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A Novel Concept for the Mechanism of Higher Oxygenate Formation from Synthesis Gas over MnO-Promoted Rhodium Catalysts

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Based on data from zeolite-supported catalysts, a new model is proposed for the formation of higher oxygenates from syngas over MnO-promoted Rh. Oxygenate precursors, $C_xH_yO_z$, are formed at MnO sites in close proximity to the Rh–MnO interface. The role of Rh is the formation and delivery of CH_x groups and H atoms. FTIR indicates that the $C_xH_yO_z$ complex is probably a surface acetate.

Results from ethylene hydroformylation tests at relatively low temperatures, where CO dissociation does not occur, show that the presence of MnO in the catalyst does not enhance the ability *of Rh* **to catalyze CO insertion. At higher temperatures though, where CO dissociation occurs, higher oxygenates are formed only in negligible amounts over unpromoted Rh.**

The role of MnO in enhancing the formation of higher oxygenates was tested using $CHCl_3$ as a source of CH_x groups instead of Rh. Formation of the oxygenate precursor $C_xH_yO_z$ from the surface reaction between $CHCl_3$, CO, and H_2 is detected by FTIR on MnO *in the absence of* **Rh. The same complex is formed from the same reaction over cosupported Rh/MnO and the physical mixture Rh + MnO. However, its hydrogenation to higher oxygenates, occurs** *only* **over Rh/MnO, where Rh and MnO particles are in close contact. Furthermore, this hydrogenation is apparently confined to those acetate groups located on MnO sites** *at the Rh–MnO interface.*

Summarizing, the MnO promoter basically behaves as a cocatalyst; the formation of higher oxygenates from syngas is another example of bifunctional catalysis with essential steps taking place at the interface of both catalytic functions.

1. INTRODUCTION

Rhodium is a very versatile catalyst for CO hydrogenation. Its selectivity toward different kinds of products is strongly dependent on the presence of a *promoter* in the catalyst. A catalyst promoter is defined as an element or compound without catalytic activity by itself, but when added to an active catalyst it modifies its activity, selectivity, and/or stability. In the case of Rh, the pure, unsupported metal, either as single crystal or as polycrystalline foil, yields methane as the predominant product from CO hydrogenation (1). Methanol can become the main product if a promoter such as MgO or CaO is added to the catalyst (2). Of particular interest is the formation of higher oxygenates when an appropriate promoter and proper conditions are used. Higher oxygenates are oxygen-containing molecules with two or more carbon atoms, such as alcohols, aldehydes, and carboxylic acids. Promoters known to enhance the formation of higher oxygenates from syngas when added to Rh include compounds of alkali (3, 4), rare earth (5, 6), and transition elements (7–9).

Understanding how promoters work remains a challenge for catalytic science. In this context, promoted Rh as a catalyst for the formation of higher oxygenates from syngas provides a probe reaction and a catalyst system with which hypotheses on how promoters act can be tested.

In general, the mechanism of CO hydrogenation to hydrocarbons and higher oxygenates is similar to that of a chain-growth polymerization, with well-defined initiation, propagation, and termination steps (10, 11). The initiation step includes the dissociative adsorption of CO and H_2 and the formation of CH_x units. The propagation step consists of the repeated insertion of CH_2 units into metal–alkyl bonds so that an alkyl chain results, attached to the metal at one of its ends. There are different termination steps and each one determines the kind of final product that is obtained. Thus, β-hydrogen abstraction from the alkyl chain results in the formation of alkenes; hydrogenation of the chain produces alkanes; and CO insertion in the metal alkyl bond followed by H addition yields oxygenated molecules, with the oxygen atom at one end of the chain (11, 12). The propagation and the termination steps are competing with one another during the reaction. Methanol formation is different because no CO dissociation is required and does not follow the chain-growth mechanism just described.

Although there has been much work on how promoters direct the reaction toward the formation of higher oxygenates over Rh-based catalysts (13–15), a thorough understanding of the promoting effect has not yet been achieved.

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Since undissociated CO insertion determines the formation of higher oxygenates, it has been proposed that the main function of promoters in favoring the formation of these products over Rh-based catalysts is the enhancement of the ability of Rh to catalyze CO insertion (16, 17). Direct and indirect measurements of the rate of CO insertion over promoted and unpromoted catalysts have, however, yielded conflicting results. Some researchers report an enhancement of CO insertion when a promoter is present in the catalyst (18), but other groups found no difference between promoted and unpromoted catalysts (19).

An intriguing concept assumes that the promoter provides new sites where CO insertion and oxygenate precursors are formed. For methanol formation from syngas over Pd promoted by CaO or MgO, Prins recently proposed (20) that the intermediate, presumably a formate, is formed not on the Pd, but on the oxide. In this model, the role of Pd is merely to supply atomic hydrogen for the final hydrogenation step. Applying this concept to the formation of higher oxygenates over promoted Rh, one can speculate that the role of Rh would be limited to the dissociation of CO and H_2 and the formation of alkyl groups. These groups could then migrate over the surface to the promoter, where undissociated CO insertion and hydrogenation to form the oxygenated products take place. The principal objective of this paper is to discriminate between these mechanistic concepts.

Manganese has been shown to be an efficient promoter of Rh in the formation of higher oxygenates, particularly ethanol and acetic acid (8, 21, 22). In previous work we have demonstrated that MnO, in close interaction with Rh clusters, is the chemical species responsible for the promotion effect (21, 23), whereas Mn^{2+} ions do not exhibit this kind of promotion.

In this paper we investigate the role MnO plays in the formation of higher oxygenates, particularly in relation to the CO insertion step. First we examine the possibility that the MnO promoter enhances the CO insertion ability of Rh by using the hydroformylation of ethylene as a probe reaction. This reaction is closely related to CO hydrogenation and the products, propionaldehyde and *n*-propanol, are derived from CO insertion into the adsorbed ethylene reactant. If CO insertion takes place on the Rh surface, as has been hitherto assumed by most researchers, any enhancement by MnO on the rate of this step should be observed in ethylene hydroformylation as an increased yield of propionaldehyde or *n*-propanol. The novel alternative hypothesis, that CO insertion actually takes place on the MnO surface, is examined mainly by FTIR over Rh-free MnO samples where CH_x groups are externally supplied. Chlorinated hydrocarbons CH_xCl_{4-x} are well-proven agents delivering CH_x groups (24), and were used here for this purpose. Potential intermediates in oxygenate formation resulting from undissociated CO insertion, such as acyl and carboxylate groups, have characteristic infrared bands that ease their identification.

In previous work, the use of a zeolite as support enabled us to prepare catalysts containing manganese present as Mn^{2+} ions or as encaged MnO particles, and to unambiguously determine that only MnO promotes the formation of higher oxygenates. We have thus used zeolite NaY as a support in the research described in this paper.

2. EXPERIMENTAL

The catalysts were prepared in the same way as before, when MnO-promoted Rh was tested for CO hydrogenation (23). Zeolite NaY was kindly provided by the manufacturer, UOP (Des Plaines, IL), Lot 10027-45, and was used as received, a fine white powder without binder. The manganese and rhodium components were introduced into the zeolite cages by ion exchange. The precursors used were $Mn(NO_3)_2 \cdot 6H_2O$ and $[Rh(NH_3)_5Cl]Cl_2$. In all promoted catalysts, manganese was always introduced first. A slurry was prepared by adding 200 ml of doubly deionized water per gram of zeolite. The precursor was dissolved in doubly deionized water and the solution was added dropwise to the slurry, which was magnetically stirred. For Mn, the ion exchange lasted 1 day at room temperature; for Rh, 3 days at 85°C. The weight loadings were 3% in Rh and 5% in Mn, giving an atomic ratio of Mn/Rh of about 3. After each ion exchange the sample was washed, dried in an oven at 110°C, and calcined in O_2 in a glass U-shaped reactor at 400°C to decompose the precursor and leave bare Mn^{2+} and Rh^{3+} ions attached to the zeolite framework. All the gases were of ultrahigh purity grade and further purified by using 5A molecular sieve traps to remove traces of water. Reduction at 400°C in pure H_2 followed. Before flowing into the reactor, hydrogen flowed through a trap containing MnO/SiO_2 to remove traces of oxygen. After the reduction step, Mn^{2+} ions in the sample remain unchanged (23), but Rh^0 clusters are formed. During the reduction of Rh, acid protons are produced, which become the new charge compensating cations.

The formation of encaged MnO particles was accomplished by immersing the reduced samples into a solution of NaOH at a pH of 11. In a basic environment, Mn^{2+} ions are hydrolyzed and become first $Mn(OH)_2$, which is very quickly oxidized to hydrated MnO_2 by atmospheric oxygen. Since acid sites were found to be detrimental to the formation of oxygenated products from CO hydrogenation by transforming them into hydrocarbons through secondary reactions (25), immersion of the sample in the NaOH solution also serves to neutralize the acid protons formed during reduction of Rh^{3+} ions; i.e., Na^+ replace H^+ as charge compensating cations.

After immersion in a basic solution the sample was washed extensively to remove any unexchanged material and recalcined at 400°C in oxygen for 2 h. A final reduction step in H_2 was performed at 400°C for 1 h immediately before running any experiment. This reduction took place always *in situ*, so the sample was never again in contact with the atmosphere.

Hydroformylation of ethylene was carried out in a computer-controlled stainless-steel plug flow reactor manufactured by Xytel Corp. All gases were of ultrahigh purity grade. A mixture of CO, H_2, ethylene, and Ar with molar ratios of 1 : 1 : 1 : 19 was fed into the reactor. The GHSV was 15,000, the reaction temperature was 160°C, and the total pressure was 7 bar. Contamination in the feed from iron pentacarbonyl was removed by flowing the CO through a γ-Al_2O_3 trap before entering the reactor.

For FTIR studies, a quartz cell was used where spectra could be taken at high temperature and atmospheric pressure. The samples were pressed into thin self-supporting wafers (5–10 mg/cm^2). Data collection was done in the transmission mode with a resolution of 1 cm^{-1}. The spectrometer was a single beam Nicolet 60SX equipped with a mercury–cadmium telluride detector, cooled by liquid nitrogen. Hydrogen and syngas ($H_2/CO = 2$) flowed through a 5A molecular sieve and MnO/SiO_2 traps to remove water and oxygen contamination, respectively. In addition, syngas flowed through a γ-Al_2O_3 trap to remove any contamination, such as iron pentacarbonyl. In some experiments, methylene chloride, CH_2Cl_2, and chloroform, $CHCl_3$ were used as sources of CH_x groups. Both reagents were obtained from Fisher Scientific and their purity was 99.9%. They were purified by at least three freeze–thaw–pump cycles to remove dissolved gases. A carrier gas, usually H_2, was flowed through a gas space saturated with the vapor of the chlorinated hydrocarbon. The reservoir was kept at a temperature such that the chlorinated hydrocarbon vapor pressure was about 60 Torr: −18°C for CH_2Cl_2 and 0°C for $CHCl_3$. Infrared spectra were taken at 250°C, which is a typical temperature for CO hydrogenation, and the same at which our previous studies on CO hydrogenation were performed (21).

3. RESULTS

The results of ethylene hydroformylation at steady state (12 h TOS) over unpromoted and MnO-promoted Rh/NaY are summarized in Table 1. In both cases the final reduction was carried out *in situ* at 400°C for 1 h. The overall activity, as measured by the conversion of ethylene, is slightly higher in the case of Rh/NaY. However, the most important result is that the selectivity of both catalysts toward CO insertion products is essentially the same. This suggests that the promoter effect is *not* related to an enhanced ability of Rh to catalyze CO insertion. Only a small fraction of the initially formed propionaldehyde is hydrogenated to *n*-propanol. Methane may be formed by hydrogenolysis of ethane. The absence of other hydrocarbons in the product stream suggests that CO dissociation, the key step in the formation of alkyl chains, does not take place at 160°C over either catalyst.

TABLE 1

Results of Ethylene Hydroformylation over Rh/NaY and RhMnO/NaY

	Rh/NaY	RhMnO/NaY
C_2H_4 conversion (mol %)	22.1	18.4
Selectivity (mol %)		
CH_4	26.3	33.8
C_2H_6	46.5	40.4
Propionaldehyde	26.0	24.9
n-Propanol	1.2	0.9

Note. Data at steady state. Reaction conditions: $T = 160$°C; $p = 7$ bar; GHSV = 15,000; feed molar ratio $H_2 : CO : C_2H_4 : Ar = 1 : 1 : 1 : 19$. Selectivity data on the basis of one converted mole of C_2H_4.

FTIR spectra of different samples taken at 250°C after 3 h under syngas flow are shown in Fig. 1. Bands of adsorbed CO on Rh appear in both the Rh/NaY and the RhMnO/NaY samples. Their frequencies, around 2040 and 1800 cm^{-1}, indicate CO adsorption in the linear and bridged mode, respectively. No CO adsorption is evident on NaY or MnO/NaY. Their spectra are very similar and almost featureless. On the other hand, in addition to adsorbed CO, other bands are visible on Rh/NaY and particularly on RhMnO/NaY. Water, a product of CO hydrogenation, is detected as a bulge near 1630 cm^{-1} in both samples. Prominent bands appear at about 1590 and 1450 cm^{-1} on RhMnO/NaY. The same bands are barely noticeable, if at all, in Rh/NaY.

Chlorinated methanes were used as sources of CH_x groups in Rh-free MnO/NaY samples. Coadsorption of CH_2Cl_2, CO and H_2 at 250°C resulted in no new infrared bands on MnO/NaY, compared with those seen on the same catalyst when only CO and H_2 were flowed over it. In contrast, by using $CHCl_3$ as external CH_x source, and flowing it together with CO and H_2, new bands appear on MnO/NaY in the regions of 1720, 1590, 1480–1450, and 1385 cm^{-1}, which were not present when only CO and H_2 were flowed over the sample. The spectrum is shown in Fig. 2. These bands appear at approximately the same wavenumbers as observed on RhMnO/NaY after syngas flow. Clearly, they are caused by $C_xH_yO_z$ groups located on the MnO surface. To test their reactivity toward hydrogenation, the flows of CO and $CHCl_3$ were shut off and pure H_2 was left flowing over the sample. Spectra were taken after 30 and 60 min of hydrogen flushing. There were no changes in the band intensities in the regions of 1590 and 1480–1450 cm^{-1} at any time. Thus, no hydrogenation of these $C_xH_yO_z$ groups takes place on a Rh-free sample.

Figure 3 shows the infrared spectrum resulting from the coadsorption of $CHCl_3$, CO and H_2 on Rh/NaY at 250°C. The bands caused by the nondissociative adsorption of CO

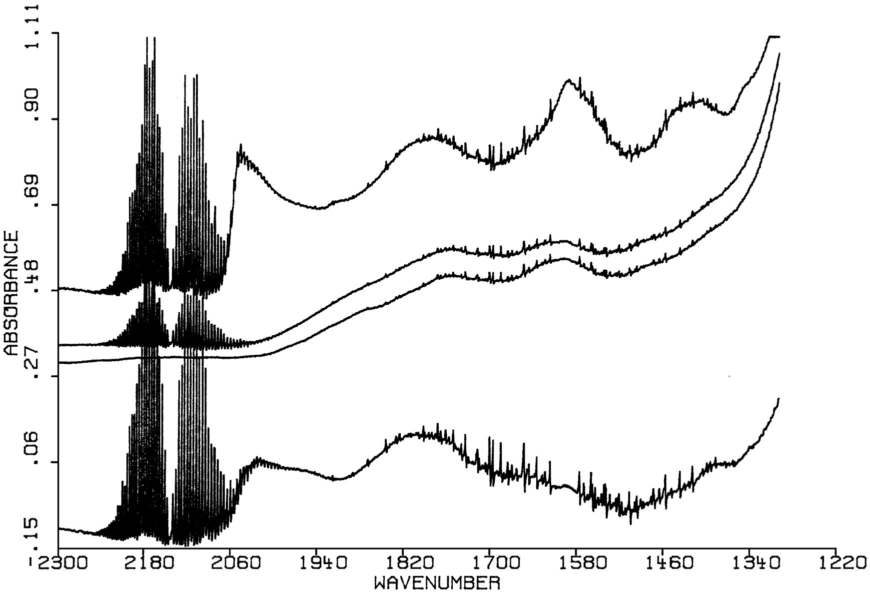

FIG. 1. FTIR spectra under synthesis gas flow ($H_2/CO = 2$) after 3 h at 250°C. From top: RhMnO/NaY, MnO/NaY, NaY, Rh/NaY.

on Rh are clearly seen in the 2040 and 1800 cm^{-1} regions. More significantly, bands at 1590 and 1480–1450 cm^{-1} are present. These bands were almost unnoticeable when CO and H_2 were flowed over Rh/NaY, but are very prominent in the case of syngas flowing over RhMnO/NaY. This means that the addition of $CHCl_3$ as a precursor of alkyl groups to the reacting mixture increases the surface concentration of the species responsible for the infrared bands at 1590 and 1480–1450 cm^{-1}, which we attribute to $C_xH_yO_z$. The reactivity of these bands toward hydrogenation was tested by flushing with pure H_2 for 30 and 60 min. In contrast to the case of MnO/NaY, some decrease in the intensity of these bands is observed after 30 min of flushing, as shown in Fig. 3. No further changes were detected after 60 min of flushing.

Coadsorption and reaction of $CHCl_3$, CO, and H_2 at 250°C was also studied on RhMnO/NaY. The top spectrum in Fig. 4 shows the results after 3 h on stream. All the bands present in this case also appeared in the spectrum obtained when only syngas was flowed over the sample. In particular, the bands in the 1590 and 1480–1450 cm^{-1}

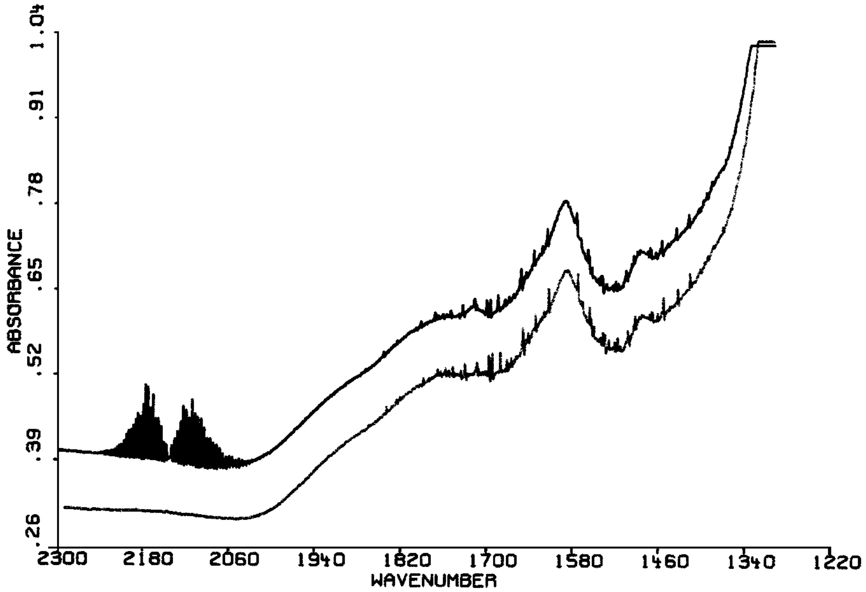

FIG. 2. FTIR spectra of MnO/NaY at 250°C. (Top) After 3 h under a flow of 60 Torr $CHCl_3$, 233 Torr CO, 466 Torr H_2. (Bottom) After flushing with 760 Torr H_2 for 30 min.

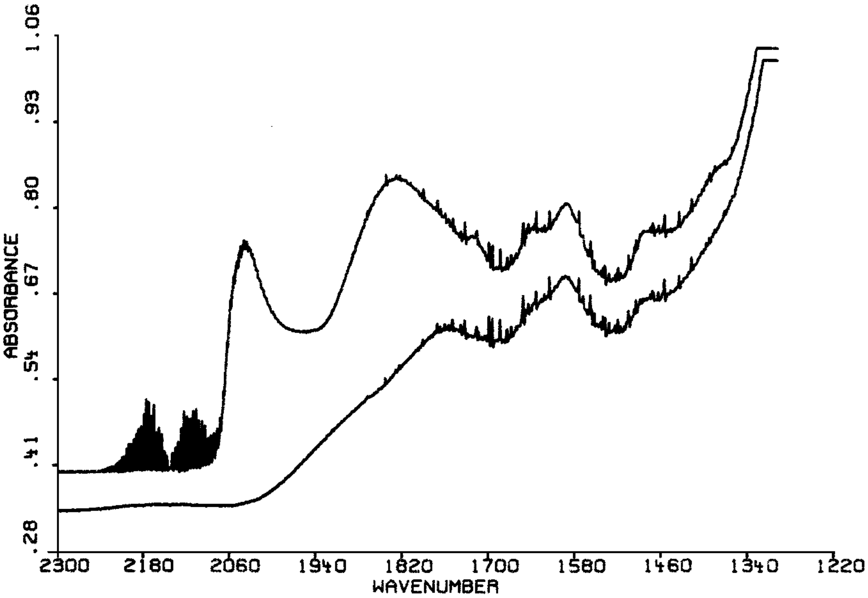

FIG. 3. FTIR spectra of Rh/NaY at 250°C. (Top) After 3 h under flowing $CHCl_3 + CO + H_2$. (Bottom) After flushing with H_2 for 30 min. Partial pressures as in Fig. 2.

regions are prominent. As with the other samples, flushing with pure hydrogen was used to determine the reactivity of these bands. The bottom spectrum in Fig. 4, obtained after flushing with H_2 for 30 min at 250°C, shows the complete disappearance of the bands due to CO adsorbed on Rh. More significant though, is the disappearance of the small bands at about 1720 and 1385 cm^{-1} and the sharp decrease in the intensity of the bands in the regions around 1590 and 1480–1450 cm^{-1}. This decrease is much more noticeable than in the case of Rh/NaY. However, the bands did not completely vanish; no further change in their intensity was observed after 30 min of flushing with H_2.

To examine a possible requirement of close proximity between Rh and MnO for the effects described, a physical mixture of Rh/NaY and MnO/NaY was exposed to $CHCl_3$, CO, and H_2 in the same way as the other samples described above. It was then flushed with pure hydrogen for 60 min. The resulting spectra are shown in Fig. 5. The top spectrum,

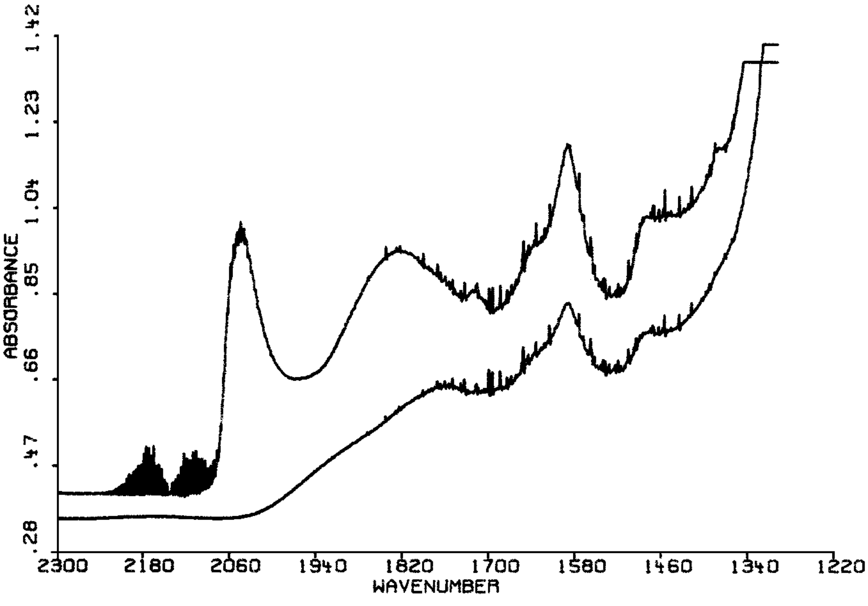

FIG. 4. FTIR spectra of RhMnO/NaY at 250°C. (Top) After 3 h under flowing $CHCl_3 + CO + H_2$. (Bottom) After flushing with H_2 for 30 min. Partial pressures as in Fig. 2.

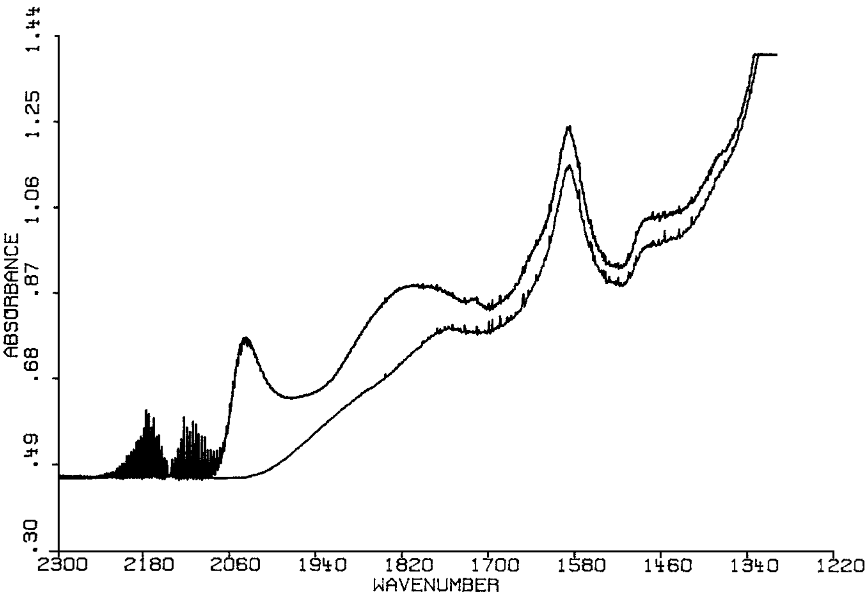

FIG. 5. FTIR spectra of a physical mixture Rh/NaY + MnO/NaY at 250°C. (Top) After 3 h under flowing $CHCl_3 + CO + H_2$. (Bottom) After flushing with H_2 for 30 min. Partial pressures as in Fig. 2.

obtained after 3 h of exposure to all three gases strongly resembles the spectrum of RhMnO/NaY exposed to flowing syngas (Fig. 1). It shows CO adsorbed on Rh and the bands in the 1590 and 1480–1450 cm^{-1} regions. The bottom spectrum, taken after flushing with H_2 for 30 min, shows no adsorbed CO. The bands at 1590 and 1480–1450 cm^{-1} did not change in intensity. No changes were observed after 60 min of flushing. Clearly, physical mixtures behave differently from samples where Rh and MnO particles are in close proximity.

4. DISCUSSION

The results of the ethylene hydroformylation tests show that at 160°C, CO insertion takes place over Rh regardless of the presence of the MnO promoter. In other words, MnO does *not* enhance the capability *of Rh* to catalyze CO insertion. The fact that the unpromoted catalyst is actually somewhat more active than the promoted one can be explained by a partial blockage or coverage of the Rh surface by the promoter, as has been shown previously by a variety of characterization techniques (23). Ethane is formed by hydrogenation of ethylene, and methane may be formed from hydrogenolysis of ethane. Since no other hydrocarbons are observed, it seems that at 160°C no CO dissociation takes place; thus, alkyl chain formation and the subsequent hydrocarbon formation do not happen. These processes are known to require somewhat higher temperatures. At these higher temperatures, oxygenate formation is negligible over unpromoted Rh in CO hydrogenation (1, 13, 21). It would therefore seem that CO insertion is favored only at low temperatures, where the rate of the competing reactions in CO hydrogenation is negligible. A survey of the literature on alkene hydroformylation over heterogeneous Rh catalysts shows that hydroformylation is generally carried out at lower temperatures than those for CO hydrogenation (26–28), thus offering support to this concept.

Upon accepting the conclusion that MnO does not appear to promote the formation of higher oxygenates from syngas by enhancing the rate of CO insertion on Rh, the alternative possibility, that CO insertion actually takes place on new sites provided by the promoter itself is worth discussing. In this context the data obtained in the absence of Rh are relevant. If Rh is only required for the dissociation of CO and H_2, and for the formation of alkyl chains, whereas formation of the C–C bond between the alkyl group and CO takes place on MnO, it should be possible to obtain oxygenates by using an alternative precursor of alkyl groups. As the use of halogenated hydrocarbons as alkyl sources is well documented in the literature (24, 29), this strategy to "replace" Rh with $CHCl_3$ has been used in this work to test this concept. The data show, indeed, that adsorbed oxygen-containing species are formed on MnO *in the absence of Rh*.

As to the identification of the observed $C_xH_yO_z$ groups, it appears that among the oxygenate precursors proposed by different researchers, acyl and carboxylate groups are most likely (5, 13, 30–32). They have characteristic infrared bands that facilitate their detection. If CO insertion results in an oxygenate precursor of this nature, it should be readily identifiable by FTIR.

The species responsible for the infrared bands at 1590 and 1450 cm^{-1} on RhMnO/NaY after exposure to syngas has been ascribed to a surface acetate (33, 34), which means that acetate ions could be likely intermediates in the formation of C_2 oxygenates (Fig. 1). Henceforth, we will call the $C_xH_yO_z$ groups acetates. Under a flow of syngas, these bands are absent on MnO/NaY and barely noticeable on Rh/NaY. However, when $CHCl_3$ is flowed together with syngas over MnO/NaY (Fig. 2), the acetate bands appear in the FTIR spectrum. Very interestingly, also present are a pair of bands at around 1720 and 1385 cm^{-1}, which have been ascribed to adsorbed acetaldehyde (34). This points to CO insertion taking place on MnO at 250°C *in the absence of Rh* if an external source of CH_x groups is used.

Coadsorption and subsequent surface reaction among $CHCl_3$, CO, and H_2 produce infrared bands on Rh/NaY and RhMnO/NaY very similar to those just described. They can be seen in Figs. 3 and 4, respectively. The intensities of the acetate bands on RhMnO/NaY were considerably higher than on the other two samples.

If these acetate groups are true precursors of higher oxygenates, they should react with H_2 to yield the final product. In the model discussed here, Rh is necessary to dissociate H_2 molecules. Indeed, the data presented in this paper confirm this: bands due to acetate groups on MnO/NaY remain unchanged in flowing H_2 and showed no reactivity, but those on RhMnO/NaY had the highest reactivity. Hydrogenation, resulting in an intensity decrease, can only occur if atomic hydrogen is available. Dissociative adsorption of H_2 readily occurs on metal surfaces, but it is much more difficult on most oxides, such as MnO. Thus, the absence of atomic hydrogen on the surface of Rh-free MnO prevents the hydrogenation of surface acetates. In contrast, when Rh is present, hydrogenation is possible, and apparently occurs, as evidenced by the drop in intensity of the acetate bands on Rh/NaY and RhMnO/NaY. Interestingly, the bands never vanish completely and have already reached their final intensity after 30 min of flushing. It could therefore be proposed that the acetate groups which are hydrogenated are only those *on* the Rh particle itself or *at its interface* with the promoter or the support. This means atomic hydrogen does *not* migrate rapidly from the Rh particle to react with acetate groups not located at the interface.

Key support for the idea that acetates are hydrogenated *only* if they are located close to the interface with the metal particle is provided by the results using a physical mixture of Rh/NaY and MnO/NaY (Fig. 5). Although the acetate bands produced by the combined action of flowing $CHCl_3$, CO, and H_2 are very prominent, their decrease in intensity upon flushing with hydrogen is negligible. Since presumably most of these surface acetates are formed on MnO, no atomic hydrogen formed on the metal surface is available for hydrogenation because of the large distance between the MnO and the Rh particles. *No measurable H_2 spillover occurs* in physical mixtures.

Figure 1 shows that under syngas flow, without additional supply of alkyl groups, the surface concentration of acetate groups is negligible on Rh/NaY, but rather prominent bands appear on RhMnO/NaY. One could argue that on unpromoted Rh at 250°C, acetate groups do not form or, if formed, tend to be unstable. TPD experiments by Barteau *et al.* (35, 36) under high vacuum conditions of adsorbed ethanol and acetaldehyde on Rh(111) show that the decomposition/desorption temperature is about 100°C higher if the metal surface is precovered with oxygen before adsorption. It is thus conceivable that oxygenate precursors are more stable on the surface of the oxide promoter.

From the present findings, we can propose that acetate groups located at the metal–promoter interface are the most likely to participate as intermediates in the formation of higher oxygenates. The main role of the promoter is then to provide new sites at the interface where these intermediates can form. Although acetates apparently can be formed on the whole surface of a MnO particle, only those groups located at or near the interface with Rh can be hydrogenated to yield the final oxygenated product. The ethylene hydroformylation experiments have shown that CO insertion occurs even on unpromoted Rh, at temperatures as low as 160°C. However, at higher temperatures, competition from other reaction steps of CO hydrogenation determine that on unpromoted Rh, CO insertion products constitute only a very small fraction of the total yield. In other words, although oxygenate intermediates can be formed on Rh, their surface concentration is very low under CO hydrogenation conditions. In order to favor the formation of higher oxygenates it is necessary to add a promoter to the catalyst, such as MnO, where oxygenate precursors are formed. If these precursors are located on MnO sites in immediate proximity to the Rh particle, they can be hydrogenated to oxygenates such as ethanol and acetaldehyde.

A variant of this scenario which cannot be ruled out is that a fraction of the oxygenate precursors is formed on the Rh surface and migrates to nearby MnO particles. These $C_xH_yO_z$ precursors are stabilized *on the promoter surface* as acetate groups that are subsequently hydrogenated to yield the final oxygen-containing products. In this case the promoter prevents oxygenate precursors from decomposing prior to their hydrogenation. The data presented here, however, do not make this alternate explanation necessary, since it is shown (Fig. 2) that CO insertion can take place on MnO in the absence of Rh.

Of course, acetates need not be the only or even the main intermediates in oxygenate formation. However, the present results show, contrary to some literature reports (30, 37), that at least a fraction of these groups is sufficiently reactive to participate in a reaction pathway leading to oxygenate formation. The presence of the promoter provides the sites for their formation. The possible participation of acetate groups in the formation of higher oxygenates is particularly interesting in relation to the observation that ethanol and ethyl acetate are the main oxygenated products obtained from CO hydrogenation over RhMnO/NaY

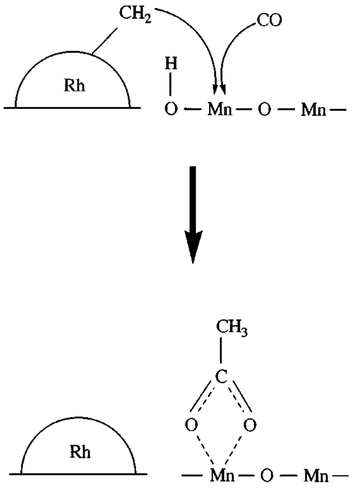

FIG. 6. Scheme representing the crucial step in the formation of the oxygenate precursor from an adsorbed CH_x group, here shown as CH_2, CO, and a surface hydroxyl on an MnO site at the metal–promoter interface.

(21, 23). Most likely, ethyl acetate is formed through a secondary reaction between, for example, ethanol and a surface acetate.

A model can be proposed that includes the formation and participation of acetate groups located at interfacial sites as precursors of higher oxygenates. The key steps are shown in Fig. 6. Here, an alkyl group formed on the metal surface migrates to the hydroxylated promoter surface across the interface and reacts with CO to yield the carboxylate intermediate. Oxygenates are formed by hydrogenation of the carboxylate. Atomic hydrogen, as discussed, is furnished by the metal.

5. CONCLUSION

As determined from the study of ethylene hydroformylation, the ability of Rh to catalyze CO insertion is not enhanced by the presence of MnO as a promoter. However, over unpromoted Rh catalysts, CO insertion products can only predominate at temperatures below that where CO dissociation occurs. Above it, the formation of hydrocarbons predominates.

At temperatures where CO dissociation occurs, the formation of oxygenated products can be favored over Rh-based catalysts by the presence of a promoter, such as MnO, which provides sites for the formation and stabilization of $C_xH_yO_z$ intermediates. As detected by FTIR, among these intermediates are surface acetate groups very likely formed on the MnO surface. These groups can be hydrogenated to the final oxygenated products if they are located in immediate proximity to a Rh particle, that is, at the Rh–MnO interface. By providing new sites where CO insertion happens, MnO behaves as a *cocatalyst* in the formation of higher oxygenates from syngas.

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REFERENCES

1. Castner, D. G., Blackadar, R. L., and Somorjai, G. A., *J. Catal.* **66**, 257 (1980).
2. Ichikawa, M., *Bull. Chem. Soc. Jpn.* **51**, 2268 (1978).
3. Kagami, S., Naito, S., Kikuzono, Y., and Tamaru, K., *J. Chem. Soc., Chem. Commun.* 256 (1983).
4. Orita, H., Naito, S., and Tamaru, K., *Chem. Lett.* 1161 (1983).
5. Kiennemann, A., Breault, R., Hindermann, J. P., and Laurin, M., *J. Chem. Soc., Faraday Trans. I* **83**, 2119 (1987).
6. Rieck, J., and Bell, A. T., *J. Catal.* **99**, 278 (1986).
7. Ichikawa, M., *Bull. Chem. Soc. Jpn.* **51**, 2273 (1978).
8. Ellgen, P. C., Bartley, W. J., Bhasin, M. M., and Wilson, T. P., *Adv. Chem. Ser.* **178**, 147 (1979).
9. Kip, B. J., Smeets, P. A. T., van Grondelle, J., and Prins, R., *Appl. Catal.* **33**, 181 (1987).
10. Biloen, P., and Sachtler, W. M. H., *Adv. Catal.* **30**, 165 (1981).
11. Sachtler, W. M. H., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. I, p. 151. Dechema, Frankfurt-am-Main, 1984.
12. Orita, H., Naito, S., and Tamaru, K., *J. Chem. Soc., Chem. Commun.* 150 (1984).
13. Ichikawa, M., *in* "Tailored Metal Clusters" (Y. Iwasawa, Ed.), p. 183. Reidel, Dordrecht, 1986.
14. Bastein, A. G. T. M., van der Boogert, W. J., van der Lee, G., Luo, H., Schuller, B., and Ponec, V., *Appl. Catal.* **29**, 243 (1987).
15. Burch, R., and Petch, M. I., *Appl. Catal. A* **88**, 39 (1992).
16. Ichikawa, M., *Polyhedron* **7**, 2351 (1988).
17. Sachtler, W. M. H., Shriver, D. F., Hollenberg, W. B., and Lang, A. F., *J. Catal.* **92**, 429 (1985).
18. Mori, Y., Mori, T., Hattori, T., and Murakami, Y., *Catal. Lett.* **10**, 171 (1991).
19. Koerts, T., Ph.D. thesis, Eindhoven Technical University, 1992.
20. Prins, R., Presentation at the Special Symposium on Mechanisms of Heterogeneous Catalysis in honor of Prof. Wolfgang M. H. Sachtler. Baltimore, MD, July 6, 1996.
21. Treviño, H., and Sachtler, W. M. H., *Catal. Lett.* **27**, 251 (1994).
22. Van den Berg, F. G. A., Ph.D. thesis, State University of Leiden, 1983.
23. Treviño, H., Lei, G. D., and Sachtler, W. M. H., *J. Catal.* **154**, 245 (1995).
24. Van Barneveld, W. A. A., and Ponec, V., *J. Catal.* **88**, 382 (1982).
25. Treviño, H., and Sachtler, W. M. H., *Chem. Eng. Technol.* **18**, 23 (1995).
26. Trunschke, A., Böttcher, H. C., Fukuoka, A., Ichikawa, M., and Miessner, H., *Catal. Lett.* **8**, 221 (1991).
27. Rode, E. J., Davis, M. E., and Hanson, B. E., *J. Catal.* **96**, 563 (1985).
28. Naito, S., and Tanimoto, M., *J. Catal.* **130**, 106 (1991).
29. Van der Lee, G., Ph.D. thesis, State University of Leiden, 1986.
30. Underwood, R. P., and Bell, A. T., *J. Catal.* **111**, 325 (1988).
31. Bastein, A. G. T. M., Ph.D. thesis, State University of Leiden, 1988.
32. Orita, H., Naito, S., and Tamaru, K., *J. Catal.* **90**, 183 (1984).
33. Fukushima, T., Arakawa, H., and Ichikawa, M., *J. Chem. Soc., Chem. Commun.* 729 (1985).
34. Lavalley, J. C., Saussey, J., Lamotte, J., Breault, R., Hindermann, J. P., and Kiennemann, A., *J. Phys. Chem.* **94**, 5941 (1990).
35. Houtman, C. J., and Barteau, M. A., *J. Catal.* **130**, 528 (1991).
36. Houtman, C. J., Brown, N. F., and Barteau, M. A., *J. Catal.* **145**, 37 (1994).
37. Orita, H., Naito, S., and Tamaru, K., *J. Catal.* **112**, 176 (1988).