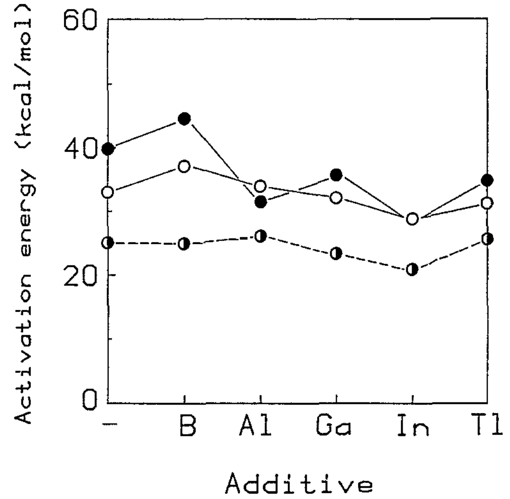

Fig. 3. The dependence of the apparent activation energies on the added 3B element in amorphous lanthanum oxides. –: without additive, $W/F = 4$ g · s/l, $CH_4/O_2 = 1$, $D = 0.13$, ●: CO_x, ○: H_2, ◑:H_2O.

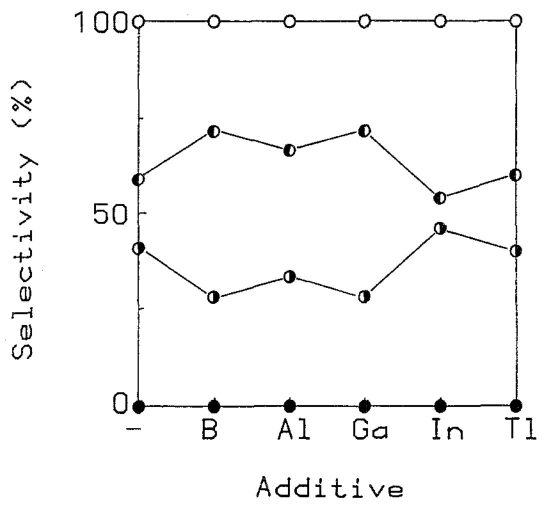

Fig. 4. The dependence of the selectivities on the added 3B element in amorphous lanthanum oxides at 500 ° C. –: without additive, $W/F = 4$ g · s/l, $CH_4/O_2 = 1$, $D = 0.13$, ○: CO_x, ●: C2, ◑: CO, ◐: CO_2.

differences decreased with increasing reaction temperature. As the result of investigation of apparent activation energy for CO_x and hydrogen, lanthanum boron oxide indicated the highest value (37.1 and 44.6 kcal/mol) while lanthanum indium oxide the lowest value (28.8 and 28.7 kcal/mol) as shown in fig. 3. Hence, we think that these differences of apparent activation energies follow a trend similar to that shown in fig. 2. In the study with a $LaAlO_3$ catalyst [12], the more strongly adsorbed oxygen species were reported to be effective for the formation of C2 hydrocarbons, while gas phase or weakly adsorbed oxygen species were effective for the formation of CO_x. The dissociation energy of the 3B element-oxygen bond decreased with increasing atomic number of the 3B element [13]. These facts suggest that the formation of CO_x increases with increasing atomic number. The dissociation energy may cause the difference of activation energy.

Fig. 3 represents that the apparent activation energy for CO_x agrees with that for hydrogen within 7 kcal/mol on each catalyst. This suggests that CO_x and hydrogen are formed via the same reaction. On the contrary, the activation energy for water (ca. 24 kcal/mol) is different from the above values. The fact shows that water is formed via the different reaction from CO_x and hydrogen, and this also supports the previously proposed reaction mechanism.

Fig. 4 shows the dependence of the selectivities of products on the added 3B elements at 500 ° C. At this temperature, CO of 28.1% and CO_2 of 71.9% in B changed to CO of 40.0% and CO_2 of 59.9% in Tl. Both selectivities of CO and CO_2, however, seem to depend only a little on the atomic number of 3B element,

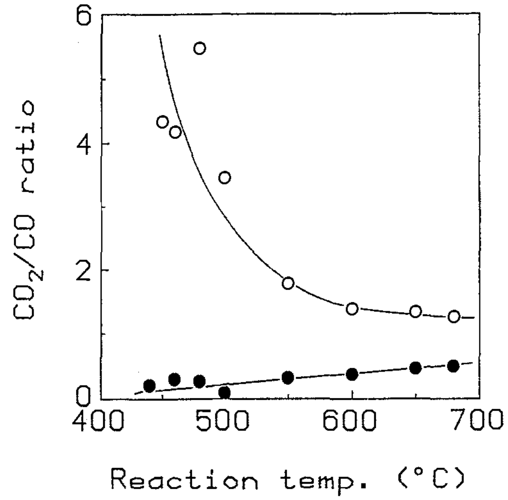

Fig. 5. The dependence of the CO_2-to-CO ratio on reaction temperature. $W/F = 4$ g·s/l, $CH_4/O_2 = 1$, $D = 0.13$, ○: lanthanum aluminum oxide, ●: yttrium aluminum oxide.

because this tendency in the formation of CO_x decreased with increasing reaction temperature (CO of 36.3% and CO_2 of 54.3% in B changed to CO of 39.7% and CO_2 of 50.8% in Tl at 650 °C). This fact reveals that the added 3B elements have no influence on the CO_2/CO ratio in lanthanum oxides.

The above results reveal that the ratio of k_9 to k_{10} (k_9, k_{10}: rate constants of CO and CO_2 formation, respectively) is almost constant despite changing the added 3B elements, while the C2 hydrocarbon-to-CO_x ratio (this ratio increases with increasing atomic number of the added 3B element [14]) and the activity per unit surface area changes with the added 3B elements. These facts suggest that the rate constants of methyl radical formation, k_2, and methyl radical consumption, k_3 and k_6, are much influenced by the added 3B elements.

In the reaction over fine particles of amorphous yttrium aluminum oxide, which was prepared in the same way from lanthanum oxides including 3B element, products were similar to those obtained over the lanthanum oxides but the formation ratios of some products, especially CO_2/CO ratio, changed. At low temperatures, CO_2/CO ratio is much greater than 1 in lanthanum aluminum oxide while in yttrium aluminum oxide this ratio is smaller than 1 as shown in fig. 5. Apparently two tendencies have quite different forms with respect to the decomposition of formaldehyde.

This result reveals that the kind of rare earth element has much influence on the reactions (9) and (10) of formaldehyde decomposition. We believe that by using suitable rare earth elements an excellent catalyst can be obtained, over which no decomposition of formaldehyde occurs.

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