# PROMOTION EFFECTS ON THE SYNTHESIS OF HIGHER ALCOHOLS. FIFTH QUARTERLY REPORT, SEPTEMBER 1983-NOVEMBER 1983

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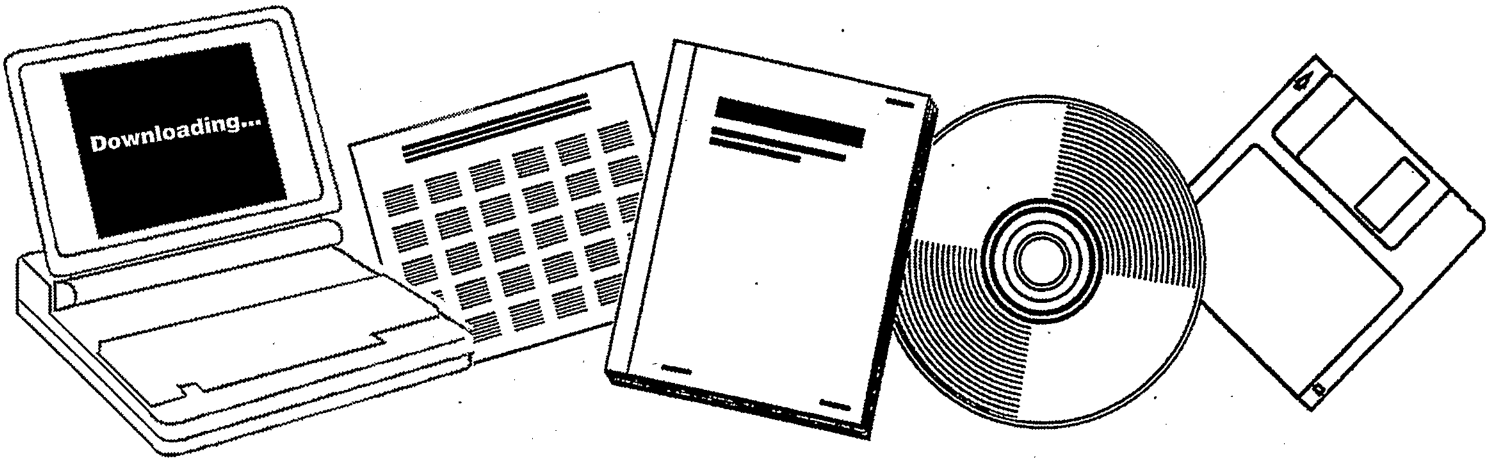

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# PROMOTION EFFECTS
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# SYNTHESIS OF HIGHER ALCOHOLS

## 5th Quarterly Report

Sept., 1983 - Nov., 1983

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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 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 fifth quarter of the project, a study of the alcohol synthesis over alkali-promoted $Rh/TiO_2$ catalysts was carried out and is detailed in Sec. 3.

## 3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

### INTRODUCTION

The synthesis of alcohols from carbon monoxide and hydrogen has been studied during the past half century. The catalysts utilized for these studies have included transition metal catalysts such as Rh, Pd, Pt, Ir,(1) and modified methanol synthesis catalysts such as alkali-promoted Cu/ZnO(2) and the IFP catalysts (3) for higher alcohol synthesis. The use of alkali-promoted methanol synthesis catalysts, prior to 1957, was reviewed by Natta, et al,(4). They concluded that alkali promoting activity may be related to alkali basicity which increases with an increase in atomic weight of the alkali metal. Recently alkali-promoted Cu/ZnO has been studied by G. A. Vedage, et al.(5) Their results indicate that the selectivity to higher alcohols may be related to the basicity of the catalyst surface. Because of the complexity of these mixed oxide catalysts, the role of alkali promoters on these catalysts is far from being fully understood.

It has been suggested (6) that higher-alcohol synthesis catalysts must dissociate the C-O bond only at a moderate rate so that the catalyst surface contains undissociated adsorbed CO and surface carbene species for the bimolecular insertion reaction. Rh appears to be an excellent candidate for the higher alcohol synthesis. This element, which lies between Ru (which can yield hydrocarbons exclusively) and Pd (which can produce only methanol), can catalyze the formation of both hydrocarbons and alcohols from synthesis gas. It appears that different chemical environments for Rh can result in very different product distributions ranging from methanol and ethanol (7) to hydrocarbons (8). It has been reported (9,10) that the CO hydrogenation selectivity to alcohols over supported Rh varies with the basicity of the support. However, remarkably little work has been done on the alkali promotion of Rh catalysts. This paper reports on a study of the alkali promotion effect on the synthesis of alcohols over $Rh/TiO_2$.

## EXPERIMENTAL

### Catalyst Preparation:

The alkali promoted Rh catalysts were prepared by the impregnation of $TiO_2$ (Degussa, P. 25) and $SiO_2$ (Strem) using $RhCl_3$ $3H_2O$ (Alfa Products) and an alkali nitrate (Li, K, Cs) in aqueous solution at pH=3-3.5 to give 3wt%Rh catalysts. The atom ratio of alkali promoter to Rh was 1/2. After impregnation, the samples were dried overnight in air at $40^0C$, then reduced in flowing $H_2$ on heating in $50^oC$ steps (30 minutes) to $400^oC$ and holding at $400^oC$ for 16 hours. Prior to reaction, the $TiO_2$-supported catalysts were again reduced in flowing $H_2$ at $500^oC$ for 1 hour to induce the strong metal support interaction (SMSI) effect. The $SiO_2$-supported catalysts were reduced at $400^oC$ for 1 hour.

### Catalytic Reactor:

The higher alcohol synthesis was carried out in a differential reactor at $250-325^oC$ and 1-30 atm with $H_2/CO=1/2$. The gases used for these reactions studies were obtained from Air Products and included $H_2$ (UHP, 99.99%), He (UHP, 99.99%) and CO (UHP, 99.99%), which were 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 remove oxygen as 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 3 mass flow control meters (Brooks 5850) for controlling $H_2$, CO, and He flow, 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 by a 8′ x 1/8" poropak Q column in series with a 6ft. x 1/8" 80/100 carbopack c/0.2% carbowax 1500 using a He carrier flow of 20cc/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 of all $C_1$-$C_6$ paraffins and olefins, $C_1$-$C_4$ alcohols, $C_1$-$C_4$aldehydes, ethylacetate, acetic acid, CO, $CO_2$, and $H_2O$ in a 50 min. analysis.

## RESULTS AND DISCUSSION

### (a) $Rh/TiO_2$ and $Rh/SiO_2$

The activity of $Rh/TiO_2$ and $Rh/SiO_2$ as a function of reaction time is shown in Fig. 1 . $Rh/TiO_2$ was several orders of magnitude more active than $Rh/SiO_2$. It is obvious that both these catalysts did not deactivate in the same manner. In the case of $Rh/TiO_2$, a rapid initial decline in the activity was observed. In contrast to $Rh/TiO_2$, the activity of $Rh/SiO_2$ showed a slight initial increase followed by a slow decline, which parallels the observation reported by van Den Berg.(11)

As shown in Table 1, the primary oxygenated products over $Rh/TiO_2$ were $C_2H_5OH$, $CH_3COOH$, and acetone, with $CH_3OH$ and $CH_3CHO$ as minor products. On the other hand, the $Rh/SiO_2$ catalyst produced mainly $CH_3CHO$ and $C_2H_5OH$. The major difference in the oxygenate selectivity between $Rh/TiO_2$ and $Rh/SiO_2$ catalysts appears to be the formation of a significant amount of acetone (10wt%) and acetic acid (13wt%) as shown in Table 1. In contrast to the results just described, acetone was not observed for CO hydrogenation over $Rh/TiO_2$ by Katzer et al,$^{(9)}$ or by Ichikawa et al.$^{(7,10)}$ The failure of these authors to observe acetone may be due to low reaction temperatures, low $CO/H_2$ ratios, different catalyst preparation methods, and/or different reduction conditions. In fact, the presence of acetone has been observed in the Fischer-Tropsch synthesis $^{(12)}$ and higher alcohol synthesis $^{(4)}$ from CO hydrogenation. It has been suggested that the acetone is formed by the secondary reaction of acetic acid:

$$2CH_3COOH \rightleftarrows (CH_3)_2CO + H_2 + CO_2$$

The formation of acetone over $Rh/TiO_2$ in this study may be explained by the above secondary rection since an appreciable amount of acetic acid formed over $Rh/TiO_2$ could result in acetone under this reaction condition: 300°C, 10 atm.

The hydrocarbon selectivity together with $CO_2$ yield is higher for $Rh/TiO_2$ than $Rh/SiO_2$. As Rh has been shown to be a poor catalyst for the water gas shift reaction,$^{(13)}$ the formation of $CO_2$ can be attributed to the Boudoward reaction. The higher yield of $CO_2$ for $Rh/TiO_2$ than for $Rh/SiO_2$ suggests that $Rh/TiO_2$ had a stronger CO dissociation ability, which may explain the higher yield of hydrocarbons. It is obvious from the data shown that the support had a strong influence on the catalytic selectivity and activity.

It has been reported that the selectivity of CO hydrogenation over supported rhodium catalysts varies with the basicity of the support.(9) Rh on MgO, a very basic support, exhibits 90% selectivity to methanol. Acidic supports, such as $Al_2O_3$, result in mainly $CH_4$, while slighltly acidic or basic supports (e.g., $SiO_2$, $TiO_2$, $CeO_2$) produce both alcohols and hydrocarbons. Thus, use of $TiO_2$ as a support which has a greater acidity than $SiO_2$ would result in higher yields of hydrocarbons. The results of this study appear to be consistent with this correlation.

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, Ir, and Rh) by Vannice(14). Katzer et al. (9) have also reported that Rh/$TiO_2$ reduced at 673°K 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. It appears that their reduction temperature may not have been high enough to induce SMSI.

High temperature reduction (> 500°C) of many $TiO_2$-supported transition metal catalysts, resulting in $H_2$ and CO chemisorption suppression and higher olefin selectivities and chain growth probabilities during CO hydrogenation, has usually been suggested to produce SMSI.(14,15,16) Meriaudeau, Ellestad and Naccache (17) have studied CO hydrogenation over supported Rh catalysts at 1 atm and 300°C. They concluded that the increase in chain length and in olefin/paraffin ratio observed for Rh on a $TiO_2$ support could be due to SMSI. However, our results show the olefin/paraffin ratio and chain length to be approximately the same for the $TiO_2$- and $SiO_2$- supported catalysts. This may be due to the high CO/$H_2$ ratio or the high pressure reaction conditions for our study. It would be interesting to understand the effect of pressure on CO hydrogenation over SMSI catalysts. No high pressure reaction study over SMSI catalysts has been found by us in the open literature.

(b) Alkali-promoted $Rh/TiO_2$ catalyst

The effect of alkali species on the catalytic performance of $Rh/TiO_2$ was studied using catalysts containing different types of alkali species (Li, K, and Cs). The effects of alkali promotion on the activity and selectivities of this catalyst for CO hydrocondensation are shown in Figures 2, 3, 4, 5, and 6. The activity of CO conversion decreased in the order:

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

The acitivities of ethanol, acetic acid, acetone, and $CH_4$ formation (as shown in Fig. 3,4) also decreased in the same order, while the formation rate of acetic acid fell to zero for the case of $Cs-Rh/TiO_2$. The rate of acetaldehyde formation appeared not to be influenced by alkali promotion. The trend in the rate of higher hydrocarbon formation ($C_2$+) seemed to follow that of $CO_2$ formation, as shown in Fig. 2 and 4, suggesting that the hydrocarbons were formed from dissociated CO. The observed decrease in CO conversion for alkali-promoted $Rh/TiO_2$ catalyst is consistent with results reported for alkali-promoted $Rh-Mn/SiO_2$ by Wilson, et al.(18)

The selectivities of oxygenated products and hydrocarbons are shown in Figures 5 and 6. As shown in Figure 5, there was little change in the selectivities for ethanol and acetone among unpromoted Li-, K-promoted catalysts. The selectivity for acetic acid, as also shown in Fig. 5, decreased in the order: unpromoted > Li > K > Cs, while acetaldehyde selectivity increased in that order. The methane and higher hydrocarbon selectivities and olefin/paraffin ratios are shown in Fig. 6. The addition of alkali to $Rh/TiO_2$ appeared to increase the olefin/paraffin ratio significantly. The finding that the alkali-promoted $Rh/TiO_2$ decreased the CO conversion activity and increased the olefin/paraffin ratio is indeed consistent with those results reported for alkali-promoted Ni, Ru, Co catalysts.(19,22) In fact, it has been well established(22) that alkali-promotion of FT catalysts results in (1) decreased CO conversion activity, (2) increased CO dissociation ability, (3) decreased hydrogenation ability resulting in higher olefin/paraffin ratios, and (4) increased selectivities to long chain hydrocarbons. A comparison of the mole ratio of various products among the promoted and unpromoted catalysts is shown in Table II.

The decrese in the mole ratio of (EtOH)/(MeCHO) paralleling that in the (paraffin/olefin) ratio as shown in Table II could be due to a decrease in the hydrogenation ability following alkali-promotion. The aldehyde formed over Rh catalysts may be partly transformed into ethanol, which has been shown by the addition of acetaldehyde into CO and $H_2$ over Rh catalysts resulting mainly in an increase in ethanol production. (11) Bhasin et al(24) have reported that during, CO hydrogenation over Rh, the carbon efficiency ratio of (EtOH)/(MeCHO) is proportional to the rate constant for hydrogenation of acetaldehyde. These results suggest that the ethanol is obtained mainly due to the hydrogenation of an acetaldehyde surface intermediate, which is consistent with our results.

Watson and Somojai(25,26) have sugested that the oxidation state of (surface) Rh is responsible for the formation of oxygenated products during CO hydrogenation while metallic Rh is responsible for the formation of hydrocarbons. They found that a slower rate of CO hydrogenation over $Rh_2O_3$ $5H_2O$ (involving the oxidized state of surface Rh) produced large quantities of aldehydes and higher olefin yields. Our results show a slower rate of CO hydrogenation and higher yields of olefins and acetaldehyde when $Rh/TiO_2$ is promoted by alkali. The rate of acetaldehyde formation was essentially invariant with the various alkali promotions suggesting that the alkali promoters may stabilize or at least not affect the oxidation state of surface Rh while suppressing the hydrogenation ability. The overall effect of alkali $Li < K < Cs$.

The results obtained in this study demonstrate four effects of alkali promotion of $Rh/TiO_2$: (a) a decrease in the activity of $Rh/TiO_2$, (b) hydrogenation suppresssion, (c) a slight modification in the hydrocarbon and alcohol chain growth, (d) a slight increase in the selectivity for oxygenated products. The major difference between alkali-promoted $Rh/TiO_2$ and alkali-promoted Cu/ZnO appears to be that alkali promotion leads to a decrease in the rate of alcohol product formation for $Rh/TiO_2$ catalysts and an increase in the rate of higher alcohol product formation for Cu/ZnO catalyst.(5)

## CONCULSIONS

The selectivity and activity of alcohol synthesis over Rh catalysts vary with the type of support and additive.

The activity of $Rh/TiO_2$ is 30 times higher than $Rh/SiO_2$.

The effect of alkali promotion of $Rh/TiO_2$ increases in the order:

$Li<K<Cs$.

The addition of alkali promoters to $Rh/TiO_2$ results in lower activity of CO hydrogenation, a slight increase in the selectivity of oxygenated products, and a high yield of olefins.

## 4. FORECAST OF WORK

Work in the next quarter will be focused on:

1. The effect of the Rh precursor on the activity and selectivity of supported Rh in CO hydrocondensation,

2. The effect of SMSI and non-SMSI states of $Rh/TiO_2$ on the catalytic activity and selectivity,

3. The alkali promotion effect on the strong basic (MgO, CaO) and acidic ($Al_2O_3$) supported Rh catalysts.

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## TABLE I

| | 3% $Rh/SiO_2$ | 3% $Rh/TiO_2$ |
|---|---|---|
| Activity (g mole/kg·hr) | 1 | 32 |
| Selectivities | | |
| $CO_2$ mole % of CO Conv. | 0 | 17 |
| MeOH wt % of HC +Ox | 0 | 1 |
| EtOH | 6 (0.025)[a] | 6 (0.562)[a] |
| MeCHO | 40 (0.155)[a] | 1 (0.145)[a] |
| MeCOOH | 0 | 13 |
| Acetone | 0 | 7 |
| Hydrocarbons | 51 | 72 |
| $\frac{C_2^{=} - C_4^{=}}{C_2^{-} - C_4^{-}}$ | 1.3 | 1.1 |

300°C 10 atm, $CO/H_2=3$

[a] activity in g mole/kg hr

# TABLE II

| Mole Ratio | $Rh/TiO_2$ | $Li\text{-}Rh/TiO_2$ | $K\text{-}Rh/TiO_2$ | $Cs\text{-}Rh/TiO_2$ |
|---|---|---|---|---|
| $\frac{[EtOH]}{[MeCHO]}$ | 12.8 | 3 | 0.34 | 0.54 |
| $\frac{\text{Paraffin}}{\text{Olefin}}$ | 0.82 | 0.262 | 0.262 | 0.251 |
| $\frac{C_2^+\ HC}{CH_4}$ | 0.33 | 0.29 | 0.24 | 0.5 |
| $\frac{C_3O_x}{C_2O_x}$ | 0.29 | 0.4 | 0.295 | 0.37 |

## FIGURE CAPTIONS –

Fig. 1 Activity of CO Conversion.

Fig. 2 Effect of Alkali Promotion on CO Conversion.

Fig. 3 Effect of Alkali Promotion on $C_2$ Oxygenates.

Fig. 4 Effect of Alkali Promotion on Hydrocarbons.

Fig. 5 Effect of Alkali Promotion on Oxygenate Selectivities.

Fig. 6 Effect of Alkali Promotion on HC Selectivities.

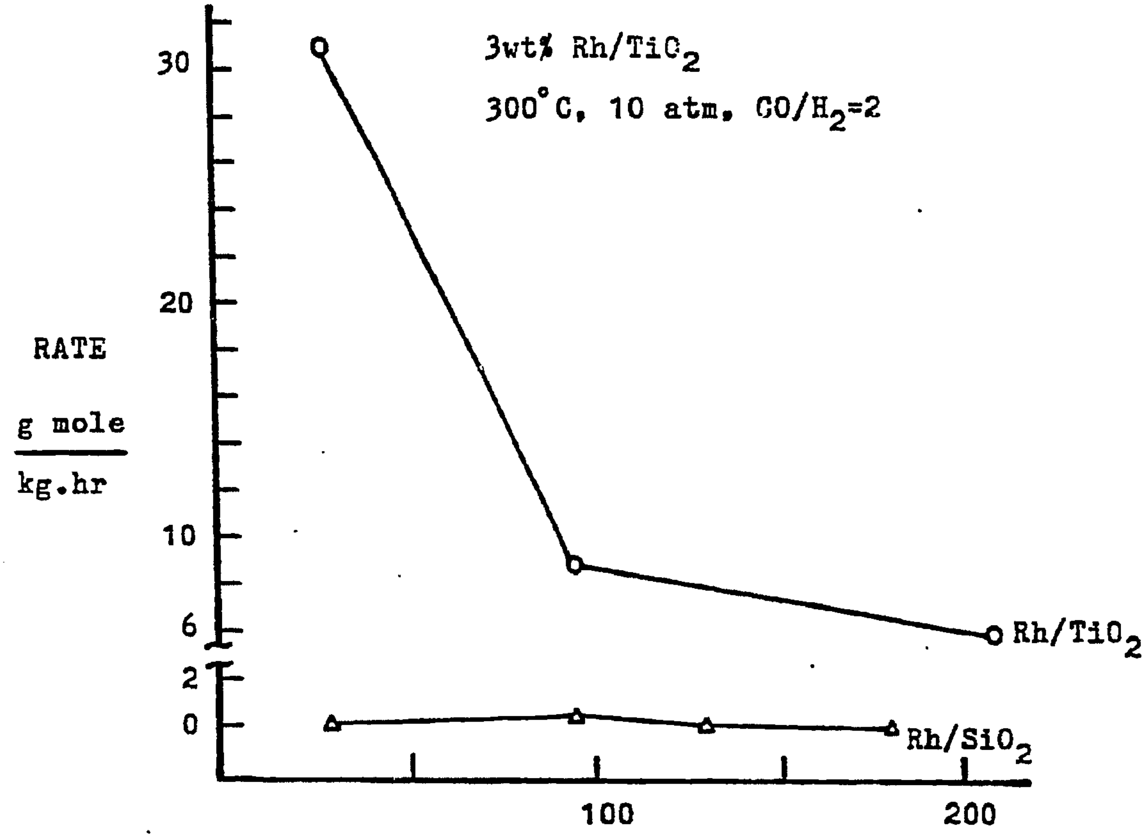

Figure 1. Activity of CO Conversion

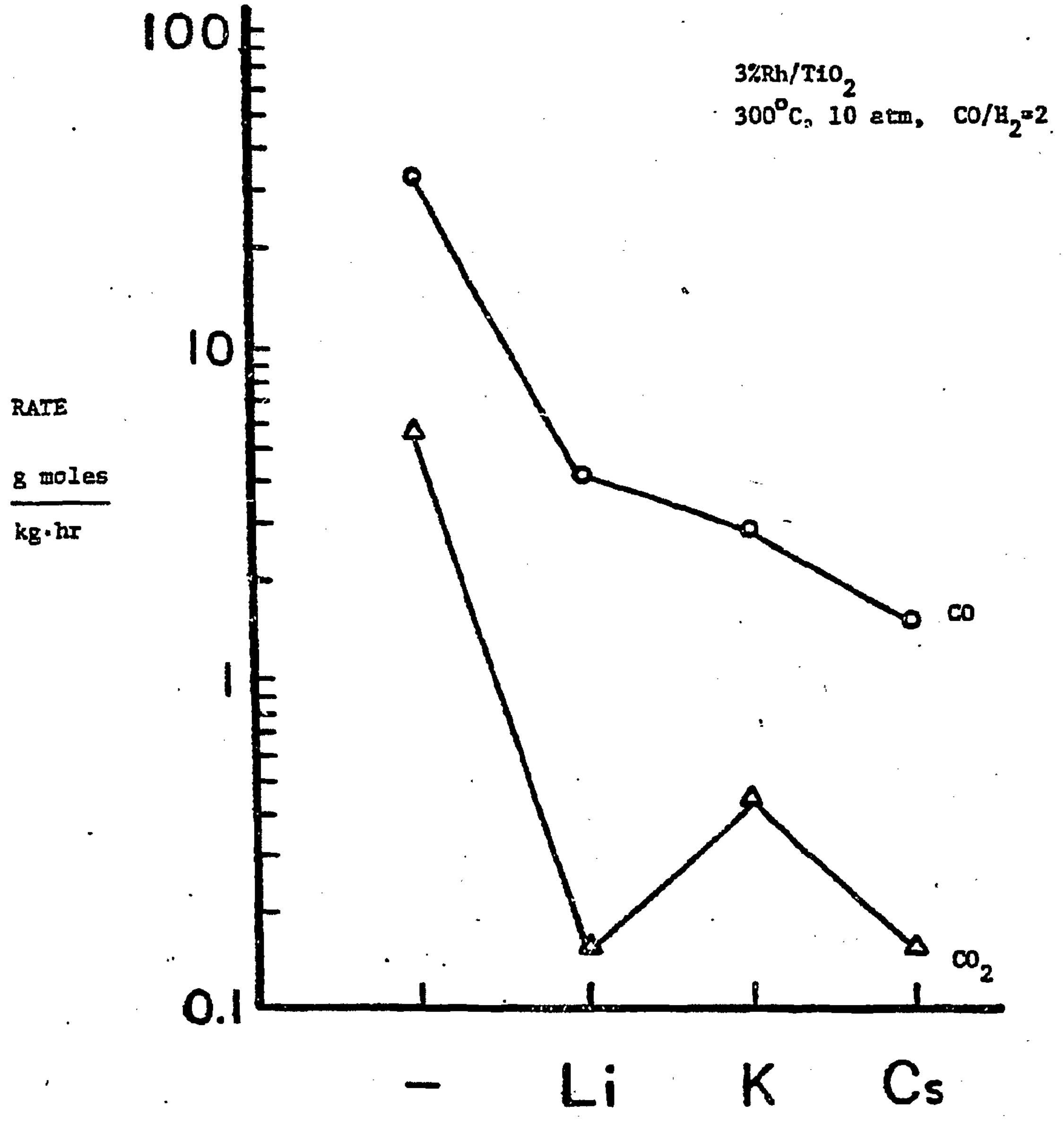

Figure 2. Effect of Alkali Promotion on CO Conversion

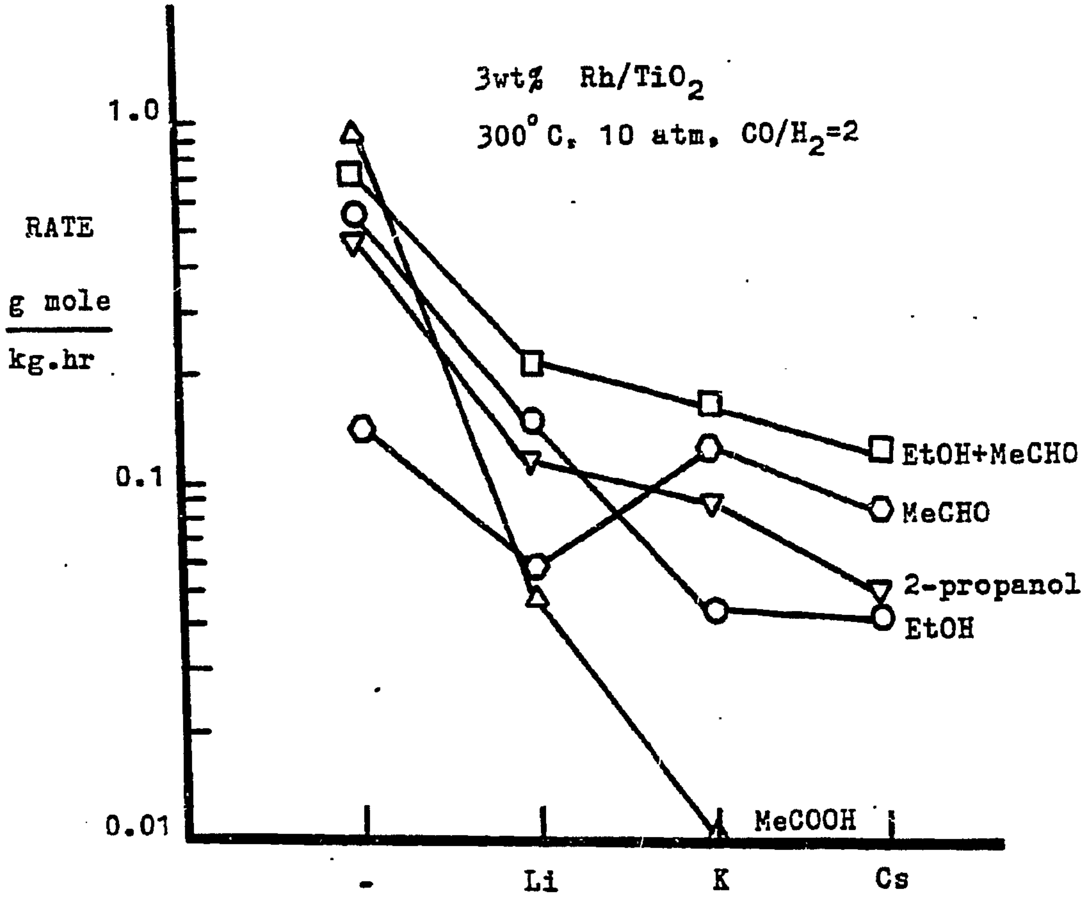

Figure 3. Effect of Alkali Promotion on $C_2$ Oxygenates

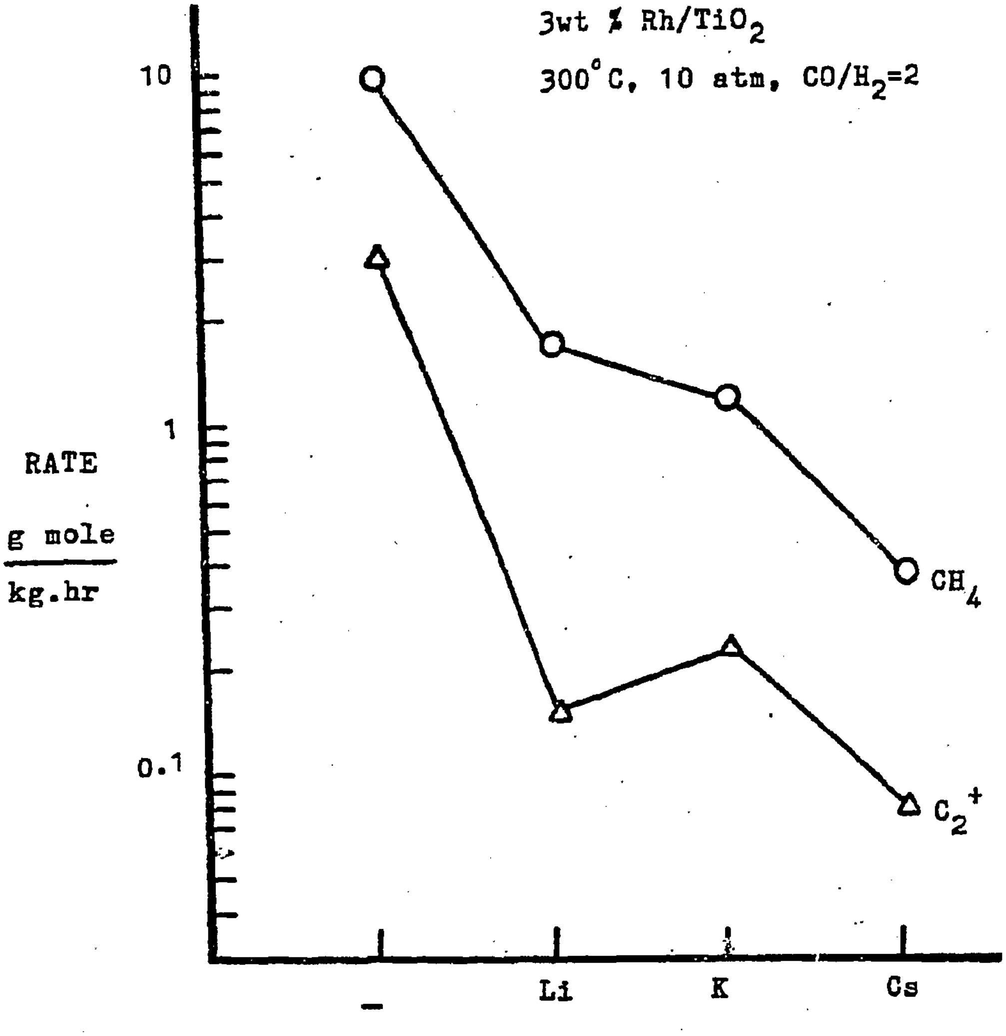

Figure 4. Effect of Alkali Promotion on Hydrocarbons

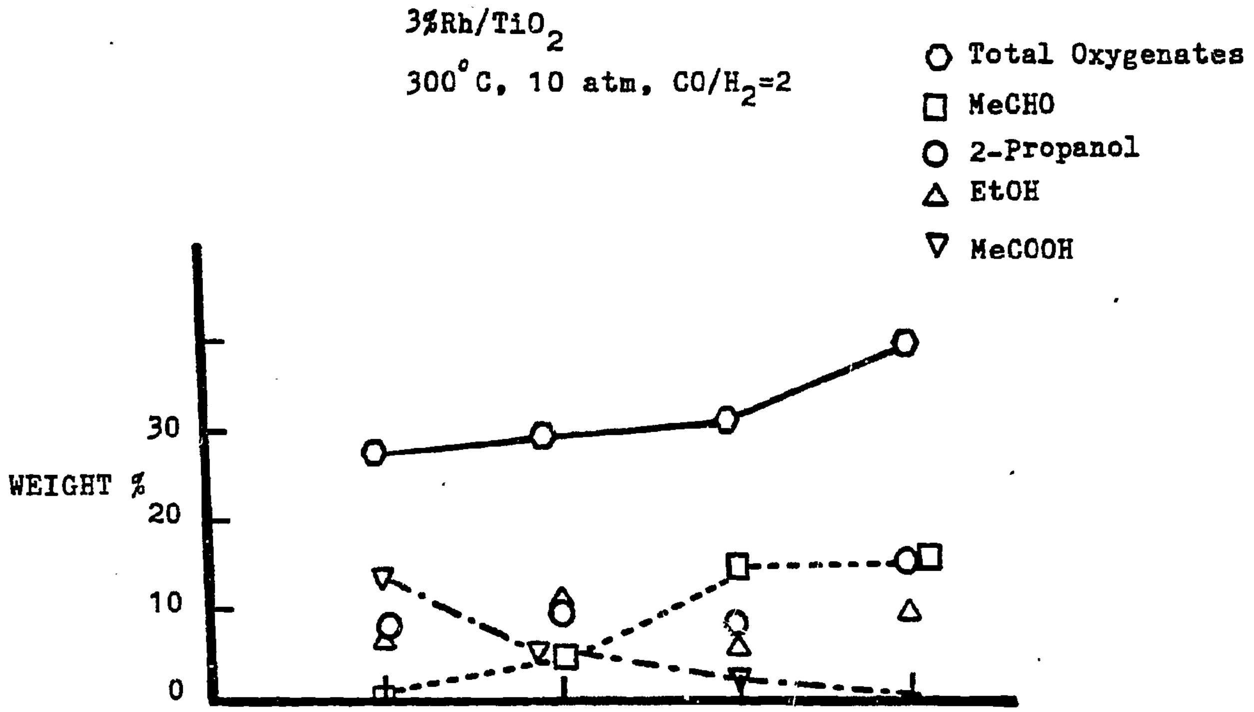

Figure 5. Effect of Alkali Promotion on Oxygenate Selectivities

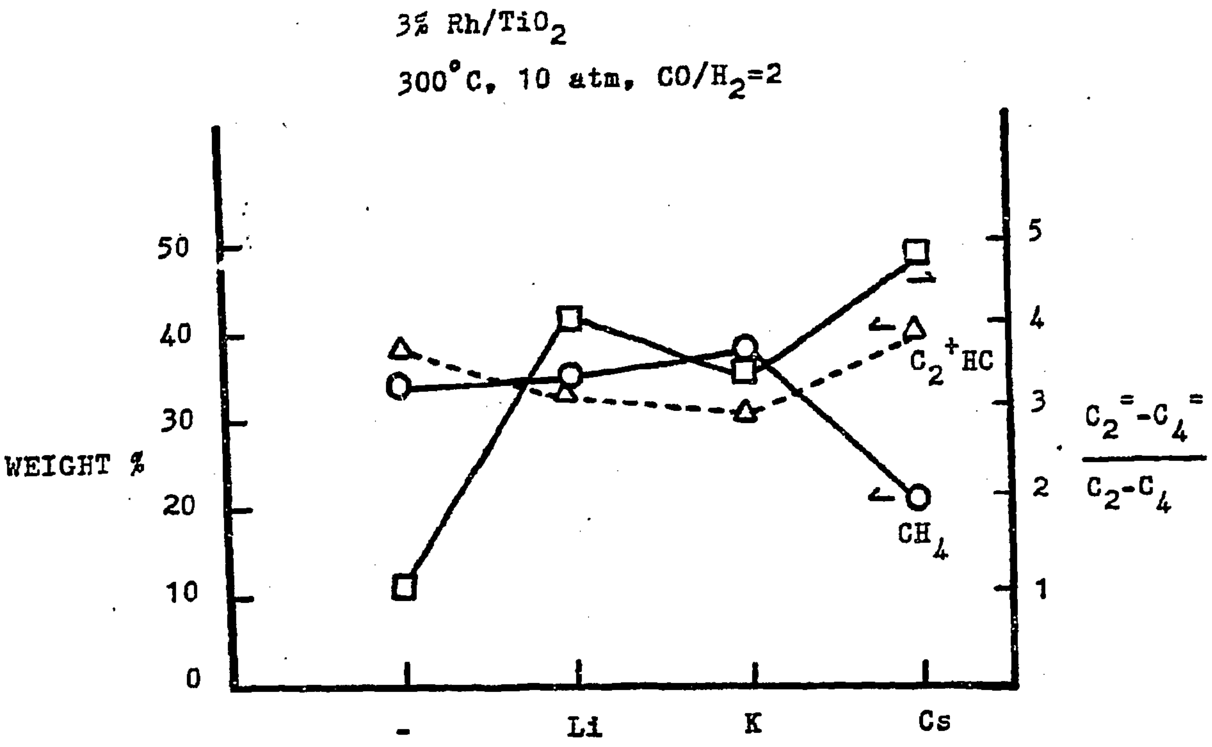

Figure 6. Effect of Alkali Promotion on HC Selectivities

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