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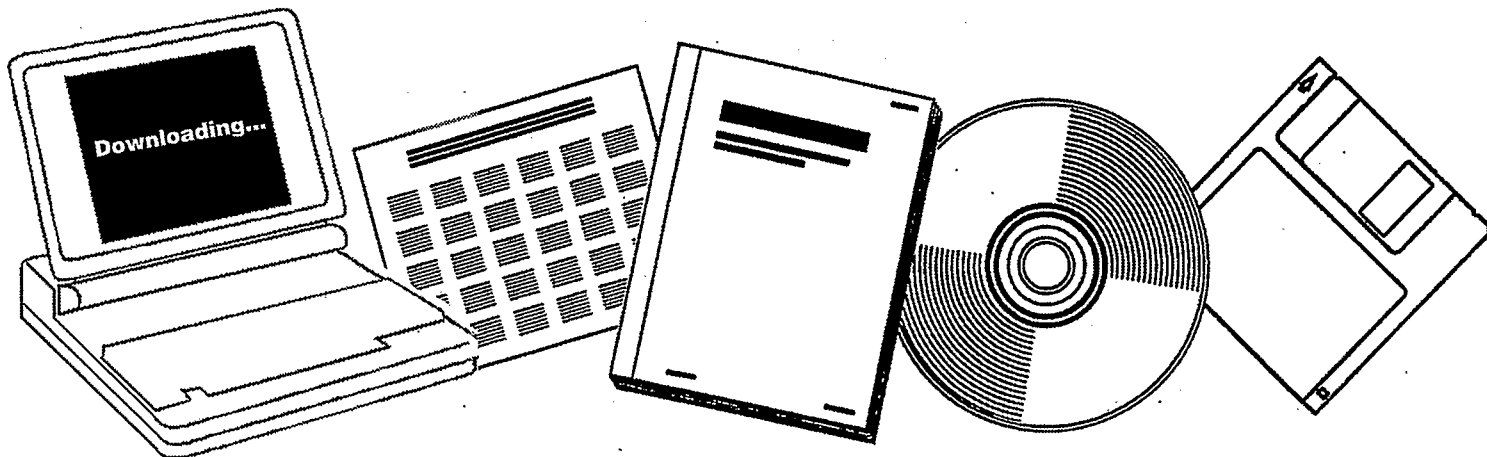
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**PROMOTION EFFECTS ON THE SYNTHESIS OF
HIGHER ALCOHOLS. NINTH QUARTERLY REPORT,
JULY 1984-SEPTEMBER 1984**

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

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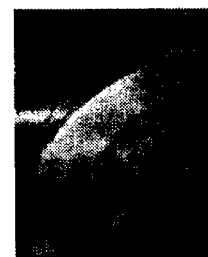
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PROMOTION EFFECTS
ON THE
SYNTHESIS OF HIGHER ALCOHOLS

9th Quarterly Report

July, 1984 - September, 1984

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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 both supported metals (such as Pd and Pt) 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 catalysts components will be attempted by ESCA.

This comprehensive research 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 9th quarter of the project, alcohol synthesis over Al_2O_3 , TiO_2 , SiO_2 and La_2O_3 -supported Rh catalysts have been studied to delineate the support effect. In addition, alkali promoted Rh/ La_2O_3 have been studied by ethylene addition and ethanol addition to determine the effect of alkali promotion on specific reaction steps during synthesis.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Support Effect

Results have been obtained for Al_2O_3 -, TiO_2 -, SiO_2 -, and La_2O_3 -supported Rh catalysts and alkali-promoted Rh/ La_2O_3 . The activity and product selectivity these Rh catalysts is presented in Table I. Under the same reaction conditions the oxygenate selectivity increased in the order: $\text{Al}_2\text{O}_3 < \text{TiO}_2 < \text{La}_2\text{O}_3 < \text{SiO}_2$. The results are not quite consistent with those reported for low temperature and low pressure reaction (1). It appears that the reaction conditions can affect the product distribution. An increase in the reaction pressure from low pressure to 10 atm resulted in an enhancement of C_2 oxygenate selectivity for TiO_2 - and SiO_2 - supported Rh catalysts and an increase in methanol selectivity for Rh/ La_2O_3 at the expense of C_{2+} hydrocarbons. The low selectivity to methanol at 300°C below 2 atm is apparently due to thermodynamic limitations (2). The conditions which favor methanol formation at the expense of hydrocarbons are low temperatures and high pressures (3).

An increase in total pressure of CO/H_2 could increase the coverage of nondissociatively adsorbed CO since CO is always more competitive for surface adsorption sites than H_2 . Ramamoorthy and Gonzales (4) have demonstrated that high coverages of CO can block CO dissociation. Somorjai (5) has pointed out that at high pressures the reaction time may be longer than the period between collisions of the reactant with the surface sites of the catalyst. Thus, the adsorbed CO could act to block the ensemble of sites needed for CO dissociation longer, resulting in a higher coverage of CO at higher pressures than at lower pressures. The increase in coverage of nondissociatively adsorbed CO could enhance those reactions which require nondissociatively adsorbed CO, such as formation of methanol and the CO insertion reaction. It

has been shown that the methanol and C₂ oxygenates are formed through two different reaction mechanisms - the first involving the hydrogenation of nondissociatively adsorbed CO and the second involving C-C bond formation between adsorbed CH_x and CO (6, 7). However, the problem of selectivity to methanol or ethanol still exists. Several speculations have been made to interpret the difference in the methanol and C₂ oxygenate selectivities among supported Rh catalysts. Ceriotti et al. (8) suggested that small modifications in the surface of a support can destabilize the hydroxymethyl species (which is assumed to be the precursor to methanol) and inhibit methanol formation. Kuznetsov et al. (9) have observed that La₂O₃ can catalyze the formation of methanol from CO hydrogenation at 250°C and 1 atm. They have suggested, based on their NMR results, that CHO and CHO₂⁻ are the precursors for the formation of methanol. On Rh/La₂O₃, these precursors could be formed on La₂O₃ then hydrogenated to methanol on the Rh.

Alkali-Promoted Rh/La₂O₃

The effect of alkali promoters on the product selectivity and activity of Rh/La₂O₃ is shown in Table II and III. The suppression of hydrogenation over alkali-promoted Rh/La₂O₃ is evidenced by the decrease in rate of formation of methane and the increase in the ratio of C₄⁼/C₄. The use of C₄⁼/C₄ as an index for hydrogenation ability is due to the lower incorporation ability of C₄⁼. As shown in Table II, Li promotion of Rh/La₂O₃ resulted in a significant increase in selectivity of C₂ oxygenated compounds whereas the selectivity of methane was decreased. The rate of CO conversion and the rate of formation for all the products decreased for K-promoted catalysts while the product selectivities were only slightly affected, as shown in Table II. Cs-promoted catalyst exhibited decreases not only in formation rate for the products but also in selectivity for the oxygenated compounds.

Ethylene Addition into CO/H₂

A small amount of ethylene (2.6 mole %) was added to the CO/H₂ reaction mixture to clarify the effect of alkali promotion on specific reactions and to elucidate the nature of the adsorbed species during the reaction. The rates of formation of the major products from the added ethylene are presented in Table IV. The major products produced included ethane, C₃⁺ hydrocarbons (mainly C₃⁼), propionaldehyde, and 1-propanol. The formation rates of methane, acetone, ethyl acetate, and C₁ and C₂ oxygenated compounds from CO and H₂ were virtually unaffected. It appears that hydrogenolysis of ethylene did not occur significantly as indicated by the constant rate of formation of CH₄ both before and during ethylene addition. The formation of C₃ oxygenated compounds could occur by insertion of CO into the adsorbed ethylene. The constant rates of formation for acetone, ethyl acetate, and C₁ and C₂ oxygenated compounds during ethylene addition indicate that the adsorbed CO or the active sites for CO insertion were abundant for reaction to oxygenated compounds under the conditions of differential reaction.

As shown in Table IV, relative to the unpromoted catalyst, hydrogenation of ethylene was unaffected for Li-promotion, slightly decreased for K promotion and severely suppressed for Cs promotion. The observed decrease in the rate of hydrogenation of ethylene for K- and Cs-Rh/La₂O₃ may be due to a strong suppression of hydrogenation for these catalysts. Li⁺ appeared to promote the rate of formation of oxygenated compounds while a marked decrease was observed for the Cs promoted catalyst. K promotion also produced a decrease in the rate of formation of C₃ oxygenated compounds.

From ethylene addition results, we can conclude that the increase in the oxygenate selectivity over Li-Rh/La₂O₃ is due to the promotion of CO insertion rather than the suppression of hydrogenation. The increase in C₄⁼/C₄ upon

alkali promotion is due to the suppression of hydrogenation caused by alkali promotion rather than the low CO conversion activity for K- and Cs-promoted Rh/La₂O₃.

Ethanol Addition into CO/H₂

The amount of ethanol added was controlled in the range of 0.1-0.99 mole %. The only possible effect of the concentration of added alcohols on the reaction of alcohols is the selectivity toward the formation of ether (10). However, ether is known to be readily decomposed over Rh catalyst at temperature above 200°C (10). It is no surprise that ether was not formed in this reaction system at 300°C. Although the amount of ethanol added are not equal for each catalyst, the trend for relative rates and selectivities of these specific reactions such as dehydration, dehydrogenation, dehydroxymethylation and chain incorporation still can be clearly discerned. As shown in Table V, the selectivity of decomposition of ethanol to C₁ and C₂ hydrocarbons decreased in the order: unpromoted > Li > K, Cs. Dehydrogenation selectivity of ethanol increased in the order: unpromoted < Li > K, Cs, while dehydrogenation activity was very low for both K- and Cs-Rh/La₂O₃. Besides the reaction of ethanol, the addition of ethanol results in a decrease in rates of formation of methanol and C₃ oxygenates for promoted and unpromoted catalysts. As both Rh metal and metal oxide are known to be able to dehydrate and dehydrogenate alcohols (10-13) addition of ethanol into CO/H₂ was also carried out over La₂O₃ to determine the contribution of La₂O₃ in decomposition of ethanol. La₂O₃, as shown in Table V, did not exhibit any dehydration and dehydroxymethylation activities but dehydrogenation activity under 300°C and 10 atm. Since La₂O₃ (Table V) is inactive in dehydration and dehydroxymethylation of ethanol, the dehydration and dehydroxymethylation activities of Rh/La₂O₃ must be attribute to Rh metal. The inability of K- Cs- promoted

Rh/La₂O₃ to catalyze dehydration and dehydroxymethylation of ethanol as shown in Table VI seems to suggest that the K and Cs promoters or at least part of them are located on Rh metal poisoning dehydration and dehydroxymethylation of ethanol.

CONCLUSIONS

This study has demonstrated that the synthesis of C₂ oxygenates from CO hydrogenation is closely related to the synthesis of C₃ oxygenates from reaction of C₂H₄ with CO/H₂. It also confirms the reaction scheme for the synthesis of hydrocarbons and oxygenates as proposed by various investigators (6, 7, 14, 15). The selectivity and activity of a Rh catalyst is dependent on its ability to catalyze those specific reaction steps such as CO dissociation, hydrogenation and CO insertion. These specific reaction steps were found to be strongly dependent on the type of alkali promoter, support and reaction conditions.

The overall effect of alkali promoters on Rh/La₂O₃ in the synthesis of oxygenated compound can be summarized as follows:

1. Li-promotion enhances CO insertion step and slightly affects hydrogenation steps over Rh/La₂O₃ resulting in an increase in selectivity and rate of the formation of C₂ oxygenated compounds during CO hydrogenation and an increase in selectivity and rate of the formation of C₃ oxygenated compounds during reaction of ethylene with CO/H₂.

2. K and Cs promoters suppress both CO insertion and hydrogenation over Rh/La₂O₃ resulting in a decrease in selectivity and activity to oxygenated compounds and a decrease in overall activity.

4. Forecast of Work

During the 10th quarter, Rh black catalyst and a series of alkali promoted Rh/Al₂O₃ and Rh/SiO₂ will be studied to elucidate the effects of alkali promoters and support on the synthesis of alcohols over Rh metal.

Table I Effect of Pressure on the Product Selectivity

Catalysts	Rh/Al ₂ O ₃ ^a	Rh/TiO ₂ ^b		Rh/SiO ₂ ^a		Rh/La ₂ O ₃ ^a	
Press. atm	10	1.3	10	1.6	10	1.3	10
Rate (mole/kg/hr)	7.73	1.49	17.31	0.395	1.099	0.68	0.772
Selectivity wt %							
CH ₄	70.0	44.2	49.9	28.9	22.0	20.6	22.8
C ₂ +	13.7	53.8	32.4	33.2	8.0	43.5	18.9
Total OX	16.3	2	17.7	37.9	70.0	35.9	58.3
MeOH	2.1	0	0.3	1.2	1.2	1.7	21.6
C ₂ OX	8.7	2	10.4	32.2	50.3	29.5	30.9

- a. CO/H₂ = 1, 300°C
 b. CO/H₂ = 2, 300°C
 c. GHSV = 7000 - 11,000 Hr.
 d. C₃+ O_x are included in Total OX

Table II Effect of Alkali Promoters on the Product Selectivity

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃
Rate of CO Conv. to OX and HC (mole/kg/hr)	0.772	1.02	0.348	0.213
<u>Selectivity wt %</u>				
CH ₄	22.8	10.0	14.1	24.5
C ₂ ⁺	18.9	22.1	21.3	32.7
Total OX*	58.3	67.9 ^o	64.6	42.8
MeOH	21.6	16.0	2.5	13.8
C ₂ OX	30.9	43.1	31.4	15.8

Reaction Conditions: 300°C, 10 atm, and CO/H₂ = 1
 *Acetone, EtAc, C₃ - C₄ OX are included in Total OX.

Table III Effect of Alkali Promoters on the Mole Ratio of Specific Products

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃
\bar{C}_4/C_4	5.76	7.67	8.40	8.32
MeCHO/EtOH	0.19	0.15	0.24	4.30

Table IV Products Formed as a Result of Ethylene Addition

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃
Rate of C ₂ H ₄ Conversion (mole/kg/hr)	2.528	2.639	1.231	0.209
Rate of Product Formation (mole/kg/hr)				
C ₂ H ₆	2.170	2.210	1.020	0.119
C ₃ ⁺	0.008	0.009	0.069	0.035
EtCHO	0.072	0.127	0.049	0.041
1-Propanol	0.278	0.293	0.093	0.014

2.6 mole % of C₂H₄ in CO/H₂ = 1, at 300°C and 10 atm

Table V: Products Formed as a Result of Ethanol Addition

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃	La ₂ O ₃
% of EtOH Added	0.11	0.28	0.47	0.68	0.99
Mole %					
CH ₄	84	58	0	0	0
C ₂	6	19.4	0	0	0
C ₃ +	9	3.6	0	0	0
MeCHO	0.5	19	100	100	100
Acetone	0.5	0	0	0	0
Overall Rate mole/kg/hr	0.27 (81%)	0.15 (18%)	0.038 (2.7%)	0.002 (0.09%)	0.028 (1%)
Decrease in Product Formate Rate During EtOH Addition mole/kg/hr					
MeOH	0.04	0.03	0.01	0.007	-
C ₃ OX	0.007	0.017	0.004	0	-

300°C, 10 atm and CO/H₂ = 1

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