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Inactivity of Surface Carbon to Hydrogenation on Supported Rhodium

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Carbon atoms deposited on Rh/TiO_2 were not readily hydrogenated to form methane, methanol, or ethanol in CO hydrogenation at 393 and 422 K. This result is in contrast to the behavior of supported Ni and Co for which similarly deposited surface carbon is readily hydrogenated to hydrocarbons. Two possibilities for the different behavior are discussed.

INTRODUCTION

There is much evidence that carbon atoms on metal surfaces are reactive species for hydrogenation to produce hydrocarbons (*1–3*). Labeled carbon deposited on a Ni surface by the dissociation so ^{13}CO was hydrogenated more rapidly than ^{12}CO in a $^{12}CO + H_2$ mixture (*1*). Biloen *et al.* (*2*) showed that labeled (^{13}C) carbon atoms deposited on the surface of Ni, Co, and Ru are statistically incorporated into higher hydrocarbons during reaction in the presence of $^{12}CO + H_2$. These results strongly suggest that surface carbon is an intermediate of the Fischer–Tropsch reaction on these metals, imply that CO dissociation is a prerequisite to hydrocarbon formation, and imply that metals that readily dissociate CO should be good Fischer–Tropsch catalysts if the surface carbon is not bound too strongly.

On the other hand, metals that do not readily dissociate CO are good catalysts for methanol synthesis (*4*), which has been shown to involve a nondissociative mechanism (*5*). Thus Pd, Pt, and Ir give very high selectivities to methanol (*4*). Rh, lying between Ru (hydrocarbons) and Pd (methanol), synthesizes methanol, ethanol, higher alcohols, and higher hydrocarbons (*6, 7*), raising questions concerning the mechanisms of the simultaneous reactions occurring and the role of surface carbon. Adsorbed CO dissociates on polycrystalline Rh (*8*) and on stepped single crystal Rh surfaces (*9*) above 573 K. Starting with C_2H_4, temperatures of 1073 K were required to make a graphitic surface (*9, 10*). In contrast, on Ni, CO dissociation results in carbidic carbon at temperatures below 600 K; graphitic carbon is formed above 700 K (*3, 11*).

EXPERIMENTAL

In this study, labeled carbon was deposited on Rh/TiO_2 by the dissociation of adsorbed CO according to:

$$^{13}C^{16}O(ad) \rightarrow {}^{13}C(ad) + {}^{16}O(ad)$$

$$^{13}C^{16}O(ad) + {}^{16}O(ad) \rightarrow {}^{13}C^{16}O_2$$

Table 1 summarizes the results. Three wt% Rh/TiO_2 was used in an internal recycle reactor, product analysis was done by GC, and isotopic composition was determined by mass spectrometry. Details are given elsewhere (*5*).

RESULTS AND DISCUSSION

The dissociation of CO on the Rh/TiO_2 was slow (Table 1), even though temperatures of 523 and 573 K were employed. The

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TABLE 1

$^{13}C^{16}O$ Dissociation on Rh/TiO_2

Catalyst amount g[a]	0.31	1.36
$^{13}C^{16}O$ pressure, Torr[b]	56	91
Temperature, K	522	573
Contact time, hr	3	24
$^{13}C/Rh$[c]	0.41	1.97

[a] Catalysts (3.0 wt% Rh/TiO_2) reduced in 250 Torr H_2 at 573 K for 18 hr.

[b] Purity was 90% (1 Torr = 133.3 N m^{-2}).

[c] The amount of ^{13}C deposited on the catalysts was calculated from CO_2 produced; $2^{13}C^{16}O \rightarrow {}^{13}C(ad) + {}^{13}C^{16}O_2$; the total amount of Rh contained in the catalyst was used to calculate $^{13}C/Rh$.

$^{13}C/Rh$ ratios were determined from the amount of CO_2 produced as determined by GC. On Ni and Ru the rate of CO dissociation is more rapid (*3*, *11–13*), whereas on Pd, adsorbed CO does not undergo substantial dissociation at 573 K (*14*). After depositing ^{13}C on Rh/TiO_2 and evacuating, a mixture of $^{12}C^{16}O$ plus H_2 was added, and the products of the hydrogenation reaction and their isotopic composition were analyzed (Tables 2 and 3). The selectivity (mol% of total product formed) to CH_4, CH_3OH, and C_2H_5OH was 84.8, 2.2, and 0.85%, respectively, for the Rh/TiO_2 with $^{13}C/Rh = 0.41$. No other oxygen-containing species were observed. The selectivity to CH_4 was 84.3 mol% for the Rh/TiO_2 with $^{13}C/Rh = 1.97$. This latter catalyst made essentially no alcohols. However, the selectivity to alcohols depended on the amount of catalyst used. Clearly, the catalyst was either adsorbing the alcohols and forming stable species such as alkoxides or was catalyzing their conversion to dehydration products.

TABLE 2

Isotopic Composition of Ch_4 and CO from Reaction of $^{12}C^{16}O$ Plus H_2 over Rh/TiO_2 Containing Deposited ^{13}C

Reactions conditions	$^{13}C/Rh$		
	0.41[a]	1.97[b]	
$^{12}C^{16}O$ pressure, Torr	26.5	24.2	
H_2 pressure, Torr	603.0	626.9	
Temperature, K	422	393	
	Reaction time (hr)		
	4	3	9
CO conversion, %	26	11	36
Isotopic composition, %[c]			
$^{13}C^{16}O$	0 ± 0.2	0.1 ± 0.3	0.6 ± 0.2
$^{12}C^{16}O$	100 ± 0.2	99.9 ± 0.3	99.4 ± 0.2
$^{13}CH_4$	0 ± 1.0	0 ± 0.5	4.3 ± 0.3
$^{12}CH_4$	100 ± 1.0	100 ± 0.5	95.7 ± 0.3

[a] This catalyst, after the ^{13}C deposition reaction and evacuation, was contacted with 52 Torr $^{12}C^{16}O$ at 453 K to remove adsorbed $^{13}C^{16}O$ by exchange and evacuated prior to the hydrogenation of $^{12}C^{16}O$ (*2*).

[b] This catalyst was evacuated at 573 K for 2 hr to remove adsorbed ^{13}CO and was then cooled to 393 K.

[c] Corrected for the natural abundance of ^{13}C.

The ^{13}C deposited on the Rh/TiO_2 was essentially unreactive to exchange with gas phase $^{12}C^{16}O$. Only in the case of 9 hr reaction at 393 K with 36% conversion of $^{12}C^{16}O$ was there sufficient $^{13}C^{16}O$ to be detectable above experimental error (Table 2). The reactivity of the deposited ^{13}C with respect to hydrogenation was also low as indicated by the low concentration of $^{13}CH_4$ in all cases (Table 2). Only after 9 hr for the 1.97 $^{13}C/Rh$ case was the $^{13}CH_4$ concentration (4.3 mol% of total CH_4 producted) above the error. If all the deposited ^{13}C had been converted to $^{13}CH_4$, the CH_4 produced would

TABLE 3

Isotopic Composition of Alcohols from Reaction of $^{12}C^{16}O$ plus H_2 over Rh/TiO_2 Containing Deposited ^{13}C[a]

Isotopic species	MW	Composition[b] mol%
$^{12}CH_3{}^{16}OH$	32	100 ± 0.1
$^{13}CH_3{}^{16}OH$	33	0 ± 0.1
$^{12}C_2H_5{}^{16}OH$	46	97.9 ± 2.4
$^{12}C^{13}CH_5{}^{16}OH$	47	1.0 ± 1.6
$^{13}C_2H_5{}^{16}OH$	48	1.1 ± 0.9

[a] $^{13}C/Rh$ = 0.41; CO conversion = 26%; reaction conditions given in Table 2.

[b] Isotopic composition determined by GC–mass spectroscopy using a duPont 21-492B chemical ionization mass spectrometer and methane as a reactant; a carbowax 1500 column was used for the GC separation; corrected for natural abundance of ^{13}C.

have contained 14.0 mol% $^{13}CH_4$ for the 0.31 g of Rh/TiO_2 at 26% conversion, and 84.3 mol% $^{13}CH_4$ for the 1.36 g Rh/TiO_2 at 36% conversion. Similarly, the rate of conversion of deposited ^{13}C to alcohols was so low that ^{13}C-containing alcohols could not be reliably detected (Table 3). Clearly, the deposited carbon reacts with H_2 very slowly relative to the rate that $^{12}C^{16}O$ from the gas phase is hydrogenated to $^{12}CH_4$ and to alcohols.

The reactivity of carbon deposited on Rh/TiO_2 appears to be much less than that of carbon deposited on supported Ni where reactivity with H_2 was detected at 50°C and a maximum amount of the carbon was rapidly hydrogenated to CH_4 at 195°C (*3*). The rate of hydrogenation of carbon deposited on Ni is more rapid than the hydrogenation of gas phase ^{12}CO (*1, 2, 13, 14*). Analogous experiments on Ru and Co reveal that deposited ^{13}C is not as reactive as on Ni (*12*). In the case of Rh/TiO_2, the deposited ^{13}C appears to be even less reactive. Thermally stabilized or polymerized carbon on Ni is much less reactive, being rapidly hydrogenated only at 680 K (*3*). The conversion of reactive surface carbidic carbon atoms to a less reactive polymerized carbon species has been shown for Ni (*3, 14*) and Fe (*15, 16*), and has been proposed to be the cause of the observed lower activity of deposited ^{13}C (*12*). The slow rates of CO dissociation observed for Rh/TiO_2 which forced the use of longer CO contact times could have also resulted in a thermal annealing or polymerization of the deposited carbon and a reduction in its reactivity toward hydrogenation.

The role of the TiO_2 in the observed behavior is unclear. Based on its other observed effects in CO hydrogenation, its potential involvement cannot be eliminated.

If the deposited carbon did not undergo polymerization to less reactive species, these results raise questions about the generality of the CO dissociation mechanism for methane and higher hydrocarbon formation over metals in CO hydrogenation. The large amount of carbon on Rh/TiO_2 contacted with CO for 24 hr at 573 K ($^{13}C/Rh$ = 1.97) suggests that chains of polymerized carbon atoms were formed, or that carbon was either incorporated into the Rh particles forming a non-surface carbide, or was somehow introduced onto the surface of the TiO_2. Metal carbides have formulas of the form M_xC where $x > 1$.

After the $^{12}C^{16}O + H_2$ reaction over the Rh/TiO_2 containing 0.41 $^{13}C/Rh$ was completed, the sample was evacuated at 373 K for 4 hr and then treated in 290 Torr H_2 at 573 K for 20 hr. CH_4, C_2H_6, and C_2H_4 were detected after 3.4 hr of reaction, but only CH_4 was detected after 20 hr (Table 4), indicating that hydrogenolysis of the C_2 hydrocarbons was occurring. The amount of CH_4 produced after 20 hr reduction corresponds to a C/Rh ratio of 2.6. The CH_4 contained 92% $^{12}CH_4$, showing that more than chemisorbed ^{12}CO not removed by the 373 K evacuation was contributing to the $^{12}CH_4$. These results suggest that ^{12}CO was undergoing dissociation during the CO + H_2 reaction, forming carbidic carbon on the Rh which was not being immediately and entirely hydrogenated. Carbonaceous deposits of many "monolayers" have been

TABLE 4

H_2 Reaction on Catalyst Containing Deposited ^{13}C ($^{13}C/Rh$ = 0.41) after $^{12}C^{16}O + H_2$ Reaction Study[a]

Reduction time, hr	3.4	20
Production time composition, Torr in 290 Torr H_2		
CH_4	6.64	7.45
C_2H_6	0.024	ND[b]
C_2H_4	0.002	ND[b]
$\geq C_3$	ND[b]	ND[b]
Isotopic composition of CH_4, mol%[c]		
$^{13}CH_4$	7.2 ± 0.2	8.0 ± 0.7
$^{12}CH_4$	92.8 ± 0.2	92.0 ± 0.7

[a] After $^{12}C^{16}O + H_2$ reaction study was completed, the Rh/TiO_2 was evacuated at 373 K for 4 hr, then H_2 was admitted; reaction temperature 573 K; H_2 pressure 290 Torr.

[b] ND, Not detectible.

[c] Corrected for natural abundance of ^{13}C.

reported for CO hydrogenation over polycrystalline Rh foil (*8*). Therefore, if the route to CH_4 and higher hydrocarbons on Rh involves dissociation of CO, then the surface carbide species resulting from CO dissociation must have two reaction paths: one leading to hydrocarbon products via hydrogenation, the other involving a polymerization reaction to less reactive carbon. However, other characterization studies of these Rh/TiO_2 catalysts (*18*) show that the Rh is highly dispersed and that a large fraction of the CO is adsorbed as dicarbonyl species that is not fully removed at 373 K. This CO would contribute significantly to the total $^{12}CH_4$.

The CH_4 produced contained 8 mol% $^{13}CH_4$ after 20 hr of H_2 reaction. This amount of $^{13}CH_4$ corresponds to 50% of the ^{13}C initially deposited by $^{13}C^{16}$ dissociation. The chemical state of this carbon is unclear; that which eventually underwent hydrogenation must be carbidic or an amorphous polymer because the rate of hydrogenation of graphite impregnated with Rh became measurable only at 1070 K (*17*), and the graphitic carbon on Ni is not hydrogenated below 830 K (*3*).

These results may be explained by two possibilities:

(1) CO dissociates slowly at 523 K in the absence of H_2, and it therefore takes a long time to build up an appreciable amount of carbon on the Rh. Because of the slow rate of formation, the deposited carbon may have sufficient time to change to less active form. Under reaction conditions in the presence of H_2, CO dissociation may be more rapid, and the freshly deposited carbon may be more reactive.

(2) The rate of CO dissociation is slow on Rh compared with that for Ni at 523 K. Therefore the rate of CO dissociation may be so slow around 423 K that CO undergoes hydrogenation preceding C–O bond rupture. Only 50% of the ^{13}C deposited was ultimately hydrogenated to $^{3}CH_4$ at 573 K for the case of $^{13}C/Rh = 0.41$; the remainder was either unreactive (graphitic) or not directly associated with the metal.

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