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separate layers of noble metals in pellets,[112] or separate layers of washcoats, each containing one noble metal, on a honeycomb support. Segregation can be obtained on a macroscale by using separate pellet beds in series, or separate honeycombs in series, each containing one noble metal.

A segregation arrangement where the exhaust gas first contacts Pt before contacting Rh or Pd has been suggested by Hegedus et al.[112] in order to increase the resistance of the catalyst to lead deactivation. The Pt catalyst produces SO_3 from SO_2 in the exhaust under oxidizing conditions which fixes the lead as a sulfate before it contacts the Pd or Rh and to some extent the Pt itself.

Segregation has been suggested for kinetic reasons. A system where the exhaust gas of near stoichiometric composition first contacts Rh before it contacts Pt in order to prevent NH_3 formation has been proposed.[56,58,93,113]

A dual system of Pd followed by Pt–Rh has been suggested for the purpose of lowering the use of Pt–Rh in TWC catalyst systems.[114]

Segregation can be used so that each noble metal can be supported on an optimum support for that particular metal. For example, one may want to employ CeO_2 in a Pd–Al_2O_3 catalyst to increase the dispersion of Pd at high temperatures, or to use Pt–Al_2O_3 without CeO_2 so as to prevent the dispersion of Pt produced by CeO_2,[50] and as a result to increase alkane oxidation activity. One may want to employ Rh on a support such as zirconia, α-alumina, or doped γ-alumina in order to prevent Rh loss by dissolution into the support in a high-temperature oxidizing atmosphere.[101]

Conclusion

This paper has described the behavior of Pt, Pd, and Rh in some of the simple catalytic reactions of interest in auto exhaust catalysis as observed in laboratory experiments and reported in the literature. These experimental results have been a most valuable guide in formulating new catalyst systems that have improved catalyst durability, that make efficient use of noble metals, and that enable vehicles to operate at high fuel economy.

However, the use of the numerical values of the rate constants found in the laboratory for simple two-component reactions to predict the rates of oxidation and reduction in actual vehicle use is not feasible. This is because many of the catalytic reactions described above are occurring simultaneously, and a description of the species on the catalyst surface as a function of temperature, and gas-phase composition, which can change rapidly from oxidizing to reducing and back, has yet to be obtained. For this reason, the kinetic expressions used to model catalytic behavior on the vehicle have been obtained by using a laboratory flow reactor with a simulated exhaust gas. The exhaust gas composition and its cyclic variation, the temperature, and the space velocity have been varied over a wide range as expected in practice. The resultant kinetic expressions have numerous empirical constants that were computer-evaluated by optimization procedures.[37,115–117] This work consumed 15–20 man-years.

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Catalytic Site Requirements for Elementary Steps in Syngas Conversion to Oxygenates over Promoted Rhodium

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(Received: December 20, 1985; In Final Form: March 24, 1986)

Following P. H. Emmett's pioneering work, much research was focused on the mechanism of Fischer–Tropsch catalysis, and it has been discovered that certain base metal ions promote the activity and selectivity of Rh metal to catalyze the conversions of CO + H_2 to aldehydes and alcohols. Recent IR, Mössbauer, and EXAFS evidence in conjunction with catalytic tests suggests that the highly oxophilic ions Mn, Ti, Zr, and Nb, when located at the Rh surface, enhance CO dissociation, possibly through direct interaction with the oxygen atom of tilted adsorbed CO. A different mechanism emerges for Fe and Zn ions. These seem to block sites, thus inhibiting the formation of bridging CO and its dissociation to C + O. These steps are characterized by large ensemble requirements. Remarkably, the rate of CO insertion on Rh appears enhanced but the rate of hydrogenation is markedly suppressed by Zn. Consequently, the hydroformylation of olefins and the synthesis of methanol are efficiently catalyzed. This result suggests that the latter reactions require only very small Rh ensembles; possibly they are catalyzed by single Rh atoms.

Introduction

Following the pioneering work by Paul Emmett and his associates,[1,2] numerous studies have been done to unravel the elementary steps of hydrocarbon synthesis on Fischer–Tropsch catalysts such as Fe, Ni, Co, and Ru.

At present there appears to be a fair consensus that the following steps are involved:[3,4]

(1) Dissociation of H_2

$$H_2 \rightarrow 2H_{ads} \tag{1}$$

(2) Adsorption of CO and the dissociation

$$CO \rightarrow CO_{ads}$$

$$CO_{ads} \rightarrow C_{ads} + O_{ads} \tag{2}$$

(3) Reaction of adsorbates with each other, resulting in $CH_{x,ads}$,

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CO_2, H_2O, $CH_{x,ads}$ followed by formation of methyl groups and methane

$$CH_{x,ads} + (3 - x)H_{ads} \rightarrow CH_{3,ads}$$

$$CH_{3,ads} + H_{ads} \rightarrow CH_4 \qquad (3)$$

(4) Chain propagation, e.g., by insertion of $CH_{2,ads}$ in a $CH_{3,ads}$–M bond

$$CH_{3,ads} + CH_{2,ads} \rightarrow C_2H_{5,ads} \qquad (4)$$

and repetition of this step with longer alkyl groups

$$C_nH_{2n+1,ads} + CH_{2,ads} \rightarrow C_{n+1}H_{2n+3,ads} \qquad (5)$$

(5) Termination either by β-hydrogen abstraction, leading to α-olefins

$$C_nH_{2n+1,ads} \rightarrow C_nH_{2n} + H_{ads} \qquad (6)$$

or by hydrogen addition, leading to paraffins

$$C_nH_{2n+1,ads} + H_{ads} \rightarrow C_nH_{2n+2} \qquad (7)$$

The relative chances for either of these termination steps depend on the catalyst and can be influenced widely by other variables including promoters and reaction conditions (space velocity, temperature, pressure, CO/H_2 volume ratios).

Even for this relatively simple case of hydrocarbon synthesis, it is not certain whether all steps mentioned proceed on the same site or whether surface migration of an intermediate occurs between the elementary steps. In Emmett's pioneering work,[1,5] isotopic labeling was used to study the reaction mechanism. In those days only C-14 labeled molecules were available and isotopic enrichment was low. At present C-13 labeled molecules with high enrichment are available and have widely been used to clarify the mechanism of the Fischer–Tropsch process. Researchers at Koninklijke/Shell-Laboratorium, Amsterdam,[6,7] found by precovering Ni or Ru with C-13 atoms that in the synthesis of hydrocarbons the dissociative adsorption of CO is essential and that C-13 atoms carrying no oxygen are readily built in the growing alkyl chains. By combining in situ FTIR with C-13 labeling, Tamaru et al.[8] confirmed that all hydrocarbon molecules are formed via dissociatively adsorbed CO. It follows that the most demanding step of Fischer–Tropsch synthesis as regards site requirement is CO dissociation, which needs a fairly large ensemble of metal atoms, to accommodate both the carbon and oxygen, for instance on two adjacent Freundlich sites. It can be assumed that sites which are able to catalyze this critical step would also be able to dissociate H_2 and form C–H bonds ($CH_{x,ads}$) and to manage CH_2 insertion into M–alkyl bonds and the termination steps.

The classical Fischer–Tropsch catalysts Fe or Co, usually promoted with alkali metal and alumina, convert part of the syngas to primary alcohols and aldehydes. Addition of an α-olefin with n carbon atoms to the syngas results in an enhanced formation of the aldehyde with $n + 1$ carbon atoms, i.e., hydroformylation

$$C_nH_{2n} + H_2 + CO \rightleftarrows C_{n+1}H_{2n+1}CHO \qquad (8)$$

can take place under the conditions of the Fischer–Tropsch process and was indeed first discovered in this way by Roelen and Büchner[9] in 1938. The term "hydroformylation" was coined much later.

TABLE I: Characteristics of the SiO_2-Supported Rh Catalysts

catalyst (atomic ratio)	Rh metal loading, wt %	Rh dispersion	
		D[CO/Rh][a]	EM,[b] Å
Rh	4.0	0.32	30–40
	2.0	0.38	30
Re–Fe	4.0		
(1:0.1)		0.43	
(1:0.3)		0.28	25
(1:0.5)		0.23	30
Rh–Zn	4.0		
(1:0.3)		0.19	30
Rh–Mn	4.0		
(1:1)		0.34	40
Rh–Ti	4.0		
(1:1)		0.46	30
Rh–Zr	4.0		
(1:1)		0.38	35

[a] Rh dispersion determined from CO chemisorption at 25 °C. [b] Average Rh particle size estimated from electron microscopy.

The involvement of sites of a nature different than those required for hydrocarbon synthesis has been discussed for the formation of oxygenates. In particular, a high yield in alcohols and aldehydes has been found in the trend-setting work of Wilson et al. at Union Carbide in 1975[10] with rhodium catalysts. Among the group VIII (groups 8–10)[40] metals, Rh is unique in its ability to catalyze predominantly the formation of C_2–oxygenates from CO + H_2, and numerous studies have been made in recent years in view of the value of these oxygenate products. One of the present authors[11] observed (Table I) that highly dispersed Rh prepared by decomposing $Rh_4(CO)_{12}$ on ZrO_2, TiO_2, or La_2O_3 is a particularly effective catalyst for the formation of ethanol, but on ZnO and MgO methanol is predominantly formed, and on SiO_2 and Al_2O_3 hydrocarbons prevail in the reaction product. High yields of ethanol and higher alcohols with up to eight carbon atoms are achieved with SiO_2-supported Rh catalysts promoted with Mn and Mo,[12] suggesting that under these circumstances an alkyl chain growth takes place very similar to that which leads to hydrocarbons. Recent studies demonstrated that early transition metals such as Mn,[10a,13] Ti, and Zr[14] (existing most likely as oxides on the reduced Rh catalysts) provide a significant enhancement of the CO conversion rate (ca. 10–50 times that with Rh/SiO_2), whereas the selectivity is still high for C_2–oxygenates. In contrast to these oxophilic metal additives the addition of Fe to Rh/SiO_2[11] does not influence the CO conversion rate, but it does affect the oxygenate selectivity, changing the product from a mixture of CH_3CHO and CH_3COOH to a mixture of EtOH and MeOH. The need to understand these promoting effects caused by metal ions or oxides forms a major challenge to fundamental research in this area of catalysis.

Ichikawa et al.[16] conducted ^{13}C labeling studies using enriched ^{13}CO and $^{13}CH_3OH$ and promoted Rh catalysts such as Rh–Ti/SiO_2. When the catalysts were precovered with $^{13}C_{ads}$ by means of the Boudouard reaction

$$2CO \rightarrow C + CO_2$$

and subsequently exposed to unlabeled CO + H_2, a selective incorporation of the ^{13}C label into the methyl group of ethanol

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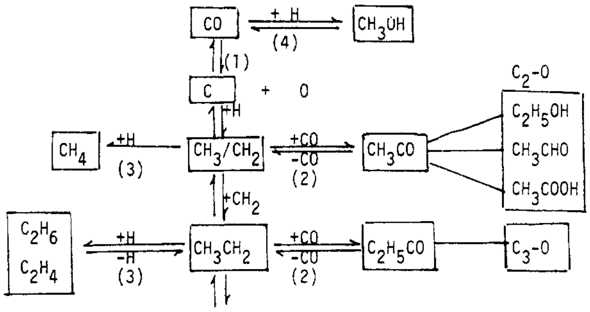

Figure 1. Scheme of elementary steps for syngas conversion to oxygenates and hydrocarbons: (1) CO dissociation, followed with formation of alkyl group; (2) CO migratory insertion in H alkyl group to form acyl species; (3) H addition and β-H elimination of surface alkyl group; (4) CO migratory insertion to metal–H, resulting in methanol.

and acetaldehyde was observed, but essentially no label appeared in the oxygen-carrying group of these molecules. These results confirm that methanol homologation is only a minor process in the formation of the C_2–oxygenates on promoted Rh catalysts. The virtual absence of any ^{13}C label in the methanol formed on these catalysts proves that this molecule is formed by hydrogenation of undissociated CO, as was shown earlier by Katzer et al.[17] These authors claimed that methanol and ethanol are formed on different sites. The mechanism which we propose for the production of oxygenates on promoted Rh catalysts is consistent with that previously reported by Tamaru et al. for unpromoted Rh/SiO_2.[18]

Consequently, a unifying general scheme for hydrogenation of CO over metal catalysts and including the formation of hydrocarbons and oxygenates consists of the following processes depicted in Figure 1:

(1) Dissociation of adsorbed CO to form CH_3/CH_2 (this step requires the largest ensemble of metal atoms) eventually followed by growth of alkyl chains via CH_2 insertion.

(2) Migratory CO insertion in surface–alkyl bonds, resulting in acyl species, as has been supported by spectroscopic studies.[19] Their hydrogenation leads to oxygenates, e.g., higher alcohols and aldehydes.

(3) The formation of hydrocarbons by hydrogen addition to or β-hydrogen elimination from surface alkyl groups.

(4) Nondissociatively adsorbed CO is hydrogenated to methanol (possibly via CO insertion in a M–H bond).

The problem will be addressed whether these requirements can lead to sites fulfilling all requirements for each elementary step or whether a bifunctional operation is more likely, which might be associated with the particular promoting effects caused by the different metal ions/oxides in the promoted Rh catalysts.

Thus, to understand the promoting role of metal ions or oxides which affect one or more of the elementary steps of the reaction scheme described in Figure 1, we have used TPR and IR spectra of chemisorbed CO to evaluate the dissociation of CO and the reactivities of various surface species on promoted Rh. Additionally, to study the relative activities for the competitive elementary steps, e.g., steps 2 and 3 of two termination processes, we have carried out ethylene hydroformylation as a diagnostic test reaction. In this way the effect of each metal additive on the CO insertion process can be identified. The catalyst site requirements for elementary steps in syngas conversion to oxygenate products catalyzed on promoted Rh will also briefly be discussed.

Experimental Section

1. Catalysts. SiO_2-supported Rh catalysts were prepared by a conventional impregnation method. SiO_2 gel (Carb-o-sil 300 and 60–80 mesh granule, Davison #62, surface area = 260–280 m^2/g) was impregnated with $RhCl_3 \cdot 3H_2O$ (Johnson-Matthey Inc.) and $MnCl_2$, $FeCl_3 \cdot 6H_2O$ (Merck Chem. Reagent Co.), and $ZnCl_2$ (Mallinckrodt, Inc.) from methanol solutions. After removal of the solvent, the impregnated catalysts were reduced in flowing H_2 (1 atm, 35–40 mL/min) at a temperature increasing from 200 to 400 °C and then held at 400 °C for 6 h, prior to the CO + H_2 and/or hydroformylation reactions. The Rh dispersion was determined by adsorption of CO and the metal particle sizes by electron microscopy. The relevant data are compiled in Table I. For IR observation, the samples were dried and pressed into a disk wafer of 20 mm diameter (70 mg each), which was also reduced in flowing H_2 as above. After cooling down to room temperature, H_2 was replaced by argon and the sample disk was passivated by introducing several small air pulses and stored in air. Each catalyst is rereduced in the IR cell or in the catalytic reactor in a H_2 flow at 400 °C for 2 h, prior to admitting the gas to be tested.

2. CO Hydrogenation and Olefin Hydroformylation. Hydrogenation of CO and hydroformylation of ethylene were carried out in a flow reactor of Pyrex glass (inner diameter = 6 mm, length = 200 mm) in which 0.4–0.5 g of catalyst was charged. A gas mixture of CO, H_2, and/or ethylene (1:1:1 vol ratio) was introduced by flowing at 30–100 mL/min and 150–220 °C. The oxygenated products such as MeOH, EtOH, CH_3CHO, C_2H_5CHO, and C_3H_7OH were dissolved in a water-trap (25 mL H_2O) by bubbling the effluent gas. They were analyzed by FID (flame ionization detector) GLC using a Porapak P column (4 m, He flow) at 165 °C. The effluent gas is analyzed by a gas/liquid chromatograph, Hewlett Packard 57909, using a capillary column, "Pona" (50 m, diameter = 0.2 mm) for the separation of C_1–C_5 hydrocarbons by programmed temperature control from −40 to 70 °C. For a series of the SiO_2-supported Rh and Rh–Zn catalysts, the conversion of CO and ethylene, the product yields (mmol/min/g of catalyst), and the selectivities based on the consumption of CO or C_2H_4, respectively, were measured at a standard set of operation conditions.

The gases C_2H_4 (Union Carbide, CP grade), H_2, CO, and CO + H_2 (Mattheson Gas Products Inc.) had a purity higher than 99.9 vol % and were pretreated with deoxo-trap (Mn/MnO) and MS-5A trap to eliminate oxygen, moisture, and possible carbonyls such as $Fe(CO)_5$ and $Ni(CO)_4$.

3. TPR Studies. A pulse-reactor test unit was constructed, consisting of a pulse injection valve (1–3 mL, STP), a microreactor (using a catalyst charge of 0.1–0.5 g), and a GC mass spectrometer with a 1-m column. A CO/Ar pulse was injected in the He flow passing over the catalyst, the Ar serving as internal reference. The uptake of CO and the formation of CH_4, H_2O, and CO_2 were then determined quantitatively from the ratios of the MS peaks to the Ar peak (m/e 40). After the catalyst had been exposed to CO at 200 °C for 2 h, it was cooled to 25 °C and exposed to H_2 at a flow rate of 50 mL/min, while the temperature was raised by 10 °C/min up to 500 °C.

Results and Discussion

1. Promoting Effects due to "Oxophilic" Ions. Results in Table II from ref 11 show that the oxidic promoters can be classified in at least two distinct groups which we shall further describe as "oxophilic" and "basic" promoters, respectively.

To study the role of oxophilic metal additives in affecting the CO dissociation, we have measured[20] the temperature at which CO_2 was produced due to the Boudouard reaction on reduced Rh catalysts. We found that the oxophilic promoters lower this characteristic temperature. Whereas the formation of CO_2 became detectable at 210 °C with unpromoted Rh/SiO_2, the temperatures in the presence of Mn, Ti, or Zr ions are as follows: Mn + Rh at 167 °C, Ti + Rh at 182 °C, and Zr + Rh at 175 °C. In the TPR profiles shown in Figure 2a–c, the peak for methane formation due to hydrogenation of adsorbed CO shifted to lower temperatures from 195 °C on Rh/SiO_2 to 136–165 °C on Mn

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TABLE II: Performance of Catalysts Prepared from $Rh_4(CO)_{12}$ Impregnated on the Different Metal Oxides Catalyzed in an Atmospheric CO–H_2 Reaction[a]

support	T,	CO conv,	selectivity (CE,[b] %)		
MO_x	°C	%/h	MeOH	C_2–O	HC
ZnO	220	1.6	94		4
MgO	220	2.6	88	2	7
CaO	230	0.8	92	1	2
La_2O_3	205	3.0	38	43	10
Nd_2O_3	210	3.8	24	47	21
ZrO_2	215	4.4	13	50	36
TiO_2	210	6.0	6	40	51
Nb_2O_5	195	5.8	7	39	51
MnO_2	205	1.2	4	25	63
SiO_2	235	1.7	tr[c]	6	92
γ-Al_2O_3	250	8.6	tr[c]	tr[c]	99

[a] Rh, 0.5 wt % loading from $Rh_4(CO)_{12}$; P_{CO} = 200 Torr, P_{H_2} = 450 Torr; a closed circulating reactor (volume: 400 mL STP) cited in ref 11. $Rh_4(CO)_{12}$ was impregnated from hexane solution at each oxide powder, followed by decomposing at 120–200 °C under vacuum. [b] CE = carbon efficiency; CE (%) = $100n_jC_j(\sum_j n_jC_j)^{-1}$; n_j = number of carbon atoms in the jth molecule; C_j = concentration of the jth product. C_2–O, C_2–oxygenates, mostly consisting of EtOH. [c] tr = trace.

TABLE III: IR Spectral Changes in CO Chemisorption on Oxophilic Metal Ion Promoted Rh Catalysts[a]

	ν_{CO},[d] cm^{-1}		
catalyst[b]	linear	bridging	ref
Rh/SiO_2	2040–2060 (S)	1880–1900 (S, Br)	22
$Rh–Mn/SiO_2$			
(1:1)	2045 (S)	1750 (S, Br), 1520	
(1:2)	2040 (S)	1700 (S, Br), 1520 (M)	
$Rh–Zr/SiO_2$			
(1:1)	2060 (S)	1830 (S, Br), 1670 (Sh)	
$Rh–Ti/SiO_2$[c]			this work
(1:1)	2075 (S)	1830 (S, Br), 1720 (Sh)	
$Rh–V/SiO_2$[c]			
(1:1)	2075 (S)	1760 (S, Br), 1650 (Sh)	
$Rh–Nb/SiO_2$[c]			
(1:1)	2080 (S)	1750 (S, Br), 1620 (Sh)	

[a] Rh loading, 4 wt %. IR in CO chemisorption: P_{CO} = 150 Torr, 25 °C. [b] Metal atomic ratios. [c] In a CO flow at 1 atm, 25 °C. [d] S = strong; Br = broad; Sh = shoulder; M = medium.

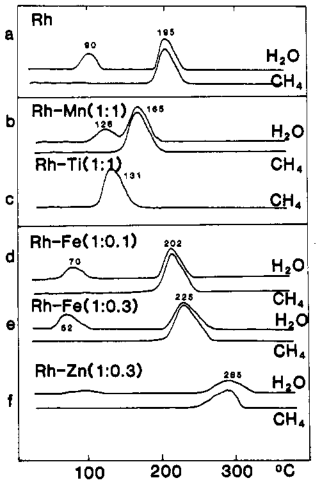

Figure 2. TPR profiles of CH_4 and H_2O formation in flowing H_2 on Rh, and oxophilic and base-metal-promoted Rh catalysts which were precovered with CO at 25 °C: a–e, ref 20.

+ Rh (Mn/Rh atomic ratios of 0.5:1 and 2.0:1, respectively), 165 °C on Rh + Zr (1:1), and 131 °C on Rh + Ti (1:1). For all samples, methane appears at the same temperature as H_2O. This confirms the model that the surface is predominantly covered with undissociated CO; its dissociation followed by fast hydrogenation of the fragments leads to CH_4 + H_2O.

The shifts in these peaks toward lower temperature for some promoted catalysts therefore indicate that these promoter ions enhance the CO dissociation and thus increase the rate of the CO conversion on Rh. In this category are the oxophilic promoters Mn^{2+}, Ti^{3+}, and, because of its very similar promoting action, Zr^{3+}/Zr^{4}. Here, integer numbers for the valencies of these ions are used only for convenience and in conformity with results by XPS[14a,21] and EPR,[13] although the actual charge of these ions on the Rh surface is presumably significantly lower.

A different type of evidence on the effects of promoter ions has been obtained by the IR spectra of chemisorbed CO. Two strong bands at 2040–2060 and 1880–1890 cm^{-1} are reasonably assigned to linear and bridging carbonyls, respectively, on Rh/SiO_2.[23] As shown in Table III, the stretching frequency of the bridging carbonyl is dramatically reduced in the presence of oxophilic metal promoters, e.g., 1760 cm^{-1} on Rh + Ti (1:1), 1670 cm^{-1} on Rh + Zr (1:1), and 1735 cm^{-1} on Rh + V (1:1), respectively. In particular, a very low frequency band appeared on Rh + Mn/SiO_2 catalysts at 1520–1540 cm^{-1} and a second band at 1870–1700 cm^{-1} (depending on the Mn contents).[22] In contrast to the bands of the bridging CO, those of linear carbonyl remain basically unchanged at 2030–2080 cm^{-1} upon adding the oxophilic metal promoters. This evidence is similar to the one found by Shriver for carbonyl complexes in the adduct formation with Lewis acids such as $AlBr_3$ and BF_3[24] or on γ-alumina.[25] These observations are interpreted in terms of C- and O-bonded CO. Likewise, Anderson et al.[26] recently showed on Pt + Ti alloys that CO is C bonded to Pt atoms but O bonded to Ti. We therefore assume a tilted mode of CO adsorbed on Rh (Pt) with coadsorbed oxophilic promoters, e.g., Mn and Ti ions on the same surface. This important function of the oxophilic promoter to enhance CO dissociation has been discussed in previous papers by us[22,27] but it is not necessarily the only function of these oxides.

By using high-pressure IR spectroscopy, one of the present authors obtained additional evidence[19,28] on the role of oxophilic promoters. They appear capable of stabilizing surface species which are thought to be precursors to C_2–oxygenates. The in situ IR spectra at 31 bar and 230–270 °C showed distinct bands on Rh + Mn (1672–1682 cm^{-1}), Rh + Ti (1620 cm^{-1}), and Rh + Zr (1654 cm^{-1}). These bands were growing with time and are ascribed to an acyl species CH_3CO_{ads} which is the primary intermediate resulting from CO insertion into metal–alkyl bonds. Bands at 1564 and 1442 cm^{-1} on Rh + Mn/SiO_2 and at 1547 and 1456 cm^{-1} on Rh + Zr/SiO_2 have also been observed during hydrogenation of CO; they are assigned to acetate, attached to the corresponding oxophilic metal ion. In contrast to this, only very weak bands are detectable on unpromoted Rh/SiO_2 at similar conditions of syngas conversion and temperature. These bands are located at 1658 (acyl), 1750, 1540, and 1435 cm^{-1}; the latter three bands are assigned to silyl acetate, possibly at the Rh/SiO_2 interface. The intensities of the IR bands due to the acyl and the acetate species on umpromoted Rh/SiO_2 are roughly 1 order of magnitude smaller than those of the same species in the presence of oxophilic promoters such as Mn.

In concluding we state that oxophilic promoters, probably located at the surface of Rh particles, enhance the CO dissociation rate and therefore also the steady-state coverage of the surface with alkyl groups. They also appear to stabilize acyl species which are the precursors for C_2–oxygenates. As a result, CO conversion is increased while the selectivity to oxygenates is high.

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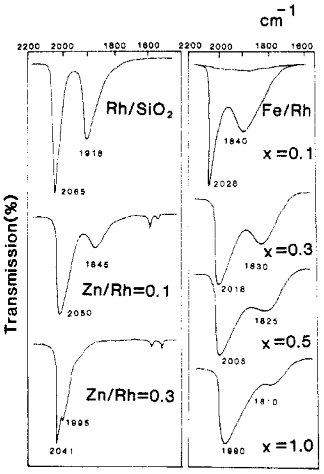

Figure 3. IR spectra of CO chemisorption on Rh/SiO$_2$, Rh–Zn/SiO$_2$, and Rh–Fe/SiO$_2$ (ref 22) catalysts having different metal contents (x = Fe/Rh); CO 1 atm, 25 °C; P_{CO} = 100–150 Torr, 25 °C.

2. Promoting Effects due to "Basic" Ions. A. Spectroscopic Evidence. In contrast to the oxophilic metal additives, the addition of Fe and Zn to Rh substantially suppresses the CO dissociation. In fact, CO_2 formation in flowing CO over the base-metal-promoted Rh catalysts started at higher temperatures, i.e., 225 and 235 °C on Rh–Fe/SiO$_2$[20] with Fe/Rh = 0.10 and 0.30, respectively, compared with 195 °C on Rh/SiO$_2$. Moreover, the CH_4 peak in the TPR profiles shifted by addition of Fe and Zn to Rh/SiO$_2$ toward higher temperatures as shown in Figure 2d–f.

Additionally, it was found that Fe added to Rh strongly suppresses the abundance of bridging carbonyl chemisorption on Rh surface,[22] as shown in Figure 3a. Along with this, the nature of CO chemisorption was studied by infrared spectroscopy on 4 wt % loading Rh–Zn/SiO$_2$ and increasing quantities of Zn. Infrared spectra for these samples in CO chemisorption are shown in Figure 3b. Two strong bands at 2065 (HF band) and 1918 (LF band) cm^{-1} for CO on Rh/SiO$_2$ are of comparable intensity, but with increasing Zn content the LF band attributed to bridging CO decreases significantly and the HF band broadens. A new band appears at 1995 cm^{-1} on the shoulder of the linear CO band at high Zn content, e.g., Zn/Rh = 0.3. Yates et al.[29] and Solymosi et al.[30] have previously pointed out that the chemisorption of CO on Rh can exert a dramatic influence on the state of Rh dispersed (0.5–1.0 wt. % Rh) on Al_2O_3. They claimed that twin carbonyls giving two bands at 2100 and 2030 cm^{-1} due to symmetric and asymmetric stretching vibrations are formed on isolated Rh$^+$ sites of a highly dispersed Rh crystallite possibly consisting of 10–20 Rh atoms. In our present Rh–Zn/SiO$_2$ catalysts the metal particles vary in size between 20 and 40 Å, as shown by TEM observation and a preliminary analysis of EXAFS data of the Rh–K edge.[31] These provided evidence for predominant Rh–Rh bonding in the catalysts before and after CO chemisorption. Therefore, we do not assume a disintegration of the Rh particles, but we attribute the dramatic change in the intensity ratios of bridging and linear CO (Figure 4) to a site isolation of the Rh ensembles as found earlier, e.g., for AgPd alloys.[32] In the case of the Zn promoter it appears likely that an incomplete overlayer is formed with the Zn ions, possibly located on the Freundlich sites of the Rh surface. In this arrangement a high coordination between Rh and Zn is achieved. On such a surface the bridging sites would be blocked with Zn so CO could be confined to the linear mode. This interpretation is in accord with studies of CO on Pd–Ag and Ni–Cu alloys[33] and Rh–Fe/SiO$_2$[20,22] as mentioned, and such a surface impedes CO dissociation, e.g., methanation, for which large ensembles of contiguous metal atoms are required.

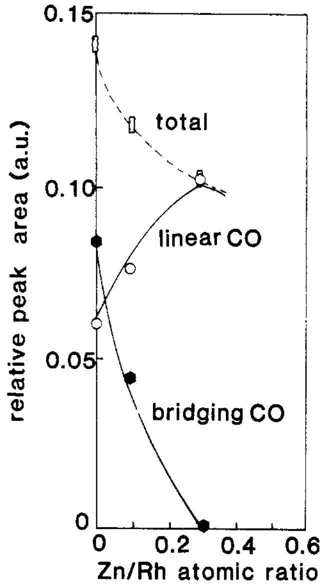

Figure 4. Relative concentrations of linear and bridging CO on Rh–Zn/SiO$_2$ depending on Zn content.

It is interesting that Fe ions also seem to act as breakers of ensembles, like Cu in Ni or Ag in Pd.[32,33] Indeed, the Mössbauer data show that Fe in Rh–Fe/SiO$_2$ is present as highly dispersed Fe^0 and Fe^{3+}.[35] On Fe metal surfaces CO dissociates readily due to the favorable situation on large Fe^0 ensembles.

The lower frequency linear band appearing at 1995 cm^{-1} on Rh–Zn/SiO$_2$ might be due to an electronic effect in supported Rh–Zn bimetal catalysts; an increased electron density due to the Zn could lead to enhanced back-donation from Rh to adsorbed CO.

Additionally, in the presence of Zn, weak but distinct bands are observed at 1620 and 1580 cm^{-1}. They may arise from CO which is C-coordinated to Rh and O-coordinated to Zn ions, acting as Lewis acid sites possibly located at the Rh/SiO$_2$ interface.

From a thermodynamic consideration on the reduction of Zn ions ($Zn^{2+} \rightarrow Zn^+$ or $Zn^{2+} \rightarrow Zn^0$) it is conceivable that the adsorbed Zn ions on the Rh surface could be reduced to Zn^+/Zn^0 under the strong reduction by H_2 flow at 400–500 °C, in forming Rh–Zn bimetal ensembles at the Rh surface. Recently, an in situ EXAFS study has been made[34] on Rh–Fe/SiO$_2$ and the results can be combined with those of a parallel Mössbauer study.[35] From these data, in particular the analysis of the EXAFS data on the K edges of Rh and of Fe, it appears that Fe is present most likely as Fe^{3+} in these catalysts with an atomic ratio of Fe/Rh = 0.3–1.0. The Fe^{3+} ions are directly bonded to Rh atoms. Their coordination number, i.e., the average number of nearest Rh neighbors to each Fe ion, is low, viz., 3–4, which suggests that the Fe ions are present on the surface of the Rh particles. It therefore appears reasonable to imagine that the Fe ions together with their counterions form an incomplete overlayer, as found previously for analogous, so-called SMSI systems.[36] In this overlayer the Freundlich sites of the Rh surface are preferred positions for the Fe^{3+} ions. In this way the adsorbed Fe ions block the sites for the CO chemisorption in the bridging or multiple bonding mode.

B. Ethylene Hydroformylation on Zn-Promoted Rh. The addition of base metals such as Zn is effective in blocking CO dissociation on the Rh surface, so that methanation and C$_2$–

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TABLE IV: Kinetic Values for Ethylene Hydroformylation on Rh/SiO_2 and Rh-Zn/SiO_2[a]

catal Rh-Zn/SiO_2, Zn/Rh atomic ratio	tot conv, %	activity, mmol/(min g of catalyst)		
		C_2H_5CHO	C_3H_7OH	C_2H_6
Rh/SiO_2	21.8	0.012	0.0003	0.185
0.05	25.7	0.105	0.0015	0.125
0.10	12.1	0.058	0.0020	0.046
0.20	8.8	0.042	0.0022	0.035
0.30	5.7	0.028	0.0035	0.018
0.50	3.3	0.015	0.0038	0.011

[a] SiO_2 Davison #62 SiO_2 gel (20 mesh) used for support. C_2H_4:CO:H_2 = 10:10:10 mL/min; 1 atm, 180 ± 2 °C. Zn/Rh = 0.05–0.5 atomic ratios. Rh, 4.0 wt % loading (0.50 catalyst).

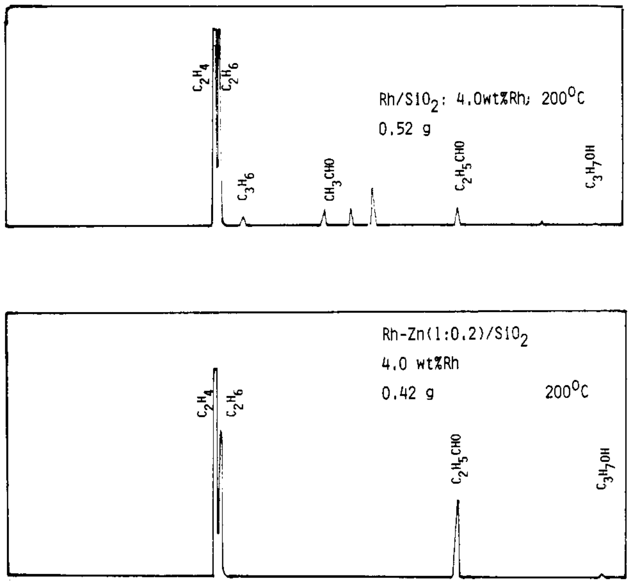


Figure 5. GLC spectra of products in ethylene hydroformylation reaction on Rh/SiO_2 (0.52 g) and Rh–Zn (1:0.2)/SiO_2 (0.42 g) catalysts at 200 °C. C_2H_4:CO:H_2 = 10:10:10 mL/min, 1 atm.

oxygenate formation are substantially suppressed on Rh–Zn/SiO_2 and Rh/ZnO, as presented in Table II. On the other hand, methanol formation in a CO–H_2 conversion is enhanced by the presence of Zn or Fe or Rh catalysts.[11,15,37] Owing to the complexity of CO hydrogenation, it is difficult to discriminate between the influence of promoters on the individual elementary steps for oxygenate formation as depicted in Figure 1. In the present research on the Zn-promoted Rh catalysts, we have therefore chosen to study the influence of Zn ions on hydroformylation. As the CO cleavage and the subsequent formation of surface CH_3/CH_2 groups are almost completely blocked by Zn, this test reaction enables us to observe the specific influence of Zn ions on the CO migratory insertion and the H addition to ethyl groups on Rh. As shown in Figure 5, the formation of hydrocarbons and C_2-oxygenates in the conversion of synthesis gas over Rh catalysts is completely suppressed by adding limited quantities of Zn to the Rh/SiO_2 catalysts; methanol is the sole product in the properly promoted catalysts. Upon addition of ethylene to synthesis gas, a very simple product distribution is obtained, viz. C_2H_6 and C_2H_5CHO with C_3H_7OH as a minor byproduct. Hydroformylation and hydrogenation are thus the predominant reactions. The most striking result of these studies is, however, the dramatic increase in hydroformylation yield brought about by the addition of Zn (Zn/Rh = 0.05–0.3 atom ratios) to Rh/SiO_2, while the simple hydrogenation is effectively suppressed. Consequently, the selectivity toward hydroformylation, expressed by the ratio of C_2H_5CHO to C_2H_6 is dramatically improved by a factor of 15.

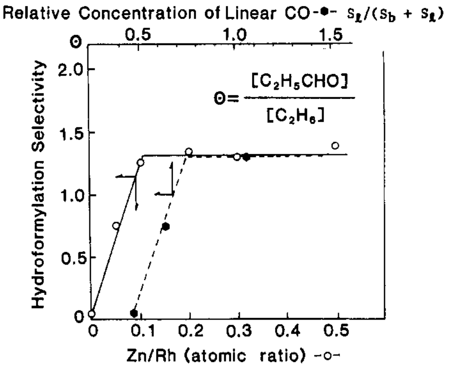
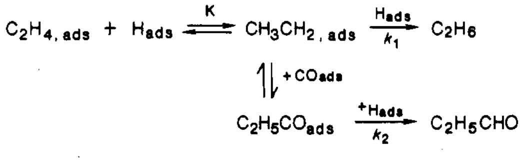


Figure 6. Hydroformylation selectivity of Rh–Zn/SiO_2 plotted against the relative concentration of linear CO, i.e., $S_l/(S_b + S_l)$ and Zn/Rh atomic ratio.

The selectivity is plotted in Figure 6, both against the Zn/Rh ratio and against the relative intensity of the linear CO band in the IR spectrum (data from Figure 4). The results show that Zn strongly blocks the simple hydrogenation of ethylene. Apparent activation energies for hydroformylation were found to be 17 ± 2 kcal/mol for Rh/SiO_2 and 14 ± 2 kcal/mol for Rh–Zn (1:0.3)/SiO_2, and those for hydrogenation of ethylene were 29 ± 1 kcal/mol for Rh/SiO_2 and 34–40 kcal/mol for Rh–Zn/SiO_2 (Zn/Rh = 0.05–0.2).

The preferential suppression of hydrogenation over hydroformylation due to Zn addition to Rh might indicate that Zn not only blocks sites for the dissociation of CO but also impedes the H_2 dissociation, while the CO insertion remains active. A decreased rate of H_2 dissociation on the surface which is mainly covered with linearly adsorbed CO and Zn ions and their counterions implies a low steady-state concentration of H_{ads} and, therefore, a low chance for addition of *two* H atoms in rapid succession to an adsorbed C_2H_4 molecule. This is, in the most primitive form (to avoid additional assumptions), illustrated by the following scheme



which leads to kinetic equations of the type

$$V_{C_2H_6} = k_1KP_{C_2H_4}[H_{ads}]^2 \propto [H_{ads}]^2$$

$$V_{C_2H_5CHO} = k_2KP_{C_2H_4}[CO_{ads}][H_{ads}] \propto [H_{ads}]$$

where $[CO_{ads}] = (1 - [H_{ads}]) \simeq 1$.

Thus, the simple hydrogenation of ethylene is effectively suppressed by decreasing the H concentration, resulting from a decrease of the effective ensemble size of Rh. This interpretation is also consistent with recent results[38] on Rh–Ir/SiO_2 catalysts.

The C- and O-bonded carbonyl, indicated by an IR band at very low frequency of the CO stretch near 1600 cm⁻¹, might provide a different clue to the high hydroformylation rate of the Zn-promoted catalysts. It is conceivable that the intrinsic rate constant of the CO insertion step in the above scheme is increased by the interaction of adsorbed CO with an electron acceptor. That this is indeed a very realistic probability has been proven in recent elegant work by Shriver,[39] who found a very dramatic increase

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in CO insertion rate for organometallic compounds when a Lewis acid interacts with the O atom of the carbonyl ligand.

Conclusions

The reaction network of growing chains on the surface of Fischer–Tropsch catalysts, which fascinated Emmett, can now be visualized as a chain growth initiated by dissociation of adsorbed CO. The sites where this occurs have to be large ensembles. This dissociation rate is enhanced by oxophilic metal ions or oxides. In combination with Rh they induce a CO adsorption mode with C and O bonding, which is an obvious precursor to CO dissociation. Three termination steps enable the alkyl groups to leave the catalyst surface. Two of them result in the formation of hydrocarbons, viz., H addition and β-H abstraction. The third termination "step" is initiated by CO insertion in the metal–alkyl bond resulting in the formation of an acyl group. Subsequently, hydrogen atoms are added to this acyl group, resulting in higher oxygenates (aldehydes and primary alcohols). This third termination mode is identical with the hydroformylation of olefins, once the adsorbed olefin has added one hydrogen atom. This CO insertion is favored by isolated metal atoms, e.g., Rh. Base metal additives such as Fe and Zn ions on the surface of Rh effectively block the large Rh ensembles required for CO dissociation and possibly H_2 dissociation. Their presence, therefore, results in a depression of methanation and of the simple olefin hydrogenation. A site isolation of surface Rh is also indicated by IR data which show that bridging CO chemisorption is completely suppressed when the catalyst contains Fe and Zn. Increased hydroformylation in the presence of Zn might be attributed to Zn ions, which induce a Lewis acid promoted CO insertion. Along with this, the addition of base metals such as Fe and Zn to Rh improves the methanol synthesis, possibly due to the same Lewis acid promotion favoring CO insertion into M–H bonds. In this case, formyl is an intermediate of methanol formation.

Acknowledgment. The authors are greatly indebted to the Monsanto Co. for a donation to the Catalysis Center at Northwestern University, and to Johnson Matthey Inc. for a loan of rhodium.

Registry No. CO, 630-08-0; Rh, 7440-16-6; Zn, 7440-66-6; Fe, 7439-89-6; Mn, 7439-96-5; ZnO, 1314-13-2; MgO, 1309-48-4; CaO, 1305-78-8; La_2O_3, 1312-81-8; Nd_2O_3, 1313-97-9; ZrO_2, 1314-23-4; TiO_2, 13463-67-7; Nb_2O_5, 1313-96-8; MnO_2, 1313-13-9; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1; Zr, 7440-67-7; Ti, 7440-32-6; V, 7440-62-2; Nb, 7440-03-1; ethylene, 74-85-1.

Hydrogen Control of Platinum-Catalyzed Skeletal Reactions of Alkanes: Selectivities and Surface Species

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(Received: November 14, 1985; In Final Form: April 1, 1986)

Conversions of *n*-pentane, *n*-hexane, 3-methylpentane, *n*-heptane, 2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,2-dimethylpentane, 3,3-dimethylpentane, *n*-octane, and 2-methylheptane to aromatics, skeletal isomers, C_5-cyclic products, and fragments were studied on Pt black catalysts and compared to each other. Yields of these skeletal reactions show maxima as a function of the hydrogen pressure between 5 and 60 kPa (35 and 450 Torr) hydrogen pressure. Low hydrogen pressures favor highly dehydrogenated surface intermediates leading to aromatization and/or hydrogenolysis. Under higher hydrogen pressures, C_5-cyclic intermediates prevail: these give cyclopentane and/or skeletal isomers. Radiotracer studies confirm that the main route of skeletal isomerization involves C_5-cyclic intermediates. A new type of hydrogenolysis, "C_5-unit splitting", is reported. Comparison of the present results with single-crystal data by Somorjai et al. permits us to suggest that the hydrogen control of the selectivities by controlling the surface intermediates may be valid for both types of catalysts.

Introduction

The mechanisms of skeletal reactions—formation and rupture of C_5-ring, aromatization, isomerization, and hydrogenolysis—over dispersed and single-crystal Pt catalysts have been discussed extensively during recent years; still, there is no consensus on this question.[1] Hydrogenolysis likely involves multidissociated intermediates attached to the catalysts via more than one C atom of the alkane.[2] Two of the present authors reported evidence that—at least over monofunctional Pt catalysts—aromatization involves dehydrogenation into di- or trienes followed by ring closure.[3,4] Gault and his school postulated at least four different surface intermediates for C_5-cyclization and the related isomerization, all of them being greatly dehydrogenated.[1b,5] This concept was seriously criticized; instead, the loss of one H atom from each carbon atom to form a C_5-ring was suggested to be sufficient.[6] The role of surface hydrogen for such "associative" surface species was first stressed by Liberman.[7] We also suggested earlier[8,9] a less dehydrogenated, flat surface intermediate for the C_5-cyclic reaction. The presence of a tertiary C atom in the molecule would facilitate the formation of the necessary surface species; this route was also supported by the predominance of *cis*-dimethylcyclopentanes among the products of cyclization.[9] The occurrence of a parallel C_5-cyclization via more dehydrogenated intermediates at lower hydrogen pressure has also been pointed out.[1a,d,6,8] All these experiments were carried out in a large excess of hydrogen (1:5 to 1:200) and with total pressures up to 1 bar.

The other mechanism of isomerization, the so-called bond shift[10] or C_3-cyclic route,[11] has also been disputed. Our previous results are in agreement with the intermediate proposed by McKervey

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