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A Mechanistic Study of Carbon Monoxide Hydrogenation over Rhodium Catalysts using Isotopic Tracers

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The medium-pressure (1.01 MPa) hydrogenation of carbon monoxide has been investigated over rhodium catalysts in the steady state (at typically 523 K) by use of isotopic labeling ([^{13}C]CO, [^{18}O]CO, and [^{2}H]H_2). When labeled carbon monoxide was introduced, neither methane nor ethanol nor methanol showed any incorporation; however, the labels were rapidly incorporated into the aldehydic function of ethanal. Labeled water, produced from the hydrogenation of [^{18}O]CO, took more than 0.3 h to desorb. The results suggest that (i) ethanol and ethanal are produced independently with no common intermediate, (ii) the formation of alcohols is slow (taking over 0.5 h), and (iii) carbon monoxide is not hydrogenated directly to methane but goes through the hydrocarbonaceous residue present on the surface. The carbonaceous residue was found to play a central role in the mechanism, supplying in effect both hydrogen and CH_2 units to other reactive surface species. © 1987 Academic Press, Inc.

INTRODUCTION

The hydrogenation of carbon monoxide has been the subject of considerable study over the last decade by groups in both university and industrial research laboratories (*1*). Many advances have been made in our understanding of the processes involved, but equally many questions remain unresolved. This is due partly to the different metals, supports, and conditions used in the various studies, but partly also to the complexity of the systems under study. In this study we have made use of isotopic tracers to investigate the mechanism of formation of both hydrocarbon and oxygenate products at medium pressure and steady-state operation. In many ways use of the isotopic tracer is ideally suited to investigating carbon monoxide hydrogenation, since carbon, hydrogen, and oxygen isotopes are readily available. We are not the first to tackle the mechanism by the use of tracers; Takeuchi and Katzer (*2*), using a subatmospheric recirculating system, concluded that methanol was formed by a nondissociative mechanism, while Orita, Naito, and Tamaru (*3*) in a similar system have shown that ethanol is not a hydrogenation product of ethanal.

EXPERIMENTAL

The apparatus used for this study was constructed throughout of stainless-steel tubing. Carbon monoxide, hydrogen, and nitrogen could all be fed into the system, either separately or mixed, up to a total pressure of 1.01 MPa with a typical GHSV of 1200 h^{-1}. The reactor consisted of a glass-lined 0.64-cm o.d. stainless-steel tube in which the catalyst (typically 1 cm^3) was placed. The reactor was surrounded by an electric furnace which maintained the temperature at the desired value to ±1 K. Temperatures were measured by a thermocouple placed in contact with the center of the catalyst bed. All postreactor tubing was heated to prevent condensation of prod-

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TABLE 1

Steady-State Activities and Selectivities of Major Products[a]

Catalyst	Product	Yield[b]	Selectivity[c]	Total conv.[c]
Rh(chloride)/ silica	Methane	83.3	32	
	Ethane	2.3	2	
	C3–C6	0.4	1	2.5
	Ethanal	64.4	49	
	Ethanol	5.1	4	
Rh(nitrate)/ silica	Methane	70.9	36	
	Ethane	2.2	2	
	C3–C6	4.5	8	2.0
	Ethanal	30.8	31	
	Ethanol	7.3	8	
Rh(chloride)[d]/ tungsten trioxide	Methane	18.3	23	
	Ethane	1.9	5	
	C3–C6	3.2	16	4.4
	Methanol	24.1	30	
	Ethanol	6.7	17	

[a] Conditions: 523 K, 1.01 MPa, $CO:H_2$ 1:2, GHSV 1200 h^{-1}.
[b] Units: nmol · (g · catalyst)$^{-1}$ · s^{-1}.
[c] Units: %.
[d] Conditions: 458 K, 1.01 MPa, $CO:H_2$ 1:2, GHSV 1200 h^{-1}.

ucts. The system was run continuously with the reactor effluent being sampled at regular intervals. The products were analyzed by gas chromatography (*4*). Isotopically labeled species, at 0.10 MPa, were introduced into the feedstream via a sample valve and were analyzed by a mass spectrometer (Spectramass Dataquad, fitted with a high-resolution RF head) connected to the reactor outlet.

The catalysts used in this study, rhodium trichloride/silica, rhodium trichloride/tungsten oxide, and rhodium nitrate/silica, were prepared by impregnation. The samples were reached *in situ* by a 4:1 nitrogen:hydrogen stream (100 cm^3 min^{-1}) at 573 K for 30 min. The catalysts were then cooled in flowing nitrogen/hydrogen to the desired temperature and the flow switched to carbon monoxide/hydrogen 1:2 (20 cm^3 min^{-1}) at 1.01 MPa. The dispersion of the catalysts, estimated from carbon monoxide chemisorption on the basis of (No. of CO molecules adsorbed/No. of Rh atoms present) × 100% was 113% for Rh[Cl]/silica, 33% for Rh/WO_3, and 93% for $Rh[NO_3]$/silica. Carbon monoxide (99.99%), hydrogen (99.99%), and nitrogen (99.9995%) were all used as received. Isotopically labeled gases, [^{13}C]carbon monoxide (99 at.%, Amersham), carbon [^{18}O]monoxide (99 at.%, Amersham), and [^{2}H]hydrogen (99.7 at.%, Matheson), were all used as received.

RESULTS

Unless otherwise stated all results quoted have been obtained while the catalysts were in a steady state with respect to activity and selectivity. The yields and selectivities obtained are shown in Table 1. To investigate whether unreacted carbon monoxide retained its molecular integrity or whether there was rapid C—O bond breaking and making, a 50/50 mixture of [^{13}C]carbon monoxide and carbon [^{18}O] monoxide was pulsed into the feedstream. All four carbon monoxide masses responded simultaneously; the results are shown in Fig. 1.

The time taken for [^{18}O]- or [^{13}C]-containing ethanal to be detected after a pulse of carbon [^{18}O]monoxide or [^{13}C]carbon monoxide is shown in Fig. 2. However,

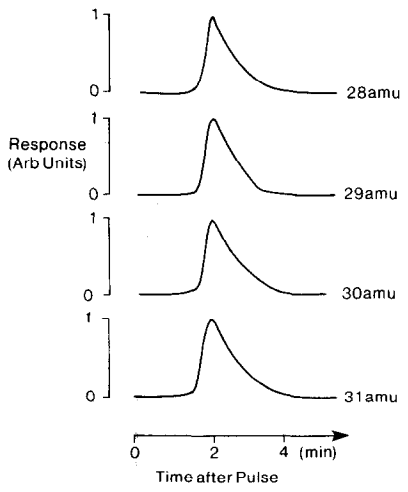


FIG. 1. Response of masses 28, 29, 30, and 31 after injection of [^{13}C]CO and [^{18}O]CO (0.5 cm^3, 1.01 MPa) into the feedstream. Catalyst $Rh[Cl]/SiO_2$; conditions: 548 K, GHSV 1200 h^{-1}, $CO:H_2$ 1:2.

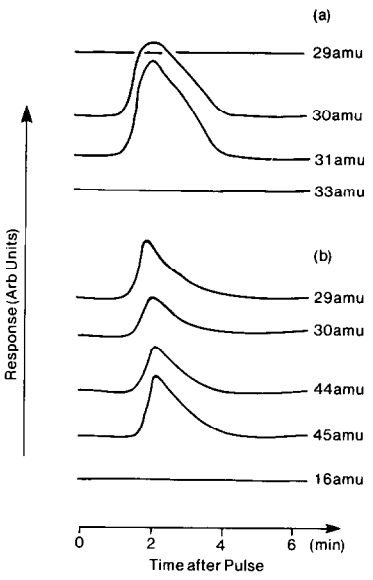


FIG. 2. (a) Response of masses 29, 30, 31, and 33 after injection of [^{18}O]CO (0.5 cm^3, 1.01 MPa) into the feedsteam. Catalyst Rh[Cl]/SiO_2; conditions: 523 K, GHSV 1200 h^{-1}, CO : H_2 1 : 2. (b) Response of masses 16, 29, 30, 44, and 45 after injection of [^{13}C]CO (0.5 cm^3, 1.01 MPa) into the feedstream. Catalyst and conditions as for (a).

when a similar experiment was carried out to study the production of ethanol, no evidence for incorporation was observed. To confirm this result the same experiments were repeated over a Rh/WO_3 catalyst which only produces alcohols; again there was no evidence for incorporation. The incorporation of [^{18}O]oxygen from carbon [^{18}O]monoxide into water was examined and a slow evolution of [^{18}O]water was observed as shown in Fig. 3. No evidence was found for incorporation of [^{13}C]carbon monoxide into methane.

To investigate whether the hydrocarbonaceous residue is actively involved in hydrogen transfer the system was precipitated into a nonsteady state by switching from a feedstream of carbon monoxide/hydrogen to one of [^{2}H]hydrogen and then back to carbon monoxide/hydrogen. The behavior of the hydrogen isotopes and the water isotope mixtures are shown in Figs. 4 and 5.

DISCUSSION

It is appropriate to point out at the outset of this discussion that as the catalysts were in the steady state, with respect to activity and selectivity, hydrocarbonaceous residues are present on the surface. These residues have been suggested (*5*) to play a major role in hydrogenation reactions and the results will be discussed in this light.

When both labeled carbon monoxide were copulsed all four isotopic masses responded. Therefore there is scrambling of nonreacted carbon monoxide. It is worth noting, however, that the result is valid only because all four masses responded; masses 29, 30, and 31 would all be observed even if there was no scrambling (see below). This result was not unexpected; in a study of carbon monoxide adsorption and thermal desorption over these catalysts (*6*) it was shown that there was considerable scrambling by 523 K. Therefore carbon monoxide can adsorb, scramble and desorb without necessarily being involved in hydrogenation.

When [^{13}C]carbon monoxide was pulsed into the feedstream and mass 17 was monitored, no evidence was found for incorporation of the label into the methane. This is at first sight a surprising result; however, it must be remembered that the catalyst is in a steady state and as such has a considerable reservoir of carbon in the form of a hydrocarbonaceous deposit (*4*). This result must be interpreted in that context, and we

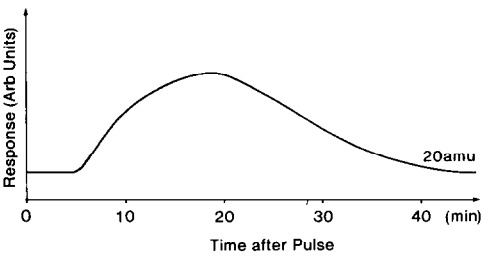


FIG. 3. Response of mass 20 after injection of [^{18}O]CO into the feedstream. Catalyst Rh[NO_3]/SiO_2, conditions: 523 K, GHSV 1200 h^{-1}, CO : H_2 1 : 2.

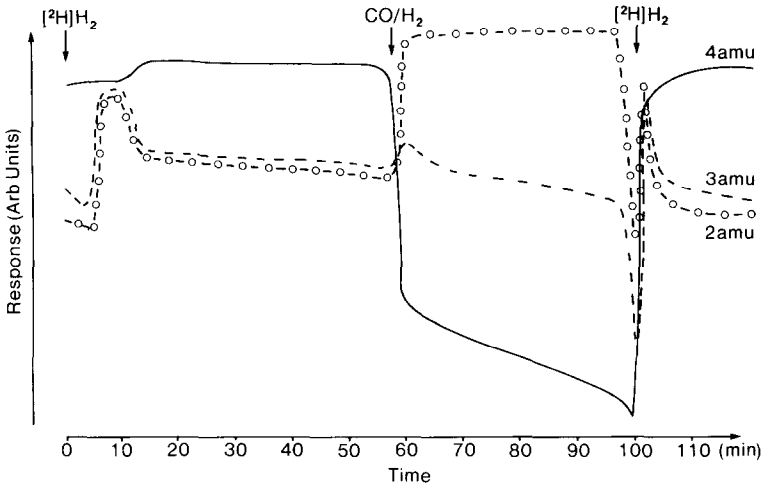


FIG. 4. Response of masses 2, 3, and 4 to flow switching from CO/H_2 to $[^2H]H_2$ to CO/H_2 to $[^2H]H_2$. Catalyst $Rh[Cl]/SiO_2$, conditions: 523 K, GHSV 1200 h^{-1}, $CO:H_2$ 1:2.

therefore propose the following. On adsorption the carbon monoxide can dissociate and be partly hydrogenated to give a CH_x species. This intermediate may react further with hydrogen to give methane or it may be incorporated into the hydrocarbonaceous residue present on the surface. From the tracer results it appears that the latter is correct. However, methane is being formed continuously at a steady rate. Therefore we suggest that on another part of the surface a C-1 fragment of the hydrocarbonaceous residue is hydrogenated to methane. This has been shown to occur over these catalysts; in recent studies (*4, 7*) the removal of the hydrocarbonaceous residue has been shown to occur principally by a hydrogenolysis mechanism

$$C_xH_y \rightarrow C_{x-1}H_{y-4} + CH_4$$

giving rise to methane as the major product. It is worthwhile to note that the hydrocarbonaceous residue will produce methane even when only an inert gas, such as nitrogen, is flowing over the catalyst (*4*). Therefore the labeled CH_x species would be mixed with a large nonlabeled population having the same statistical chance of being desorbed (ignoring any isotope effect) and so would be lost in a large dilution effect.

When carbon [^{18}O]monoxide was pulsed into the feedstream the mass that is associated with [^{18}O]ethanal, i.e., CHO, 29 amu $\rightarrow$ CH^{18}O, 31 amu, showed a response at approximately the same time as the unreacted carbon [^{18}O]monoxide. Therefore there is a relatively rapid conversion of carbon monoxide into ethanal. When [^{13}C]carbon monoxide was pulsed into the system the mass associated with $CH_3{}^{13}CHO$ responded but that associated with $^{13}CH_3CHO$ did not, i.e., CHO, 29 amu

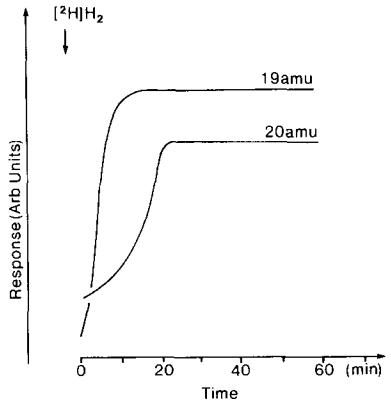


FIG. 5. Response of masses 19 and 20 to flow switching from CO/H_2 to $[^2H]H_2$. Catalyst Rh/WO_3, conditions: 458 K, GHSV 1200 h^{-1}

$\rightarrow$ ^{13}CHO, 30 amu, but no response was observed from mass 16, i.e., CH_3, 15 amu $\rightarrow$ [^{13}C]CH_3, 16 amu. The probability of double incorporation in one ethanal molecule is less than 1%. Therefore the [^{13}C]carbon went selectively into the aldehyde function. Clearly the CH_x, or possibly more correctly the hydrocarbonaceous residue, is a common intermediate for both methane and the CH_3 function of the aldehyde. A similar conclusion was reached by Orita and co-workers (*3b*) who also showed by use of isotopic labeling, in a subatmospheric circulating system, that the species which formed the methyl group in ethanal was also an intermediate for the formation of methane. Equally the aldehyde group cannot be in fast equilibrium with the hydrocarbonaceous deposit, i.e., $CHO \not\rightleftharpoons CH_x$.

Studies in this area (*3b, 8*) have shown, by examining kinetics and product distributions, that ethanol is not a subsequent hydrogenation product of ethanal and indeed the response of the ethanal peaks to the [^{18}O]-labeling of carbon monoxide while no response is observed for ethanol is a clear indication that ethanal is not hydrogenated to ethanol. This would suggest that the $-CH_2OH$ group of ethanol and the $-CHO$ group of ethanal have no common intermediate. The appearance of the [^{18}O]oxygen in the $-CHO$ of ethanal but not the $-CH_2OH$ of ethanol is in keeping with the proposed behavior of these catalysts in terms of alcohol production (*4*). By examining the nonsteady state and transient effects Gilhooley *et al.* (*4*) proposed that alcohol formation over these catalysts was slow in the order of 0.5–1 h; were that to be the case then the absence of the label as a clear peak may mean that the residence time is long enough for surface equilibration to result in a statistical amount of label to be desorbed in ethanol over a long period of time. The response obtained from water, a slow evolution over 30 min, shows the difficulty of detecting a tracer which is desorbed over a long period of time; if the period of time was doubled then we would be unable to detect the tracer unambiguously. It is interesting to note that the behavior of water appears to be similar to that of the alcohols and we may consider it to be the first in the homologous series $C_nH_{2n+1}OH$ where $n = 0$. Indeed, the results from the feedgas switching indicate that the rate-determining step in water production is the hydrogenation of an $-OH$ group. Mass 19 (Fig. 5) responds to the addition of [^{2}H]hydrogen after approximately 10 min, but mass 20 responds after 20 min. Therefore if the formation of water is represented by

$$O(a) + H(a) \rightarrow OH(a) \qquad [1]$$

$$OH(a) + H(a) \rightarrow H_2O(g) \qquad [2]$$

then reaction [2] must be slow with respect to reaction [1]. If the slow step in alcohol production is similar to reaction [2] then it is possible to envisage a situation where the difference between aldehydes and alcohols lies in their bonding to the surface, e.g.,

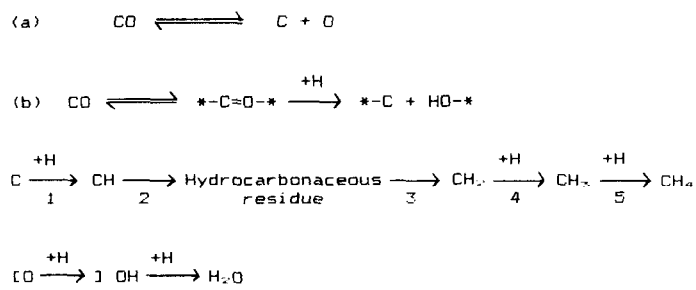
for ethanal,

$$*{-}CO(CH_3) + *{-}H \rightarrow CH_3CHO(g)$$

and for ethanol,

$$*{-}OCH_2CH_3 + *{-}H \rightarrow CH_3CH_2OH(g).$$

This difference in bonding would allow methanol to be produced by a nondissociative mechanism, as proposed by Katzer and Takeuchi (*2a*) and Orita *et al.* (*3a*), yet for the tracers still not to be detected in our system. This is possible because if the adsorbed species has a long residence time on the surface, mixing (as distinct from scrambling) can occur on the surface with a large nonlabeled population; equally even with no mixing a long residence time resulting in a slow desorption of the tracer over a period of, e.g., 40–60 min would not be detectable in our system where we are continuously monitoring the reactor effluent. It is worth noting that in the recirculating system used by Orita *et al.* (*3*) the methanol was collected over a period of 25

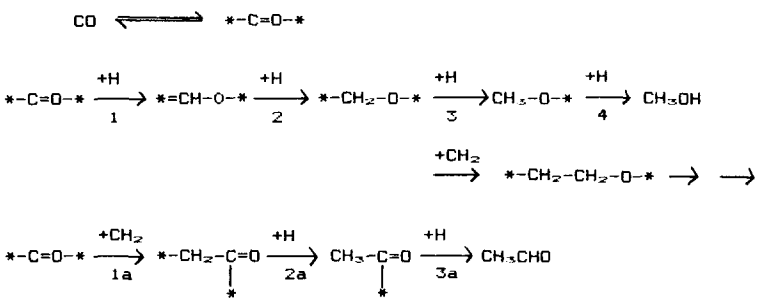


SCHEME 1

min before analysis and so can detect the tracer even though it may desorb over a long period of time.

Figure 4 shows the variation with time of the hydrogen isotopes after the feedgas has been switched from carbon monoxide/[^{1}H]hydrogen to [^{2}H]hydrogen. At a space velocity of 1200 h^{-1} the catalyst bed is swept every 3 s; therefore even if every adsorption site, as measured on a freshly reduced sample, was occupied by hydrogen, all surface [^{1}H]hydrogen should be replaced by [^{2}H]hydrogen in less than 10 s (assuming a facile adsorption/desorption equilibrium, which would be expected for hydrogen at 523 K). However, [^{1}H]hydrogen is still present after 45 min and peaked for a 5-min period when the amount of [^{1}H]hydrogen present in the gas stream was equivalent to the amount of [^{2}H]hydrogen. Therefore the hydrocarbonaceous deposit acts as a reservoir for surface hydrogen. This was confirmed by taking the catalyst into a nonsteady-state regime where the deposit was building up and then back into a stream of [^{2}H]hydrogen. In this case the amount of [^{1}H]hydrogen present is considerably smaller and hence the output peaks and declines to below the level reached after 45 min when the catalyst had been in a full steady-state regime, in less than 5 min. Clearly the role of the surface deposit in hydrogen transfer is difficult to prove unambiguously and the present study has not provided a clearcut answer: however, it has, we believe, added to the wealth of circumstantial evidence that the surface deposit is a reservoir of hydrogen which is supplied to the reactive intermediates.

In conclusion we may postulate two mechanistic schemes to accommodate the above results. Scheme 1 represents the formation of hydrocarbons. The first step, (a), dissociation of carbon monoxide, is the usual starting requirement and indeed at first sight it is needed to explain the scrambling of the desorbed and unreacted carbon monoxide; however, it is possible for there to be scrambling, in the absence of dissociation, by a concerted mechanism and this route should not be discounted. In recent studies (*9*) it has been suggested that on rhodium catalysts there is limited dissociation of adsorbed carbon monoxide but that the carbon produced in this way may also be unreactive. Recent chemisorption studies (*10*) also suggest that adsorbed carbon monoxide may scramble but not dissociate. Therefore we propose that pathway (b) is at least as likely as pathway (a). Step 2 represents the formation of the residue: its position cannot be absolutely determined but it is highly hydrogenated (*4*) and is not mononuclear (*4, 7*); therefore it cannot be far from that proposed. In step 4 addition of a CH_2 unit rather than hydrogen allows the formation of higher hydrocarbons. Scheme 2 represents the formation of oxygenates. Note that the adsorption site for carbon monoxide is not necessarily the same as that in Scheme 1; in fact if the scrambling of carbon monoxide is via a nondissociative mechanism, then the adsorption site which leads to alcohol for-



SCHEME 2

mation must be different to allow for the absence of scrambling in methanol as found by Takeuchi and Katzer (*2a*). The first step, we suggest, is the important one with respect to whether an alcohol or aldehyde is formed; reaction with H results in an alcohol while reaction with CH_2 results in an aldehyde. A similar scheme for aldehyde production has been proposed by Tamaru *et al.* (*3b*). Higher homologs can be produced by reaction with CH_2 rather than hydrogen in step 3 or 2a. It is important to note that the hydrocarbonaceous residue is the source of hydrogen and CH_2 units under reaction conditions. Clearly if these mechanisms are correct then the deposit, which is often considered detrimental to the catalyst, is in fact central to the catalysis.

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