

The Role of Promoters in CO/H₂ Reactions: Effects of MnO and MoO₂ in Silica-Supported Rhodium Catalysts

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Addition of manganese and molybdenum compounds to silica-supported rhodium catalysts results in a significant increase in their activity for synthesis gas conversion. The location of these promoter elements and their role in the CO/H₂ reaction have been studied by various techniques. The available evidence suggests that manganese and molybdenum oxides partly cover the surface of the rhodium crystallites, thereby forming mixed oxides containing Me-O-Rh bonds, which cannot be completely reduced by treatment with hydrogen at 500°C. A possible role of these mixed oxides is to weaken CO chemisorption, thereby increasing the surface concentration of hydrogen atoms. © 1985 Academic Press, Inc.

INTRODUCTION

Supported metal catalysts are used in a variety of processes in the chemical and petroleum industries. In addition to an active metal and a support, industrial catalysts often contain a number of secondary components known as promoters. Promoters are additives which, although themselves inactive, improve the activity, the selectivity, or the stability of the unpromoted catalyst (1). The term promoter is usually restricted to compounds which are added in small amounts. In recent years it has become evident that the support may also affect the performance of the active metal (2). Unfortunately, the role of promoters and supports in catalysis is only poorly understood. A better insight into the ways in which secondary components influence the behavior of an active metal may lead to significant improvements in the preparation of supported metal catalysts.

Synthesis gas (CO/H₂) reactions offer a unique opportunity to study the role of pro-

motors and supports because they exhibit a wide variation in activity and selectivity depending on the composition of the catalyst. Kikuzono *et al.* (3) noted that the rate of methanol formation over Pd/SiO₂ catalysts can be significantly enhanced by the addition of alkali. Vannice and Garten (4) reported that Ni/TiO₂ is 10 times more active (per metal atom) than Ni/SiO₂ for the formation of methane. Moreover, Ni/TiO₂ also produces a larger fraction of heavier hydrocarbons. The addition of alkali to Fe and Ru catalysts leads to a decrease in hydrocarbon formation, but increases the selectivity toward the heavier hydrocarbons (5, 6). The most pronounced effects, however, have been observed with rhodium catalysts. Ichikawa (7, 8) found that the selectivity of rhodium-containing catalysts, tested under atmospheric conditions, depends markedly on the support. The observed products range from methanol as the principal product on Rh/ZnO and Rh/MgO, to ethanol as the main product on Rh/La₂O₃, and to methane and hydrocarbons on Rh/SiO₂. These effects were thought to be related to the basicity of the support. Researchers at Union Carbide observed that at higher pressures (70 bar) Rh/SiO₂

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can also produce C₂-oxygenates (ethanol, acetaldehyde, and acetic acid) with selectivities up to 80% (9). Moreover, addition of poorly reducible oxides such as MnO leads to a dramatic increase in activity (10).

The effect of Mn addition was studied by Wilson *et al.* (11), who noted that MnO cannot be reduced to the metallic state but is present as Mn²⁺ in the actual catalyst. ESR evidence indicated that the promoter element is in close contact with the rhodium crystallites. They postulated that MnO forms a mixed oxide with an oxidized form of rhodium. The formation of a mixed oxide would decrease the rate of CO dissociation, thereby reducing the amount of carbon on the catalyst and effectively increasing the active metal surface area. The kinetic model developed by these authors requires that (a) the surface of the catalysts be practically totally covered with carbon under the reaction conditions, and (b) for the addition of promoters to result in a 20-fold increase in the surface concentration of CO.

However, in the course of an *in situ* infrared study we found that (a) the surface of both catalysts is largely covered by CO under the reaction conditions, and (b) the concentration of adsorbed CO on the promoted catalyst is actually lower than on the unpromoted catalyst (12). In order to resolve these discrepancies we decided to investigate the role of promoters in Rh/SiO₂ catalysts in more detail. Two catalysts were used in this study: unpromoted Rh/SiO₂ (2.5 wt%) and an Rh-Mn-Mo/SiO₂ catalyst (2.5-0.3-0.3%), which was claimed to be active in a recent patent (13).

EXPERIMENTAL

Catalyst preparation. Catalysts were prepared by the incipient wetness technique using RhCl₃ · xH₂O, Mn(NO₃)₂ · 4H₂O, and (NH₄)₆Mo₇O₂₄ in aqueous solution. SiO₂ from Grace (Type SP2-261.359, 307 m²/g, 14-30 mesh) was used as support material. Impregnated catalysts were dried in flowing N₂ with a temperature program

ending with 2 h at 250°C and reduced in a flow of 10% H₂ in He, using a programmed temperature rise (2°C/min) starting at 25°C and ending with 1 h at 500°C. The catalysts thus prepared were passivated with 2% O₂ in He at 25°C and stored in an inert atmosphere. Before each experiment or analysis the catalysts were rereduced at 300°C for 1 h in a flow of 10% H₂ in He.

Characterization of catalysts. Electron microscopy was performed with a Philips EM 401 transmission electron microscope.

The rhodium content of fresh and spent catalysts was determined by atomic absorption spectrometry (AAS).

Reducibility of the catalysts was studied by temperature-programmed reduction (TPR) using the apparatus described in Ref. (14). Reduction took place with a flow of 5% H₂ in N₂ and a heating rate of 5°C/min. Positive rhodium ions were extracted from fresh catalysts with acetylacetonate (acac) under a N₂ atmosphere (10 ml acac for 1 ml of catalyst) and the resulting solutions were analyzed with a Kevex energy dispersive X-ray fluorescence spectrometer (excitation via a Sn secondary target).

The CO/H₂ reaction. Reduced catalysts were tested in a stainless-steel, single-pass, fixed-bed reactor, lined with copper to prevent metal carbonyl formation. In each experiment 2 ml of catalyst was diluted with 3 ml of SiC to minimize local temperature gradients. The products of the reaction were directly fed to a three-column GLC system via a heated sampling line and analyzed on-line (further details on the analytical system are given in Ref. (12)).

Ethane hydrogenolysis. Hydrogenolysis of ethane was carried out at atmospheric pressure in a stainless-steel flow reactor. A mixture of ethane (2.5%), hydrogen (12.5%), and nitrogen (85%) was used as a feed gas. Products were analyzed with a Hewlett-Packard 5710A gas chromatograph equipped with a Poropak Q column and a flame ionization detector.

Analysis of carbon on spent catalysts. The nature of the carbon-containing species

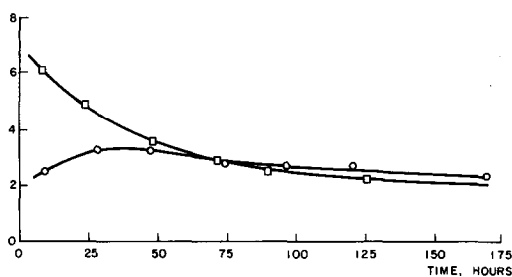


FIG. 1. Activity of promoted and unpromoted rhodium catalysts. Reaction conditions: $P = 10$ MPa; $\text{CO}/\text{H}_2 = 1$; $\text{GHSV} = 5000 \text{ h}^{-1}$. (○) Rh/SiO_2 ; $T = 250^\circ\text{C}$. (□) $\text{RhMnMo}/\text{SiO}_2$; $T = 210^\circ\text{C}$.

accumulating on the catalysts was analyzed by PCME (Pyrolysis Combustion Mass spectrometric Element analysis). The basis of this technique is the following: a small amount of sample (ca. 50 mg) is weighed accurately and placed in the first compartment of an oven. In the first stage of the analysis (the pyrolysis mode) the sample is heated in a stream of helium, using a temperature program starting at 25°C and ending at 1000°C . The gaseous pyrolysis products are oxidized in a second compartment of the oven with a mixture of helium and oxygen at 1000°C , and the combustion products (CO_2 and H_2O) are analyzed by mass spectrometry. In the second stage (the combustion mode) the sample itself is moved into the second compartment of the oven and any remaining carbon is burned off. PCME not only allows quantitative determination of elements (C, H, and also Cl, S, and N), but also provides information about the chemical nature of the products on the surface (from the C/H ratio and desorption temperature).

RESULTS

The CO/H_2 Reaction

The two catalysts, Rh/SiO_2 and $\text{RhMnMo}/\text{SiO}_2$, were tested for synthesis gas conversion in continuous runs lasting 168 h. Reaction conditions were: pressure 10 MPa, space velocity $5000 \text{ l (l cat)}^{-1} \cdot \text{h}^{-1}$ and $\text{CO}/\text{H}_2 = 1$. With a view to keeping the

conversion below 10%, the promoted catalyst was tested at a lower temperature than the unpromoted catalyst (210 vs 250°C).

The activity of both catalysts as a function of time-on-stream is shown in Fig. 1. The promoted catalyst is indeed much more active than the unpromoted catalyst. Using a value of 100 kJ/mol for the activation energy, it can be calculated that the promoted catalyst is almost 10 times more active after 24 h of testing. It is also apparent that the two catalysts do not deactivate in the same way. In the case of the promoted catalyst, a rapid initial decline is followed by a slow continuous decline. The unpromoted catalyst declines only slowly and even shows an initial increase; however, this is entirely due to an increase in methanol formation (methanol selectivity increases from ca. 50% initially to 77% after 168 h; see Table 2). Throughout the experiment the promoted catalyst remains considerably more active than the unpromoted catalyst, taking into account the difference in reaction temperature.

As illustrated in Tables 1 and 2, the selectivity also changes during the experiment. On the promoted catalyst, the selectivity to hydrocarbons increases as a function of time, mainly at the expense of formation of methanol and C_3^+ -oxygenates. The selectivity to C_2 -oxygenates shows a slight in-

TABLE 1
Selectivity of $\text{RhMnMo}/\text{SiO}_2$ as a Function of Time

	Selectivity ^a					
	8 h ^b	24 h	48 h	72 h	90 h	136 h
CH_4^a	6.0	6.6	7.8	8.5	9.3	10.0
C_2^+ hydrocarbons	5.3	5.8	5.7	6.1	8.5	9.0
Methanol ^c	12.0	11.4	9.5	9.3	9.2	9.3
Ethanol ^c	27.4	24.8	22.9	21.7	21.1	19.5
Acetaldehyde	3.0	3.8	4.6	7.8	6.9	8.1
Acetic acid ^c	9.0	20.1	23.8	24.0	25.9	27.3
C_3^+ oxygenates	36.7	27.5	25.7	22.6	19.1	16.8

^a Selectivities are expressed in percentage carbon efficiency.

^b Time-on-stream.

^c Esters were counted as alcohol + acid.

TABLE 2
Selectivity of Rh/SiO₂ as a Function of Time

	Selectivity ^a						
	9 h ^b	28 h	47 h	74 h	96 h	120 h	168 h
CH ₄ ^d	5.3	3.2	3.1	2.4	2.7	2.7	2.7
C ₂ ⁺ hydrocarbons	0.8	0.1	0.1	—	—	—	—
Methanol ^c	49.7	66.4	69.0	71.1	72.7	76.3	76.6
Ethanol ^c	27.2	22.1	19.9	18.6	17.4	15.1	14.7
Acetaldehyde	1.9	1.7	1.4	1.6	1.5	1.3	1.2
Acetic acid ^c	10.7	4.6	3.9	3.3	3.8	3.0	3.0
C ₃ ⁺ oxygenates	4.4	1.9	2.6	3.0	1.9	1.6	1.8

^{a-c} For footnotes see Table 1.

crease, but there is a clear trend from ethanol as the major product in the beginning of the run toward acetic acid and acetaldehyde at later stages. In the case of the unpromoted catalyst the selectivity to most products decreases in favor of methanol.

Separate experiments were conducted to investigate the CO hydrogenation activity of the promoter oxides themselves. Two catalysts, containing 5 wt% Mo/SiO₂ and 5 wt% Mn/SiO₂, respectively, were prepared and tested at 250°C and under otherwise identical reaction conditions. Both catalysts produced only traces of methane and methanol under these conditions. Moreover, a physical mixture catalyst, prepared by grinding Mo/SiO₂, Mn/SiO₂, and Rh/SiO₂ into particles <40 μm, mixing the resulting fines in a 1:1:1 ratio and pressing this mixture into larger particles (550–1200 μm), gave results which were similar to those obtained with the catalyst containing only Rh/SiO₂.

Ethane Hydrogenolysis

Previous investigations provided evidence for the hypothesis that the promoter oxides in promoted rhodium catalysts are located on the surface of the rhodium particles (11, 12). If so, we expect that a structure-sensitive reaction such as hydrogenolysis of alkanes will be significantly affected by the presence of a promoter oxide. This is indeed found to be the case (Fig. 2): on the unpromoted catalyst hydrogenolysis of ethane

has a lower activation energy and a lower preexponential than on the promoted catalyst. Furthermore, the promoter oxides themselves were found to be completely inactive for this reaction.

Electron Microscopy

Electron micrographs of the fresh and spent catalysts, the latter after 168 h reaction with CO/H₂, are shown in Figs. 3 and 4. A comparison of the two catalysts shows that the freshly reduced catalysts are very much alike: both exhibit rhodium particles with an average particle size of 2.0–2.5 nm. The particle size distribution of the promoted catalyst does not change at all during the reaction. The unpromoted catalyst does show some larger rhodium particles (10–40 nm) after prolonged reaction, but the bulk (>99%) of the small particles remains unchanged. These data should be treated with some caution since electron microscopy, by its nature, sees only a very limited part of the total catalyst surface. However, after analyzing a large number of micrographs we feel confident that the two catalysts do not differ significantly in either their particle size distribution or their resistance to sintering.

Determination of Rhodium Content

During an earlier study we found that rhodium carbonyl species can be formed at

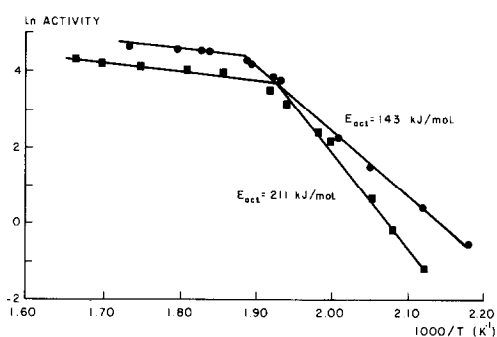


FIG. 2. Ethane hydrogenolysis over promoted and unpromoted rhodium catalysts. Reaction at atmospheric pressure: C₂H₆:H₂:N₂ = 1:5:34; GHSV = 20,000 h⁻¹. (●) Rh/SiO₂. (■) RhMnMo/SiO₂.

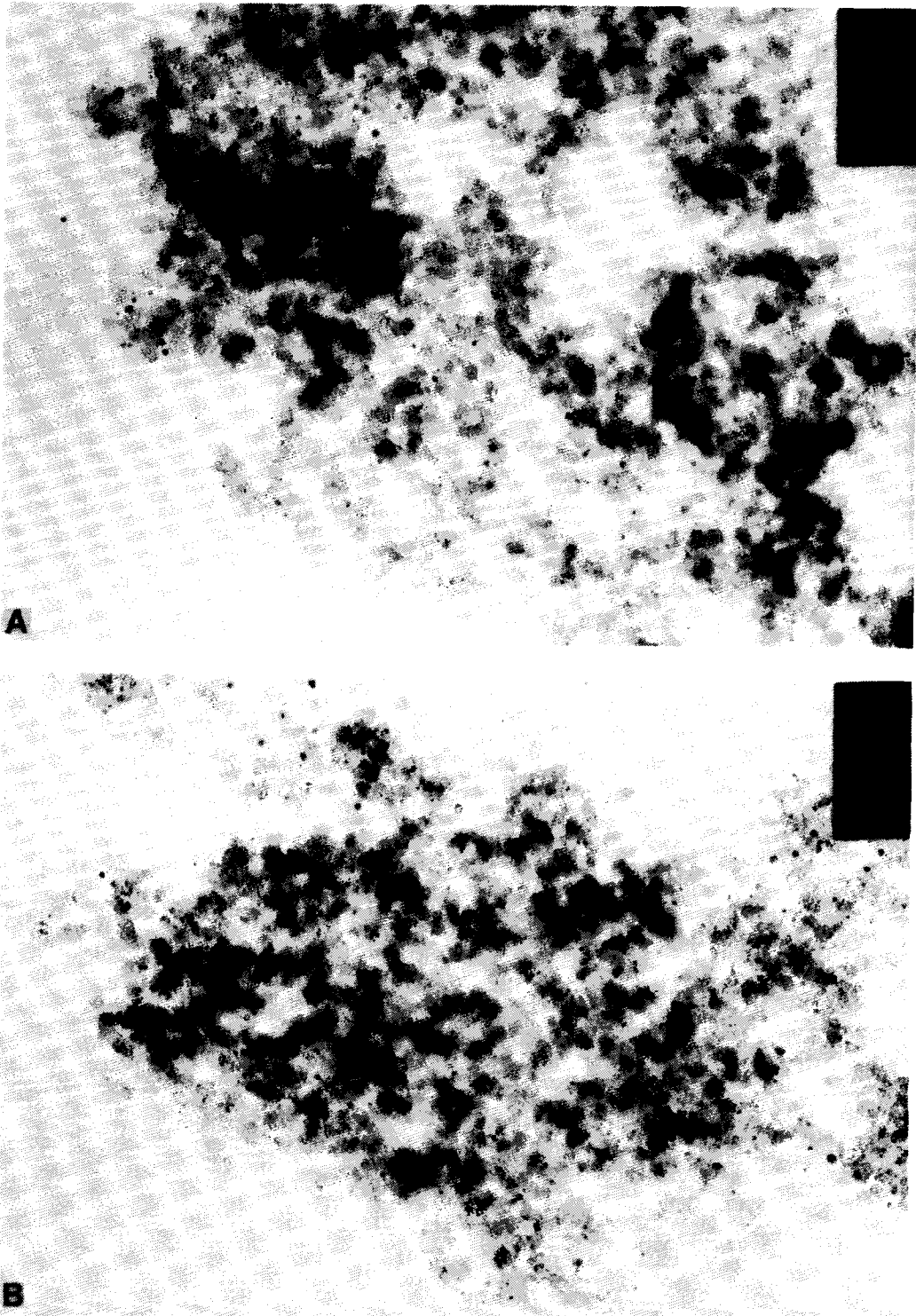


FIG. 3. Electron micrographs of RhMnMo/SiO₂ catalysts. (A) Freshly reduced catalyst and (B) after 168 h reaction with CO/H₂. Magnification 306,000 \times .

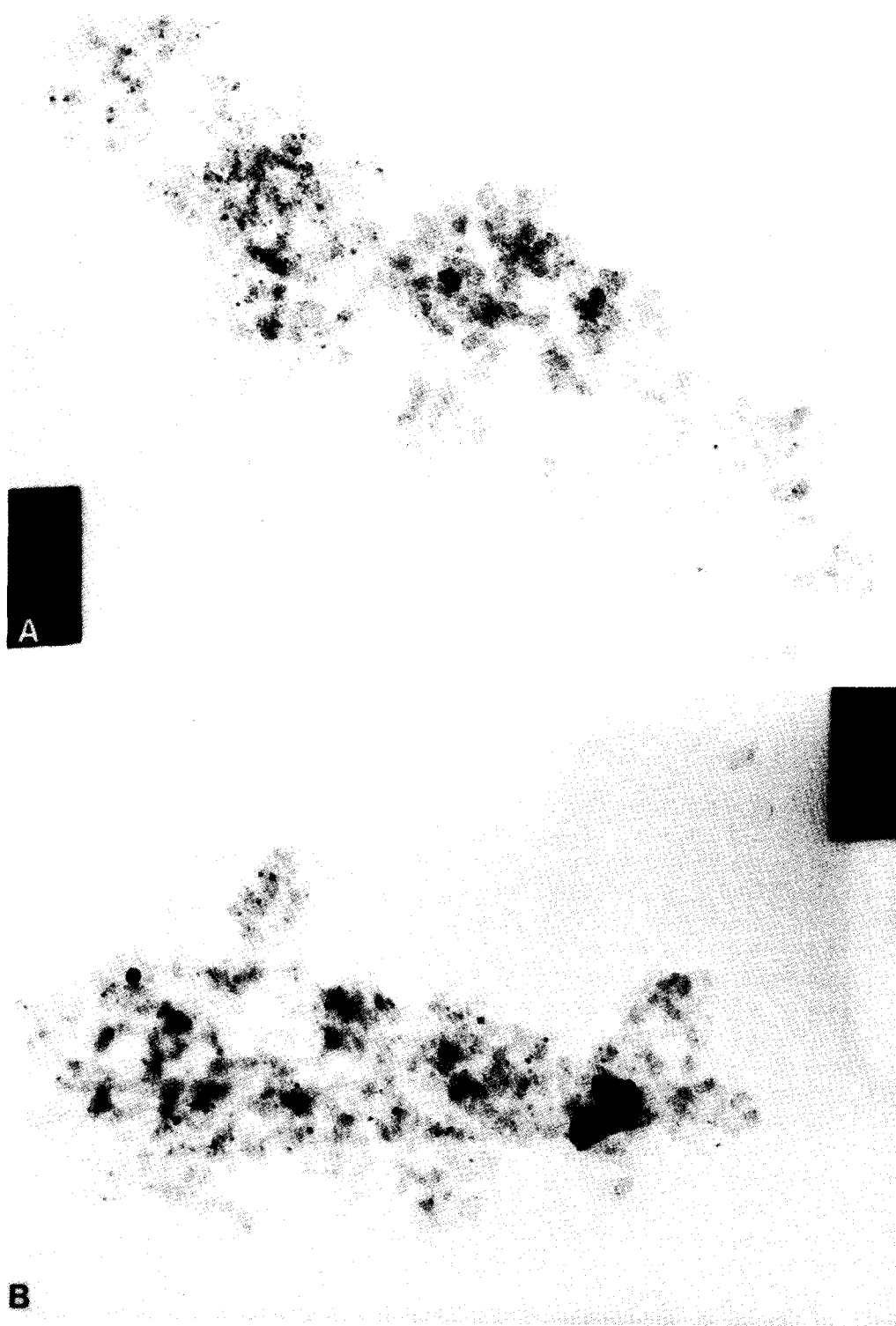


FIG. 4. Electron micrographs of Rh/SiO₂ catalysts. (A) Freshly reduced and (B) after 168 h reaction with CO/H₂. Magnification 306,000 \times .

TABLE 3
Rhodium Content of Fresh and Spent Catalysts

	Rh/SiO ₂ (wt%)	RhMnMo/SiO ₂ (wt%)
Unreduced	2.32 ± 0.12	2.34 ± 0.12
Reduced	2.44 ± 0.12	2.46 ± 0.12
After 168 h	2.33 ± 0.12	2.43 ± 0.12

low temperatures (298 K) and high CO pressures (12). Moreover, Vannice and Garten (4) have shown that formation of Ni(CO)₄ is 10 times less rapid on Ni/TiO₂ than on Ni/SiO₂, while Ni/TiO₂ is the more active catalyst. This suggests that the differences in activity may be due to the fact that the promoters inhibit the rate of carbonyl formation and therefore reduce metal loss. However, our AAS data (Table 3) show that, within the accuracy of the analysis, no rhodium is lost during reduction or during the reaction with synthesis gas (10 MPa, CO/H₂ = 1).

Analysis of Carbon-Containing Species on Spent Catalysts

The carbon content of both catalysts was measured after 24 and after 168 h of reaction. Heating the spent catalysts in helium from 25 to 1000°C produced a number of carbon-containing species, which can be divided into three groups (Table 4):

(i) A small amount of species desorbing at 200°C (ca. 0.05 wt%), which could be related to the formation of carbonates after adsorption of CO₂ from the air.

(ii) Species with a H:C ratio ≥ 2, desorbing at around 680°C. The amount of these species is related to the catalytic activity: it is initially higher on the promoted catalyst and it decreases with time. These products may be due to adsorbed intermediates and/or to relatively short hydrocarbon chains located on the support.

(iii) Species with a H:C ratio of 2, desorbing around 900°C. The amount of these species increases with time-on-stream on both catalysts. We assume that these are

hydrocarbons of very long chain length, which are built up during the reaction and cannot desorb under the reaction conditions. The existence of such long paraffinic chains is a familiar phenomenon in Fischer-Tropsch catalysis (15).

Following the pyrolysis treatment, the remaining carbon was removed by combustion with oxygen at 1000°C. On both catalysts a small amount of "elementary" carbon (C:H ratio > 10) was observed. After 168 h on-stream the amount of this "elementary" carbon corresponds to a Rh:C ratio of 1:0.3. However, since part of this carbon may have been formed during the pyrolysis stage, this number can only be used as an upper limit to estimate the amount of elementary carbon which was present on the catalyst surface.

TEMPERATURE-PROGRAMMED REDUCTION (TPR)

For the TPR experiments the catalysts were first reduced via a standard reduction procedure and then oxidized at 500°C for 1 hr in a stream of 5% O₂ in helium. TPR profiles of the two catalysts are shown in Fig. 5. Reduction of the promoted catalyst occurs at a significantly higher temperature than reduction of the unpromoted catalyst

TABLE 4
Analyses of Carbon-Containing Species on Spent Catalysts

	Rh/SiO ₂ (wt%)	RhMnMo/SiO ₂ (wt%)
"Carbonate"		
after 168 h	0.05 ^a	0.05
First desorption peak		
After 24 h	0.43	1.77
After 168 h	0.28	0.82
Second desorption peak		
After 24 h	0.48	0.19
After 168 h	0.80	0.82
"Elementary" carbon		
After 24 h	0.17	0.23
After 168 h	0.08	0.09

^a Weight percentage of carbon in sample.

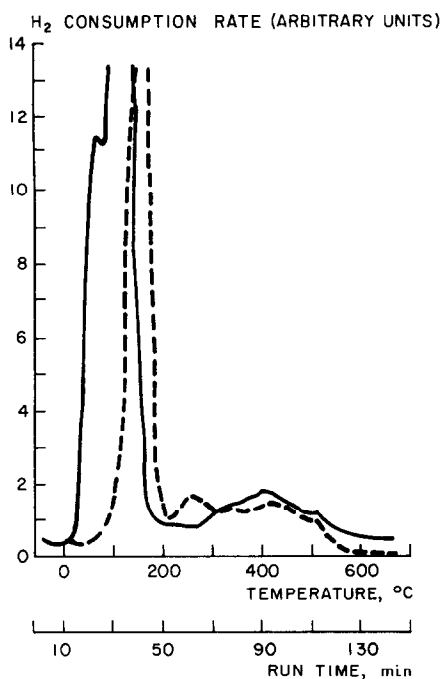


FIG. 5. TPR profile of promoted and unpromoted rhodium catalysts. (—) Rh/SiO₂ and (---) RhMnMo/SiO₂.

(166 vs 122°C). Unfortunately, the accuracy of the measurements is not sufficiently high to determine whether all the rhodium oxide is reduced to rhodium metal.

Extraction of Rhodium Ions

Acetylacetonone is known to form very stable complexes with positive metal ions. We therefore extracted the reduced catalysts with acetylacetonone, following the procedure used by Driessen *et al.* (16). X-Ray fluorescence spectra of the resulting solutions are shown in Fig. 6. Both catalysts were found to contain positive rhodium ions: in the case of the unpromoted catalyst the amount of rhodium ions corresponds to $4 \pm 1\%$ of the total amount of rhodium, while $15 \pm 3\%$ of rhodium ions can be extracted from the promoted catalyst. This shows that the promoters increase the number of extractable rhodium ions. It should be noted that, while Rh(I) is completely extractable under these conditions, Rh(III) may be partially unextractable.

DISCUSSION

The Location of the Promoter Oxides in RhMnMo/SiO₂ Catalysts

The first question we wish to consider concerns the location of the promoter elements. Results of an ESR study on a Mn-promoted Rh/SiO₂ catalyst led Wilson *et al.* (11) to suggest a close contact between

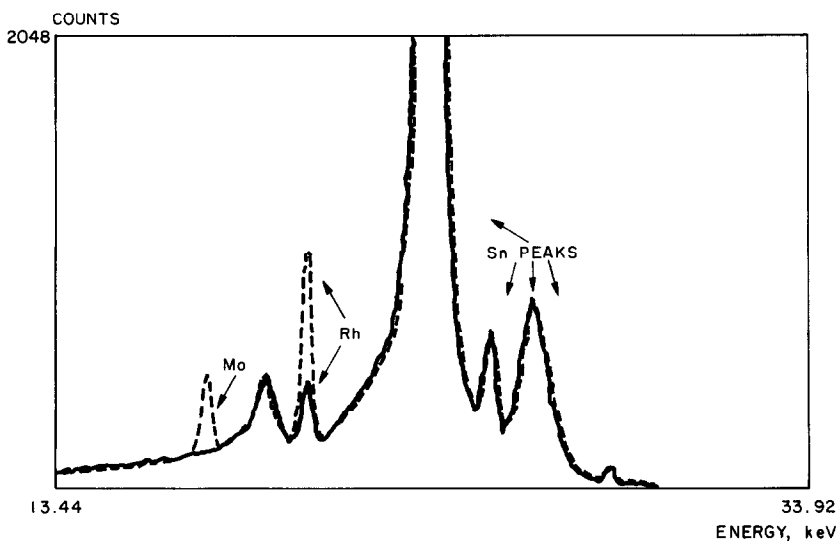


FIG. 6. X-Ray fluorescence spectra of solutions obtained by extracting rhodium catalysts with acetylacetonone. (—) Extract from Rh/SiO₂ and (---) extract from RhMnMo/SiO₂.

Mn^{2+} and the rhodium crystallites. In the course of an *in situ* ir study we observed that the intensity of the ir signal of adsorbed CO on a Mn- and Mo-promoted Rh/SiO₂ catalyst is considerably lower than on an unpromoted catalyst, both at room temperature and under reaction conditions (12). Since the two catalysts had approximately the same average rhodium particle size, the decrease in CO chemisorption strongly suggests that the promoter oxides partially cover the rhodium particles. In fact, it can be calculated that in order to decrease CO chemisorption to the extent observed in ir (by a factor of 2 to 3), the promoter oxides have to be spread over the rhodium surface as near-monolayers. The existence of such an intimate contact between rhodium and the promoter oxides was supported by a significant shift in the stretching frequency of both linear- and bridge-bonded CO (from 2050 to 2030 cm^{-1} and from 1900 to 1870 cm^{-1} , respectively, when comparing the unpromoted and the promoted catalyst) (12). The interaction of this shift would be in accordance with a reduced dipole-dipole coupling of adsorbed CO on promoted rhodium. A different model assumes that the oxygen atom of the Rh-C-O adsorption complex interacts with a contiguous manganese or molybdenum ion, leading to a somewhat tilted orientation of adsorbed CO. Spectroscopic data on such complexes show that the CO stretching frequency is lowered.

The present results do not permit us to decide between these models; they do show, however, that in the promoted catalyst rhodium and the promoter ions are in close contact on an atomic scale. This can be described as an overlayer of promoter and oxygen ions, covering some part of the rhodium crystals. The increase in the fraction of extractable rhodium ions could then be rationalized in terms of a stabilization of Rh^+ ions by the interaction of the overlayer with the metal surface. The overlayer might then be described as consisting of patches

of a mixed oxide. Rhodium ions are also present in unpromoted catalysts, and Huizinga (17) has argued that they are instrumental in the interaction between Rh metal particles and the supporting oxide.

The assumption that Rh ions are stabilized by the interaction with the promoter would not only explain the observed increase in reduction temperature, the shift of the ir bands and the differences in the fraction of extractable rhodium ions, but also the observed differences in ethane hydrogenolysis activity. In the case of the promoted catalyst, the active sites for this reaction are presumably ensembles of several contiguous Rh atoms. In the promoted catalyst part of the Rh metal surface is covered by an oxidic overlayer and hydrogenolysis will make use of mixed ensembles.

The spreading of an oxidic overlayer over a noble metal assumes a rather strong interaction between metal atoms and the ions of another transition metal, as this process has to compete with the formation of two separate phases. The electrostatic Madelung energy will be lower in the two-dimensional overlayer than in the bulk oxide. The idea of a strong mutual interaction between metal crystal and transition metal ions has, however, received considerable support in recent work on the metal-support interaction, in particular the so-called SMSI (strong metal-support interaction). TiO₂ is reduced to Ti₄O₇ which forms a semiconducting and a metallic phase (18), and there are strong experimental data proving that this oxide spreads over Ni and other transition metals forming incomplete overlayers. For oxides such as MnO and MoO₂, which form layer lattices, the loss in lattice energy is small if the layers are separated from each other. The existence of a mixed oxide phase becomes further understandable when considering the radii of the cations: $r(\text{Rh}^{2+}) = 0.086$ nm, $r(\text{Mn}^{2+}) = 0.080$ nm, and $r(\text{Mo}^{4+}) = 0.06$ nm. Mixed oxides of Rh and Mn and of Mn and Mo are known to exist (19).

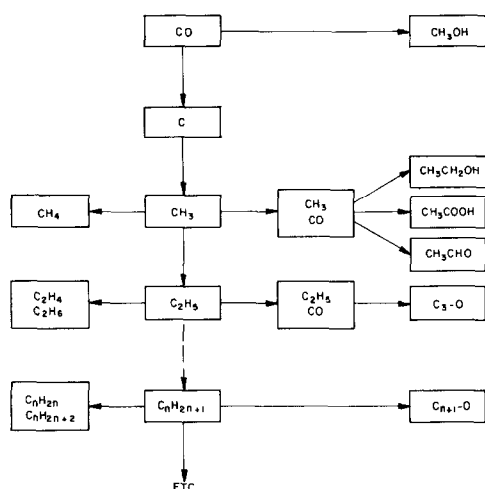


FIG. 7. Schematic model for the synthesis of hydrocarbons and oxygenates.

The Role of Mn and Mo Oxides in CO/H₂ Conversion

The promoting effects of MnO and MoO₂ can be rationalized by using the model of the surface described above.

First of all, the results described above eliminate some trivial effects. Electron microscopy has shown that the unpromoted catalysts have similar dispersions and are not much less resistant to sintering than the promoted catalysts. Elemental analyses of fresh and spent catalysts revealed that loss of rhodium metal does not play a significant role. The amount of carbonaceous residues on the promoted catalyst was not lower than on the unpromoted catalyst; a lower quantity would have been expected on the model of Wilson *et al.* (11). Discounting such effects, we believe that the increase in activity on the promoted catalysts is related to an enhanced rate of the rate-determining step (RDS) in the reaction mechanism. The nature of this RDS will therefore be discussed first.

The formation of hydrocarbons and oxygen-containing products from synthesis gas is believed to proceed via the reaction scheme outlined in Fig. 7 (12, 20). The main steps in this mechanism are CO dissociation

and hydrogenation of the resulting carbon to give CH₂ and CH₃ species. Once formed, the CH₃ groups can undergo a number of competing reactions, viz., hydrogenation to give CH₄, CO insertion to give precursors leading to C₂ oxygenates, and addition of CH₂ units giving longer alkyl groups. For a number of CO/H₂ reactions it has been possible to conclude that CO dissociation is not rate determining under the reaction conditions. In the case of methanation over nickel catalysts it was found that the slowest step in the reaction is hydrogenation of surface carbon (21) and that the concentration of adsorbed hydrogen atoms on the surface is the limiting factor (22). van Dijk *et al.* concluded that CO dissociation on iron is rapid compared with the rate of the overall reaction (23). Using transient isotope techniques Biloen *et al.* (24) obtained evidence suggesting that CO dissociation is rapid on nickel, cobalt, and ruthenium.

Assuming that hydrogenation of surface carbon is the RDS in the overall reaction on rhodium, which would be consistent with the positive reaction order in hydrogen (10), it follows that the addition of MnO and MoO₂ must be related to an increase in the rate of hydrogenation. This theory is supported by kinetic data: Ellgen *et al.* (10) studied the kinetics of the CO/H₂ reaction and expressed the rate of the reaction on unpromoted and Mn-promoted rhodium catalysts as power law equations of the type $r = k \cdot \exp(-E_a/RT) \cdot p_{\text{H}_2}^x \cdot P_{\text{CO}}^y$. The values of the power law parameters reported by the authors are given in Table 5. The small changes in activation energy and CO pressure dependence upon Mn addition suggest that the reaction mechanism remains similar. However, the decrease in H₂ pressure dependence (from 0.87 ± 0.08 to 0.58 ± 0.12) seems to be significant, indicating that the concentration of hydrogen adsorbed on the catalyst has indeed become less limiting. Our own data show that the decrease in activity as a function of time is

TABLE 5
Power Law Parameters for Promoted and
Unpromoted Rhodium Catalysts^a

Catalyst	E_{act}^b	x^b	y^b
5% Rh/SiO ₂	26 ± 0.7	0.87 ± 0.08	-0.40 ± 0.08
1.8% Rh-0.8% Mn on SiO ₂	24 ± 2	0.58 ± 0.12	-0.48 ± 0.12
2.5% Rh-1.0% Mn on washed SiO ₂	24 ± 2.5	0.64 ± 0.1	-0.33 ± 0.1

^a From Ref. (10).

^b For meaning of symbols see text.

accompanied by a decrease in the hydrogenating power of the catalysts (see, e.g., the change from ethanol to acetic acid and acetaldehyde as the major C₂ product).

The increase in the hydrogenation rate can be caused by two different phenomena. First, it is conceivable that the promoter oxides act as a hydrogen reservoir via spill-over of adsorbed hydrogen and/or formation of hydroxyl groups. However, this explanation is not consistent with the fact that MnO and MoO₂ lower the hydrogenation activity of other Fischer-Tropsch catalysts (25). We therefore prefer the second explanation, which assumes that the true function of the promoter oxides is to decrease the heat of CO chemisorption via the formation and stabilization of rhodium ions. It seems highly likely that positive rhodium ions would not chemisorb CO as strongly as rhodium metal, since rhodium ions have less capacity for back-donation of electrons from occupied metal orbitals to the unoccupied 2π* orbitals of CO. Since the surface of the catalyst is practically covered with CO under the reaction conditions, a small change in the heat of chemisorption of CO, leading to a small decrease in θ_{CO} (e.g., from 0.999 to 0.99), could result in a 10-fold increase in θ_{H} and therefore a 10-fold increase in activity. Thus we propose that the role of MnO and MoO₂ is to change the relative surface concentrations of CO and H₂.

This conclusion does not seem to be limited to the effects of MnO and MoO₂ on

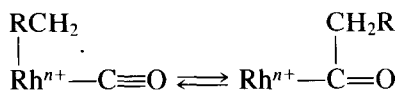
rhodium catalysts. It is very well possible that the increased activity of Ni/TiO₂ compared with Ni/SiO₂ is also due to the formation of mixed oxides. Various authors have reported that iron oxide is much more active than reduced iron (23, 26), a result which might be due to changes in the relative surface concentrations of CO and H₂. Interestingly, the effects of adding alkali to Ni, Fe, and Ru catalysts are usually rationalized by a similar, but opposite, reasoning: potassium increases the heat of CO chemisorption and decreases the surface concentration of hydrogen. This lowers the rate of the overall reaction and increases the selectivity toward heavier hydrocarbons and, especially in the case of Fe, toward oxygen-containing products.

Up to this point we have only discussed the effects of promoters on activity. Their effect on selectivity is more complicated. Watson and Somorjai (20), studying model rhodium catalysts, found that oxygen-containing products are only formed in the presence of oxidized rhodium. They therefore proposed that both rhodium metal and rhodium ions play a role in the reaction mechanism. Our finding that silica-supported rhodium catalysts still contain positive rhodium ions after a high-temperature reduction supports this idea. It is well known that CO dissociation on transition metals requires an ensemble of several metal atoms (27) and it is logical to assume that rhodium metal is necessary for this function. On the other hand, it now seems likely that activation of undissociated CO, e.g., for methanol formation over Cu-ZnO or Pd/SiO₂ catalysts involves positive metal species (16, 28).

The coexistence of rhodium metal and rhodium ions leads to the hypothesis that the various products of the CO/H₂ reaction are formed via three different pathways: (i) hydrocarbons are formed via CO dissociation and hydrogenation of surface carbon; this reaction is thought to occur on metallic rhodium; (ii) methanol is formed on rhodium ions; and (iii) other oxygen-containing

products (C₂⁺) are formed via a dual-site mechanism: alkyl groups are formed on metallic rhodium, migrate to the rhodium ions, and added there to an undissociated CO molecule.

The concept of such a dual-site mechanism is not unknown in heterogeneous catalysis. In the case of methanol formation over Cu-ZnO catalysts, Herman *et al.* (28) suggested that CO is activated on Cu⁺ ions, while H₂ adsorbs dissociatively on ZnO and migrates to the Cu⁺ ions. Hoek and one of us (29) showed that enantioselective hydrogenation of methyl acetoacetate requires the presence of Ni⁰ (for H₂ dissociation) and a Ni⁺ complex (to form an asymmetric intermediate). The hypothesis that CO insertion requires a positive rhodium ion may be understood by assuming that formation of acyl groups takes place via nucleophilic attack of an alkyl group to a Rhⁿ⁺-coordinated CO molecule:



Coordination of the CO to a metal in a higher oxidation state results in a reduced back-donation and an increased positive charge on the carbonyl carbon atom, thus activating the CO ligand toward nucleophilic attack.

We therefore believe that the behavior of the catalyst is determined not only by the relative concentrations of CO and H₂ on the surface, but also by the relative concentrations of rhodium metal and rhodium ions. This may explain the widely varying rates and product distributions that have been reported in the literature. Moreover, changes in the relative concentrations of rhodium metal and rhodium ions may occur during the reaction as a result of reduction of rhodium ions and selective poisoning of rhodium metal by carbon deposition. Such processes may explain the decline in activity and the changes in selectivity as a function of time-on-stream.

Until recently, little attention has been

paid to the presence of metal ions in supported metal catalysts and their behavior under reaction conditions. Driessen *et al.* (16), studying methanol formation over promoted Pd catalysts, found a linear relation between activity and the amount of Pd ions in the used catalysts. Our own data suggest that both the activity and the selectivity of rhodium-containing catalysts are affected by the presence of positive rhodium ions. Further research into the behavior of transition metal ions, their interaction with the surface of a transition metal lattice, and their function as adsorption sites, will be needed, especially under actual research conditions of CO hydrogenation, to improve our understanding of the processes on the catalyst surface.

CONCLUSIONS

1. Rhodium oxide, supported on silica, is not completely reduced by treatment with hydrogen at 500°C.
2. Poorly reducible oxides may act as promoters by stabilizing rhodium ions.
3. The concentration of hydrogen atoms on the surface is the rate-limiting factor in the conversion of synthesis gas over rhodium catalysts.
4. The promoter effect of Mn²⁺ and Mo⁴⁺ can be understood by assuming that the presence of rhodium ions decreases the heat of CO chemisorption. This results in an increase in the surface concentration of hydrogen and an increase in the reaction rate.
5. It is probable that the presence of positive rhodium ions under the reaction conditions is responsible for the formation of oxygen-containing products.

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