Catalytic properties of supported cobalt catalysts for steam reforming of ethanol

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Steam reforming of ethanol, $C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$, was carried out over Co/Al_2O_3, Co/SiO_2, Co/MgO, Co/ZrO_2 and Co/C. The properties of the Co catalysts were greatly affected by the supports. Co/Al_2O_3 exhibited the highest selectivity for steam reforming of ethanol by suppression of methanation of CO and decomposition of ethanol.

Keywords: steam reforming of ethanol, Co/Al_2O_3, supported cobalt catalysts

1. Introduction

At present, there is an increasing world-wide interest in renewable energies, bioenergy in particular, arising from the concern for the environment and also from needs for sustainable development [1]. The bioenergy may be realized either by burning biomass directly or upgrading it into useful and more valuable materials, such as fuel gas, fuel oil and materials for chemical industries. Fuel ethanol is currently manufactured from sugar cane in Brazil and from corn and other starch-rich grains in the United States by biochemical conversion. In this case, ethanol is obtained as an aqueous solution of concentration less than 15%. If it is possible to manufacture some valuable materials from the solution without distillation, the advantage of the process utilizing biomass would become much higher.

One of such processes is the manufacture of hydrogen by steam reforming of ethanol or the manufacture of acetone from ethanol and water. Ethanol forms acetone and carbon dioxide on some metallic oxide catalysts which have both acidic and basic sites in the presence of water vapor [2–4]. On the other hand, the steam reforming of ethanol proceeds on transition metal catalysts, especially on cobalt catalyst [5,6]. In the present study, we will report that the catalytic properties of the cobalt catalyst are controlled by the support.

2. Experimental

The catalyst supports (32–42 mesh) used were Al_2O_3 (Catalysis Society of Japan, JRC-ALO-1), SiO_2 (Catalysis Society of Japan, JRC-SIO-5), ZrO_2 (Catalysis Society of Japan, JRC-ZRO-1), MgO (Catalysis Society of Japan, JRC-MGO-3), and Activated Carbon (Wako Pure Chemicals Ltd., extra pure grade). Co/Al_2O_3, Co/SiO_2, Co/ZrO_2, and Co/C were prepared by impregnation of an aqueous solution of cobalt(II) nitrate (Wako Pure Chemicals Ltd., extra pure grade). Co/MgO was prepared by impregnation of an ethanol solution of cobalt(II) nitrate. Co loading was adjusted to 7.4 wt% for all these supports. The resulting precursors were dried at 383 K for 3 h and subsequently calcined in air at 773 K for 3 h except for Co/C. The calcined ones were reduced by hydrogen at 773 K for 3 h prior to reaction experiments.

Reactions were carried out at atmospheric pressure by use of a conventional flow reactor. A helium stream of 40 ml min^{-1} was passed through a bubbler containing aqueous ethanol solution kept at 313 K, and then the stream was fed into the reactor stuffed with 0.3 g of catalyst. The partial pressures of ethanol and water were 1.7 and 7.2 kPa, respectively. Experiments of steady-state reaction were carried out at the lowest temperature where the ethanol conversion reached 100%. The same reactor was used in temperature-programmed reaction (TPR) experiments, where the catalyst temperature was raised at a rate of 2 K min^{-1}. Reactants and products were analyzed by using a Shimadzu gas chromatograph GC-8AIT. The separation column used was a 2 m glass column packed with PEG6000/Shimalite TPA or activated charcoal, and both packings were supplied by Shimadzu Manufacturing Co. Hydrogen yields were calculated on the basis of reaction stoichiometries for by-products.

3. Results and discussion

Product compositions and ratios [COx]/[C-products] obtained in the steady-state conversion of ethanol ($W/F = 0.45$ (g s)/cm^3), mean crystallite size and surface area on Co/Al_2O_3, Co/SiO_2, Co/ZrO_2, and Co/C are given in table 1. Formation of carbon dioxide, carbon monoxide, methane, and hydrogen was observed. It

Table 1
Steam reforming of ethanol over various Co catalysts [a]

Catalyst [b]	Product composition (%)				$[CO + CO_2]/[C\text{-products}]$ molar ratio (%)	Mean crystallite [c] size (nm)	Surface area [d] (m^2/g)
	CO_2	CO	CH_4	H_2			
Co/Al_2O_3	19	7.9	6.0	67	81	13	130
Co/ZrO_2	23	3.1	8.9	65	74	27	13
Co/MgO	23	2.5	9.2	65	74	10	18
Co/SiO_2	24	2.0	11	63	69	16	159
Co/C	23	2.4	16	58	61	4	659
Co/C [e]	4.3	28	23	45	58	4	659

[a] Reaction temperature 673 K, W/F 0.45 (g s)/cm^3.
[b] Co loading 7.4 wt%.
[c] Calculated from the half-maximum width of the peak using XRD.
[d] BET surface area is measured by N_2 adsorption.
[e] Reaction temperature 613 K.

is clear that the product composition varies with the support materials of the catalysts. The formation of hydrogen decreased in the order: $Co/Al_2O_3 > Co/ZrO_2 > Co/MgO > Co/SiO_2 > Co/C$. Values of the ratio [COx]/[C-products] indicated that the selectivity for the steam reforming of ethanol decreased in the same order. The difference in selectivity was not related to the mean crystallite size and surface area. These facts suggest that not Co dispersion, but the properties of the support surface are the decisive influencing factors regarding the selectivity for steam reforming. An important side reaction was the methane-forming reaction. Morita et al. [7] and Luengo et al. [8] reported that methane was formed on nickel and platinum catalysts solely by decomposition of ethanol, $C_2H_5OH \rightarrow CH_4 + CO + H_2$. In general, transition-metal catalysts are known to be active for the CO hydrogenation (methanation), $CO + 3H_2 \rightarrow CH_4 + H_2O$. Therefore, a part of methane observed here is thought to be formed by the hydrogenation of CO which was generated by the steam reforming of ethanol.

In figure 1 are the effects of carbon monoxide added to the reactant mixture, i.e., the mixture of ethanol and water vapors. On addition of carbon monoxide, the outlet partial pressures of carbon dioxide and methane were increased. When the addition of carbon monoxide was stopped, the outlet gas compositions reverted to their own original values. These results suggest that the water–gas shift reaction and methanation are involved in the conversion of ethanol on Co/SiO_2. The contact time dependence of the selectivity of the products is shown in figure 2 . As the contact time decreased, the formation of carbon monoxide increased and those of carbon dioxide and methane decreased. This fact suggests that a part of carbon dioxide and methane were produced via carbon monoxide by the water–gas shift reaction and methanation on Co/SiO_2, respectively. Similar results were obtained on Co/MgO and Co/ZrO_2, suggesting that the same reactions proceed on these catalysts.

Figures 3 and 4 show the results of the same experiments as shown in figures 1 and 2 carried out on Co/

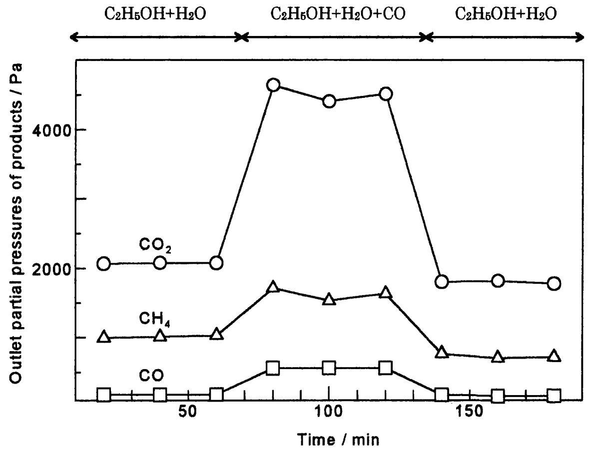

Figure 1. Effect of carbon monoxide upon steam reforming of ethanol over Co/SiO_2. Experiment was carried out at 673 K. Co loading 7.4 wt%.

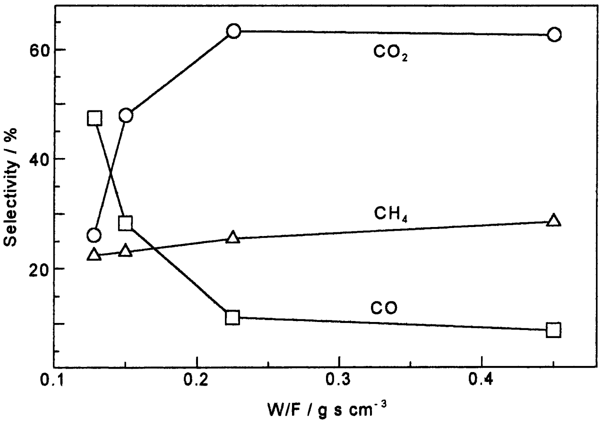

Figure 2. Selectivity of products over Co/SiO_2 versus W/F. Experiment was carried out at 673 K. Co loading 7.4 wt%.

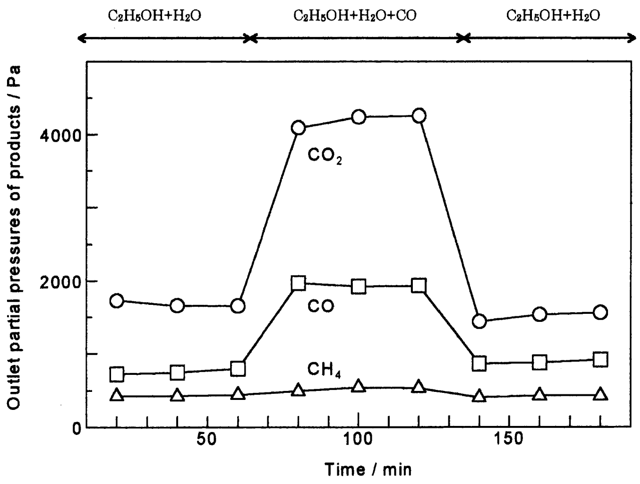

Figure 3. Effect of carbon monoxide upon steam reforming of ethanol over Co/Al_2O_3. Experiment was carried out at 673 K. Co loading 7.4 wt%.

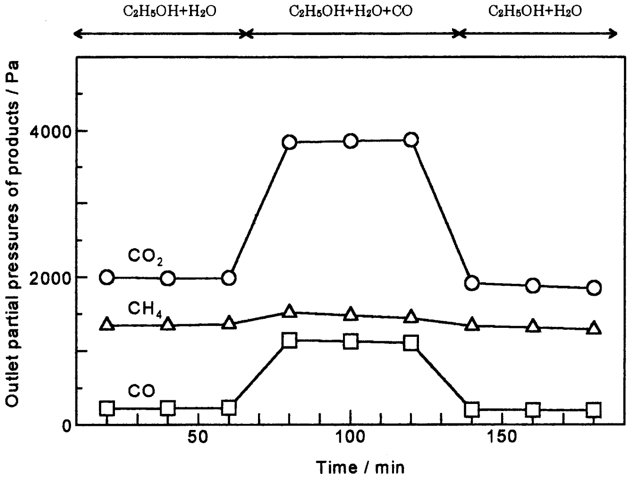

Figure 5. Effect of carbon monoxide upon steam reforming of ethanol over Co/C. Experiment was carried out at 673 K. Co loading 7.4 wt%.

Al_2O_3, respectively. When carbon monoxide was fed together with the mixture of ethanol and water vapor, the outlet partial pressure of carbon dioxide increased, but that of methane scarcely increased. As the contact time decreased, the formation of carbon monoxide increased and that of carbon dioxide decreased, but the selectivity of methane scarcely changed. These results suggest that the water–gas shift reaction is involved in the conversion but the methanation hardly proceeds on Co/Al_2O_3.

Figures 5 and 6 show effects of the addition of carbon monoxide and the contact time upon the conversion of ethanol on Co/C. The catalyst exhibited the highest selectivity of methane, however, the outlet partial pressure of methane hardly increased on addition of carbon monoxide. As the contact time decreased, the formation of methane remained constant and that of carbon monoxide and carbon dioxide did not change very much by reason of large surface area. These facts suggest that methane formation on Co/C occurs by decomposition of ethanol, not by methanation.

For the purpose of thermodynamic analyses of the steam reforming and the decomposition of ethanol, standard free energy changes were calculated using the standard Gibbs free energies and enthalpies of formation [9] and isobaric heat capacities of the components [10,11]. Figure 7 illustrates the relationship between the temperature and the standard free energy changes of the reactions. At 500 K, the steam reforming of ethanol hardly occurs by reason of $\Delta G^o > 0$. On the other hand, the decomposition of ethanol is easy to occur at the same temperature because the value of ΔG^o is sufficiently negative. Methane reforming hardly occurs below 800 K by reason of $\Delta G^o > 0$. These results suggest that the steam reforming occurred directly without going through methane formation.

Figures 8A and 8B show temperature dependences of the reactions disclosed by the temperature-pro-

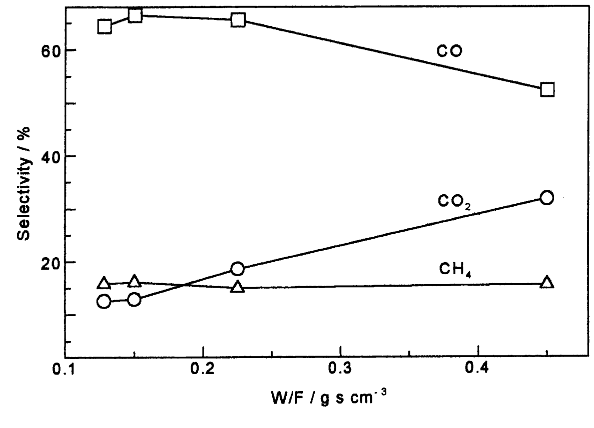

Figure 4. Selectivity of products over Co/Al_2O_3 versus W/F. Experiment was carried out at 673 K. Co loading 7.4 wt%.

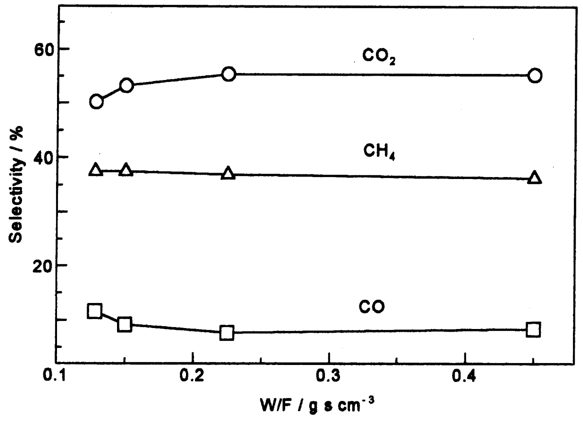

Figure 6. Selectivity of products over Co/C versus W/F. Experiment was carried out at 673 K. Co loading 7.4 wt%.

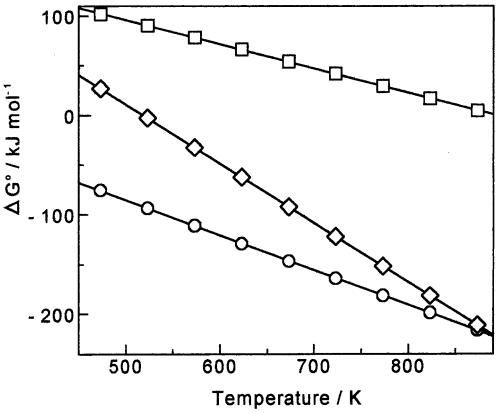

Figure 7. Gibbs free energy versus temperature. (◇) $C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$; (○) $C_2H_5OH \rightarrow CH_4 + CO + H_2$; (□) $CH_4 + H_2O \rightarrow CO + 3H_2$.

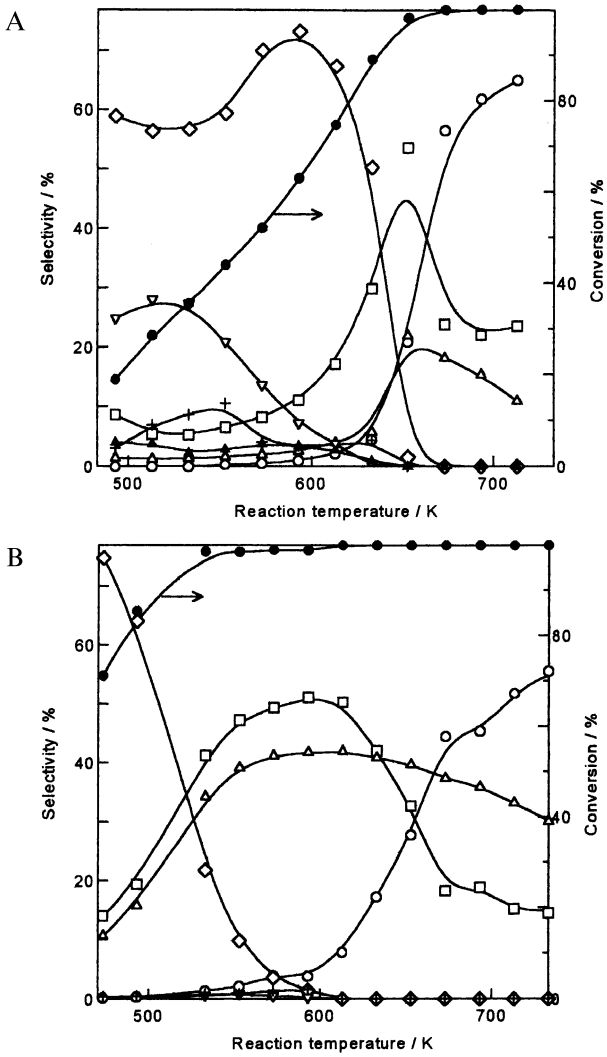

Figure 8. Selectivity of products and conversion of ethanol on (A) Co/Al_2O_3 and (B) Co/C versus reaction temperature. (○) CO_2, (□) CO, (△) CH_4, (▲) CH_3OH, (+) CH_2CH_2, (◇) CH_3CHO, (▽) $C_2H_5OC_2H_5$, (●) conversion.

grammed reactions on Co/Al_2O_3 and Co/C. The conversions of ethanol and selectivities for products were plotted against reaction temperatures elevated at a rate of 2 K min^{-1}. The conversion of ethanol ascended monotonously with elevation of the temperature, and was 20% at 500 K on Co/Al_2O_3 (A). However, the conversion reached 90% over Co/C (B) at the same temperature. Methane and carbon monoxide were produced in nearly 1 to 1 ratio on Co/C. From the results, it was concluded that the main reaction occurring on Co/C is the decomposition of ethanol.

Based on these findings, we conclude that the steam reforming of ethanol selectively occurs on Co/Al_2O_3 and Co/SiO_2. On the other hand, the decomposition of ethanol mainly occurs on Co/C. Our recent study using X-ray photoelectron spectroscopy (XPS) revealed that the degree of reduction increased with following order: $Co/Al_2O_3 < Co/SiO_2 \ll Co/C$ [12]. This suggests that the decomposition of ethanol mainly occurs on cobalt metal.

4. Conclusion

The conversion of ethanol on Co is greatly influenced by the support. The steam reforming of ethanol on Co/SiO_2, Co/MgO, and Co/ZrO_2 was accompanied by the methanation. Methane was mainly produced by the decomposition of ethanol on Co/C. Co/Al_2O_3 exhibited high selectivity for the steam reforming of ethanol by reason of restraint of the methanation of carbon monoxide and the decomposition of ethanol.

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