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Reactivity of Surface Carbon Deposited on Supported Rh Catalysts by the Disproportionation of CO

Recent investigations on hydrocarbon synthesis from CO and H_2 over Group VIII metals (*1–7*) have proposed that the surface carbon formed by the dissociation of CO is an intermediate for hydrocarbon formation. It implies that metals which dissociate CO readily (e.g., Ni, CO, and Ru) are good catalysts for hydrocarbon synthesis unless the surface carbon is bound too strongly. There is a certain controversy in the literature on whether CO undergoes dissociation on Rh surfaces under UHV conditions (*8*). In the case of supported Rh, Solymosi and Erdöhelyi (*9*) reported that the dissociation of CO takes place on Rh/Al_2O_3 above 473 K. They also examined the effect of the support on the disproportionation of CO and the reactivity of dissociated surface carbon toward hydrogenation after the desorption of molecularly adsorbed CO with He at 548 K. They found that TiO_2 was the most effective support for the disproportionation of CO and that different kinds of surface carbon were produced by CO dissociation (*10*). The same group also reported previously that a large amount of carboneous species was formed on Rh/TiO_2 in the CO + H_2 reaction and that most of them were very unreactive and could not be hydrogenated even at high temperatures (*11*). In all of these works (*9–11*), the reactivity of surface carbon was investigated after the desorption of molecularly adsorbed CO with He flushing at 548 K. Some aging of surface carbon might occur in the flushing step and direct comparison of the reactivity of adsorbed CO with that of surface carbon could not be performed. Recently, Takeuchi and Katzer (*12*) reported that carbon atoms deposited on Rh/TiO_2 were not readily hydrogenated to form methane, methanol, or ethanol in CO hydrogenation. However, they deposited carbon atoms at relatively higher temperatures (522–573 K), and so the deposited carbon might undergo transformation into less reactive species.

In the present work, we have investigated the reactivity of surface carbon deposited on TiO_2- or SiO_2-supported Rh catalysts in the presence of molecularly adsorbed CO by means of the isotopic tracer technique and have made a direct comparison of the reactivity of adsorbed CO with that of surface carbon. It has been revealed that three forms of carbon produced by the disproportionation of CO.

The catalysts were prepared by impregnating aqueous solutions of metal salts ($RhCl_3$, Na_3RhCl_6, and a mixture of $RhCl_3$ and alkaline chloride) onto TiO_2 (P-25, Nippon Aerosil, anatase ≈90%, 50 m^2/g) and SiO_2 (Aerosil 380, Nippon Aerosil, 380 m^2/g). After impregnation, the catalysts (5 wt% Rh) were dried in air at 383 K for 12 h. These materials were ground into a fine powder, put into a U-shaped glass reactor, which was connected to a closed gas circulation system, and further dried by air circulation ($P \approx 150$ Torr) at room temperature with a liquid nitrogen cold trap for 15 h in order to condense water. The hydrogen reduction was carried out between 473 and 723 K for several hours (P = 400–150 Torr).

The reaction products were analyzed by gas chromatography using molecular sieve 5A and Porapak Q columns. The isotope distribution of products was determined by a quadrupole mass filter (UTI 100c).

Hydrogen gas was purified by passing it through an Engelhard Deoxo unit and a liq-

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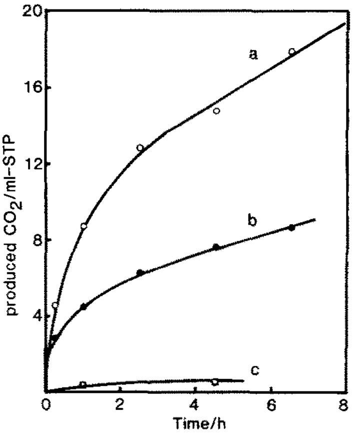

FIG. 1. CO disproportionation over Rh catalysts (5 wt% Rh, 5 g-catalyst, P^0 = 200 Torr); (a) Rh/TiO_2, T = 473 K; (b) $Rh–Na/TiO_2$, T = 473 K; (c) Rh/SiO_2, T = 453 K.

uid nitrogen cold trap. Carbon monoxide was passed through a liquid nitrogen cold trap immediately before use in order to remove water impurity. Isotope-labeled carbon monoxide (^{13}CO, 90% purity; $C^{18}O$, 99%) was purchased from Prochem and used without further purification.

The disproportionation of CO ($2CO \rightarrow C(a) + CO_2$) over various supported Rh catalysts was examined and the results are shown in Fig. 1. The activity of disproportionation was very dependent on the metal precursors and supports (the metal precursors are shown in parentheses). The Rh/TiO_2 ($RhCl_3$) catalyst exhibited the highest activity, and the constant rate of CO_2 formation was observed from 6 h to more than 30 h (the support TiO_2 alone was not active in the disproportionation of CO). The amount of produced CO_2 was much larger than that of adsorbed CO (12 ml-STP/5 g-cat., CO/Rh = 0.24), suggesting that most of dissociated carbon might be deposited on the support. The addition of sodium cation ($Rh–Na/TiO_2$ (Na_3RhCl_6) catalyst) reduced the activity of CO disproportionation as well as that of CO hydrogenation as reported previously (*13*). The Rh/SiO_2 ($RhCl_3$) showed the lowest activity and the isotopic mixing reaction ($^{12}C^{18}O + {}^{13}C^{16}O \rightarrow {}^{12}C^{16}O + {}^{13}C^{18}O$, $P(CO) \approx 40$ Torr) did not proceed at all over this catalyst in the presence of hydrogen ($P(H_2)$ = 14 Torr, T = 423–453 K). The $Rh–Cs/SiO_2$ ($RhCl_3$ + 3CsCl) showed the disproportionation activity to be similar to that of Rh/SiO_2, but the isotopic mixing reaction reached equilibrium within 10 min at 423 K in the absence of hydrogen. In the presence of hydrogen, it took about 6 h to reach equilibrium. When only $C^{18}O$ was introduced onto SiO_2-supported catalysts (T = 423 K), the considerable incorporation of ^{16}O from the support to gaseous CO was observed for alkali halide doped catalysts but not for Rh/SiO_2. These results might suggest that the isotope mixing reaction proceeds by the participation of the support but not through the dissociation of CO.

The reactivity of surface carbon and adsorbed CO was investigated by means of the isotopic tracer method. The experimental procedures and results are shown in Scheme 1. The disproportionation of ^{13}CO (^{13}C 90%) was carried out over Rh/TiO_2 at 473 K for 6.5 h (step I). In this step, 17.9 ml-STP of CO_2 was produced. The catalyst was cooled to room temperature and evacuated for 5 min. A known amount of ^{12}CO was introduced repeatedly in order to replace the molecularly absorbed ^{13}CO (step

Rh/TiO_2
(5 wt% Rh, 5 g-catalyst, CO(a) = 12 ml-STP)

I. ^{13}CO disproportionation at 473 K for 6.5 h
$2{}^{13}CO \rightarrow {}^{13}C(a) + {}^{13}CO_2$
CO_2 = 17.9 ml-STP

II. Replacement of $^{13}CO(a)$ with ^{12}CO
$^{13}CO(a) + {}^{12}CO(g) \rightarrow {}^{12}CO(a) + {}^{13}CO(g)$
$^{12}CO(a)$ = 6 ml-STP

III. Hydrogenation of surface species at r.t.–423 K
$C(a), CO(a) + H_2 \rightarrow CH_4$
$^{13}CH_4$ = 7.0 ml-STP, $^{12}CH_4$ = 6.6 ml-STP

IV. Oxidation of C(a) at 473 K
$C(a) + O_2 \rightarrow CO_2$
CO_2 = 6 ml-STP

SCHEME 1

II). The amount of adsorbed CO after the disproportionation was determined from the amount of ^{13}CO which appeared in the gas phase in step II. After the above-mentioned treatments, 17.9 ml-STP of C(a) (^{13}C 90%) and 6 ml-STP of $^{12}CO(a)$ existed on the catalyst surface. The hydrogenation of surface species was carried out by raising the temperature stepwise from room temperature to 423 K (step III). A decrease in hydrogen pressure was observed at ≈423 K and methane began to appear in the gas phase. The isotopic composition of produced methane was determined as follows: $^{13}CH_4$ = 7.0 ml-STP and $^{12}CH_4$ = 6.6 ml-STP. This result indicates that all of CO(a) and ≈40% of C(a) are hydrogenated to methane at 423 K and that more than half of C(a) is less reactive than molecularly adsorbed CO. It is interesting to note that the surface carbon on Rh catalysts is not as reactive as that on Ru/SiO_2 (*14*). In the case of Ru, the surface carbon was hydrogenated to methane even at room temperature. In the oxidation at 473 K (step IV), 6 ml-STP of CO_2 was produced. Even after this treatment, 4 ml-STP of C(a) remained on the catalyst. From the above-mentioned results, three forms of surface carbon have been identified, designated as C_α, C_β, and C_γ: (i) C_α is hydrogenated to methane at temperatures up to 423 K and has almost the same reactivity toward hydrogenation as the molecularly adsorbed CO; (ii) C_β is oxidized to CO_2 at temperatures up to 473 K; (iii) C_γ is the least reactive and not oxidized to CO_2 at 473 K. The same experiments were carried out for Rh–Na/TiO_2 catalyst, and three forms of surface carbon were also observed in this case.

The chemical state of deposited carbon is not clear in the present work; however, C_α, which undergoes hydrogenation, may be carbidic or an amorphous carbon because the hydrogenation of graphite impregnated with Rh occurred only above 1070 K (*15*). Recently, Shincho *et al.* (*16*) reported that the disproportionation of CO proceeds rapidly on a Ru(1,1,10) stepped surface, and they examined the reactivity of surface carbon with O_2 by thermal desorption spectroscopy and revealed that at least four types of carbon exist. Furthermore, Bell and co-workers (*17*) have investigated the nature of carbon species deposited on supported and unsupported Ru catalysts during CO hydrogenation by ^{13}C NMR and identified four forms of nonoxygenated carbon on the catalysts.

In summary, the activity of Rh catalysts in the disproportionation reaction was very dependent on the metal precursors and supports. Rh/TiO_2 catalyst showed the highest activity, and the amount of surface carbon produced was larger than that of adsorbed CO. Three forms of carbon were identified, designated C_α, C_β, and C_γ: (i) C_α was hydrogenated at temperatures up to 423 K and had a reactivity similar to that of adsorbed CO; (ii) C_β was oxidized to CO_2 at temperatures up to 473 K; (iii) C_γ was the least reactive and not oxidized at 473 K.

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