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NOTE

Comments on the Use of Carbon-13 Tracer Experiments to Determine the Role of Surface Carbon in Catalytic Reactions

The role of surface carbon in methanation and Fischer–Trospch reactions has been demonstrated by the use of carbon-13 as a tracer (*1–3*). Typically, reactive carbon-13 on a metal surface is formed from ^{13}CO by disproportionation or dissociation reactions and subsequently the catalyst is exposed to ^{12}CO and H_2. The presence of ^{13}C in the hydrocarbons initially formed confirms the role of the surface carbon in these reactions.

In an attempt to determine the importance of surface carbon in the water gas shift (WGS) reaction over RuY zeolites we have found that under normal operating conditions, ^{13}C from the surface does not appear in the CO_2; however, the results are ambiguous because of other reactions (*4*). The purpose of this note is to describe these complicating reactions which occur when water and carbon monoxide are present in the system.

A 2 wt% RuY catalyst was prepared from a $[Ru(NH_3)_6]Cl_3$ salt and a NaY zeolite by standard ion exchange techniques as described elsewhere (*4*). All of the experiments were carried out using a glass recirculation system which was attached to an online gas chromatograph (*5*). Pretreatment of the RuY samples consisted of evacuation at 25°C to less than 10^{-3} Torr (1 Torr = 133.33 N m^{-2}) followed by H_2 reduction. During the reduction step, the temperature was raised from 25 to 380°C at 1°C/min. The total reduction time was 17 hr. Following pretreatment, the ruthenium was present in the form of small particles having an average particle size of 20 Å (*4*). The amount of exposed ruthenium, as determined by H_2 chemisorption at 25°C (*4*), was 37 μmol H_2 g cat^{-1}.

When 30 Torr of CO was recirculated in a 326 cm^3 system over a freshly pretreated RuY catalyst (0.35 g) at 300°C the results shown in Fig. 1 were obtained. After 60 min of exposure to CO the surface coverage of carbon, based on the amount of CO_2 produced by the reaction

$$2CO + s \rightarrow CO_2 + C_s \qquad (1)$$

approached 50%, which agrees with the value previously reported for a 1.2 wt% Ru/SiO_2 catalyst (*6*). When the gas phase was evacuated to 5 × 10^{-5} Torr (6 min) at 300°C and 20 Torr of H_2O was recirculated over the RuY catalyst, H_2 was the only product initially observed in the gas phase. The rapid decrease in the amount of gas phase H_2 between 5 and 15 min is attributed to the hydrogenation of excess surface carbon to form CH_x species although no hydrocarbons were observed in the gas phase. When H_2 instead of H_2O was admitted to a RuY catalyst with surface carbon, CH_4 was the only product observed in the gas phase, which is consistent with previous studies.

In a similar manner a layer of carbon-13 was formed at 250°C on a fresh RuY catalyst. Following carbon deposition a mixture of 27 Torr ^{12}CO (1.5 mmol g^{-1}) and 24 Torr H_2O was admitted to the catalyst and the reaction products monitored. As surface carbon has been reported to deactivate on a Ru-molecular sieve catalyst (*7*), the total time between the initial exposure of the catalyst to ^{13}CO and the reaction of the $^{12}CO/H_2O$ mixture was always less than 10 min. The CO_2 formed during the reaction of the CO/H_2O mixture over the catalyst at 250°C contained no $^{13}CO_2$ above that expected from the natural abundance of the isotope.

One might take this as negative evidence for the participation of surface carbon in

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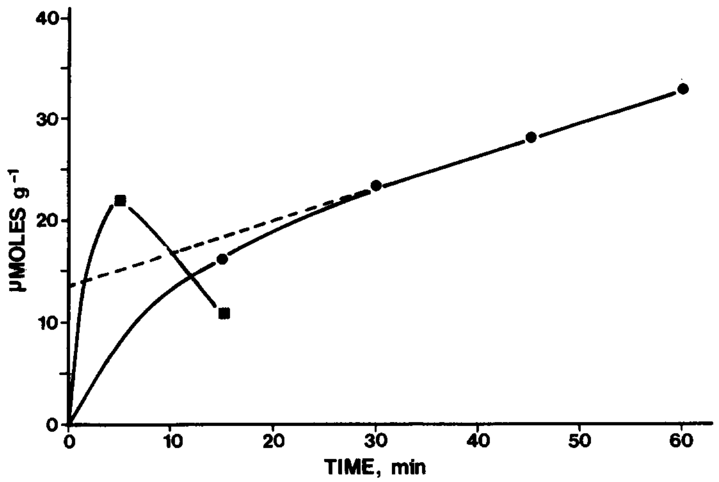

FIG. 1. CO_2 and H_2 production vs time over RuY at 300°C. (●) CO_2 produced via disproportionation of CO at 300°C; (■) H_2 formed from addition of H_2O to surface carbon at 300°C.

the formation of CO_2; however, additional experiments suggest that the interpretation may not be so straightforward. Upon decreasing the system volume to 55 cm^3 and the partial pressures of ^{12}CO and H_2O to 5 Torr (58.5 μmol g^{-1}, 0.29 g RuY), reaction with surface ^{13}C yielded both ^{13}CO and $^{13}CO_2$ as significant fractions of the gas phase (Table 1). Moreover, the amount of ^{13}C containing species observed was an order of magnitude greater than the amount of carbon thought to be on the surface, based on the $^{13}CO_2$ derived from Reaction (1).

No infrared bands due to chemisorbed ^{13}CO or carbonate species were observed after the deposition of the surface carbon and the removal of excess ^{13}CO at 250°C. Exposure of the sample containing surface ^{13}C to ^{12}CO at 250°C did not lead to the appearance of ^{13}CO in the gas phase (see below). It seems unlikely, therefore, that a strongly bound, infrared inactive molecular form of ^{13}CO was present on the surface.

These results may be understood if the reaction

$$^{13}C_a + H_2O \rightleftarrows {}^{13}CO_a + H_2 \qquad (2)$$

occurs, followed by the displacement of CO from the surface:

$$^{12}CO + {}^{13}CO_a \rightleftarrows {}^{13}CO + {}^{12}CO_a \qquad (3)$$

The latter reaction is known to occur over Rh catalysts at relatively low temperatures (*8*). In the present experiment, this exchange was confirmed over RuY using infrared spectroscopy. A strong infrared band was noted at 1985 cm^{-1} upon exposure of the RuY sample to 20 Torr of ^{13}CO at 25°C followed by brief evacuation. When 22 Torr of ^{12}CO was admitted to the cell at 25°C, the band at 1985 cm^{-1} slowly shifted to higher wavenumbers. After 4 hr the band was at 2040 cm^{-1}, which corresponds to the

TABLE 1

Interaction of ^{13}C with $^{12}CO/H_2O$ Mixture at 250°C

Species	Amount[a,b]	$^{13}C/^{12}C$
^{13}C[c]	3.2	—
CO	48.0	0.45
CO_2	10.5	0.69
CH_4	0.0	—

[a] Analyzed at 18% CO conversion. Initial amount of ^{12}CO in reaction mixture was 58.5 μmol g^{-1}.

[b] μmol g^{-1}.

[c] Calculated from $^{13}CO_2$ produced during carbon deposition.

position reported by several authors for ^{12}CO on supported ruthenium (*9, 10*).

Thus, it appears that the ^{13}C reacts with H_2O forming ^{13}CO, which is then displaced from the surface and becomes diluted by the gas phase ^{12}CO. If the relative amount of ^{12}CO is large with respect to the original amount of ^{13}C on the surface, then the percentage of $^{13}CO_2$ in the product would be small as was observed. Reactions (2) and (3) not only make it difficult to determine the role of surface carbon in the WGS reaction but they would also complicate the interpretation of labeling experiments involving surface carbon during any reaction in which CO and H_2O were present.

Since the amount of CO_2 produced by Reaction (1) has been frequently used as a measure of the amount of surface carbon (*3, 6, 7*), it is also significant that under the relatively mild conditions of this experiment, i.e., deposition of the carbon at 250°C, the total amount of ^{13}C recovered as gas phase products (Table 1) greatly exceeded the amount of $^{13}CO_2$ detected during the deposition step. This result suggests that the reaction

$$CO_a \rightarrow C_a + O_a \qquad (4)$$

serves as the dominant source of surface carbon. Somorjai and co-workers (*11*) also have provided evidence for this reaction over rhodium films. Under these conditions the reaction

$$CO + O_a \rightarrow CO_2 \qquad (5)$$

must be incomplete. The species which Rabo *et al.* (*6*) refer to as nondissociated CO that reacts with H_2 to form CH_4 may in fact be surface carbon which is derived from Reaction (4). Clearly some caution needs to be exercised in determining the amount of surface carbon simply by measuring the amount of CO_2 produced in the disproportionation reaction.

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