PROMOTION EFFECTS ON THE SYNTHESIS OF HIGHER ALCOHOLS. SIXTH QUARTERLY REPORT, DECEMBER 1983-FEBRUARY 1984

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
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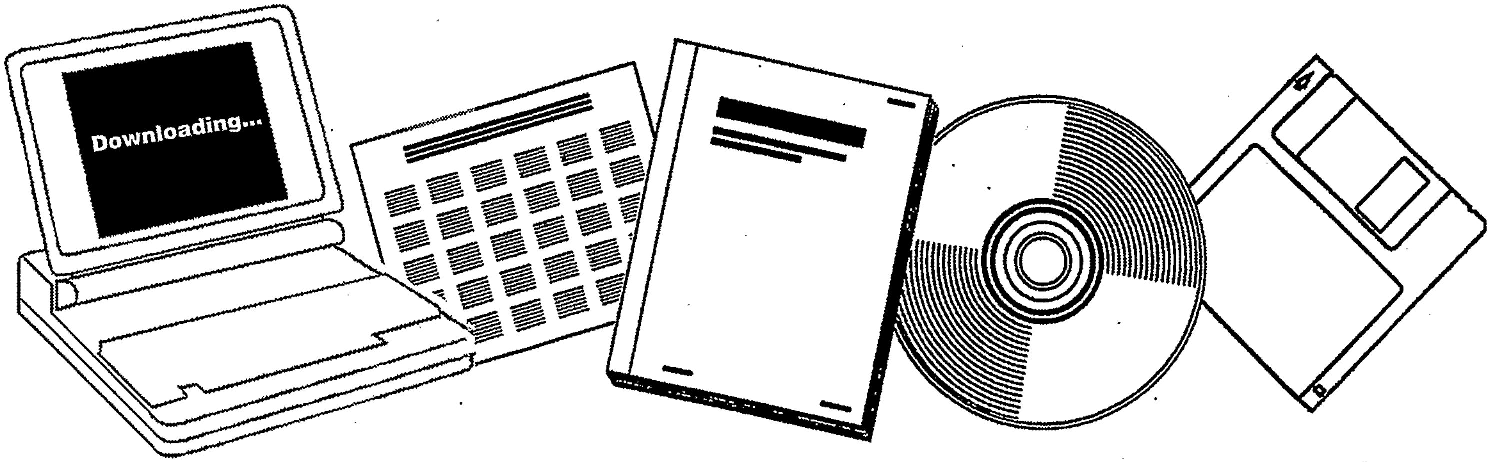

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SYNTHESIS OF HIGHER ALCOHOLS

6th Quarterly Report

Dec., 1983 - Feb., 1984

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 catalyst 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 the higher alcohol synthesis, and on the deactivation characteristics of the catalyst will be determined for both supported metals (such as Pd and Rh) and mixed metal-metal oxide catalysts (such as Cu/ZnO and Cu/ZnO/Co). Direct measurement of electronic interactions between the alkali promoters and the other catlysts components will be attempted by ESCA.

This comprehensive research program involves members of the Departments of Chemical Enginerring and of Chemistry. There is aa 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 sixth quarter of the project, a study of CO hydrogenation over alkali-promoted Rh/TiO_2 catalysts was carried out by addition of ethylene to clarify the alkali promotion effect on the specific reactions in this synthesis.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

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 oxygenated 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 supported Rh catalysts. Recently, it has been reported that alkali promotion of Rh/Al_2O_3 or $Rh-Mn/SiO_2$ enhances the oxygenate yield (4,5). A dual-site mechanism for formation of oxygenates over supported Rh catalysts has been 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.

In order 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 was 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. Small quantities of ethylene were added to the reaction mixture to help clarify promotion effects on specific reactions in the synthesis.

EXPERIMENTAL

TiO_2-supported Rh catalysts were prepared using the incipient wetness method and an aqueous solution of $RhCl_3.3H_2O$ 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 like manner using an aqueous solution of $RhCl_3.3H_2O$ 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 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 three hours of reaction. It constituted only 2.3 mole % of the mixture. The ethylene addition was utilized for three hours and then discontinued. By calculation of the product distribution before, during, and after the addition of ethylene and by taking catalyst deactivation into account, hydrogenation, chain incorporation, carbonylation, and hydrogenolysis of ethylene could be accurately delineated.

This addition did not result in any modification of the formation of products by CO hydrogenation.

The average Rh particle sizes for the catalysts were determined by X-ray diffraction line broadening using a MoKα radiation source.

RESULTS AND DISCUSSION

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

Because of the complex distribution of reaction products, only the major hydrocarbon and oxygenated products are reported in Table I. Specific activities in mole/kg/hr have been used to compare catalytic activity rather than turnover frequencies as there are uncertainties in the determination of the number of Rh surface sites in promoted and SMSI catalysts. These uncertainties can arise from (a) suppression of H_2 chemisorption caused by alkali promoters (8), (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 (9, 10). From the results of X-ray diffraction it was found that all of the catalysts had average Rh particle diameters less than 4 nm.

As shown in Table I, the rate of CO conversion decreased in the order: unpromoted > Li > K > Cs. Although the rates for all the products formed decreased upon alkali promotion, there were significant variations in 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 [illegible]. It appears that alkali promoters have different effects on the formation of oxygenated compounds than on that of hydrocarbons. The diminution of hydrogenation ability by the alkali promoters is also demonstrated in Table I, as indicated by the increase in mole ratios of C_3-C_5 olefins-to-paraffins and acetaldehyde-to-ethanol 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 rates for all the products formed 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), Kagami et al. (4) have reported that alkali species promote the oxygenate formation rate on Rh/Al_2O_3 in the order: Na > K > unpromoted. This trend is different from our results and from those reported by Wilson et al. (5). 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 sodium.

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. The formation rates of the major products [C_2H_6, C_3^+, C_2H_5CHO, $C_2H_5CH_2OH$] from ethylene are shown in Table II. 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 intermediate, 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 chemical nature of the additive, or (b) blockage of surface sites by the physical presence of the additive. If the active sites of Rh were to be affected only by blockage by the alkali species rather than by chemical promotion, then based on the physical sizes of the alkali atoms, the rates for all the products formed should decrease only by a factor of 3 within the set of promoted catalysts. 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 chemical properties 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 (8, 11-13). 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 serve as electron donors (14, 15). 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), 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. However, the ethylene added served as a probe to distinguish between hydrogenation and CO reactions in this synthesis.

The rates of incorporation of ethylene into higher hydrocarbons and the hydrogenolysis of ethylene to methane are shown in Table II. Hydrogenolysis of ethane and ethylene did not occur to any detectable extent for both promoted and unpromoted Rh/TiO_2 catalysts. Ko and Garten (16) 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 (17). The rates of incorporation of ethylene into higher hydrocarbons decreased in the order: unpromoted > Li > K > Cs. Hall et al. (18) have reported that K-promoted F-T catalysts exhibit less ethylene incorporation into higher hydrocarbons than unpromoted ones. Nijs and Jacobs (19) 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 (20). The lower rate of incorporation of ethylene into higher hydrocarbons on alkali-promoted catalysts may be 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.

CONCLUSIONS

The following 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 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) 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 provided an excellent way to probe modifications in a number of the reactions as a result of alkali promotion.

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Table I: 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 $(\frac{Ole.}{Par.})$	$\frac{MeCHO}{EtOH}$
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

reaction conditions: $CO/H_2 = 2$, 300°C, 10 atm

Table II: Effect of Ethylene Addition on Product Formation Rates

Catalysts	rate of C_2H_4 conversion (mole/kg/hr)	product formation rate (mole/kg/hr)				
		EtCHO	n-Propanol	CH_4	C_2H_6	Other HC's
Rh/TiO_2	8.30	0.132	0.075	0	7.70	0.39
$Rh-Li/TiO_2$	3.49	0.140	0.070	0	2.93	0.35
$Rh-K/TiO_2$	1.20	0.129	0.033	0	1.02	0.011
$Rh-Cs/TiO_2$	0.19	0.108	0.006	0	0.073	0.001

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

4. FORECAST OF WORK

Work in the next quarter will focus on the effect of alkali promotion on CO hydrogenation over Rh/La_2O_3 catalysts. These catalysts are very selective for oxygenated products.

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