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Unique Temperature Dependence of Acetic Acid Formation in CO_2 Hydrogenation on Ag-promoted Rh/SiO_2 Catalyst

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The rate of acetic acid formation in CO_2 hydrogenation on Ag-Rh/SiO_2 catalyst took two maxima at 463 K and 553 K. At 463 K, the rate was much faster than that of C_2-oxygenates formation in CO hydrogenation. It was suggested that, at lower temperature, acetic acid is formed through the direct incorporation of adsorbed CO_2.

The hydrogenation of CO_2 is characterized by much lower activity for C-C bond formation in comparison with CO hydrogenation. Although the latter reaction is known to produce various products depending on the catalysts,1) CO_2 hydrogenation is said to produce exclusively C_1 compound such as methane and methanol.2) Higher hydrocarbons3) and C_2-oxygenates4) were confirmed to be formed on Rh catalysts, but the selectivities were much lower than those in CO hydrogenation. Further, these products are said to be formed via gas phase CO.3,4) The present letter reports unique temperature dependence of acetic acid formation on Ag-Rh/SiO_2 catalyst suggesting the possibility of direct incorporation of adsorbed CO_2 into acetic acid.

Rh/SiO_2 catalyst was prepared by impregnation of SiO_2 (Davison 57) with an aqueous solution of $Rh(NO_3)_3$ followed by drying and reduction at 673 K for 2 h in H_2. Rh content was 5 wt%. Ag-Rh/SiO_2 catalyst was prepared by impregnation of the Rh/SiO_2 with an aqueous solution of $AgNO_3$ followed by the same treatment as above. Ag content was 0.2 in atomic ratio of Ag/Rh. The catalytic run was conducted by using a conventional flow reaction apparatus under the following condition: total pressure was 2.0 MPa, catalyst amount was 0.5 g, total flow rate was 100 ml(STP)/min., and molar ratio of CO_2/H_2 or CO/H_2 was 2.

In CO_2 hydrogenation on Ag-Rh/SiO_2, the major product was CO: its selectivity exceeded 90% in whole temperature range examined. Figure 1 indicates the rates of formations of hydrogenates as a function of reaction temperature. Among the hydrogenated products, acetic acid was the major product below 473 K, but CH_4 became the most abundant above 483 K. The rate of acetic acid formation took two maxima at 463 K and 553 K, respectively. This is in marked contrast with those of the other products which increased monotonously with the reaction temperature. The twin peaks of the rate of acetic acid formation clearly indicate that acetic acid is formed through two reaction pathways. In high temperature pathway, acetic acid seems to be formed via gas phase or adsorbed CO. This is because the temperature range is identical to that where the selectivity of C_2-oxygenates in CO hydrogenation was the highest.

At lower temperature, however, acetic acid does not seem to be formed via CO, because, in this temperature range, only trace amounts of C_2-oxygenates were formed in CO hydrogenation. Table 1 also strongly suggests that acetic acid is formed in CO_2 hydrogenation through a pathway entirely different from that in CO hydrogenation. The addition of Ag suppressed the formation of C_2-oxygenates in CO hydrogenation, while in

Table 1. Hydrogenations of CO and CO_2 on Rh/SiO_2 and $Ag\text{-}Rh/SiO_2$ catalysts at 473 K

Reactant	CO		CO_2	
Ag/Rh	0	0.2	0	0.2
Rate of formation / μmol g^{-1} h^{-1}				
CO	-	-	676	670
Hydrogenates	5.1	3.7	37.4	28.1
C_2-oxygenates	1.3	0.1	9.4	18.7
Distribution of hydrogenates / C%				
CH_3COOH	0.0	0.0	19.0	61.3
CH_3CHO	24.7	3.6	0.9	1.1
C_2H_5OH	0.0	0.0	5.2	4.1
CH_3OH	0.0	0.0	1.2	2.4
$C_{2+}HC$	10.9	22.8	1.5	0.4
CH_4	64.4	73.5	72.2	30.6

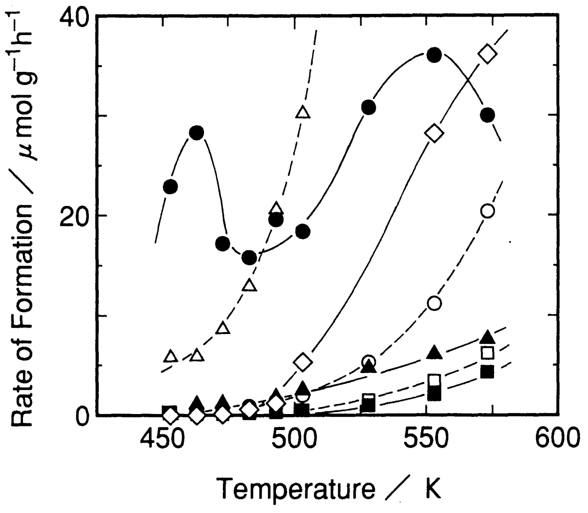

Fig. 1. Rates of hydrogenated products formations on $Ag\text{-}Rh/SiO_2$ catalyst. ●, acetic acid; ■, acetaldehyde; ▲, ethanol; ○, methanol; □, C_{2+} hydrocarbon; △, methane in CO_2 hydrogenation; and ◇, total C_2-oxygenates in CO hydrogenation.

CO_2 hydrogenation, it remarkably promoted the formation of C_2-oxygenates, especially acetic acid.

Another possible pathway to acetic acid from CO_2 is the direct incorporation of CO_2. The reaction of adsorbed CO_2 with methyl group to form acetate was suggested as a possibility,[1] because the reverse reaction, i.e., the decomposition of acetate into methyl group and CO_2, was observed on Rh(110).[5] HREEL and TD study also suggests the formation of acetate from CH_3I and CO_2 on Ni(110).[6] However, acetate formation has not been clearly confirmed, which was attributed to the difficulty of the reaction between adsorbed CO_2 and methyl group because of a short life of adsorbed CO_2.[1] The addition of Ag is said to destroy metal ensemble,[7] and smaller metal ensemble may be expected to be less active for the dissociation or the reduction of adsorbed CO_2 into CO. The lower reaction temperature is also expected to suppress the dissociation/reduction and the desorption of adsorbed CO_2. In the present study, both of these may stabilize adsorbed CO_2, giving more chance for the reaction with methyl group to form acetate which may be hydrogenated to acetic acid.

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