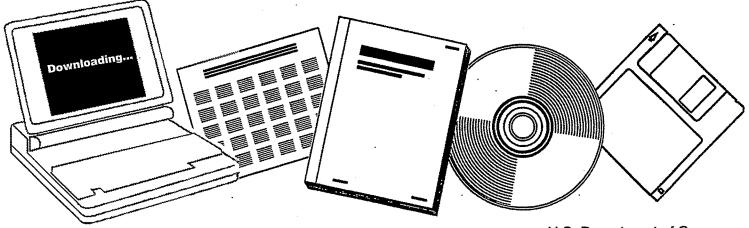**NTiS**

PROMOTION EFFECTS ON THE SYNTHESIS OF HIGHER ALCOHOLS. TENTH QUARTERLY REPORT, OCTOBER-DECEMBER 1984

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

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PROMOTION EFFECTS

ON THE

SYNTHESIS OF HIGHER ALCOHOLS

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James G. Goodwin, Jr.
S.-C. Chuang

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

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1. OBJECTIVE AND SCOPE OF WORK

The importance of the direct synthesis of higher (C_2-C_6) alcohols from synthesis gas as a promising route for providing clean fuels and petrochemical feedstocks is generally recognized. It is known that the addition of alkali salts to methanol synthesis catalysts shifts the products to higher alcohols. However, little is known about the effect of various alkali species on the catalysts components and the synthesis reaction. A series of research studies is planned which should greatly expand current knowledge in this area. In particular, the effect of various alkalis (Na, K, Rb, and Cs) on CO chemisorption, on the activity and selectivity for higher alcohol synthesis reaction, and on the deactivation characteristics of the catalyst will be determined for supported metals (such as Pd and Rh). Direct measurement of electronic interactions between the alkali promoters and the other catalysts components will be attempted by ESCA.

This comprehensive reserach program involves members of the Departments of Chemical Engineering and of Chemistry. There is a great need for cooperation between researchers in the areas of catalysis and surface science. This research project seeks to accomplish this and utilize the resulting synergism in illuminating the precise function of alkali promotion in the higher alcohol synthesis.

2. SUMMARY OF PROGRESS

During the 10th quarter of the project, alcohol synthesis over Pd/SiO$_2$, K-Pd/SiO$_2$, Rh/MgO, and K-Rh/MgO catalysts have been studied to elucidate the role of K on methanol synthesis. This study provides a means to compare the effect of K promotion on C_1 oxygenates (MeOH) to that on C_{2+} oxygenate species.

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3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

INTRODUCTION

Pd, Pt, Ir and Rh catalysts have been found to be active in methanol synthesis (1-5). Although the mechanism for methanol synthesis over these catalysts is still not clear, the good methanol synthesis activities of these catalysts have been identified to be due to their high hydrogenation ability coupled with their ability to activate nondissociatively adsorbed CO (1,4). Several recent studies have revealed that the selectivities and activities of Pd and Rh catalysts are greatly affected by the composition of the support (2,3) and the presence of promoters (6-8,14). Pd supported on certain types of silica (3) or basic supports (2) exhibited high activity and selectivity for methanol formation. For Rh, even more basic supports (4,5), such as MgO and ZnO, than those for Pd catalysts are required in order to promote the production of high yields of methanol. Addition of alkali promoters on Rh catalysts produce a marked modification in the selectivity for methanol synthesis (8). Although the effects of supports and alkali promoters have been identified, the mechanisms of these effects are still not clear. In the present work, methanol synthesis over K-promoted Pd/SiO_2 and K-promoted Rh/MgO has been studied to establish the relative methanol synthesis capabilities of these two supported metals and to elucidate the role of potassium on methanol synthesis.

EXPERIMENTAL

Catalyst Preparation and Characterization

2.3 wt% Pd/SiO_2 catalyst was prepared by impregnation of SiO_2 (Strem) using an aqueous solution of palladium chloride (Alpha Chemical). 3 wt%

Rh/SiO$_2$ was also prepared in the same manner but using rhodium chloride. Two samples of potassium-promoted Pd/SiO$_2$ were prepared by impregnation of Pd/SiO$_2$ using a KNO$_3$ solution resulting in atom ratios of K to Pd of 0.6 and 1.8. Potassium-promoted Rh/MgO was obtained by impregnation of MgO using rhodium chloride and potassium nitrate (atom ratio of K/Rh = 0.5). The samples, except part of Rh/MgO, were then reduced in flowing hydrogen on heating in a temperature ramp of 1°C/min to 400°C and holding at that temperature for 16 hours and then stored. In order to study the effect of reduction temperatures on the performance of Rh/MgO, part of Rh/MgO was reduced in a similar manner but a maximum temperature of only 250°C was used. Prior to reaction, the catalysts which had been reduced at 400°C were re-reduced in flowing hydrogen at 400°C for three hours. Rh/MgO (reduced at 250°C) was re-reduced at 250°C.

The metal particle sizes of these supported metal catalysts were determined by static hydrogen chemisorption at 25°C (9) and X-ray diffraction using a MoKα radiation source. The results are shown in Table I. Due to suppression of hydrogen chemisorption brought about by potassium promotion, hydrogen chemisorption appears to be inappropriate for measuring average metal particle size in these alkali-promoted catalysts (9).

Apparatus and Procedures

The apparatus used for this study is described elsewhere (19). The major parts of this apparatus consist of H$_2$, CO and He flow controllers, a stainless steel microreactor containing 0.2 to 0.75 g of the catalyst in a furnace, an on-line GC using a 12 ft x 1/8" poropak Q column in series with a 12 ft x 1/8" 80/100 carbopak c/o.2% carbowax 1500 column, and an Apple II computer with an interface for automatic control. The CO hydrogenation and ethylene addition studies were carried out at 300°C, 10 atm, CO/H$_2$ = 1 and space velocity of 1,100 to 2,700 hr^{-1}. After more than 12 hours of just CO hydrogenations, a

small amount (3-3.5 mole % of CO/H$_2$) of ethylene was added to the feed. It was continued for two hours then terminated. The reaction was carried out for another three hours to establish the reference data to estimate the rate of product formation that resulted from ethylene addition. 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.

RESULTS

Due to uncertainty in measuring the number of surface atoms for alkali-promoted catalysts (9,10) and to the fact that selectivity is the property of interests, the activity of these catlaysts for metahnol synthesis is expressed in mole/kg/hr. The product distribution for methanol synthesis over Pd/SiO$_2$, K-Pd/SiO$_2$, Rh/MgO, and K-Rh/MgO is shown in Table II and III. Pd/SiO$_2$ demonstrated a very high selectivity for methanol formation. The addition of K promoters to Pd/SiO$_2$ resulted in decreases in both the selectivity and the activity for methanol formation while it increased the activity and selectivity for the formation of methane and higher hydrocarbons. For Rh/MgO, the product distribution is strongly dependent on the reduction temperature. Rh/MgO reduced at 250°C produced higher yields of methanol than that reduced at 400°C. An increase in reduction temperature enhances the selectivity for C$_2$ oxygenate (OX) formation. The addition of K to Rh/MgO (reduced at 400°C) decreased the overall rate of CO conversion while it increased the selectivities for methanol and higher hydrocarbon (HC) formation. This increase in selectivities over K-Rh/MgO was due to a decrease in rate of formation of CH$_4$ and C$_{2+}$ oxygenates rather than to increases in the rates of formation of methanol and higher hydrocarbons.

In order to determine the effect of potassium promoters on the hydrogenation ability of these catalysts, a small amount of an unsaturated hydrocarbon (ethylene) was added to the CO/H_2 reactant stream. The added ethylene, CO, and H_2 may compete with one another for the same active sites. In addition, the added ethylene may incorporate with intermediates produced from CO hydrogenation (11). The product distribution from reaction of the added ethylene over Pd/SiO_2, $K-Pd/SiO_2$, Rh/MgO, and $K-Rh/MgO$ is shown in Tables IV and V. It is interesting to note that the addition of ethylene results in a decrease in methanol formation for Pd/SiO_2, $K-Pd/SiO_2$ and Rh/MgO (reduced at $250^\circ C$). The extent of suppression in methanol formation seems to parallel the activity of methanol formation of these catalysts (Tables II and III). This suppression was not observed for Rh/MgO (reduced at $400^\circ C$) and $K-Rh/MgO$ (reduced at $400^\circ C$) which are not very active for methanol synthesis.

The addition of potassium promoters to Pd/SiO_2 resulted in a decrease in rate of ethylene hydrogenation while it slightly increased the rate of formation of C_3 oxygenated compounds. Similiar suppression of ethylene hydrogenation was also found to occur for K-promoted Rh/MgO.

DISCUSSION

Pd/SiO_2 vs Rh/MgO

The most interesting point of this study is the product distribution from reaction of ethylene added during CO hydrogenation obtained for Rh/MgO after H_2 reduction at $250^\circ C$ and Pd/SiO_2 (Tables IV and V). The result of adding ethylene was a significant suppression of the formation of methanol during CO hydrogenation over these catalysts while there was little effect on methane formation. This clearly suggests that (a) part of the adsorbed ethylene competed with CO for the same hydrogenation sites, (b) active sites for the

formation of methanol are different from those for the formation of methane. Similiar suppression in methanol formation during the addition of 1-hexene to CO/H_2 over Cu/ZnO has been reported by Vedage and Klier (12). They suggested that CO and 1-hexene compete for the same active sites resulting in this suppression.

The suppression of methanol formation was also observed for Rh/MgO (after H_2 reduction at 250°C) which is capable of producing a marked yield of methanol. This suggests that the active sites for methanol formation on Rh/MgO have certain similiar characteristics to those on Pd/SiO_2. Rh/MgO after H_2 reduction at 250°C also produces significant amounts of C_2 oxygenated compounds. This suggests that this catalyst possesses the ability for CO insertion into C_yH_x to form C_{2+} oxygenated compounds (18,19). This CO insertion capability displayed by Rh/MgO after H_2 reduction at 250°C is also demonstrated by the formation of C_3 oxygenated compounds during the addition of ethylene to the CO/H_2 reactant mixture. In contrast to Rh/MgO (reduced at 250°C), such a CO insertion capability was not observed for Pd/SiO_2. Though both Pd/SiO_2 and Rh/MgO are not very active for CO dissociation (1,14), they exhibit a dramatic difference in capability for the insertion of CO into adsorbed ethylene. It appears that the formation of C_{2+} oxygenated compounds during CO hydrogenation is controlled by not only the concentrations of surface carbidic species and nondissociatively adsorbed CO (13) but also its capability for insertion of CO into surface C_yH_x species. The poor CO insertion activity of Pd/SiO_2 may be due to its relatively high hydrogenation activity. For Rh/MgO it would appear that active sites for CO insertion into adsorbed C_yH_x are different from those for methanol formation, as indicated by significant different dependence of the formation of these two species on the reduction temperatures (Table III).

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Potassium-Promoted Pd/SiO$_2$

Addition of a potassium promoter to Pd/SiO$_2$ caused a marked decrease in activity and selectivity for methanol formation while it increased the activity and selectivity for the formation of both methane and higher hydrocarbons. This presence of this potassium promoter also caused a suppression of ethylene hydrogenation during the addition of C$_2$H$_4$ to the CO/H$_2$ reactant stream. It seems to suggest that potassium promoters may preferentially block the active sites for methanol synthesis and ethylene hydrogenation over Pd/SiO$_2$. However, the effect of alkali promotion is generally considered to be electronic in nature (15-19). If the electronic factor play a major role in the effect of alkali promotion, such similar suppression of activities for these two reactions may suggest that some steps of these two reaction take place on the same active sites or at least on sites which have certain similar chemical properties. These active sites are subject to modification brought about alkali promotion. This is somewhat confirmed by the fact that the rate of methanol formation decreases so significantly upon the addition of ethylene, suggesting competition for the same sites. It also suggests that not only CO hydrogenation to methanol but also at least most of ethylene hydrogenation take place on different active sites than methane formation.

Suppression of ethylene hydrogenation has been observed for K-promoted Rh/MgO. In fact, potassium promoters have long been recognized to be effective in hydrogenation suppression for transition metal catalysts including Fe (15), Ru (16), Ni (17), and Rh (18). Potassium promotion exhibits a stronger ability to suppress ethylene hydrogenation than CO insertion into adsorbed ethylene thereby resulting in higher selectivities for the formation of C$_3$ oxygenated comounds over K-promoted catalysts like Rh (18).

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Our previous studies of Rh/TiO_2 (18) and Rh/La_2O_3 (19), several other investigations of supported Rh and Pd (13,14), and this study have revealed that different active sites may be responsible for the formation of methanol, C_2 oxygenated compounds, and hydrocarbons. There still exists controversy concerning the precise nature of active sites responsible for the formation of methanol. The formation of methanol has been suggested to take place (a) on Pd ions (14), (b) on small sized crystallites of Pd metal (3), (c) more actively on Pd (100) than on Pd (111), (d) at the interface of Pd metal and the support (6), and (e) on Rh^{+2} for supported Rh catalysts (14).

As stated earlier, while we are still not able to differentiate what type of active sites is responsible for the methanol formation, it can be suggested that active sites for methanol formation are different from those for methane formation. Fajula et al. (3) have observed that the formation of methane over supported Pd catalysts is directly related to the density of acidic sites at the surface of the support. Accordingly, the addition of potassium to Pd/SiO_2 should decrease the acidity of the catalysts (21) so that the formation of methane would also decrease. On the contrary, an enhancement of methane and hydrocarbon formation was observed for potassium-promoted Pd/SiO_2. Fajula et al. (3) have also pointed out that the formation of methane via CO dissociation followed by hydrogenation of resulting surface carbon can not definitely be ruled out for Pd catalysts. They have further noted that, if this is the case, the reasons for their observed correlation is not apparent. K promoters are knwon to be effective in promoting CO dissociation over Ru (16), Ni (17), and Rh catalysts (22). Mori et al. (23) have observed that the addition of alkali promoters to Pd/Al_2O_3 causes a shift in the wave number of adsorbed CO to a lower value. They have suggested that alkali promoters, mostly located on the Al_2O_3 support, decrease the dissociation

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probability of CO on Pd/Al$_2$O$_3$. It is still not clear how alkali promoters modify CO dissociation activity of supported Pd catalysts. A further study on this issue would provide a better understanding of the alkali promotion effect on CO hydrogenation over Pd catalysts.

The major effect of alkali promoter on methanol synthesis over Pd/SiO$_2$ and Rh/MgO catalysts have been suggested to be

   (a) a modification of active sites (interface of the metal and the support) by alkali promoters (6),

   (b) stabilization of some ions (assumed to be active sites for methanol formation) by the alkali promoters against reduction in hydrogen atmosphere (14),

   (c) creation of a defect structure which is beneficial for the activity of the catalyst (14).

All these propositions appear to indicate alkali promoters is effective in promoting methanol formation. Kikuzono et al. (6) have observed that Li and Na cations promote methanol formation over Pd/SiO$_2$ while K and Cs cations decrease it. Klier (24) has found that Cs promoters suppress the methanol synthesis activity of Pd/SiO$_2$ but increase its activity for the water-gas-shift reaction. In contrast, Tatsumi et al. (7) have reported that methanol synthesis over Pd/SiO$_2$ was promoted when Li, Na, K, Rb, and Cs were used as promoters. However, they pointed out that the addition of alkali promoters to Pd/SiO$_2$ has certain opposite effects on methanol synthesis and they have further sugested that this effect may be electronic in nature.

.. In this study, we found K promotion (alkali promotion) to be effective in decreasing the hydrogenation ability of Pd/SiO$_2$ (suppressing CO hydrogenation to methanol and ethylene hydrogenation to ethane). Thus, alkali promoters appear to have two major effects on methanol synthesis which are opposite to

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each other. One effect is hydrogenation suppression which can decrease the activity of methanol synthesis. The other one is beneficial to the activity of active sites to activate CO or stabilize precursor to methanol (6,14). Hence, the observed effect of alkali promotion on methanol synthesis may be due to the net effect of these two factors. A quantitative study of the effects of these two factors would be important for gaining a better understanding of alkali promotion on methanol synthesis.

Conclusions

The results of this study have suggested that the active sites for methanol formation are different from those for methane formation over Pd/SiO_2 and Rh/MgO (reduced at $250^{\circ}C$). Both Pd/SiO_2 and Rh/MgO (reduced at $250^{\circ}C$), which are active in methanol synthesis, showed a similar decrease in methanol formation during the addition of ethylene to the CO/H_2 reactant stream. The major effect of potassium promoters were identified to be (a) suppression of ethylene hydrogenation over Pd/SiO_2 and Rh/MgO and (b) suppression of hydrogenation of CO to methanol over Pd/SiO_2.

4. FORECAST OF WORK

During the next quarter, methodology dealing with probing the nature of the fundamental reactions occurring on the surface during CO hydrogenation by the addition of ethylene, ethanol, and acetaldehyde to the CO/H_2 reactant stream will be developed. Such a methodology, in providing a way in which to understand how these fundamental reactions are modified, will enable us to better understand overall modification in catalyst activity and selectivity. A deeper insight into the effect of metal-promoter-support interactions on higher alcohol synthesis obtained from these experiments and previous work will be reported and summarized in the next quarterly report.

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Table I: The Average Metal Particle Sizes of Pd/SiO_2, $K-Pd/SiO_2$, Rh/MgO, and $K-Rh/MgO$

Catalysts	Average Metal Particle Size (Å)
Pd/SiO_2	$41^{(a)}$ $< 40^{(b)}$
$K-Pd/SiO_2$ (K/Pd = 0.6)	$87.3^{(a)}$ $< 40^{(b)}$
$K-Pd/SiO_2$ (K/Pd = 1.8)	$140^{(a)}$ $< 40^{(b)}$
Rh/MgO	$< 40^{(b)}$
$K-Rh/MgO$ (K/Rh = 0.5)	$< 40^{(b)}$

(a) Determined by static hydrogen chemisorption at 25°C, $H_{irr}/Pd = 1$.
(b) Estimated by X-ray diffraction using MoKα

Table II: Activity and Product Selectivity During CO Hydrogenation over Pd/SiO_2 and $K-Pd/SiO_2$

Atom Ratio of K to Pd	0	0.6	1.8
r_{CO} (moles/kg/hr)	2.7	0.534	0.38
Selectivity (wt%)			
CH_4	0.4	3.9	12.5
C_2+ HC	2.3	36.0	42.0
MeOH	97.3	60.1	40.7
C_2 OX	0	0	4.8
Activity (mole/kg/hr)			
CH_4	0.023	0.028	0.056
C_2+HC	0.051	0.092	0.091
MeOH	2.5	0.216	0.09
C_2OX	0	0	0.008

$300^{\circ}C$, 10 atm., $CO/H_2 = 1$, 2.3 wt% Pd/SiO_2

Table III: Activity and Selectivity During CO Hydrogenation over Rh/MgO and K-Rh/MgO

Catalyst	Rh/MgO	Rh/MgO	Rh/MgO	K-Rh/MgO	K-Rh/MgO
Reduction Temp(°C)	250	400	400	400	400
Reaction Temp(°C)	250	250	300	250	300
r_{CO}, mole/kg/hr	0.254	0.515	5.23	0.125	0.53
Selectivity (wt %)					
CH_4	17.5	9.9	31.6	8.6	18
C_2+HC	13.8	10	26.8	29.6	54.6
MeOH	22.6	1.6	.6	6.7	3
C_2 OX	43.4	78	37.8	52.8	20.4
C_3 OX	2.7	0.5	3.2	2.3	4.0
Activity (mole/kg/hr)					
CH_4	0.058	0.054	1.7	0.018	0.094
C_{2+}HC	0.018	0.026	0.58	0.022	0.124
MeOH	0.037	0.006	0.17	0.005	0.008
C_2OX	0.05	0.4	0.76	0.027	0.039

CO/H_2 = 1, 300°C, 10 atm.

Table IV: Product Formation Rates and Selectivities
from Ethylene Reaction During CO Hydrogenation
over Pd/SiO_2 and $K-Pd/SiO_2$

Atom Ratio of K to Pd	0	0.6	1.8
r_{CO} during CO/H_2[a]	2.7	0.53	0.38
R_{CO} during $CO/H_2/C_2H_4$[a]	1.75	0.66	0.55
$r_{C_2}^=$[a]	36.17	35.0	5.8
Conversion of $C_2^=$ %	99	90	16.1
Selectivity (mole %)			
CH_4	0	0	0
C_2H_6	99.5	95.5	96.5
C_3+	0.3	0.1	0.5
C_3 OX	0.2	0.4	3.0
Activity[a]			
CH_4	0	0	0
C_2H_6	36.0	34.8	5.59
C_3+	0.1	0.035	0.03
C_3OX	0.07	0.14	0.17
Change in r_{CH_3OH} during addition C_2H_4	-1.1	-0.032	-0.005
(%)	57	14.8	5

3.3 ~ 3.5 mole % in $CO/H_2 = 1$, 300°C, 10 atm.
[a] All rates are expressed in mole/kg/hr

Table V: Product Formation Rates and Selectivities from Ethylene Reaction During CO Hydrogenation over Rh/MgO and K-Rh/MgO

	Rh/MgO	Rh/MgO	Rh-K/MgO
Reduction Temp($^{\circ}$C)	250	400	400
Reaction Temp($^{\circ}$C)	250	300	300
r_{CO} during CO/H$_2$ [a]	0.254	5.23	0.53
r_{CO} during CO/H$_2$/C$_2$H$_4$ [a]	0.565	5.764	0.667
r_{C_2} [a]	2.399	5.37	0.72
Conversion of C$_2$ = (%)	27.3	61.1	8.2
Selectivity (mole %)			
CH$_4$	0	0	0
C$_2$H$_6$	86.3	87.6	80.5
C$_3$+	0.4	2.4	0.4
C$_3$ OX	13.3	9.9	19.1
Activity [a]			
CH$_6$	0	0	0
C$_2$H$_6$	2.07	4.7	0.58
C$_3$+	0.009	0.14	0.003
C$_3$OX	0.32	0.53	0.137
Change in r_{CH_3OH} during C$_2$H$_4$ addition (mole/kg/hr)	-0.012	0	0
(%)	32	0	0

3 mole % C$_2$H$_4$ in CO/H$_2$ = 1, 10 atm.
(a)All rates are expressed in mole/kg/hr