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, CO₂, 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 N₂O or O₂ 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,

\[ \frac{C_2}{CO_2} \approx \frac{k_2^{0.5} \cdot k_3^{0.5} \cdot K_1^{0.5} \cdot P_M^{0.5}}{k_6 \cdot P_O^{0.75}} \]

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 \( \text{CH}_3\text{OO} \) radicals by the oxidation of methyl radicals, respectively, and \( K_1 \) the equilibrium constant of adsorbed oxygen species. This expresses that the formation of \( \text{CO}_x \) via formalde-
hyde 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(NO₃)₃·6H₂O (Soekawa), H₃BO₃ (Wako), Al(NO₃)₃·9H₂O (Wako), Ga(NO₃)₃·nH₂O (Soekawa), In(NO₃)₃·3H₂O (Soekawa), Ti(NO₃)₃·3H₂O (Aldrich), and Y(NO₃)₃·6H₂O (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 m²/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].