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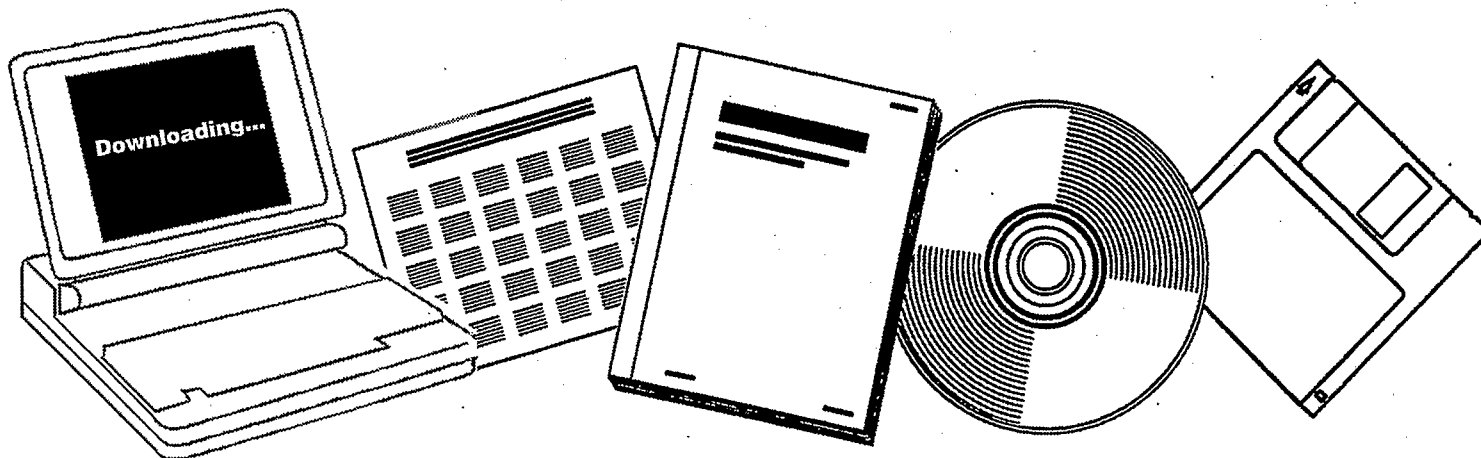
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**PROMOTION EFFECTS ON THE SYNTHESIS OF
HIGHER ALCOHOLS. SEVENTH QUARTERLY REPORT,
MARCH 1984-MAY 1984**

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

JUL 1984



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PROMOTION EFFECTS

ON THE

SYNTHESIS OF HIGHER ALCOHOLS

7th Quarterly Report

March 1984 - May 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 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 on 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 seventh quarter, a study of CO hydrogenation over alkali-promoted Rh/La₂O₃ 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

It is known that the catalytic hydrogenation of carbon monoxide can produce a wide spectrum of products including paraffinic and olefinic hydrocarbons, alcohols, aldehydes, acids, esters (1,2,3), and ethylene glycol (4). The oxygen containing species are very desirable in terms of not only their potential application as a fuel but also the current extensive use as of them chemical feedstocks or intermediates. Rh catalysts have been found to actively catalyze both homogeneously and heterogeneously the formation of C₂ oxygenated compounds from synthesis gas (4,5). Depending on the chemical environment of Rh catalysts and reaction conditions, the products may consist of ethylene glycol (4), alcohols, aldehydes, acetic acids (6), and/or hydrocarbons (9). The chemical environment of heterogeneous Rh catalysts can be modified both by the support and by the presence of additives. Recently, it has been reported that alkali promoters can enhance the oxygenate selectivity of supported Rh catalysts (8,9,10). While depending on the type of support, precursor, and reaction conditions, the absolute rate of C₂ oxygenate formation may be increased or slightly suppressed by alkali promoters. Kagami et al. (10) found the rate of formation for C₂ oxygenated compounds over Rh/Al₂O₃ was promoted by the presence of sodium. Orita et al. (11) reported that the addition of alkali metal cations to Rh/TiO₂ enhanced both the activity and selectivity for C₂ oxygenate formation. These investigators have suggested that doping TiO₂- and Al₂O₃-supported Rh catalysts with alkali metal cations results in the creation of active sites for C₂ oxygenated compound formation. On the contrary, a slight suppression in rate of formation of C₂ oxygenated compounds has been observed for Li-, Na-promoted Mn-Rh/SiO₂ (12), Na promoted Mn-Mo-Rh/SiO₂ (8), and alkali-promoted Rh/TiO₂ (9). An extensive study on the alkali promotion on differently

supported Rh catalysts would greatly help to elucidate the role of alkali promoters on alcohol synthesis over supported Rh catalysts. La_2O_3 -supported Rh catalyst (13) is known to be highly selective for the synthesis of alcohol from synthesis gas. A study of alkali promotion of Rh/ La_2O_3 would increase our knowledge of the effect of alkali promoters on the yield of C_2 oxygenated compounds during CO hydrogenation.

This paper presents the results from a study of the synthesis of alcohols over Li, K, and Cs-promoted Rh/ La_2O_3 during CO hydrogenation under the reaction conditions of $\text{CO}/\text{H}_2 = 1$, 523-573 $^\circ\text{K}$ and 0.1 - 1 MPa using a differential reactor. The addition of ethylene into the CO/H_2 mixture was carried out at 573 $^\circ\text{K}$ and 1 MPa to elucidate the effect of alkali promotion on specific reactions occurring during the synthesis such as hydrogenation, CO insertion, and chain incorporation.

EXPERIMENTAL

Material

Alkali-promoted 3 wt % Rh catalysts were prepared by impregnation of La_2O_3 using an aqueous solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Alfa Products) and an alkali nitrate (Li, K, Cs) at $\text{pH} = 3-3.5$. The atom ratio of the particular alkali element to Rh was 1/2. After impregnation, the samples were dried overnight in air at 313 $^\circ\text{K}$, then reduced in flowing H_2 on heating in 50 $^\circ\text{K}$ steps (30 minutes) to 673 $^\circ\text{K}$ and holding at that temperature for 16 hours. Prior to reaction, the catalysts were again reduced in flowing H_2 at 673 $^\circ\text{K}$ for 3 hours.

Apparatus and Procedures

The gases used for these reaction studies were obtained from Air Products and included H_2 (UHP, 99.995%), He (UPC, 99.998%) and CO (UHP, 99.8%), 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 the interface between the computer and 3 mass flow control meters (Brooks 5850) for controlling H₂, 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 using an poropak Q column in series with a 80/100 carbopack c/0.2% carbowax 1500 using a He carrier flow of 20 cc/min. The GC columns were initially held at 40°C for 2 minutes and then temperature programmed at 15°C/min to 160°C, permitting a good on-line separation of all C₁-C₆ paraffins and olefins, C₁-C₄ alcohols, C₁-C₄ aldehydes, acetone, ethyl acetate, acetic acid, CO, CO₂, and H₂O in a 60 minute analysis.

The reaction study was carried out in a differential reactor at 523-573°K and 0.1 - 1 MPa with H₂/CO = 1. High space velocities of 7000 to 11,000 hr⁻¹ were used to keep CO conversion below 5% in order to minimize heat and mass transfer effects and secondary reactions. A small amount of ethylene (2.6 mole % of reactant mixture) was added to the CO/H₂ reactant mixture in the last three hours of each experiment run. The relative hydrogenation, chain incorporation, carbonylation, and hydrogenolysis activities were estimated by determination of the product distribution before, during, and after the addition of ethylene.

RESULTS AND DISCUSSION

Effect of Reaction Conditions on Product Distribution

The effect of pressure on the product selectivity over Rh/La₂O₃ is presented in Table I. Although the residence time for the study under different pressure was different, it was found that this parameter had little effect on the selectivity of primary products over supported Rh catalysts (8). At 0.1 MPa and 573°K, a significant amount of oxygenated compounds including ethanol and acetaldehyde were produced. An increase in the reaction pressure from 0.1 MPa to 1 MPa resulted in an enhancement of oxygenate selectivity at the expense of C₂⁺ hydrocarbons. The increase in the selectivity of oxygenated compounds was mainly due to an increase in the formation rate of methanol at the higher pressure. The rates of formation for CH₄ and C₂ oxygenated compounds showed only a slight increase and the formation rate of C₂⁺ hydrocarbons was decreased (Table II). The low rate of formation of methanol at 0.1 MPa and 573°K is apparently due to thermodynamic limitations (14). The conditions which favor methanol formation at the expense of hydrocarbons are low temperatures and high pressures (15).

Although there still exists controversy (13,15,16,17,18,19) about the precursors and active sites for formation of oxygenated compounds, it is generally accepted that formation of methanol occurs by a nondissociative CO mechanism (18) and formation of C₂⁺ oxygenated compounds requires insertion of undissociatively adsorbed CO into a C_yH_x surface species which is generated by CO dissociation (17,19). A reaction scheme based on this argument is shown in Figure 1.

An increase in total pressure of CO/H₂ could increase the coverage of nondissociatively adsorbed CO since CO is always more competitive for surface adsorption sites than H₂. Ramamoorthy and Gonzales (21) have demonstrated

that high coverages of CO can block CO dissociation. Somorjai (22) 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 by nondissociatively adsorbing CO could enhance those reactions which require nondissociatively adsorbed CO, such as formation of methanol and the CO insertion reaction. As shown in Table II, an increase in total pressure of CO/H₂ resulted in a significant increase in the formation rate of methanol but very little increase in that of C₂ oxygenated compounds. Thus, the significant difference in variation of formation rate as a function of total pressure for methanol and C₂ oxygenated compounds indicates that the precursors for formation of methanol are probably different from those for C₂ oxygenated compounds.

The effect of temperature on the product distribution is shown in Table III. Methanol was a dominant product at temperatures below 543°K. The selectivity for C₂ oxygenated compounds increased with increasing temperature to a maximum at around 559°K. Watson and Somorjai (19) divided CO hydrogenation over LaRhO₃ into three temperature regions where different reactions, i.e., formation of methanol, of C₂ oxygenates and of hydrocarbons, were predominant. It appears that such significant predominance of these reactions at different temperatures on Rh/La₂O₃ was not the case.

Effect of Alkali Promotion on Rh/La₂O₃

The effects of alkali promoters on Rh/La₂O₃ may be classified into (1) the chemical effect of the promoters on the Rh metal and La₂O₃ and (b) physical blockage of the surface by these promoters. Alkali promoters

themselves are known to be inactive for CO hydrogenation. Thus, physical blockage of the surface active sites by alkali promoters would greatly affect the dissociation of CO which requires large ensembles of surface atoms (23). On the other hand, a reaction which does not need such large ensembles of surface atoms, such as hydrogenation (23) and CO insertion (9) would be only slightly affected by the physical blockage of the surface by alkali promoters. Thus, the physical blockage of surface atoms could lead to an enhancement in the selectivities for those products which form on small ensembles of surface atoms. However, it is generally recognized that the chemical effect of alkali promoters on CO hydrogenation is more significant than that due to physical blockage. A number of studies (24,25) have shown that the addition of alkali promoters on supported group VIII transition metal catalysts results in a higher CO dissociation probability, a suppression of hydrogenation, an increase in selectivity to long chain hydrocarbons, a decrease in CO conversion for Ru (25) and Ni (26), and an increase in yields of oxygenated compounds (27). It would be expected that some of these effects would be exhibited by alkali-promoted Rh/La₂O₃.

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 C_4^-/C_4 (Tables IV, VI). The use of C_4^-/C_4 as an index for hydrogenation ability is due to the lower incorporation ability of C_4^- . As shown in Table IV, Li-promoted catalyst showed a significant increase in rate of formation of C₂ oxygenated compounds whereas the rate of formation of methane was decreased. Li⁺ appeared to promote the rate of formation of C₂ oxygenated compounds and C₂⁺ hydrocarbons at the expense of CH₄. The rate of CO conversion and the rate for all the products formed decreased for K-promoted catalysts while the product selectivities were only slightly

affected, as shown in Table V. Cs-promoted catalyst exhibited decreases not only in formation rate for all the products but also in selectivity for the oxygenated compounds.

It has been suggested that the rate determining step for the formation of C_2 oxygenated compounds is the formation of CH_x on the surface (19). However, the variation in product distribution among alkali-promoted and unpromoted Rh/La₂O₃ can not be simply explained by this argument. It appears that the adsorbed CO, H, and CH_x compete for the available surface CH_x species resulting in the variation in selectivity among these catalysts (6). It was found that the selectivity in CO hydrogenation over supported Rh catalysts varies with the basicity of the support (28). Rh on MgO, a very basic support, exhibits 90% selectivity to methanol. Acidic supports, such as Al₂O₃, result in mainly CH₄, while slightly acidic or basic supports (e.g., SiO₂, TiO₂, CeO₂) produce both alcohols and hydrocarbons. It has been suggested (29) that surface hydroxyl groups are effective in converting Rh⁰ to Rh⁺, which has been proposed to be involved in the formation of C_2 oxygenated compounds (19). Rh⁺ was found to be stable on MgO (30), which is a strongly basic support. MgO-supported Rh (13,31) and MgO promoted Rh (31) was observed to be more active for the formation of methanol than C_2 oxygenated compounds. Katzer et al. (28) reported from an XPS study that there was no evidence for the existence of Rh⁺ on Rh/TiO₂, which is known to be active for the formation of C_2 oxygenated compounds.

Alkali promoters have been used to poison support acidity (32). Ichikawa (33) reported that the rate of formation of and selectivity for C_2 oxygenated compounds can be enhanced by modification of the acidity-basicity of the support through addition of Zr- and Ti-oxide to the support. It is speculated that there may exist an optimum basicity-acidity of the support which best

promotes the formation of C₂ oxygenated compounds over La₂O₃. The basicity of alkali promoters increases in the order: Li < Na < K < Cs. The Li promoter is known to be more basic than La₂O₃. The enhancement of the basicity of the support may be related not only to the quantity and basicity of the alkali promoter but also its distribution on the support and the metal surface. It appears that the acidity-basicity of the support has a significant effect on the oxygenate selectivity of supported Rh catalysts. However, an XPS study of supported Rh catalysts (28) did not show any pronounced effect of the support on the oxidation state of Rh. Recently, Kagami et al. (10) have suggested that the active sites for the formation of C₂ oxygenated compounds are located at the interface of the metal and the support, and it is this interface which is modified by the alkali promoter. A further study on the effect of Rh particle size on the formation of C₂ oxygenated compounds would be helpful to elucidate the possibility of this argument. Vis (34), based on a study of CO hydrogenation over Rh/La₂O₃ at 4 MPa and 550°, has suggested that CO may be hydrogenated to oxygenated compounds on adsorption sites on a support such as La₂O₃. However, a TPR study (35) of co-adsorption of CO, H₂, and C₂H₄ demonstrated that these species could not interact with one another to form C₃ oxygenated compounds on La₂O₃ at 10 torr and 293°K.

Ethylene Addition to the CO/H₂ Reaction Mixture

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 VII. 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 H_2 were virtually unaffected. It appears that hydrogenolysis of ethylene did not occur significantly as indicated by the constant rate of formation of CH_4 both before and during ethylene addition. The formation of C_3 oxygenated compounds could occur by insertion of CO into the adsorbed ethylene. The constant rates of formation for acetone, ethyl acetate, and C_1 and C_2 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 VII, relative to the unpromoted catalyst, hydrogenation of ethylene was unaffected for Li-Rh/ La_2O_3 , slightly decreased for K-Rh/ La_2O_3 and severely suppressed for Cs-Rh/ La_2O_3 . It is possible that the hydrogenation of added ethylene could occur partially on active sites of the La_2O_3 , since the added ethylene would have a higher probability for adsorption on the support compared to the ethylene formed in F-T. It has been reported that La_2O_3 is active for hydrogenation of ethylene after a high temperature ($>773^\circ K$) pretreatment (35). The catalysts for this study have been reduced at $673^\circ K$ for 16 hr. A long period of reduction at $673^\circ K$ for La_2O_3 might result in the same state as a $773^\circ K$ treatment in a short period. It is speculated that the alkali promoters might also have effects on the hydrogenation ability of La_2O_3 . The observed decrease in the rate of hydrogenation of ethylene for K- and Cs-Rh/ La_2O_3 may be due to a strong suppression of hydrogenation for these catalysts.

Li^+ appeared to promote the rate of formation of C_3 oxygenated compounds while a marked decrease was observed for the Cs promoted catalyst. K-Rh/ La_2O_3 also showed a decrease in rate of formation of C_3 oxygenated compounds. These results appear to be consistent with those reported in the previous section. The incorporation of ethylene into C_3^+ hydrocarbons appeared to be enhanced

for the K- and Cs-promoted catalysts. This is in general agreement with the belief that alkali promotion effect leads to higher yields of long chain hydrocarbons (26).

CONCLUSIONS

1. The effect of alkali promotion on the activity and selectivity for CO hydrogenation over Rh/La₂O₃ is dependent upon the type of alkali promoter.
2. The effect of alkali promotion on La₂O₃ can be summarized as follows:
 - a. Li-promotion enhances the rate of formation and selectivity of C₂ oxygenated compounds while Cs-promotion decreases both.
 - b. The suppression of hydrogenation increases in the order: unpromoted < Li < K < Cs.
 - c. The rate of CH₄ formation decreases in the order: unpromoted > Li > K > Cs.
 - d. The rate of CO conversion to hydrocarbons and oxygenates decreases in the order: Li > unpromoted > K > Cs.

4. FORECAST OF WORK

During the eighth quarter, alkali promoted Rh/ZnO and Rh/Al₂O₃ will be studied. Small quantities of ethylene, ethanol and acetaldehyde will be added to the reaction mixture to help clarify the promotion effects on specific reaction in the synthesis.

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Table I: Effect of Pressure on the Product Selectivity

Reaction Pressure	0.1 MPa	1 MPa
Selectivity Wt %		
CH ₄	20.6	22.8
C ₂ ⁺	43.5	18.9
Total OX*	35.9	58.3
MeOH	1.7	21.6
C ₂ OX	29.5	30.9

Space Velocity: 1,100-11,000 hr⁻¹

Reaction Temperature: 573°K, CO/H₂ = 1

*Acetone, EtAc, C₃-C₄ OX are included in Total OX.

Table II: Effect of Pressure on the Product Formation Rate
Over Rh/La₂O₃

Reaction Pressure	0.1 MPa	1 MPa
Rate of CO Conversion mole/kg hr	0.364	0.502
Product Formate Rate mole/kg hr		
CH ₄	0.150	0.213
C ₂ ⁺	0.119	0.071
MeOH	0.006	0.101
MeCHO	0.021	0.016
EtOH	0.054	0.085
Acetone	0.008	0.009

Reaction Temperature : 573°K, CO/H₂ = 1
Space Velocity: 1,100-11,000 hr⁻¹

Table III: The Effect of Temperature on the Product Distribution over Rh/La₂O₃

Reaction Temperature °K	528	543	559	573
Selectivity Wt %				
C ₁	6.9	14.2	16.2	22.8
C ₂ ⁺	10.7	11.4	15.5	18.9
MeOH	56.7	43.2	28.7	21.6
EtOH	17.0	22.5	28.7	26.7
MeCHO	5.4	5.2	4.8	4.8
Total OX	82.4	74.5	68.3	58.3

1 MPa, CO/H₂ = 1

* Acetone, EtAc, and C₃-C₄ OX are included in Total OX

Table IV: Effect of Alkali Promoters on the Product Formation Rate

	CO Conversion to OX and HC	C ₁	C ₂ ⁺	MeOH	MeCHO	EtOH	EtCHO	1-Propanol
Rh/La ₂ O ₃	0.772	0.213	0.071	0.102	0.016	0.085	0.001	0.003
Li-Rh/La ₂ O ₃	1.020	0.126	0.111	0.101	0.025	0.165	0.002	0.016
K-Rh/La ₂ O ₃	0.348	0.060	0.043	0.048	0.009	0.038	0.002	0.003
Cs-Rh/La ₂ O ₃	0.213	0.058	0.030	0.016	0.011	0.003	0.002	0.003

Rate in mole/kg hr.

Rate for EtAC < 0.001

Reaction Conditions: 573°K, 1 MPa, and CO/H₂ = 1

Table V: 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
<u>Selectivity wt%</u>				
CH ₄	22.8	10.0	14.1	22.5
C ₂ ⁺	18.9	22.1	21.3	32.7
Total OX*	58.3	67.9	64.6	44.8
MeOH	21.6	16.0	22.5	13.8
C ₂ OX	30.9	43.1	31.4	15.8

Reaction Conditions: 573°K, 1 MPa, and CO/H₂ = 1

*Acetone, EtAc, C₃ - C₄ OX are included in Total OX.

Table VI: Effect of Alkali Promoters on the Mole Ratio of Specific Products

	$C_2^= / C_2$	$C_3^= / C_3$	$C_4^= / C_4$	MeCHO/EtOH	C_2OX / CH_4
Rh/La ₂ O ₃	1.69	3.95	5.76	0.19	0.47
Li-Rh/La ₂ O ₃	2.68	6.06	7.67	0.15	1.50
K-Rh/La ₂ O ₃	1.74	2.35	8.40	0.24	0.78
Cs-Rh/La ₂ O ₃	1.78	2.40	8.32	4.30	0.23

573°K, 1 MPa and CO/H₂ = 1

Table VII: Effect of Alkali Promoters on the Product Formation Rate from 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 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 573°K and 1 MPa

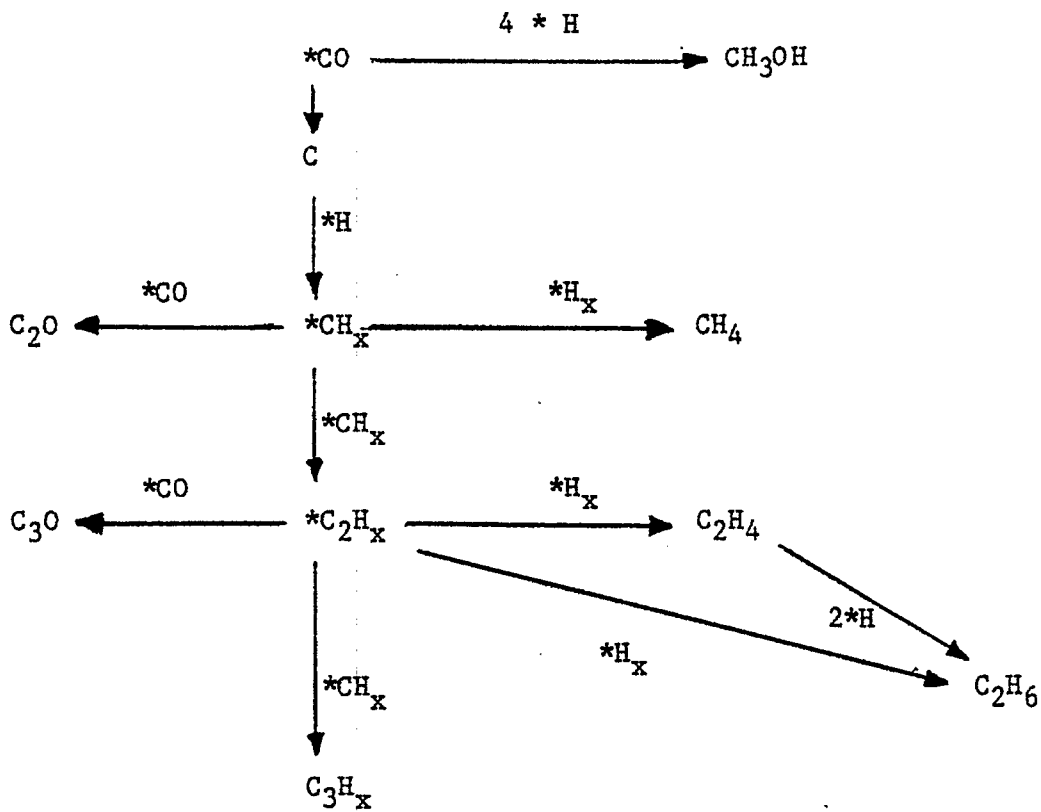


Figure 1: Reaction Scheme for Formation of Oxygenated Compounds and Hydrocarbons

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