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EFFECTS OF ADDITIVES ON THE SELECTIVITY IN FISCHER-TROPSCH SYNTHESIS BY ALUMINA-SUPPORTED RUTHENIUM CATALYSTS

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Addition of K and P to Ru/Al_2O_3 changed the selectivity of Fischer-Tropsch synthesis by affecting mainly the electronic state of Ru; the K increased olefin/paraffin ratio and decreased the methane formation, and the effect of P was opposite. In contrast, the addition of V suppressed the methane formation with only a slight decrease in the olefin/paraffin ratio. These changes were not due to the electronic effect.

Alkali metals have widely been used as promotors to improve the activity and selectivity in the CO hydrogenation.[1-3] In Fischer-Tropsch synthesis, the addition of K to Fe and Ru catalysts enhances the olefin/paraffin ratios in the hydrocarbons produced.[4-7] Besides alkali metals, V and Mn are important components in composite catalysts which yield lower olefins selectively.[8] In addition, V_2O_3 is reported to be an effective support for Ru for the formation of lower olefins.[9] In this communication, we report that there are distinct differences among the effects of these additives.

The first series of catalysts was prepared by impregnation of $Ru_3(CO)_{12}$ onto γ-Al_2O_3 (Reference Catalyst of Catalysis Society of Japan, ALO-4) which had been impregnated with an aqueous solution of K_2CO_3 or P_2O_5, and calcined at 500 °C for 10 h.[5,10] These catalysts contained, in addition to 2.5% Ru, 1.0% K or 0.9% P by weight (1:1 in atom), and are denoted as $Ru/K\text{-}Al_2O_3$(A) or $Ru/P\text{-}Al_2O_3$(A). The second series was prepared by impregnating an aqueous solution of $RuCl_3$ or a mixture of $RuCl_3$ and VCl_3 onto Al_2O_3. These catalysts contained 1.6% Ru, and 4% V by weight (1:5 in atom). These are denoted as, for example, $Ru\text{-}V/Al_2O_3$(B). The hydrogenation of CO was carried out in a continuous flow reactor at 260 °C under atmospheric pressure of a 1:2 mixture of CO and H_2. C_1-C_{12} hydrocarbons produced were analyzed by gas chromatography.

Figure 1 summarizes the effects of these additives on the CO hydrogenation over these catalysts. The addition of P enhanced the activity, while K or V decreased it to 1/3 or 1/5. As for selectivity, the addition of K increased the selectivity of C_2-C_4 olefins from 19% (obtained over Ru/Al_2O_3(A)) to 35% in weight and decreased methane, and the effect of P was opposite to K. On the other hand, in the case of the addition of V, the fraction of methane became lower, while the olefin-selectivity remained almost unchanged.[11] Under the reaction conditions, the hydrogenolysis of primary products to methane was negligible, since the distributions of carbon number in the products little changed at least up to 30%-conversion over these catalysts.

Catalyst	H/Ru[a)]	Rate[b)]	Conv./%
Ru/K-Al_2O_3(A)	0.69	2.5	5.3
Ru/Al_2O_3(A)	0.80	6.0	7.3
Ru/P-Al_2O_3(A)	0.61	7.1	7.7
Ru/Al_2O_3(B)	0.20	6.1	5.0
Ru-V/Al_2O_3(B)	0.10	1.3	5.9

a) Based on H_2 adsorption at 25 °C.
b) 10^{-3} mol(CO)·g^{-1} h^{-1}.

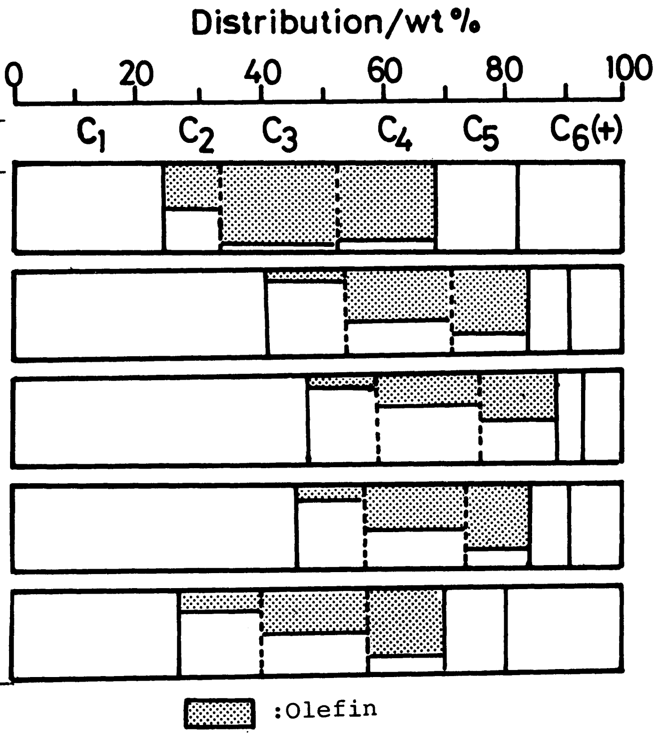

Fig. 1. Hydrogenation of CO over various Ruthenium catalysts.
The reaction was carried out at 260 °C under 1 atm (H_2/CO = 2).

Figure 2 shows the changes of propene/propane ratio in the products as a function of the conversion. Over Ru/K-Al_2O_3(A) which showed a high olefin/paraffin ratio, the ratio retained the high value at high conversions, while the ratio decreased greatly over Ru/P-Al_2O_3(A). The addition of V also decreased the ratio, but the effect was not significant. The changes in the olefin/paraffin ratio caused by the additives are mainly due to differences in contribution of the secondary hydrogenation of olefins formed primarily as described below.

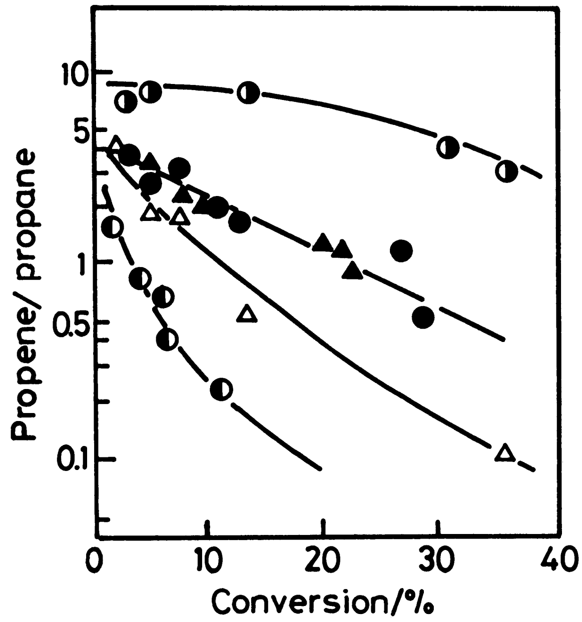

Fig. 2. Propene/propane ratio vs. conversion.

○: Ru/Al_2O_3(A)

◑: $Ru/K-Al_2O_3$(A)

◐: $Ru/P-Al_2O_3$(A)

▲: Ru/Al_2O_3(B)

△: $Ru-V/Al_2O_3$(B)

The reaction was carried out at 260 °C under 1 atm (H_2/CO = 2).

To elucidate these effects, infrared spectra of CO adsorbed on these catalysts were measured. The C-O stretching band near 2036 cm^{-1} observed over Ru/Al_2O_3(A) shifted to lower frequency by 40 cm^{-1} upon the addition of K, and to higher frequency by 16 cm^{-1} upon the addition of P. This indicates that K (probably K_2O) increases electron density of Ru, resulting in an increase in the strength of carbon-metal bond by back donation, and the effect of P (probably P_2O_5) is opposite to K. In contrast, the bands at 2017 and 2087 cm^{-1} observed on Ru/Al_2O_3(B) shifted only slightly (less than 8 cm^{-1}) to higher frequencies by the addition of V, showing that V little affected the electronic state of Ru.[11) Little shift in ir band of CO on Ru/Al_2O_3 upon the addition of V was recently observed also by Mori et al.[12) Thermal desorption of CO showed that the strength of CO adsorption changed by the additives as expected from ir band shift. For example, after evacuation at 200 °C, the amounts of CO remaining on the Ru relative to that after evacuation at 25 °C were 0.2, 0.08,and 0.0 for $Ru/K-Al_2O_3$(A), Ru/Al_2O_3(A),and $Ru/P-Al_2O_3$(A), respectively.

Increase in the strength of CO adsorption will increase the surface coverage of CO adsorbed and therefore lower the ability of the Ru surface to dissociate H_2

and to adsorb olefins from gas phase. This effect explains the high olefin/paraffin ratio and the decrease in activity observed for Ru/K-Al_2O_3(A). Similarly, the effect of P may be explained by the lower CO coverage brought about by the weakening of CO adsorption. Thus the effects of K and P are mainly attributed to the change in the strength of CO chemisorption through electronic effect. On the other hand, the selectivity change caused by V is not the electronic effect, since little change in CO adsorption and olefin/paraffin ratio vs. conversion curve was found. The effect of V is probably due to a geometrical effect like "ensemble effect" which is encountered in catalysis of alloy or bimetallic catalysts.[13,14] It was observed that the turnover frequency of hydrogenolysis of ethane which was carried out at 150 °C in a closed circulation system decreased to 1/50 by the addition of V to Ru/Al_2O_3(B), while that of the CO hydrogenation was lowered only to 1/2.5. This trend observed for Ru-V system is consistent with that reported for Ru-Cu/SiO_2 catalysts.[15,16)]

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