JOURNAL OF CATALYSIS 95, 435–446 (1985)

The Effect of Alkali Promotion on CO Hydrogenation over Rh/TiO$_2$

S. C. CHUANG, J. G. GOODWIN, JR.,[1] AND I. WENDER

Department of Chemical and Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania 15261

Received July 18, 1984; revised April 16, 1985

To develop a better understanding of the link between alkali promotion of hydrocarbon synthesis and that of oxygenate synthesis, CO hydrogenation over both unpromoted and promoted Rh/TiO$_2$ was studied in a differential reactor at 250–300°C, 1–10 atm, and CO/H$_2$ = 2. The ability of the alkali species to promote the selectivity for oxygenated compounds increased in the order unpromoted < Li < K = Cs, while the overall activity decreased in the order: unpromoted > Li > K > Cs. The promoters also showed a strong hydrogenation–suppression ability which may have caused the decrease in hydrocarbon selectivity and activity. The activities and selectivities of Rh/TiO$_2$ and alkali-promoted Rh/TiO$_2$ appear to be correlated with their catalytic abilities for hydrogenation, CO dissociation, and CO insertion. Results for unpromoted Rh/SiO$_2$ are also presented for comparison purposes.

INTRODUCTION

The synthesis of alcohols from carbon monoxide and hydrogen has been the subject of a number of past studies. The catalysts utilized for these studies have included transition metal catalysts such as Rh (*1*), Pd, Pt, Ir (*2*), Fe (*3*), and modified methanol synthesis catalysts (*4–7*). It is known that the addition of alkali salts to methanol synthesis catalysts often results in increased yields of higher alcohols. However, many questions still remain concerning the effect of various alkali species on the catalyst components and mechanism(s) of alcohol synthesis.

Rh catalysts provide excellent model systems for studying the effects of alkali promoters on the alcohol synthesis. Depending on the oxide support used and reaction conditions, the products over Rh may be primarily hydrocarbons or alcohols (*8–10*). It has been reported that the selectivity of CO hydrogenation over supported rhodium catalysts varies with the basicity of the support (*11, 12*). Rh on MgO, a very basic support, exhibits a 90% selectivity to methanol. Use of acidic supports, such as Al$_2$O$_3$, results mainly in CH$_4$ formation, while use of slightly acidic or basic supports (e.g., SiO$_2$, TiO$_2$, CeO$_2$) produces both alcohols and hydrocarbons. Rh/TiO$_2$ is a useful catalyst for studying alkali promotion effects on alcohol selectivity since it can produce significant quantities of both alcohols and hydrocarbons from the reaction of CO with H$_2$. Thus, one is able to simultaneously determine how both alcohol and hydrocarbon synthesis reactions are affected by the presence of a promoter. This paper reports on an investigation of the effect of various alkali species (Li, K, and Cs) on the activity and selectivity of Rh/TiO$_2$ for CO hydrogenation and on the deactivation characteristics of these catalysts. Rh/SiO$_2$ was also studied in order to compare the effect of the support.

EXPERIMENTAL

Material

Rh catalysts containing 3 wt% metal were prepared by impregnation (incipient wetness) of TiO$_2$ (Degussa) and SiO$_2$

---

[1] To whom all correspondence should be addressed.

0021-9517/85 $3.00

(Strem) using an aqueous solution of $RhCl_3 \cdot 3H_2O$ (Alfa Products). The TiO_2 used was Degussa P-25 which consists primarily of anatase (80%). Impregnation with $RhCl_3 \cdot 3H_2O$ and alkali nitrate (Li, K, Cs) in aqueous solution at pH = 3–3.5 produced the promoted catalyst. The atom ratio of the particular alkali element to Rh was 1/2. After impregnation, the samples were dried overnight in air at 40°C. Reduction was carried out in flowing H_2 on heating in 50°C steps (30 min) to 400°C and held at that temperature for 16 h. Prior to reaction, the TiO_2-supported catalysts were again reduced in flowing H_2 at 500°C for 3 h to induce strong metal–support interaction (SMSI) (*13*). The SiO_2-supported catalysts were reduced at 400°C for 1 h. The average Rh particle sizes for these catalysts were determined by X-ray diffraction (XRD) line broadening using a Mo$K\alpha$ radiation source and by hydrogen temperature-programmed desorption (TPD) in flowing Ar at 1 atm using a heating rate of 40°C/min from 25 to 400°C. Chlorine content of these catalysts were analyzed by Galbraith Laboratories, Inc. Average metal particle size and chlorine content for these catalysts are listed in Table 1. The higher chlorine content of alkali-promoted catalysts compared with that of unpromoted catalysts is likely due to a strong affinity between the chlorine and alkali ions (*14*).

TABLE 1

Metal Particle Size and Chlorine Content

Catalyst	Average metal particle diameter (Å)		Cl content (%)
	XRD	TPD (H_2)	
TiO_2	—	—	0.1
Rh/TiO_2	<40	24	0.044
$Li–Rh/TiO_2$	<40	27	0.43
$K–Rh/TiO_2$	<40	25	—
$Cs–Rh/TiO_2$	<40	36	0.39
Rh/SiO_2	40	46	0.068

Apparatus and Procedures

The gases used for these reaction studies were obtained from Air Products and included H_2 (UHP, 99.995%), He (UHP, 99.998%), and CO (UHP, 99.8%), which were further purified by passing through molecular sieve traps to remove water. Prior to passage through the molecular sieve trap, the hydrogen was passed through a Deoxo unit to convert oxygen to water.

The reaction temperature, pressure, and reactant flows were controlled by an Apple II computer. A Cyborg Isaac 91A served as an interface between the computer and three mass flow control meters (Brooks 5850) for controlling gas flows (H_2, CO, and He), a relay (Grayhill, Inc.) for controlling the reaction temperature, and a Brooks flow control valve for the reactor pressure control. The reactor effluent stream was analyzed by an on-line (Perkin–Elmer Sigma 1B gas chromatograph. The products were separated using an 8-ft. × $\frac{1}{8}$-in. Poropak Q column in series with a 6-ft × $\frac{1}{8}$-in. 80/100 Carbopack c/0.2% Carbowax 1500 using a He carrier flow of 20 cm^3/min. The GC columns were initially held at 40°C for 2 min and then temperature programmed at 15°C/min to 160°C, permitting a good on-line separation in a 60-min analysis of all C_1–C_7 paraffins and olefins, C_1–C_4 alcohols, C_1–C_4 aldehydes, acetone, ethyl acetate, acetic acid, CO, CO_2, and H_2O.

The reaction study was carried out in a differential reactor at 250–435°C and 1–10 atm with $CO/H_2 = 2$. High space velocities of 1100 to 11,000 h^{-1} were used to keep CO conversion below 5% in order to minimize heat and mass transfer effects and secondary reactions. A small amount of ethylene (2.3 mole% of reactant mixture) was added to the CO/H_2 reactant mixture in the last 3 h of each experimental run. The relative hydrogenation, chain incorporation, carbonylation, and hydrogenolysis activities were estimated by determination of the product distribution before, during, and after the addition of ethylene.

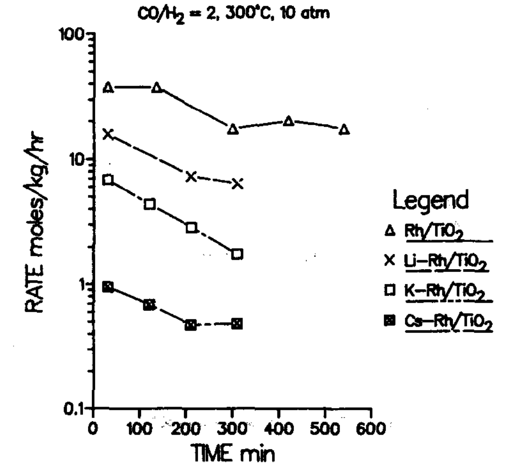

FIG. 1. Effect of alkali promotion on the rate of CO conversion.

RESULTS

Alkali-Promoted Rh/TiO$_2$

The activities of alkali-promoted and unpromoted Rh/TiO$_2$ for CO conversion as a function of time are shown in Fig. 1. An expression of activity in moles per kilogram per hour has been used due to the uncertainty in the estimation of the number of Rh surface atoms as a result of the suppression and/or slow uptake of H_2 or CO chemisorption caused by alkali promotion (*14–16*) and SMSI (*17, 18*). However, from the results of X-ray diffraction it was found that all of the catalysts before and after reaction had average Rh particle diameters less than 4 nm. In addition, analysis of the amount of H_2 desorbed during TPD assuming all the hydrogen was adsorbed only on the metal suggests that the TiO$_2$-supported catalysts had similar Rh dispersions and surface areas. The rate of CO conversion decreased in the order unpromoted > Li > K > Cs. The unpromoted Rh/TiO$_2$ exhibited a relatively stable activity after an initial decline in CO conversion during the first 300 min. The rates of formation of the major products as a function of time for Rh/TiO$_2$ are shown in Fig. 2. Since the rates of formation of all higher hydrocarbons behaved very similarly, only C_3 is shown in Fig. 2.

TABLE 2

Effect of Alkali Promotion on the Product Formation Rate

Catalyst:	Rh/TiO$_2$	Li–Rh/TiO$_2$	K–Rh/TiO$_2$	Cs–Rh/TiO$_2$
Rate of CO conversion (mole/kg/h):	17.31	6.37	1.79	0.48
	Product formation rate (mole/kg/h)			
CH_4	7.56	2.70	0.67	0.10
$C_{2+}HC$	1.3	0.68	0.108	0.06
MeOH	0.026	0.024	0.008	0.0064
EtOH	0.44	0.20	0.029	0.0022
MeCHO	0.11	0.12	0.08	0.023
Acetone	0.106	0.040	0.052	0.018

Note. Reaction conditions: CO/H_2 = 2, 300°C, 10 atm, and 300 min time-on-stream.

Although deactivation was not exactly the same for all the catalysts, similar patterns for the rate of product formation vs time, as shown in Fig. 2 for Rh/TiO$_2$, were observed for both the unpromoted and the promoted catalysts. The rate of methanol formation increased with time while the rates of formation for all the other products (hydrocarbons and oxygenates) exhibited an initial decline followed by a leveling off. An increase in the rate of methanol formation with time initially has also been reported for LaRhO$_3$ (*19*), Mn–Mo–Rh/SiO$_2$ (*20*), and Pd catalysts (*21, 22*).

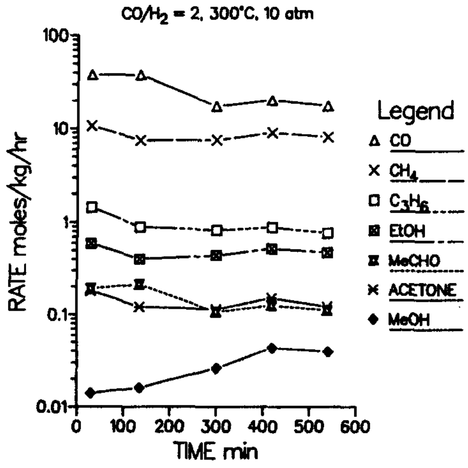

FIG. 2. Product formation rate vs time over Rh/TiO$_2$.

The effects of alkali promotion on the rates and selectivities of product formation are presented in Tables 2 and 3. The rates

TABLE 3

Effect of Alkali Promotion on Product Selectivity

Selectivity (wt%) to	Rh/TiO_2	$Li-Rh/TiO_2$	$K-Rh/TiO_2$	$Cs-Rh/TiO_2$
CH_4	49.9	46.6	37.7	20.6
C_{2+}	32.4	31.1	15.7	33.2
Total OX[a]	17.7	22.3	46.5	46.1
MeOH	0.3	0.8	0.8	2.5
EtOH	8.4	9.2	4.6	1.2
MeCHO	2.0	5.4	12.4	12.8
Acetone	2.5	2.4	10.4	13.5

Note. Reaction conditions: $CO/H_2 = 2$, 300°C, 10 atm, and 300 min time-on-stream.

[a] C_{3+} oxygenates are included in total OX (OX: oxygenated compounds).

for all the products formed decreased upon alkali promotion while the selectivity for oxygenated compounds increased. Similar results have also been reported for alkali-promoted $Mn-Rh/SiO_2$ (*23*). The Anderson–Schulz–Flory (A–S–F) distributions based on the mole fraction of both hydrocarbon and oxygenated compounds are shown in Figs. 3 and 4. The oxygenated products observed were methanol, ethanol, acetaldehyde, acetone, and ethyl acetate, while only trace amounts of C_{3+} straight-chain oxygenated compounds were detected. Because of the lack of straight-chain oxygenates above C_3 and the uncertainty in counting acetone as a C_2 or a C_3 species in A–S–F distribution, it is difficult to determine the chain-growth probability for the oxygenated compounds. A detailed mechanism for the formation of acetone and ethyl acetate is discussed later. The deviation of the C_2 mole fraction from an Anderson–Schultz–Flory distribution, as shown in Figs. 3 and 4, decreased in the order unpromoted > Li > K > Cs. The chain-growth probability of hydrocarbons appeared to be affected only slightly by the alkali promoters.

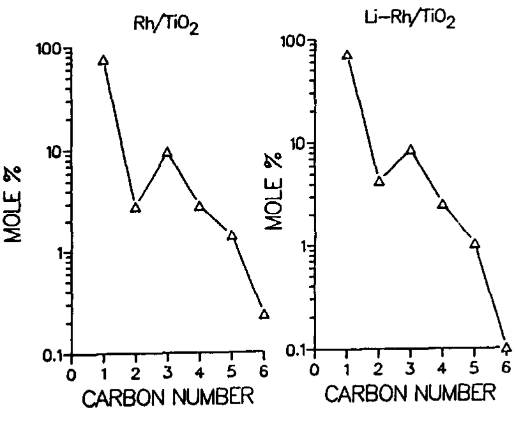

FIG. 3. Total hydrocarbon distribution over Rh/TiO_2 and $Li-Rh/TiO_2$.

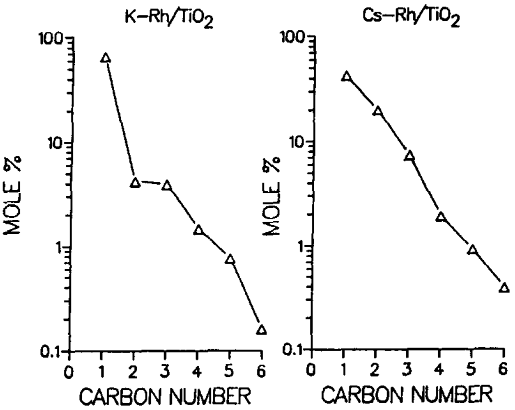

FIG. 4. Total hydrocarbon distribution over $K-Rh/TiO_2$ and $Cs-Rh/TiO_2$.

The apparent activation energies determined from Arrhenius plots for CO conversion and the formation of the major products are presented in Table 4. It is evident that the apparent activation energies for CO conversion and for the formation of certain products such as CH_4 and EtOH are not greatly affected by alkali promotion. This suggests that the reaction mechanism is not modified by alkali promotion. The values for the apparent activation energy for CO conversion agrees well with those previously reported for Rh catalysts while those for CH_4 formation are somewhat high (*9, 19, 23*). The higher values for E_{CH_4} may be due to the high CO/H_2 ratio used in this study. The inconsistency of the activation energies for acetaldehyde and acetone formation among promoted and unpromoted catalysts indicates that these species may have been involved in secondary reactions.

TABLE 4

Activation Energies (kcal/mole K) for CO Conversion and Product Formation

	Rh/TiO_2	Li–Rh/TiO_2	K–Rh/TiO_2	Cs–Rh/TiO_2	Rh/SiO_2
CO conversion	33.0	28.9	29.3	24.3	24.0
CH_4	41.5	33.1	32.9	31.9	36.4
MeCHO	20.7	9.1	NA	23.4	33.0
EtOH	24.4	21.5	—	[a]	28.8
Acetone	8.7	7.4	16.9	[a]	NA
MeOH	—	10.9	—	[a]	14.5

Note. Reaction conditions: CO/H_2 = 2, 250–300°C, and 10 atm.

[a] Low activity.

Rh/TiO_2 and Rh/SiO_2

It is obvious that the product distribution from a reaction may be strongly affected by reaction conditions. The product distributions for Rh/TiO_2 at 300°C under both 1 and 10 atm pressure are presented in Table 5. Under the 1-atm condition, only very small amounts of acetaldehyde were observed. The major products formed (more than 98 wt%) were hydrocarbons. When the pressure was increased to 10 atm, a significant amount of oxygenated compounds (up to 17 wt%) was observed, while the ratio of olefins to paraffins and chain-growth probability were essentially not affected. These results are generally consistent with those previously reported for Rh/TiO_2 under 1- (*24*) and 10-atm reaction conditions (*12*). As shown in Table 5, the use of SiO_2 as a support, which has a greater basicity than TiO_2 (*25*), resulted in higher yields of oxygenated compounds. The SiO_2-supported Rh catalyst also showed a significantly lower activity for the formation of all the products compared to Rh/TiO_2. The variation in product formation rates with time for Rh/SiO_2, depicted in Fig. 5, is similar to that

TABLE 5

Product Formation Rate for Rh/TiO_2 and Rh/SiO_2

Catalyst:	Rh/TiO_2	Rh/TiO_2	Rh/SiO_2
Reaction conditions:	300°C, 1 atm	300°C, 10 atm	300°C, 10 atm
Rate of CO conversion (mole/kg/h):	1.49	17.31	1.04
	Product formation rate (mole/kg/h)		
CO_2	0.054	1.93	0.034
CH_4	0.63	7.56	0.162
C_{2+}	0.17	1.3	0.065
MeOH	0	0.026	0.003
MeCHO	0.0016	0.12	0.14
EtOH	0	0.44	0.082
Acetone	0	0.106	0
EtOAc	0	0.043	0.052
	Selectivity (wt%)		
C_1	44.2	49.9	12.8
C_{2+}	53.8	32.4	11.3
OX	2.0	17.7	75.9

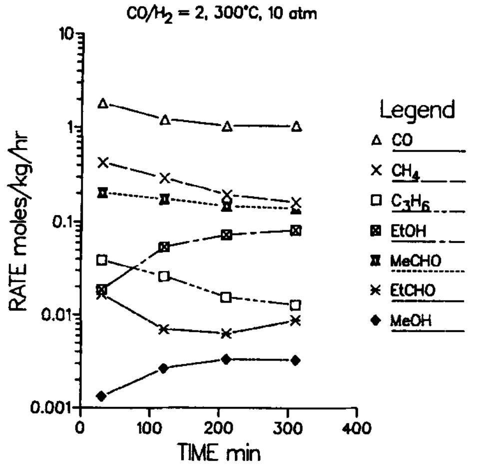

FIG. 5. Product formation rate vs time over Rh/SiO_2.

found for Rh/TiO_2 except for the rate of formation of ethanol (Fig. 2). The decrease in the formation rate of acetaldehyde with time was found to parallel the increase in the formation rate of ethanol. The dramatic modification in the rate of formation of ethanol with time indicates that the nature of the catalyst surface may have been significantly altered during reaction.

The formation rates of the major products from ethylene addition to the reaction mixture over Rh/TiO_2 and Rh/SiO_2 are presented in Table 6. The formation rates of C_1 and C_2 oxygenated compounds and CH_4 were essentially unaffected by the ethylene addition. In the case of ethylene addition to the reaction mixture over Rh/TiO_2, an increase in pressure from 1 to 10 atm resulted in an increase in the hydrogenation rate of ethylene by a factor of 46, the rate of CO insertion by a factor of 10, and the rate of chain incorporation to higher hydrocarbons by a factor of 2. In contrast to Rh/TiO_2, Rh/SiO_2 showed a higher rate of CO insertion to form C_3 oxygenated compounds (propionaldehyde and 1-propanol) and a much smaller rate for ethylene incorporation in hydrocarbon chain growth. Since the product distribution changed more with time for Rh/SiO_2 than Rh/TiO_2, it would be expected that Rh/SiO_2 after re-reduction by H_2 would perform differently than before re-rereduction. After 20 h of reaction, the Rh/SiO_2 was re-reduced in flowing H_2 at 300°C for 16 h. During the initial stage of reduction a substantial amount of CH_4 was detected. This indicates that the surface of Rh/SiO_2 was covered by carbonaceous overlayers which may have been active for hydrogenation to CH_4 or may have been in the form of an essentially inactive graphite (*26*). In comparison with the used Rh/SiO_2, Rh/SiO_2 after re-reduction demonstrated a higher hydrogenation ability while the extent of CO insertion was only slightly affected. The carbonaceous overlayer, thus, seemed to have a greater effect on hydrogenation ability (*26*) than on CO insertion.

TABLE 6

Products Formed as Result of Ethylene Addition

Catalyst	Reaction conditions		Rate of C_2H_4 conversion (mole/kg/h)	Product formation rate (mole/kg/h)				
	°C	atm		EtCHO	1-Propanol	CH_4	C_2H_6	$C_{3+}HC$
Rh/TiO_2	300	1	0.35	0.0125	0	0	0.133	0.204
	300	10	6.54	0.078	0.042	0	5.98	0.448
Rh/SiO_2	300 (used)	10	0.61	0.54	0	0	0.064	<0.001
	300 (regenerated)	10	1.72	0.57	0.4	0	0.75	<0.001

Note. 2.3 mole% of C_2H_4 was added to CO/H_2.

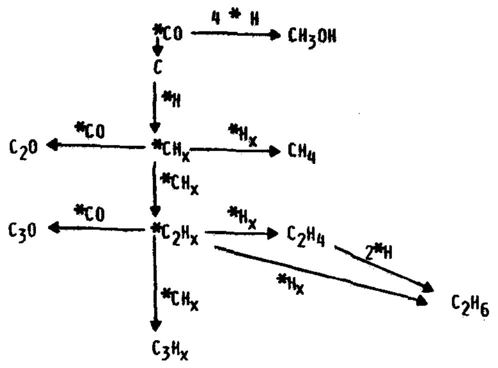

FIG. 6. Reaction scheme for the formation of oxygenated compounds and hydrocarbons.

DISCUSSION

Reaction Mechanism

The pronounced differences in activation energy and activity vs time behavior between hydrocarbons and C_{2+} oxygenated compounds as a group and MeOH suggest that the active sites and/or precursors for the formation of methanol may be different from those for hydrocarbons and C_{2+} oxygenated compounds. The formation of methanol has been shown to occur by a nondissociative CO mechanism over Rh/TiO_2 (*27*), and Rh ions have been suggested to be the sites for this formation (*20*). It has been suggested by Takeuchi and Katzer (*28*) that higher alcohol synthesis catalysts must dissociate the C—O bond only at a moderate rate so that the catalyst surface contains both undissociated adsorbed CO and surface carbene species for the bimolecular insertion. A reaction scheme based on CO insertion to form oxygenated compounds (shown in Fig. 6) has been proposed by various investigators for Rh catalysts (*8, 10, 20, 28, 29*). Takeuchi and Katzer (*28*) have suggested, based on their isotopic scrambling results, that the formation of C_2 oxygenates involves a ketene intermediate which is formed by CO insertion into an adsorbed carbene species. An acyl precursor to C_2 oxygenated compounds has been suggested by Ichikawa (*8*) and CO insertion into methyl and alkyl species to form oxygenated compounds has also been proposed by various investigators (*10, 29*). Although there still exists a controversy about intermediates to C_2 oxygenates, it is generally agreed that the formation of C_{2+} oxygenated compounds requires insertion of undissociated adsorbed CO into a C_xH_y species which is generated by CO dissociation. The CO insertion step has also been suggested to result in chain termination (*20, 29, 30*). Based on the above reaction scheme, CH_4 and C_2 oxygenated compounds would be produced from the same precursor, i.e., CH_x. A high selectivity for C_2 oxygenated compounds (even up to 90 wt%) has been observed for Rh catalysts (*20*). This can be compared to the maximum yield (25 wt%) of C_2 products predicted by the A–S–F distribution. Thus, it has been suggested that C_2 oxygenated compounds should be viewed as a "C_1" compound in the A–S–F distribution, which could, in principle, be produced with 100% selectivity (*20*). Although there still exists controversy about the rate-determining step for hydrogenation of surface carbon species (*31–34*), it is unlikely, in a reaction involving surface carbon species (CH_x surface intermediates), that some CH_4 would not be formed. This is especially true since CH_4 is more thermodynamically stable than C_2 oxygenates, and transition metals are good hydrogenation catalysts.

Formation of Acetone and Ethyl Acetate

The presence of acetone has been observed in the Fischer–Tropsch (*35*) and higher alcohol synthesis (*6*). It has been suggested that the acetone is formed by the secondary reaction of acetic acid (*37*):

$$2CH_3COOH \rightarrow (CH_3)_2CO + H_2O + CO_2.$$

However, acetic acid was not observed in this study during steady-state reaction conditions over Rh/TiO_2 and alkali-promoted Rh/TiO_2. In addition to the above reaction, Schulz and Zein El Deen (*36*) have proposed that acetone may be formed from a combination of the acetaldehyde surface intermediate and a surface methyl species. The fact that the selectivity of acetone parallels that of acetaldehyde, as shown in Table 3, supports such a conclusion. In contrast to our results, acetone was not observed during CO hydrogenation over Rh/TiO_2 by Katzer *et al.* (*12*) or by Ichikawa (*8*). The failure of these authors to observe acetone may have been due to low reaction temperatures, low CO/H_2 ratios, different catalyst preparation methods, and/or different reduction conditions. Dry (*37*) has pointed out that acetone is always present during F–T synthesis at high reaction temperatures.

It is obvious that the ethyl acetate could have been formed by the esterification of ethanol with acetic acid. However, there exist other possible routes for forming ethyl acetate not requiring acetic acid. Recently, Morrison *et al.* (*38*) have shown that a ketene complex is able to react with methanol to form methyl acetate. A ketene surface species has also been suggested to be a surface intermediate for forming C_2 oxygenated compounds, as discussed in the previous section. Thus, the ethyl acetate may have been formed from a reaction of the ketene intermediates with adsorbed ethanol. Although there are alternate pathways to form acetone and ethyl acetate not requiring the presence of acetic acid, the reaction pathways to these two species via acetic acid still can not be ruled out. At high reaction temperatures, acetic acid could easily be depleted by secondary reactions and esterification.

Effect of Reaction Conditions on Product Distribution

The reaction conditions appear to have had a strong effect on the reaction mechanism and product distribution. Although the formation of C_2 oxygenated compounds are not thermodynamically unfavorable at 1 atm and 300°C, only very small amounts of acetaldehyde were observed. As the pressure increased up to 10 atm, the formation rate of and selectivity to C_2 oxygenated compounds were enhanced (Table 5). CO insertion would appear to have been more favorable than hydrogenation at high-pressure conditions. However, considering the results of ethylene addition over Rh/TiO_2 given in Table 6, the rate of ethylene hydrogenation increased five times as much as that of CO insertion into an ethyl surface species formed from adsorbed ethylene when the pressure was raised from 1 to 10 atm. Thus, the hydrogenation of adsorbed ethylene appeared to be more favored than CO insertion at 10 atm. The difference between these two results indicates that either adsorbed ethylene from ethylene addition is not the same precursor as that in the F–T synthesis or the rate-determining step for formation of C_3 oxygenates from the adsorbed ethylene may be different from that for C_2 oxygenates from CO hydrogenation. Watson and Somorjai (*19*) have suggested that the rate-determining step for formation of C_2 oxygenated compounds is the formation of CH_x from hydrogenation of carbidic species. One may speculate based on the same argument that the rate-determining step for formation of C_3 oxygenates during CO hydrogenation is also the formation of CH_x or C_2H_y species. Van den Berg (*20*) has proposed that ethylene adsorption occurs preferentially on rhodium ions during ethylene addition. The present authors have suggested, based on an ethylene addition study, that either the active sites for hydrogenation of readsorbed ethylene or most of the adsorbed ethylene surface species are different from those normally involved in chain growth and CO insertion (*39*).

It should be noted that CO insertion into readsorbed ethylene to produce propionaldehyde and 1-propanol is very similar to the homogeneous hydroformylation of ethylene. Rh complexes are known to be excellent catalysts for the homogeneous hydroformylation reaction (*40*). Zeolite-supported Rh catalysts (*41*) and supported Rh catalysts prepared by decomposition of Rh clusters (*42*) have been demonstrated to catalyze the hydroformylation of ethylene

TABLE 7

Effect of Alkali Promotion on the [MeCHO]/[EtOH] and Olefin Selectivities[a]

	Rh/TiO_2	$Li–Rh/TiO_2$	$K–Rh/TiO_2$	$Cs–Rh/TiO_2$
[MeCHO]/[EtOH]	0.25	0.61	2.79	10.45
$[C_3^{=}–C_5^{=}]/[C_3–C_5]$	2.7	5.8	4.6	4.2

Note. Reaction conditions: 300°C, 10 atm, and 300 min time-on-stream.

[a] Before ethylene addition.

and propylene at temperatures below 130°C at 1 atm pressure. It is as yet not clear whether this reaction is homogeneously or heterogeneously catalyzed under our reaction conditions.

Alkali Promotion Effect

The effects of alkali promotion on CO hydrogenation over group VIII transition metal catalysts, such as Ru (*14*), Ni (*15*), and Fe (*43, 44*), have been identified as (a) a suppression of hydrogenation ability, (b) an increase in the ability to dissociate CO, (c) an increase in the selectivity to long-chain hydrocarbons, and (d) a decrease in CO conversion activity (Ru, Ni). It would be expected that similar effects of alkali promotion might occur for Rh catalysts. The suppression of hydrogenation was evidenced by an increase in the ratios of $C_3–C_5$ olefins-to-paraffins and of acetaldehyde-to-ethanol upon alkali promotion, as presented in Table 7.

The enhancement of CO dissociation and the "supposed" electron donation properties of the alkali promoters (*23, 45*) should result in a decrease in the product selectivity toward oxygenated compounds. On the contrary, upon alkali promotion, product selectivity for oxygenated compounds increased while the formation rates for all the products decreased (Tables 2 and 3). This clearly indicates that there was less suppression in the rate of oxygenated product formation than in that of hydrocarbon formation. Recent evidence indicates that the CO insertion step to form oxygenated compounds over Rh/TiO_2 is not strongly affected by the chemical nature of the alkali promoter (*39*). If the enhancement of CO dissociation did occur on the alkali-promoted Rh catalysts, it seemed to have little effect on CO insertion. The ethylene-addition study over used and re-reduced Rh/SiO_2 (Table 6) also indicated that the carbonaceous overlayer has little effect on CO insertion. The decrease in the rate of formation of oxygenated compounds upon alkali promotion may be mainly due to a lower rate of formation of the precursor, CH_x, as result of hydrogenation suppression by alkali promoters since CO insertion is not strongly affected by the chemical nature of the alkali promoter (*39*). The smaller deviation in mole fraction of ethylene upon alkali promotion as shown in Figs. 3 and 4 may be due to the lower rate of incorporation of ethylene into higher hydrocarbons on alkali-promoted catalysts. It was found in our previous ethylene-addition study (*39*) that the rate of incorporation of ethylene into higher hydrocarbons decreased in the order: unpromoted > Li > K > Cs.

The effect of alkali promotion to decrease overall activity of Rh catalysts for CO hydrogenation at temperatures above 275°C and pressures above 10 atm has been reported by van den Berg (*20*), Wilson *et al.* (*23*), and this paper. Contradictory results reported by Orita *et al.* (*46*) and Kagami *et al.* (*47*) for alkali-promoted Rh/TiO_2 and Rh/Al_2O_3 have shown the alkali promoter increases the formation rate of oxygenated compounds under low-temperature and low-pressure conditions (180°C and <1 atm). They have suggested that the active sites may be located near the juncture of the rhodium metal and the support and that those sites are modified by the addition of alkali ions. The difference in reaction conditions may be related to these contradictions. It has been suggested that Rh catalysts can dissociate adsorbed CO at temperatures of 200–300°C (*48*). Thus, alkali promotion may enhance CO dissociation excessively at high temperatures (>200°C) resulting in a high coverage of carbon species and leading to a decrease in overall activity. However, such a promotion of CO dissociation at low temperatures (<200°C) may greatly increase the formation rate of CH_x, a precursor for CO insertion, without contributing to catalyst deactivation.

Support Effect

The ability of Rh catalysts to catalyze CO dissociation, insertion, and hydrogenation is affected not only by the presence of an alkali promoter but also by the support. Recently, Edröhelyi and Solymosi (*49*) have reported that the effect of supports in promoting the dissociation of CO over Rh decreases in the order $TiO_2 > Al_2O_3 > SiO_2 >$ MgO. It may be expected that oxygenated compound selectivity would follow the reverse order. Katzer *et al.* (*12*) have reported, in fact, that alcohol selectivity over Rh catalysts increases in the order: $TiO_2 < Al_2O_3 < SiO_2 <$ MgO. They have concluded that the selectivity to alcohol varies with the basicity of the support. Thus, the results from this study are consistent since SiO_2-supported Rh catalysts had higher oxygenate selectivities than Rh/TiO_2.

The observed increase in the activity of Rh when it is supported on TiO_2 parallels, in some respects, the observation reported for TiO_2-supported transition metals (including Ni, Pt, Pd, Ru, Ir, and Rh) by Vannice (*50*). Katzer *et al.* (12) have also reported that Rh/TiO_2 reduced at 673 or 473°K has a higher activity than Rh/SiO_2. These authors have concluded that SMSI was not extant for their Rh/TiO_2, and that the rate variation was due to differences in the number of active sites or other geometric factors. Orita *et al.* (*46*) have observed that Rh/TiO_2 in an SMSI state has a lower activity than when it is not in such a state. Present knowledge of metal–support interactions is not sufficient to give a satisfactory explanation for SMSI. It is still subject to much controversy (*17, 51–53*).

Edrohelyi and Solymosi (*49*) have also reported that the activation energy for the hydrogenation of reactive surface carbon increased in the order: $Rh/TiO_2 < Rh/Al_2O_3 < Rh/SiO_2$. The ethylene-addition results presented in Table 6 show that the rate of ethylene hydrogenation is 10 times greater over Rh/TiO_2 than over Rh/SiO_2, while the CO insertion rate is greater over Rh/SiO_2 than over Rh/TiO_2 by a factor of 4. Therefore, Rh/TiO_2 is a better hydrogenation catalyst than Rh/SiO_2. Thus, the high activity for CO conversion and the low selectivity to oxygenated compounds of Rh/TiO_2 can be explained not only by its strong CO dissociation and hydrogenation ability but also by its poor CO insertion ability. Rh/SiO_2, with a poor hydrogenation ability and a strong CO insertion ability, has a low activity for CO conversion but a high selectivity for oxygenates.

CONCLUSIONS

As a result of the special catalytic properties of Rh, a better understanding has been gained of the interrelationship between the formation of hydrocarbons and oxygenates during CO hydrogenation. Of particular interest in this present study was the effect of alkali promoters on the synthesis of oxygenates.

The selectivity and activity of CO hydrogenation over Rh catalysts vary with the presence of alkali promoters, the type of support, and the reaction conditions used. Rh/SiO_2 shows a better CO insertion ability than Rh/TiO_2, resulting in better selectivity to C_2 oxygenated compounds.

The effect of alkali promotion on Rh/TiO_2 can be summarized as follows:

(a) Alkali promoters have a different effect on the formation of oxygenated compounds than on that of hydrocarbons.

(b) The selectivity for oxygenated compounds increases in the order unpromoted $< \text{Li} < \text{K} = \text{Cs}$.

(c) The ability for hydrogenation in general and ethylene incorporation to higher hydrocarbons decreases in the order unpromoted $> \text{Li} > \text{K} > \text{Cs}$.

(d) The chain-growth probability is only slightly modified by the presence of alkali promoters.

The activity of a catalyst for CO dissociation is important in determining the selectivity of CO hydrogenation to oxygenated compounds. It appears, however, that the ability to activate CO insertion is crucial for improving C_{2+} oxygenate selectivity. It should be possible to optimize the activity and selectivity to oxygenated compounds of a Rh catalyst by modifying its relative hydrogenation, CO dissociation, and CO insertion abilities through proper choice of support and promoter.

ACKNOWLEDGMENT

Funding for this study was provided by the U.S. Department of Energy, Office of Fossil Energy, under Grant DE-FG22-82PC50810.

REFERENCES

1. Ichikawa, M., *Bull. Chem. Soc. Jpn* **51,** 2268 (1978).
2. Poutsma, M. L., Elek, L. F., Ibarbia, D. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52,** 157 (1978).
3. Loktev, S. M., *J. Mol. Catal.* **17,** 225 (1982).
4. Smith, K. J., and Anderson, R. B., *Canad. J. Chem. Eng.* **61,** 40 (1983).
5. Sugier, A., and Freund, E., U.S. Patent 4, 122, 110 (Oct. 24, 1978), assigned to Institut Francais du Petrole, des Carburants et Lubrifiants.
6. Natta, G., Colombo, V., and Pasquon, I., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 5, p. 131. Reinhold, New York, 1957.
7. Vedage, G. A., Himelfarb, P., Simmons, G. W., and Klier, K., Preprints of the Div. of Petr. Chem. (ACS) **28,** 1261 (1984).
8. Ichikawa, M., *CHEMTECH.*, 674 (1982).
9. Vannice, M. A., *J. Catal.* **37,** 449 (1975).
10. Ellgen, P. C., Bartley, W. J., Bhasin, M. M., and Wilson, T. P., *Adv. Chem. Ser.* **178,** 147, ACS, Washington, D.C. (1979).
11. Ichikawa, M., *J. Catal.* **56,** 127 (1979).
12. Katzer, J. R., Sleight, A. W., Gajarsdo, P., Michel, J. B., Gleason, E. F., and McMillan, S., *Faraday Discuss.* **72,** 72–77 (1979).
13. Meriaudeau, P., Ellestad, H., and Naccache, C., *J. Mol. Catal.* **17,** 219 (1982).
14. Shyu, J. Z., Ph.D. thesis. University of Pittsburgh, 1983.
15. Campbell, C. T., and Goodman, D. W., *Surf. Sci.* **123,** 413 (1982).
16. Gonzalez, R. D., and Miura, H., *J. Catal.* **77,** 338 (1982).
17. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsely, J. A., *Science* (Washington, D.C.) **211,** 1121 (1981).
18. Jiang, X. Z., Hayden, T. F., and Dumesic, J. A., *J. Catal.* **83,** 168 (1983).
19. Watson, P. R., and Somorjai, G. A., *J. Catal.* **74,** 282 (1982).
20. van den Berg, F. G. A., Ph.D. thesis. University of Leiden, the Netherlands, 1983.
21. Driessen, J. M., Poels, E. K., Hinderman, J. P., and Ponec, V., *J. Catal.* **82,** 26 (1983).
22. Ryndin, Y. A., Hicks, P. F., and Bell, A. T., *J. Catal.* **70,** 287 (1981).
23. Wilson, T. P., Bartley, W. J., and Ellgen, P. C., *in* "Proceedings, China–Japan–USA Symposium on Heterogeneous Catalysis Related to Energy Problems", Dalian, China. November 1982.
24. Solymosi, F., Tombacz, I., and Kocsis, M., *J. Catal.* **75,** 78 (1982).
25. Anderson, J. R., "Structure of Metallic Catalysts." Academic Press, New York/London, 1975.
26. Bartholomew, C. H., *Catal. Rev. Sci. Eng.* **24,** 67 (1982).
27. Takeuchi, A., and Katzer, J. R., *J. Phys. Chem.* **85,** 937 (1981).
28. Takeuchi, A., and Katzer, J. R., *J. Phys. Chem.* **86,** 2438 (1982).
29. Bell, A. T., *Catal. Rev. Sci. Eng.* **23,** 203 (1981).
30. Biloen, P., and Sachtler, W. M. H., "Advances in Catalysis," Vol. 30, p. 165 (1981).
31. Happel, H., Suzuki, I., Kokayeff, P., and Fthenakis, V., *J. Catal.* **65,** 59 (1980).
32. Van Meerten, R. Z. C., Vollenbrock, J. G., DeCroon, M. H. J. M., Van Nisselroy, P. F. M. J., and Coenen, J. W. E., *Appl. Catal.* **3,** 29 (1982).
33. Rautavuoma, A. O. I., and Van der Baan, H. S., *Appl. Catal.* **1,** 247 (1981).
34. Biloen, P., Helle, J. N., van der Berg, F. G. A., and Sachtler, W. M. H., *J. Catal.* **81,** 450 (1983).
35. Weitkamp, A. W., and Frye, C. G., *Ind. Eng. Chem.* **45,** 363 (1953).
36. Schulz, H., and Zein El Deen, A., *Fuel Process. Technol.* **1,** 45 (1977).
37. Dry, M. E., *in* "Catalysis-Science Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, p. 159. Springer-Verlag, Berlin/Heidelberg/New York, 1981.

38. Morrison, E. D., Steinmetz, G. R., Geoffroy, G. L., Fultz, W. C., and Rheingold, A. L., *J. Am. Chem. Soc.* **107,** 3541 (1985).
39. Chuang, S. C., Goodwin, J. G., Jr., and Wender, I., *J. Catal.* **92,** 416 (1985).
40. Wender, I., and Pino, P., "Organic Synthesis via Metal Carbonyls." Wiley, New York, 1968.
41. Takehashi, N., and Kobayashi, M., *J. Catal.* **85,** 89 (1984).
42. Ichikawa, M., *J. Catal.* **56,** 127 (1979).
43. Dry, M. E., Shingles, T., Boshoff, L. J., and Dosthuizen, G. J., *J. Catal.* **15,** 190 (1969).
44. Dry, M. E., Shingles, T., and Boshoff, L. J., *J. Catal.* **25,** 99 (1972).
45. Ertl, G., Weiss, M., and Lee, S. B., *Chem. Phys. Lett.* **30,** 391 (1979).
46. Orita, H., Naito, S., and Tamaru, K., *Chem. Lett.* 1161 (1983).
47. Kagami, S., Naito, S., Kikuzono, Y., and Tamaru, K., *J. Chem. Soc. Chem. Commun.*, 256 (1983).
48. Broden, G., Rhodin, T. N., Bruckner, C., Benbow, R., and Hurych, A., *Surf. Sci.* **59,** 593 (1976).
49. Edröhelyi, A., and Solymosi, F., *J. Catal.* **84,** 446 (1983).
50. Vannice, M. A., *J. Catal.* **74,** 199 (1982).
51. Chen, B. H., and White, J. M., *J. Phys. Chem.* **86,** 3534 (1983).
52. Meriaudeau, P., Ellestad, O. H., and Naccache, C., *J. Catal.* **75,** 243 (1982).
53. Goodwin, J. G., Jr., Chen, Y. W., and Chuang, S. C., *in* "Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals" (R. G. Herman, Ed.), p. 179. Plenum, New York, 1984.