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NOTES

Investigation by Ethylene Addition of Alkali Promotion of CO Hydrogenation on Rh/TiO$_2$

I. INTRODUCTION

The catalytic conversion of synthesis gas to oxygenated compounds, especially alcohols, is generally recognized as a promising route for providing clean fuels and petrochemical feedstocks. The mechanism for this synthesis, however, is not well understood. The selectivity to oxygenated compounds is generally affected by the type of transition metal catalyst, the support used, the presence of additives (i.e., promoters), and reaction conditions. Supported Rh catalysts have been demonstrated to be excellent for the synthesis of oxygenate compounds (*1–3*). It has been suggested that the selectivity to alcohols during CO hydrogenation on Rh varies with the basicity or acidity of the support (*2*). Although the influence of the support is now somewhat known, little is known about the effect of alkali promoters on the catalytic properties of Rh catalysts. Recently, it has been reported that alkali promotion of Rh/Al$_2$O$_3$ or Rh–Mn/SiO$_2$ enhances the oxygenate yield (*4, 5*). A dual-site mechanism for formation of oxygenates over supported Rh catalysts was proposed by these investigators. It was postulated that surface carbidic species are hydrogenated to C_xH_y on metallic Rh, while CO insertion takes place on Rh in an oxidized state (*6*). However, the nature of the active sites and the role of alkali promoters in oxygenate synthesis over Rh is not well understood.

To develop a better understanding of the effect of alkali species (Li, K, Cs) on the activity and selectivity of Rh catalysts for the synthesis of oxygenates, CO hydrogenation over alkali-promoted and unpromoted Rh/TiO$_2$ has been studied. Use of Rh/TiO$_2$ results in the production of significant quantities of both hydrocarbons and oxygenates, so use of this catalyst system offers us an opportunity to better understand the effect of alkali promotion on CO hydrogenation activity and selectivity. In order to probe the catalyst surface during reaction, small quantities of ethylene were added to the reaction mixture. This provided an excellent way to clarify the effects of promotion on specific reactions occurring during the synthesis of hydrocarbons and oxygenates.

II. EXPERIMENTAL

TiO$_2$-supported Rh catalysts were prepared using the incipient wetness method and an aqueous solution of RhCl$_3$ · 3H$_2$O with a pH of 3–3.5. These catalysts were then dried overnight in air at 40°C. The alkali-promoted Rh catalysts were also prepared in a similar manner using an aqueous solution of RhCl$_3$ · 3H$_2$O and an alkali nitrate (Li, K, Cs). The catalysts were prepared so that the Rh loading was 3 wt% and the atom ratio of alkali promoter to Rh was $\frac{1}{2}$. Following drying, the catalysts were reduced in flowing H$_2$ while heating in 50°C steps (30 min) to 400°C and holding for 16 hr. Prior to reaction, the catalysts were again reduced in flowing hydrogen at 500°C for 3 hr to induce the strong metal–support interaction (SMSI) (*7*).

Reaction was carried out in a differential reactor at 300°C, 10 atm, and CO/H$_2$ = 2. The reactor effluent was analyzed by gas chromatography. Ethylene was added to the CO/H$_2$ reactant mixture after 3 hr of reaction. It constituted only 2.3 mole% of the mixture. The ethylene addition was utilized for 3 hr and then discontinued. The

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rate of formation of each product after discontinuing ethylene addition essentially *returned* to the value existing before ethylene addition. The rates of formation of methane, C_1 and C_2 oxygenated compounds, and acetone were virtually unaffected during ethylene addition. The increase in the rates of formation of other products was assumed to be due to the added ethylene. By determining the difference in rate of product formation between, during, and after the addition of ethylene, the rates of hydrogenation, chain incorporation, and, hydrocarbonylation of ethylene could be estimated.

The average Rh particle sizes for the catalysts were determined by X-ray diffraction line broadening using a Mo$K\alpha$ radiation source.

III. RESULTS AND DISCUSSION

a. *CO Hydrogenation over Rh/TiO_2 and Alkali-Promoted Rh/TiO_2*

Several previous studies (*8*, *9*) have shown that Rh/TiO_2 reduced at 500°C exhibits (a) low activities for hydrogenation of olefins and hydrogenolysis of alkanes, (b) high selectivity for production of olefins and long chain hydrocarbons in CO hydrogenation, and (c) suppression of H_2 and CO chemisorption. These observations were attributed to SMSI. However, similar activities and selectivities in CO hydrogenation at 200°C and 1–10 atm have been observed after reduction of Rh/TiO_2 at 200 and 400°C (*2*). During this study, we observed that the product selectivity at 220°C and 10 atm for Rh/TiO_2 reduced at 500°C was essential the same as for Rh/TiO_2 reduced at 200°C but the rate of CO hydrogenation for Rh/TiO_2 reduced at 500°C was somewhat lower. Orita *et al.* (*10*) have also found that Rh/TiO_2 reduced at 500°C exhibits a decrease in the amount of hydrogen chemisorbed on Rh and a decrease in the rate of formation for all the products but methanol. It has been suggested that oxygen from CO dissociation and water from CO hydrogenation may remove the SMSI effect (*11*). On the contrary, Vannice has reported (*12*) that water has no effect on SMSI and he has proposed (*13*) a model to account for the increase in CO hydrogenation activity of Pt/TiO_2, relative to Pt on non-SMSI supports, after either high- or low-temperature reduction. In this study, specific activities in mole/kg/hr were used to compare catalytic activities rather than turnover frequencies due to uncertainties in the determination of the number of Rh surface sites in both promoted and SMSI catalysts. These uncertainties can arise from (a) suppression of H_2 chemisorption caused by alkali promotion (*14*), (b) blockage of surface sites by the alkali promoters, and (c) H_2 and CO chemisorption suppression [or slow uptake of H_2] due to SMSI (*13*, *15*, *16*). Average particle size of each of the Rh catalysts was determined from X-ray diffraction line broadening using the Scherrer equation. It was found that all of the catalysts had average Rh particle diameters less than 4 nm.

Because of the complex distribution of reaction products, only the major hydrocarbon and oxygenated products are reported in Table 1. As shown in Table 1, the rate of CO conversion decreased in the order

$$\text{unpromoted} > \text{Li} > \text{K} > \text{Cs}.$$

Although the rate of formation of all the products decreased upon alkali promotion, there were significant variations in the rate of formation of various products for the different alkali-promoted catalysts. The variation in activity among the unpromoted and variously promoted catalysts differed by more than a factor of 35 for CO conversion. While the rate of hydrocarbon formation varied by more than a factor of 55, the rate of formation of acetaldehyde and ethanol changed by only a factor of 22, and the rate of methanol formation decreased by only a factor of 4. It appears that alkali promoters have different effects on the formation of oxygenated compounds than on that of hydrocarbons. The diminution of hydrogena-

TABLE 1

Product Distributions over Alkali Promoted and Unpromoted Catalysts

Catalyst	Rate of CO conversion (mole/kg/hr)	Rate of CO_2 formation (mole/kg/hr)	Product formation rate (mole/kg/hr)					Mole ratio	
			CH_4	C_{2+}	MeOH	EtOH	MeCHO	C_3–C_5 Ole./Par.	$\frac{\text{MeCHO}}{\text{EtOH}}$
Rh/TiO_2	17.31	1.93	7.56	1.3	0.026	0.44	0.11	2.7	0.25
$Rh–Li/TiO_2$	6.37	0.169	2.70	0.68	0.024	0.20	0.12	5.8	0.61
$Rh–K/TiO_2$	1.79	0.12	0.67	0.108	0.008	0.029	0.08	4.6	2.79
$Rh–Cs/TiO_2$	0.48	0.023	0.10	0.061	0.0064	0.0022	0.023	4.2	10.45

Note. Reaction conditions: $CO/H_2 = 2$, 300°C, 10 atm.

tion ability by the alkali promoters is also demonstrated in Table 1, as indicated by the increase in mole ratio of C_3–C_5 olefins-to-paraffins and the increase in the acetaldehyde-to-ethanol ratio following alkali promotion.

The CO hydrogenation results reported here are consistent in most respects with those reported by Wilson *et al.* (*5*). They found that the rate of formation for all the products over $Rh–Mn/SiO_2$ catalysts decreased upon Li and Na promotion, while the selectivity to oxygenated compounds was enhanced. This clearly indicates that there is less suppression of oxygenate formation than of hydrocarbon formation. In contrast to the results of Wilson *et al.* (*5*) and those reported here, Kagami *et al.* (*4*) have found that alkali species promote the oxygenate formation rate on Rh/Al_2O_3 in the order: Na > K > unpromoted. This discrepancy may be due to differences in the catalyst precursors and supports used. It was proposed by Kagami *et al.* (*4*) that the active sites for oxygenate formation, which may be located near the juncture of the rhodium metal and the support, are modified by the addition of an alkali promoter, especially Na.

b. Ethylene Addition to the CO/H_2 Reaction Mixture

In an attempt to clarify the above findings, ethylene was added in small concentrations (2.3 mole%) to the reaction mixture. This addition did not result in any significant modification of the formation of products by CO hydrogenation as indicated by the constant formation rates of methane, methanol, and C_2 oxygenated compounds. The formation rates of the major products [C_2H_6, C_{3+} hydrocarbons, C_2H_5CHO, and $C_2H_5CH_2OH$] from ethylene are shown in Table 2. The rate of hydrogenation of ethylene to ethane decreased by as much as 2 orders of magnitude following promotion while the total rate of formation of propionaldehyde and *n*-propanol decreased only by a factor of 2. It is useful to consider these two products (propionaldehyde and *n*-propanol) together since they are probably formed from the same surface intermediate; a simple hydrogenation step converts the propionaldehyde to propanol. The smaller variation in the rate of propionaldehyde formation from ethylene compared to that of acetaldehyde formation by CO hydrogenation is expected since propionaldehyde can be formed directly by CO insertion into the adsorbed ethylenic surface intermediates, whereas acetaldehyde is probably produced via CO insertion into a CH_x–metal species which has to be generated by CO dissociation followed by hydrogenation (*2*).

The effects of additives on supported metal catalysts can generally be classified into one of two categories: (a) modification of catalytic properties of the metal by the

TABLE 2

Increase in Product Formation Rate as a Result of Ethylene Addition

Catalysts	Rate of C_2H_4 conversion (mole/kg/hr)	Increase in product formation rate (mole/kg/hr)				
		EtCHO	Propanol	CH_4	C_2H_6	Other HC's
Rh/TiO_2	8.30	0.132	0.075	0	7.70	0.39
$Rh\text{-}Li/TiO_2$	4.07	0.170	0.077	0	3.55	0.273
$Rh\text{-}K/TiO_2$	1.20	0.129	0.033	0	1.02	0.011
$Rh\text{-}Cs/TiO_2$	0.19	0.108	0.006	0	0.073	0.001

Note. Reaction conditions: $CO/H_2 = 2$, 300°C, 10 atm, 2.3 mole% C_2H_4.

chemical nature of the additive, and (b) blockage of surface sites by the physical presence of the additive. Physical blockage of the surface active sites by alkali promoters would have a great effect on those specific reaction steps which require large ensembles of surface atoms, such as CO dissociation (*17*), and would only slightly affect those steps, such as hydrogenation, which do not require such large ensembles. Thus, the physical blockage of surface atoms could lead to an enhancement in the selectivities for those products which form on small ensembles of surface atoms. However, alkali promoters are known to be able to enhance adsorption energy and dissociation probability of CO and to suppress hydrogenation of surface carbon and olefins (*14, 18–23*). This seems to suggest that the chemical effect of alkali promoters on CO hydrogenation is more significant than just that due to physical blockage. The slight decrease in the total rate of propionaldehyde and propanol formation from ethylene upon alkali promotion shows that CO insertion into the adsorbed ethylenic surface species is not greatly affected by the presence of the alkali promoters. It suggests that this insertion reaction may be structure insensitive, occurring on active sites which may be single atoms. The significant suppression of ethylene hydrogenation on Rh is reasonable since suppression of hydrogenation ability has been identified as a major effect of alkali promoters on CO hydrogenation over transition metal catalysts (*14, 18–20*). Our results are indeed consistent with previous findings that alkali promoters have different effects on the formation of oxygenates than on that of hydrocarbons. This may help to confirm that the active sites for the formation of oxygenated compounds are quite different from those for hydrocarbons, as proposed earlier by Wilson *et al.* (*5*) and Watson and Somorjai (*6*).

Although the actual state of the alkali promoter during reaction is still not clear, it is generally considered that alkali species may affect the electron density of metal catalysts (*21–23*). However, it should be emphasized that electrons cannot be expected to be donated by the alkali cations themselves (*30*). It has been suggested that the presence of alkali promoters on rhodium catalysts may result in a lowering of the average surface oxidation state of rhodium (*5*). However, if surface rhodium ions are considered to be responsible for oxygenate formation (*6*), a decrease in the average oxidation state of Rh ions should result in a decrease in the rate of formation of oxygenated compounds but not in that for hydrocarbons. No such alkali modification was evident in this study since there was only slight modification in the rate of propionaldehyde and propanol formation during ethylene addition upon alkali promotion. It should be noted that the ethylene from CO hydrogenation is not the same as the ethylene added until it desorbs from the surface of the catalyst. Specifically, the adsorbed added ethylene is not equivalent to the precursor to ethylene formed from CO hydrogenation. This can be concluded since the selectivity for the reacted, added ethylene to enter chain growth rather than to be hydrogenated to ethane is significantly different from that for the C_2H_x surface intermediate formed during CO hydrogenation (*24*). However, in this study, the added ethylene did serve as a probe to distinguish hydrogenation and CO insertion activities under synthesis conditions.

The rate of incorporation of ethylene into higher hydrocarbons and the extent of hydrogenolysis of ethylene to methane can be seen in Table 2. Hydrogenolysis of ethane and ethylene did not occur to any detectable extent for either promoted or unpromoted Rh/TiO_2 catalysts. Ko and Garten (*25*) have shown that the suppression of hydrogenolysis of ethane on TiO_2-supported metal catalysts is another manifestation of the SMSI effect. It has also been demonstrated that strongly chemisorbed CO can poison the hydrogenolysis reaction (*26*). The rate of incorporation of ethylene into higher hydrocarbons decreased in the order

$$\text{unpromoted} > \text{Li} > \text{K} > \text{Cs}.$$

Hall *et al.* (*27*) have reported that K-promoted F–T catalysts exhibit less ethylene incorporation into higher hydrocarbons than unpromoted ones. Nijs and Jacobs (*28*) found that the incorporation of α-olefins into higher hydrocarbons over Ru catalysts was higher using acidic supports than using neutral ones. In addition, alkali promoters have been used to poison the acidity of the support (*29*). Thus, the lower rate of incorporation of ethylene into higher hydrocarbons on alkali-promoted catalysts may be in part a consequence of the modification of the catalytic properties of rhodium as a result of an alteration in the acidity of the support by the alkali promoter. Aside from this indirect effect, it has been shown that alkali promotion results in slower rates of methane and hydrocarbon formation in CO hydrogenation. This appears to suggest that lower rates of formation of CH_x and C_xH_y species on alkali-promoted catalysts could also cause less incorporation of ethylene into higher hydrocarbons.

Although we still can not completely delineate the detailed mechanism of alkali promotion of Rh/TiO_2, we have demonstrated that the addition of probe molecules during synthesis conditions is an effective tool in studying effects of alkali promotion on metal catalysts. A further study of the effect of alkali promotion on variously supported and unsupported Rh catalysts using probe molecules is currently underway in our laboratory. It seeks to discriminate among the effects of alkali promoters, supports, and support–promoter interactions on the catalytic properties of Rh catalysts.

IV. CONCLUSIONS

The following important conclusions for Rh/TiO_2 catalysts can be drawn from this study:

(1) The active sites for oxygenate formation during CO hydrogenation over Rh/TiO_2 are not very sensitive to the chemical nature of the alkali promoter while the active sites for hydrocarbon formation are strongly dependent upon the chemical properties of the alkali promoter.

(2) The K and Cs promoters significantly suppress ethylene incorporation into higher hydrocarbons.

(3) The hydrogenation ability of Rh/TiO_2 catalysts decreases in the order: unpromoted > Li > K > Cs.

Finally, the addition of small quantities of ethylene to the reactant stream provides a way to probe modifications as a result of alkali promotion in a number of the reactions occurring during CO hydrogenation.

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