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The State of Manganese Promoter in Rhodium–Silica Gel Catalysts

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The ESR spectra of Mn/SiO_2 and Rh–Mn/SiO_2 compositions were investigated to learn more about the mode of action of the Mn used as a promoter for acetic acid and acetaldehyde formation from synthesis gas over Rh/SiO_2 catalysts. The Mn/SiO_2 catalyst showed a moderately strong, unresolved Mn^{2+} signal while Rh–Mn/SiO_2 catalysts showed little signal of any kind when they were reduced in H_2 at 500°C and evacuated. Adding H_2O vapor at room temperature resulted in the appearance of a moderately intense, resolved sextet Mn^{2+} signal from both catalysts. Subsequent treatment of the Rh–Mn/SiO_2 with a CO + H_2O mixture led to a threefold increase in intensity of the resolved Mn^{2+}. The same gas mixture had no effect on the signal from the Mn/SiO_2 catalyst. It is suggested that these observations are consequences of the Mn being concentrated on the surface of the Rh crystallites in the Rh–Mn/SiO_2 catalysts, probably as a mixed surface oxide with the Rh which stabilizes Rh^+ on the metal surface. The change in Rh surface chemistry resulting from this strong interaction with Mn^{2+} could be responsible for the effectiveness of Mn as a promoter in these catalysts.

INTRODUCTION

The selective conversion of synthesis gas to two-carbon chemicals by rhodium-containing silica gel-supported catalysts, operated above atmospheric pressure, has been described in previous publications from this laboratory (*1–5*). Additions of other metal cations to the basic Rh/SiO_2 catalyst recipe have striking effects on activity and selectivity. Catalysts containing only Rh produce CH_3CHO and CH_3COOH as the principal nonhydrocarbon products. Addition of Fe equivalent to 35 atom% of the Rh present does not change the rate of synthesis gas conversion greatly, but CH_3CHO and CH_3COOH disappear from the products and are replaced by C_2H_5OH. Significant yields of CH_3OH are also obtained. Addition of Mn equivalent to as little as 10 atom% of the Rh has little effect on the selectivity but increases the rate of synthesis gas conversion nearly tenfold. The use of Fe and Mn together gives a catalyst which produces the lower alcohols at a high rate.

The effects of the added metal ions are unexpectedly large and specific. To understand how such effects are produced it would be helpful to know how the additives interact with the Rh, which is known to be present as ~40-μm crystallites of metal in all the catalysts. Systems closely related to the Rh–Fe/SiO_2 system have been studied to determine the state of Fe in them. Sancier and Inami (*6*) used ESR and Garten and Ollis (*7*) used Mössbauer spectroscopy to study the Pd–Fe/Al_2O_3 system. Vannice *et al.* (*8*) used Mössbauer to study the Ru–Fe/SiO_2 system. Some zero-valent iron was found in those cases. Thus it is possible that some zero-valent iron was present in the Rh–Fe system. Manganese is much more electropositive than Fe, and therefore less likely to be reduced. The standard electrode potential for the reaction, M → $M^{2+} + 2e$,

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is 0.44 V for M = Fe and 1.18 V for M = Mn. Perhaps more to the point, at 400°C the maximum P_{H_2O}/P_{H_2} ratio at which Fe can be reduced to the metal is 10^{-1} (*9*). The ratio required for Mn is 10^{-10}, which is some five orders of magnitude lower than the specified moisture content of the commercial cylinder H_2 used for reduction. Since Mn is unlikely to be reduced, even in the presence of Rh, its state in the Rh–Mn catalysts cannot be inferred from the Pd–Fe and Ru–Fe results. Since Mn^{2+} is paramagnetic, ESR provides a sensitive tool for studying the characteristics of the Rh–Mn/SiO_2 system. The results of such a study are reported here.

MATERIALS AND METHODS

All ESR measurements were done at liquid N_2 temperature, 77°K, using a Varian E-104A X-band spectrometer. The microwave frequency locked to the loaded sample cavity was 9.128 GHz.

Three samples were examined by ESR. All were prepared using oxalic acid-washed Davison D59 silica gel as a support (*4*). Added metal contents were 0.2% Mn, 2.5% Rh–0.2% Mn, and 2.5% Rh–0.1% Mn (all percentages by weight). In each case the support was impregnated with the required quantities of $RhCl_3 \cdot xH_2O$ and $Mn(NO_3)_2$ in aqueous solution, using conventional incipient wetness techniques. Impregnated samples were first dried slowly in air at temperatures increasing to 200°C, then reduced in flowing H_2 at $\sim 10^2$ hr^{-1} space velocity, using a 5-hr programmed increase in temperature followed by 1 hr at 500°C. All samples were transferred and stored in air after reduction.

Rh dispersions were measured on freshly prepared Rh-containing catalysts by CO chemisorption and found to be approximately 30%. This is consistent with electron microscope measurements of average Rh crystallite sizes in these catalysts, which averaged 35 to 50 Å. In the 2.5% Rh–0.1% Mn catalyst, then, the Mn added is equal to 25 atom% of the Rh surface atoms. This is approximately the amount of Mn required to produce the maximum effect on catalyst activity (*5*). Further additions of Mn have relatively little effect.

RESULTS

0.2% Mn/SiO_2

The 0.2% Mn/SiO_2 sample was colorless when prepared. After standing in air for several months, it became purple but lost that color after the following sequence of reducing treatments:

(i) evacuation at 500°C, 30 min;
(ii) heating in H_2 (600 Torr, 1 Torr = 1333 N m^{-2}) at 500°C, 16 hr;
(iii) evacuation at 500°C, 45 min.

The color change suggests a reduction in the Mn valence from +4 to +2. ESR spectra observed at 77°K after these treatments are shown in Figs. 1 and 2. After room temperature evacuation, an unresolved Mn^{2+} signal was obtained as shown in Fig. 1A. On exposure to 20 Torr of H_2O vapor at room temperature for a few minutes, then cooling again to 77°K, the signal changed to the sextet pattern at $g = 2.00$, typical of magnetically isolated Mn^{2+} ions in a symmetrical (e.g., octahedral) environment.

Exposure of the H_2O-containing sample to CO at room temperature caused no further change in the signal. Exposure to NO_2 under the same conditions, however, caused an increase in Mn^{2+} signal intensity, as shown in Figs. 2A and B. The strong, sharp triplet at the center of Fig. 2B is due to adsorbed NO_2. Treatment of the original dry sample with NO_2 resulted in an increase in the signal intensity, but the signal was not resolved into a sextet pattern until H_2O was added.

2.5% Rh–0.2% Mn/SiO_2

This sample was stored in air for some months prior to the ESR study. ESR spectra were obtained before any treatment of the specimen (Fig. 3A); after it was evacu-

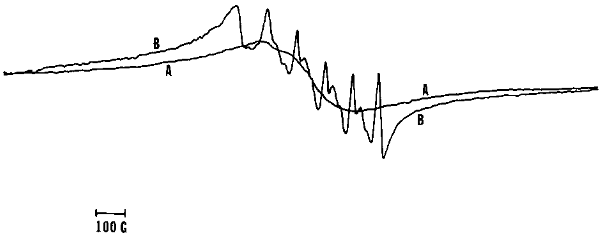

FIG. 1. Catalyst, 0.2% Mn/SiO_2: (A) reduced, evacuated; (B) after H_2O treatment.

ated at room temperature for 30 min (Fig. 3B); after it was exposed to O_2 at temperatures up to 400°C, followed by room temperature evacuation; and after it was exposed for a few minutes to 20 Torr of H_2O vapor at room temperature (Fig. 3C). The resolved sextet patterns (Figs. 3A and C) observed at $g = 2.00$ are again clearly due to magnetically dilute Mn^{2+}. Traces of structure in the sextet pattern could indicate either slight differences in the bonding of Mn^{2+} at different sites or a lack of perfect symmetry at a set of identical sites.

After the specimen was degassed at room temperature and recooled to 77°K, the original sextet pattern (Fig. 3A) virtually disappeared, leaving a small, unresolved signal (Fig. 3B). The residual signal presumably was due to some Mn^{2+} ions in a symmetrical environment such that they could interact with other paramagnetic species, possibly nearby Mn^{2+}. (Note that this catalyst could be considered to have some excess Mn present over and above that needed for maximum catalytic effect.) This faint pattern was unchanged after exposure of the specimen to O_2. However, after the specimen was exposed to H_2O vapor at room temperature, its spectrum was more intense and better resolved than the original spectrum. The integrated intensity of the H_2O-treated sample (Fig. 3C) corresponded to about one-third of the Mn present in the catalyst.

Other species capable of complexing with exposed Mn^{2+} were investigated. NH_3 (600 Torr) was shown to give results very similar to, but distinguishable from, those obtained with H_2O, as shown in Fig. 4. The isotropic coupling constants for ^{55}Mn can be determined from the spectra shown in Fig. 4 to be

$$A_{\text{iso}}\,(\text{Mn})_{\text{H}_2\text{O}} = 96 \pm 1\ \text{G},$$
$$A_{\text{iso}}\,(\text{Mn})_{\text{NH}_3} = 91 \pm 1\ \text{G}.$$

Treatment of a water-free sample at room temperature with 600 Torr of CO resulted in the slow development of a signal exhibiting

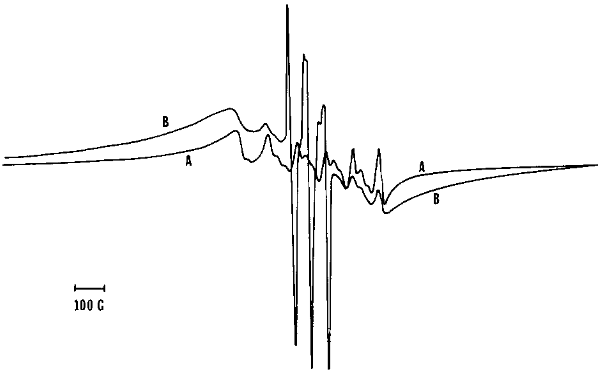

FIG. 2. Reduced, evacuated 0.2% Mn/SiO_2: (A) after H_2O treatment; (B) after H_2O + NO_2 treatment.

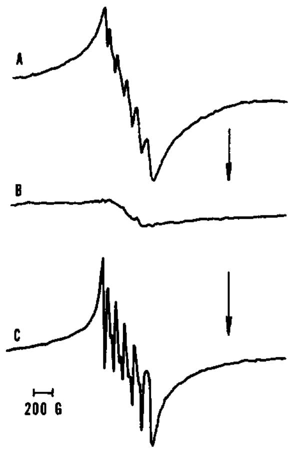

FIG. 3. (A) As received 2.5% Rh–0.2% Mn catalyst; (B) after RT evacuation; (C) after adding H_2O.

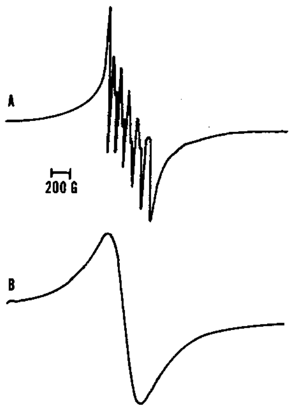

FIG. 5. Catalyst, 2.5% Rh–0.2% Mn: (A) NH_3 added; (B) H_2O + CO added (40 hr).

no fine structure. The spectrum obtained after 40 hr is shown in Fig. 5B. Again, the lack of fine structure implies that the surface Mn^{2+} complex formed as a result of the CO treatment is symmetrical but that a Mn^{2+}–Mn^{2+} interaction exists.

A change in the spectrum occurred when samples which had been treated with H_2O were exposed to 600 Torr of CO at room temperature for a few minutes without removing the H_2O, as shown in Fig. 6B. This treatment caused the Mn^{2+} signal to triple in intensity, to a point where it represented virtually all of the Mn present. The sextet pattern was well resolved, but close examination suggested the resolution was poorer than had been observed with the sample treated with H_2O or NH_3 only, and the tapering shoulders extended much farther out.

One distinction to be emphasized between the Rh–Mn/SiO_2 and the Mn/SiO_2 results is the increase in Mn^{2+} signal as a result of treatment with CO/H_2O when Rh was present, but the lack of any increase when Rh was absent.

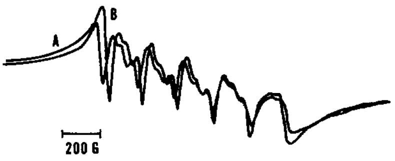

FIG. 4. Catalyst, 2.5% Rh–0.2% Mn: (A) H_2O added; (B) NH_3 added.

2.5% Rh–0.1% Mn/SiO₂

In order to eliminate the possibility that some Mn existed in valence states higher than 2+ in the 2.5% Rh–0.2% Mn/SiO_2 sample studied first, and thus that some of the Mn^{2+} observed following the CO treatment might be due to reduction of those species, a fresh sample of 2.5% Rh–0.1% Mn/SiO_2 was subjected to the same reducing treatment as that given the Mn/SiO_2 sample.

Even more than was true of the original Rh–Mn sample, very little signal was observed after evacuation of the sample at room temperature (Fig. 7A). As shown in Fig. 7B, treatment with H_2O caused the characteristic Mn^{2+} sextet pattern to appear. Treatment of the H_2O-saturated sample either with CO (Fig. 6C) or with NO_2 again caused the intensity of the signal to more than double. Room temperature treatment with O_2 (200 Torr, 16 hr) caused the signal intensity to fade. The fading could be due either to loss of H_2O, thus recreating an unsymmetrical environment around the Mn^{2+} ions, or to chemisorption of O_2, whose paramagnetism would also cause broadening of the Mn^{2+} signal. The sample could be rehydrated to reproduce the origi-

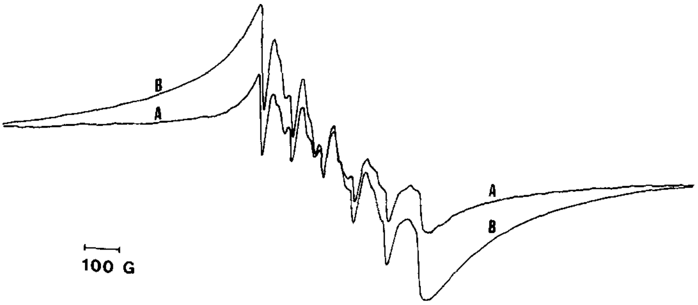

FIG. 6. Catalyst, 2.5% Rh–0.2% Mn: (A) H_2O added; (B) H_2O + CO added.

nal spectrum exactly. Subsequent treatment of the rehydrated, oxidized sample with CO gave a spectrum corresponding to that obtained on CO treatment of the original hydrated sample. Treatments with CO_2 alone or in combination with H_2O did not reproduce the effect of the CO/H_2O treatment.

DISCUSSION

The discussion will be divided into two sections, one having to do with the state of the Mn present in the Mn-only and the Rh–Mn catalysts, and the other having to do with the relation between the state of the Mn and its observed effect on CO hydrogenation.

As noted in the Introduction, the most nearly comparable studies of bimetallic supported catalysts are those of Garten, Vannice, and co-workers (*7, 8*). They found that Fe^{3+} supported on SiO_2 (Cabosil) or η-Al_2O_3 was reduced only to Fe^{2+} in an hour with flowing H_2 at 450°C, in the absence of Pd or Ru. In the presence of those platinum group metals, Fe was reduced to metal which migrated from the surface of the support and alloyed with the more reducible metals present as crystallites on the support.

In view of the much greater resistance of Mn^{2+} than of Fe^{2+} to reduction to the metal, it seems impossible to sustain the hypothesis that Mn^{2+} was reduced to metal in the absence of Rh, even though the reducing conditions employed here were slightly more forcing than those used in the earlier studies. It might be suggested that some Mn^{+} may have formed which would not be detectable by ESR, but even that seems unlikely in view of the nonexistence of Mn^{+} compounds in the conventional wet chemistry of the element. Thus, the increase in Mn^{2+} signal as a result of treatment of the Mn/SiO_2 catalyst with NO_2 is probably to be explained as due to a change in the coordination of some Mn^{2+} ions from a highly unsymmetrical to a moderately symmetrical form. Having $6s_{5/2}$ configuration, Mn^{2+} ions are subject to crystal field splitting and their ESR signal could be broadened beyond recognition by a strong asymmetric field.

The effect of H_2O appears to be to uncouple Mn^{2+} ions from nearby paramagnetic ions, probably other Mn^{2+} ions. There is no significant change in integrated signal intensity when H_2O is added to the Mn/SiO_2 catalyst, but the unresolved signal is clearly resolved into the typical sextet pattern by

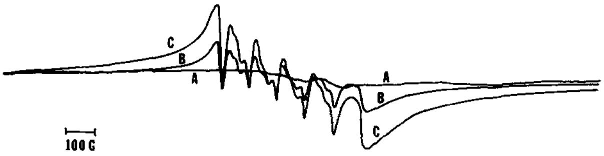

FIG. 7. Catalyst, 2.5% Rh–0.1% Mn/SiO_2: (A) evacuated; (B) H_2O added; (C) H_2O + CO added.

this treatment. Such an effect could be produced, for example, by hydrolyzing O^{2-} linkages between Mn^{2+} ions to pairs of OH^- ions. The possibility of coupling dipoles through the electrons of intervening oxide atoms is well recognized (*10*).

In the Rh-containing catalysts, particularly the one with minimal excess Mn so far as its catalytic effect is concerned, virtually all the Mn would appear to be present in asymmetric sites unless a portion of it is reduced below Mn^{2+}. Approximately one-third of the Mn present seems to be in sites such that H_2O alone generates symmetrically coordinated, magnetically isolated Mn^{2+} ions. Whether this occurs by hydrolysis of oxide linkages, simple incorporation of H_2O in the Mn^{2+} coordination sphere, or both, cannot be determined, but it is clearly a facile process. The remaining two-thirds of the Mn present can only be converted to symmetrically coordinated Mn^{2+} ions by the use of CO or NO_2, and in both those cases the Mn^{2+} generated is not magnetically isolated. Neither CO_2 nor O_2 produces the signal enhancement observed with CO and NO_2, a result more easily understood if the phenomenon is due to a change in coordination rather than a change in valence. Only by adding H_2O is the magnetically isolated form produced.

These results are evidence for strong interaction between the added Mn and the Rh crystallites, although reduction of Mn to the metallic state is highly unlikely. Formation of a stable Mn–O–Rh surface compound during the initial catalyst reduction would account for the observations. This is consistent also with the observation that only relatively small additions of Mn to the catalysts are needed to produce the maximum effect on synthesis gas conversion. The implied preferential association of Mn with the Rh in Rh–Mn/SiO_2 catalysts, despite the presence of a SiO_2 surface greater than that of Rh by a factor of $\sim 10^3$, requires a significant thermodynamic driving force. It can be calculated that the heat of interaction of Mn must be greater by 4–5 kcal/mole Mn with Rh than it is with SiO_2, if the observed distribution is an equilibrium one determined solely by relative heats of interaction. Such a difference in favor of association with Rh metal is somewhat unexpected for Mn^{2+}, since stable manganous silicates exist.

Once the idea that Mn is distributed as Mn^{2+} over the surface of the Rh crystallites in Rh/SiO_2 catalysts is accepted, a question arises as to why Mn in that state exhibits the effects it does. A comparison between the performances of a 2.5% Rh/SiO_2 catalyst and a 2.5% Rh–0.2% Mn/SiO_2 catalyst in the conversion of synthesis gas is shown in Table 1. It will be seen that the addition of 0.2% Mn resulted in increases in the overall rate of CO conversion, N, and in the selectivities to C_2 chemicals,[4] S_1, and to C_{2+} hydrocarbons, S_2. The symbols are defined as follows:

N = moles of product/sec/Rh atom on the surface. This rate is measured at 300°C and 100 atm total pressure, using 1 H_2:1 CO synthesis gas at a space velocity such that the conversion is $\leq 10\%$.
S_1 = moles of C_2 chemicals/mole CH_4.
S_2 = moles of C_{2+} hydrocarbons/mole CH_4.

If the role of Mn^{2+} is simply to form a stable mixed surface oxide phase on the Rh surface, Mg^{2+} and Zn^{2+} might be expected to have comparable effects. The three cations are of roughly comparable ionic radius (Mg^{2+} = 0.66 Å, Zn^{2+} = 0.74 Å, Mn^{2+} = 0.80 Å), and all three form stable spinel-type rhodates of composition MRh_2O_4. Ichikawa found (*11*) that catalysts made by impregnating MgO and ZnO supports with Rh carbonyl clusters gave him CH_3OH in high efficiency from synthesis gas, rather than the CH_4 he obtained from the same clusters on SiO_2 supports. The production of CH_3OH by Rh-based catalysts has also been observed by Bartley (*12*) in this labo-

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[4] Acetic acid, acetaldehyde, and ethanol.

TABLE 1

Effects of Manganese Additions on Catalyst Activity and Product Selectivities[a]

	2.5% Rh	2.5% Rh–0.2% Mn	$\frac{0.2\%\ \text{Mn}}{\text{no Mn}}$
Turnover No., $N(\simeq k_1\theta_H)$	0.03	0.30	10
Selectivity to C_2 chemicals, S_1	0.43	0.83	—
Selectivity to higher hydrocarbons, S_2	0.03	0.18	—
$NS_1\ (\simeq k_{CO}\frac{k_1}{k_4}\theta_{CO})$	0.013	0.25	20
$NS_2(\simeq k_p\frac{k_1}{k_4}\theta_{CH_2})$	0.0009	0.054	60

[a] N, S_1, and S_2 are defined in the text.

ratory. His catalysts were prepared using $RhCl_3$ as the Rh source and either using MgO as a support or adding 2% $Mg(NO_3)_2$ to the $RhCl_3$ solution during the preparation of 2.5% Rh/SiO_2 catalyst. Bartley's results demonstrate that the Rh clusters used by Ichikawa confer no special chemical properties on the resulting catalysts, though Ichikawa did obtain catalysts of very high activity.

In contrast to the results just described, when 2% $Mg(NO_3)_2$ was added to a 2.5% Rh/SiO_2 catalyst after the latter had been reduced, rather than adding it with the $RhCl_3$, there was little change in product distribution from the Rh-only case but the rate of CO conversion increased by a factor of about 3 (*12*). In other words the effect was quite similar to that obtained by adding a limited amount of Mn^{2+}.

These results seem most readily understandable in the light of Rabo and coworkers' observation (*13*) that Rh is borderline among the Group VIII metals in its ability to dissociate CO. The addition of Mg^{2+} to the catalysts would seem to modify the Rh surface chemistry in such a way as to inhibit the dissociation of CO. Without CO dissociation, surface carbon formation would be minimized and little or no CH_4 formation should occur. Instead, the CO could hydrogenate without rupture of the C–O bond.

Mg could suppress CO dissociation on Rh by forming a surface mixed oxide, presumably with Rh as Rh^+, just as Mn^{2+} has been postulated to do from the results of the ESR investigation reported here. To suppress C formation as completely as Mg and Zn appear to in Ichikawa's experiments, a high coverage of the Rh surface should be required. The effect of Mn on selectivity, i.e., the continuing formation of CH_4 and of C_2 chemicals formed from surface CH_2 and CH_3 groups, suggests that there is a lower degree of Rh surface coverage by Mn than by Mg in the catalysts prepared on MgO supports or by coimpregnation. The differences in size of the cations could be responsible for their different effects as additives. If Mg^{2+} and Zn^{2+} can fit into a two-dimensional crystalline surface oxide phase, but Mn^{2+} cannot, the differences in behavior of the ions could be accounted for.

A decrease in the rate of CO dissociation as a result of the addition of Mn to the Rh catalyst could lead to a steady-state degree of Rh surface coverage by C lower than the coverage on the Rh-only catalyst.

It seems highly likely that Rh surface atoms associated with C (or O) would not chemisorb H or CO as strongly as would bare Rh metal. Recent observations by Benziger and Madix (*14*), for example, provide direct evidence for the existence of such a phenomenon in the case of an Fe crystal. Thus decreasing θ_C should increase the surface available for the formation of CH_3 and for its conversion to stable products.

It has been argued elsewhere (*5*) that during steady-state operation of Rh catalysts the fractional coverage of the surface by C, θ_C, is close to unity. The turnover number is presumed to be proportional to the product $\theta_H\theta_C$ (*15*). If C excludes H from the catalyst surface, $\theta_H \propto (1 - \theta_C)$. Thus reducing θ_C will increase the overall rate so long as $\theta_C > 0.5$. For example, if θ_C drops from 0.999 to 0.99, or from 0.99 to 0.90, the tenfold increase in $(1 - \theta_C)$ could easily more than compensate for the slight decrease in θ_C.

An increase in the surface concentration of active sites on adding Mn to Rh/SiO_2 catalysts is not inconsistent with the observed effects of Mn on the overall conversion rate and on the selectivities. The power law rate expressions describing the overall kinetics of CO hydrogenation were found to be of the same form for Rh/SiO_2 and $Rh–Mn/SiO_2$ catalysts (*5*). This suggests that the Mn does not greatly change either the reaction mechanism or the equilibrium constants for chemisorption of reactants or products. If the changes in the elementary rate constants and the equilibrium constants are not large, changes in catalyst performance should be related to changes in the populations of various surface species.

The turnover numbers and the selectivities, defined above, can be related to surface species concentrations by assuming a specific reaction mechanism. According to the mechanism proposed previously (*5*), the rate-determining step at high pressure is

$$C + H \xrightarrow{k_1} CH,$$

whence the turnover number is (*14*)

$$N = k_1\theta_H\theta_C \simeq k_1\theta_H.$$

The competitive reactions which determine selectivity to C_2 chemicals, S_1, are

$$CH_3 + H \xrightarrow{k_4} CH_4$$

and

$$CH_3 + CO \xrightarrow{k_{CO}} CH_3CO,$$

whence

$$S_1 = \frac{k_{CO}\theta_{CO}}{k_4\Theta_H}.$$

The selectivity to C_{2+} hydrocarbons, S_2, is determined by

$$CH_3 + H \xrightarrow{k_4} CH_4$$

and

$$CH_3 + CH_2 \xrightarrow{k_p} C_2H_5,$$

whence

$$S_2 = \frac{k_p\theta_{CH_2}}{k_4\theta_H}.$$

If the rate constants are unchanged by the addition of Mn, the change in N requires a 10-fold increase in θ_H, the change in the product NS_1 requires a 20-fold increase in θ_{CO}, and the change in NS_2 requires a 60-fold increase in θ_{CH_2}. Even though there may in fact be some changes in the rate constants involved, the magnitude of these changes is great enough to suggest that an increase in the effective surface of the catalyst did occur.

The postulated decrease in θ_C on the catalyst surface as a result of Mn additions might be due to chemical effects (valence change, ligand properties) or to geometrical effects. There is evidence from earlier work on methanation over Ni (*15*) and Ru (*16*), and also from studies on Rh in this laboratory, that additions of Cu to Group VIII metal-based CO hydrogenation catalysts lower the activity of these metals in that reaction. The effect of added Cu has been ascribed to a requirement that groups of four to six adjacent metal atoms must exist on the catalyst surface before CO decomposition can occur. Copper is inactive in the CO decomposition reaction, so Cu additions reduce sharply the number of multiple Group VIII metal atom sites available. This is strictly a geometric effect and the failure to observe any increase in CO hydrogenation rate at small Cu additions indicates that other factors must be responsible for the promoter action of Mn^{2+}.

The possibility that Mn^{2+} has specific chemical properties which make it unique as a promoter in CO hydrogenation cannot be completely dismissed. $Mn(OH)_2$ on silica gel is an extremely active catalyst for the decomposition of a methanol–water mixture to produce H_2 and CO_2 (*17*). The observed increase in catalyst activity as a result of Mg^{2+} addition argues, however, for the view that most of the increased activity is due simply to the stabilization of an oxidized form of Rh on the metal surface by mixed oxide formation. That conclusion is also consistent with the recent report by Castner *et al.* (*18*) that preoxidation of Rh single crystals results in greatly increased catalyst activity and the formation of oxygen containing products.

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