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RATE MEASUREMENT BY PULSE TECHNIQUE FOR INDIVIDUAL STEPS INVOLVED IN CO HYDROGENATION AND ITS APPLICATION TO CATALYST DESIGN

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Fischer-Tropsch synthesis, reaction rate measurement, pulse technique in reaction rate measurement, transition metal catalyst, catalyst design, C–O bond dissociation, liquid fuel, C_2-oxigenate, syngas

By using pulse reaction technique, the rates were measured for the individual steps involved in CO hydrogenation over transition metal catalysts with and without promoters. On all the transition metals other than Rh, the rate constant for the dissociation of C–O bond (k_1) was much smaller than that for the hydrogenation of surface carbon species (k_2). The oxides of V, Nb, Mo, and W added to Ru/Al_2O_3 increased k_1 and decreased k_3. The Rh catalyst was unique in the sense that there was not much difference between k_1 and k_2. The characteristic feature observed was found to be useful in designing a catalyst for the production of liquid fuel or C_2-oxygenates from syngas.

1. Introduction

The hydrogenation of CO or the Fischer-Tropsch synthesis is composed of several steps involving the adsorption of H_2 and CO, the dissociation of C–O bond to form surface carbon species $[(CH_x)_{ad}]$, and their polymerization and hydrogenation to hydrocarbons with various numbers of carbon atoms [1–6]. The insertion of CO into metal-carbon bond in $(CH_x)_{ad}$ is also a requisite step for the production of C_2-oxygenates. Since the hydrogenation of CO is a complicated reaction, it would be desirable to control the activity and selectivity on the basis of the rates determined for these individual steps.

With pulse reaction technique, we have determined the rate constants for C–O bond dissociation and for the hydrogeneration of $(CH_x)_{ad}$ to CH_4 (k_1 and k_2, respectively) by measuring both dynamics of adsorbed CO and produced CH_4 [7–13]. In this paper, we will report the characteristic feature in k_1 and k_2 and its application to catalyst design.

2. Experimental

The reaction apparatus had two kinds of detectors: an emissionless infrared diffuse reflectance spectrometer (EDR) and a flame ionization detector (FID). The EDR cell was used as a pulse microreactor. When a small amount of CO was pulsed in the H_2 carrier gas, it was adsorbed on the catalyst and reacted to produce CH_4 selectively. The analyses of dynamic behaviors of adsorbed CO and produced CH_4 measured respectively with EDR and FID allowed us to determine k_1 and k_2 [7–13].

3. Results and discussion

CHARACTERISTIC FEATURE IN THE RATE CONSTANTS

Fig. 1 shows the rate constants, k_1 and k_2, determined for supported transition metal catalysts. For the metal other than Rh, k_1 was much smaller than k_2, suggesting that C–O bond dissociation is the rate-determining step. Compared to this, Rh was unique in the sense that there is not much difference between k_1 and k_2, although these two rate constants varied widely depending both on the catalyst support and on the metal loading.

Fig. 2 shows the effect of additives on k_1 and k_2. The oxides of V, Nb, Mo, and W added to Ru/Al_2O_3 catalyst greatly accelerated C–O bond dissociation accompanying the considerable suppression of the hydrogenation of $(CH_x)_{ad}$. The observed effect of the additive oxides is important in producing liquid fuel, because this condition should provide a high concentration of $(CH_x)_{ad}$ and as a result, its polymerization to higher hydrocarbons may occur favorably.

DESIGN OF CATALYST

For liquid fuel. Since higher hydrocarbons are produced via the polymerization and hydrogenation of $(CH_x)_{ad}$, a high concentration of $(CH_x)_{ad}$ provides a

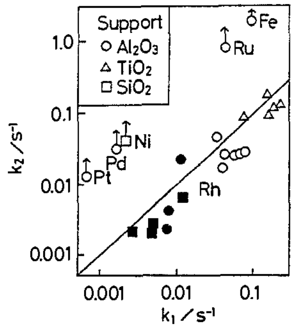

Fig. 1. Rate constants for supported transition metal catalysts. Arrow means k_2 larger than each value indicated. For Rh, metal loading was varied and closed symbols mean that these catalysts produce C_2-oxygenates in the steady-state CO hydrogenation under pressure.

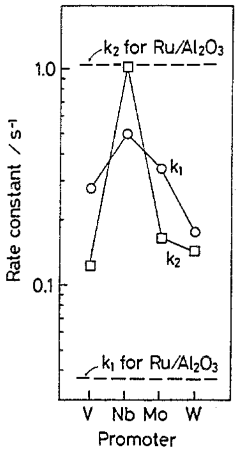

Fig. 2. Effect of additive oxides on the rate constants for Ru/Al_2O_3 catalyst.

favorable condition for the production of higher hydrocarbons. As described above, the oxides of V, Nb, Mo, and W expect us to alter the Ru/Al_2O_3 to an efficient catalyst for producing liquid fuel.

In order to confirm our expectation, steady-state CO hydrogenation was carried out under pressure. Fig. 3 shows turnover frequency and the selectivity of hydrocarbons with the numbers of carbon atoms > 4. The oxides of V, Nb, Mo, and W added considerably increased the turnover frequency. The observed enhancement is very reasonable, because according to the results with pulse reaction, these promoters accelerate the dissociation of C–O bond.

The selectivity of higher hydrocarbons was also increased by adding these promoters. Again, this is very reasonable, because these promoters accelerate the C–O bond dissociation and suppress the hydrogenation of $(CH_x)_{ad}$.

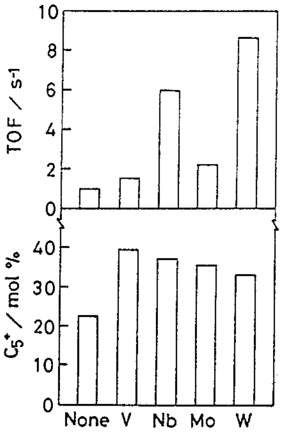

Fig. 3. Turnover frequency (TOF) and the selectivity of C_5^+-hydrocarbon for unpromoted and promoted Ru/Al_2O_3.

For C_2-oxygenates. C_2-oxygenate compounds can also be produced from syngas. It is known that Rh is an efficient catalyst and that the activity and the selectivity vary depending on the catalyst support and the dispersion of Rh metal [2,14,15]. For producing C_2-oxygenates, the CO insertion step is involved and unfortunately, our pulse technique cannot determine the rate constant of this step. However, it is expected that the selectivity of C_2-oxygenates is affected by the rates both of the C–O bond dissociation and of the hydrogenation of $(CH_x)_{ad}$. We can, therefore, discuss qualitatively about the selectivity increase on the basis of k_1 and k_2.

The rates for the polymerization of $(CH_x)_{ad}$ and for the CO insertion (r_3 and r_4, respectively) are approximated by

$$r_3 = k_3[CH_x]^n \tag{1}$$

$$r_4 = k_4[CH_x][CO] \tag{2}$$

where k_3 and k_4 are the rate constants for the respective steps and brackets mean the concentrations of respective adsorbed species. Eq. (2) indicates that large values of $[CH_x]$ and [CO] lead to the selectivity increases. However, high $[CH_x]$ leads to much more favorable condition for higher hydrocarbons, because the exponent n in eq. (1) is probably larger than 1. Therefore, rather small k_1 is preferable. Small k_1 also assures high [CO]. Large k_2, which is a better condition for CH_4 production, is not favorable for C_2-oxygenates. In conclusion, following prediction is possible: small values of k_1 and k_2 are necessary for the selective production of C_2-oxygenates. In fig. 1, it was found that C_2-oxygenates were produced on the catalysts with relatively small k_1 (indicated by closed symbols). This suggests the validity of the criterion described above.

Fig. 4 shows the selectivity of C_2-oxygenates as a function of k_1. In accordance with the prediction, as k_1 decreased, the selectivity increased. The value of k_1 was still decreased by adding K_2CO_3 to Rh/Al_2O_3. As a result, further increase in the selectivity was observed. This indicates again the validity of the prediction.

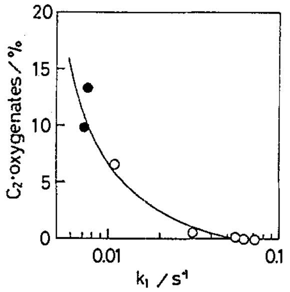

Fig. 4. Selectivity of C_2-oxygenates as a function of k_1 for Rh/Al_2O_3. Closed symbols are for K_2CO_3-added Rh/Al_2O_3.

4. Summary

From pulse reaction, the rate constants for the dissociation of C–O bond and for the hydrogenation of surface carbon species were determined. These two steps were found to be affected by the addition of a promoter or depending on the kind of support and also on the metal loading. The characteristic feature revealed from the rate measurement by pulse technique was found to be useful for catalyst design.

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