THE EFFECT OF ALKALI PROMOTION ON ALCOHOL SYNTHESIS OVER Rh/TiO_2

S.C. Chuang, J.G. Goodwin, Jr., and I.Wender

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

I. INTRODUCTION

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 often results in greater yields of higher alcohols. However, little is known about how various alkali species affect the catalyst component and alcohol synthesis reaction. Rh catalysts are simple yet model systems for studying the effect of alkali promoters on CO hydrocondensation. Depending on the oxide support used, the product catalyzed by Rh may be primarily hydrocarbons or alcohols (1, 2). This paper reports on an investigation of the effect of various alkali species (Li, K, and Cs) on CO hydrocondensation over Rh/TiO_2. Rh/TiO_2 was an attractive catalyst to study since both hydrocarbons and oxygenated compounds are formed in significant quantities during CO hydrogenation. This provided the possibility to investigate simultaneously the effect of alkali promotion on the formation of these two types of products.

II. EXPERIMENTAL

The alkali-promoted rhodium catalysts were prepared by the impregnation of TiO_2 using $RhCl_3.3H_2O$ and an alkali nitrate (Li, K, Cs) in aqueous solution having a pH of 3-3.5. The catalysts were prepared in such a way so that the Rh loading was 3 wt% and the atom ratio of alkali promoter to Rh was 1/2. After impregnation, the samples were dried overnight in air at 40°C and reduced in flowing H_2 on heating in 50°C steps (30 min.) to 400°C and holding for 16 hr. Prior to reaction, the TiO_2-supported catalysts were again reduced in flowing hydrogen at 500°C for 3 hr. to induce strong metal-support interaction (SMSI) (3). The study was carried out in a differential reactor at reaction conditions of 250-330°C, 10 atm, and CO/H_2=2. A small amount of ethylene (2.3 mole%) was added to the reactant mixture to study the specific reactions of this synthesis.

III. RESULTS AND DISCUSSION

The activity of CO conversion was observed to decrease in the order: unpromoted > Li > K > Cs. The rates of formation for all the products decreased upon alkali promotion but the oxygenate selectivities were enhanced as shown in Fig. 1. This clearly indicated that there was less suppression in the rate of oxygenate formation than in that of hydrocarbon formation. It may suggest that alkali promoters have a different effect on the formation of oxygenates than on that of hydrocarbons. The selectivity of acetone paralleled that of acetaldehyde suggesting that the acetone may be formed by the combination of the acetaldehyde intermediate and a surface methyl species as proposed by Schulz and Zein El Deen (4). The decrease in mole ratio of [MeCHO]/[EtOH] and (olefin)/(paraffin) as shown in Table I may be attributed to the suppression of hydrogenation as a result of alkali promotion. Hydrogenation suppression has been identified as a major

effect of alkali promoters on CO hydrogenation over transition metal catalysts (5, 6).

Although oxygenate selectivities were enhanced upon alkali promotion, the chain growth probability based on carbon number of both oxygenates and hydrocarbons was only increased slightly by alkali promotion. Less deviation of the ethylene fraction from the Schulz-Flory distribution was also observed on alkali-promoted catalysts, indicating that the effect of ethylene incorporation was less pronounced in the presence of alkali promoters.

In order to verify the above findings, a small amount of ethylene [2.3 mole %] was added to the reactant mixture. The results of ethylene addition are essentially consistent with the above findings.

IV. CONCLUSIONS

1. The rate of CO conversion decreased in the order: unpromoted > Li > K > Cs.
2. The hydrogenation ability also decreases in the order: unpromoted > Li > K > Cs.
3. The alkali promoters had different effects on the formation of oxygenates than on that of hydrocarbons.
4. The active sites for oxygenate formation during CO hydrogenation over Rh/TiO_2 appeared not to be sensitive to the chemical nature of the alkali promoter.

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TABLE I The Effect of Alkali Promoter on [MeCHO]/[EtOH] and [olefin]/[paraffin] Ratios

	Rh/TiO_2	$Li-Rh/TiO_2$	$K-Rh/TiO_2$	$Cs-Rh/TiO_2$
$\frac{[MeCHO]}{[EtOH]}$	0.3	0.6	2.7	10.4
$\frac{[C_3-C_5 \text{olefins}]}{[C_3-C_5 \text{ paraffins}]}$	2.7	5.8	4.6	4.2

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

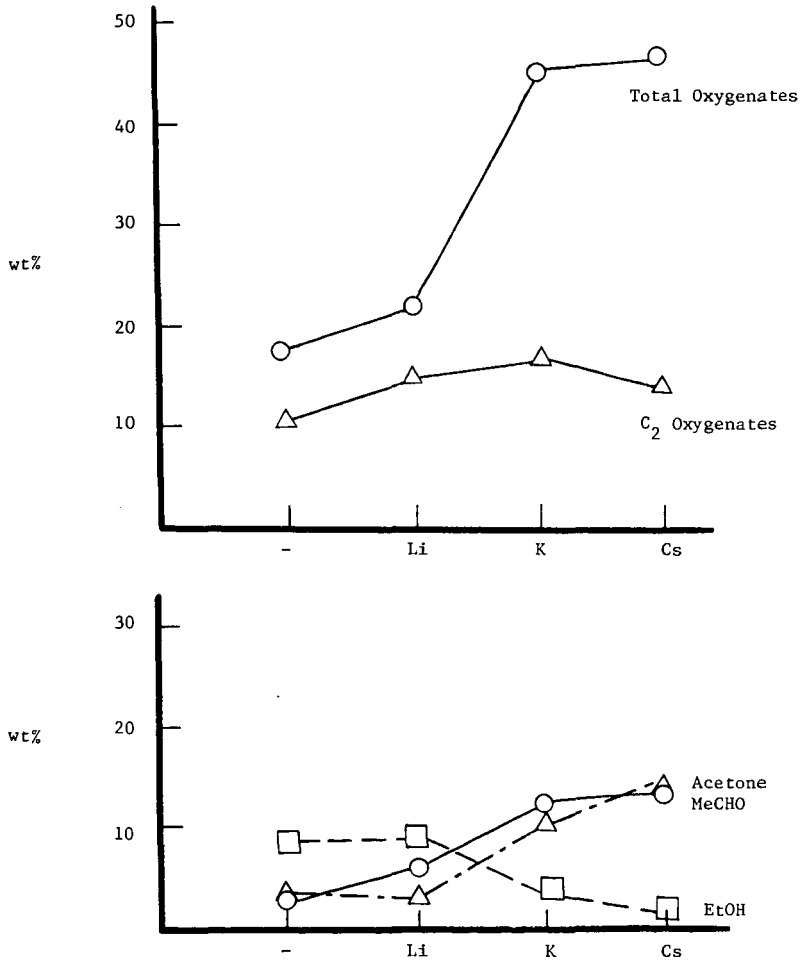

Figure 1: The Effect of Alkali Promotion on Oxygenate Selectivity for Rh/TiO_2 (CO/H_2 = 2, 300°C, 10 atm)