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EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL: TECHNICAL PROGRESS REPORT 3, MARCH 16, 1987-JUNE 15, 1988

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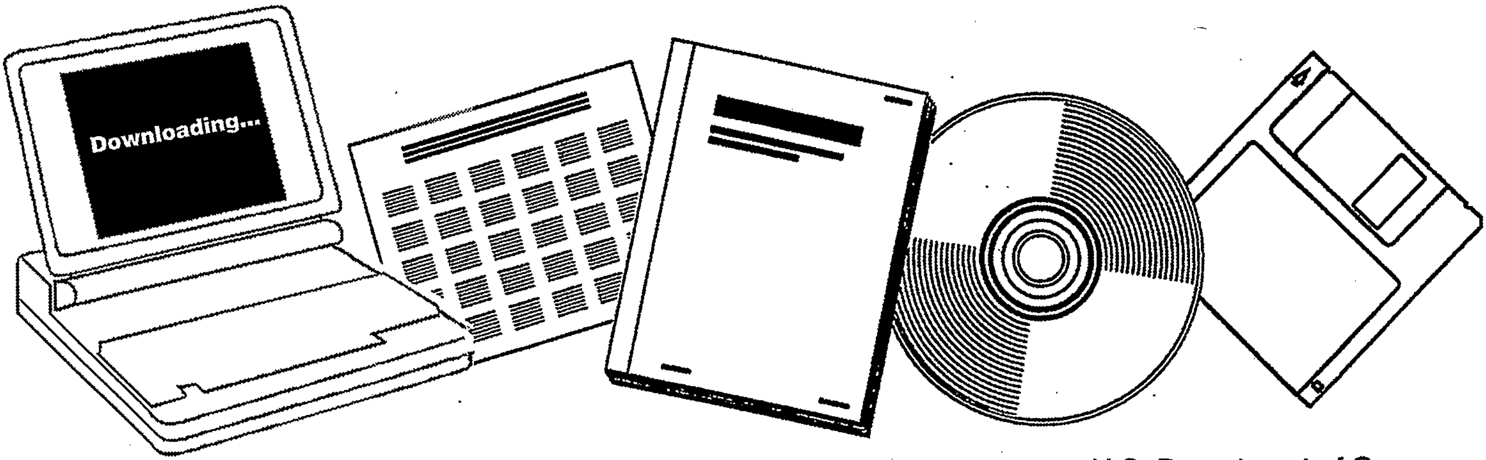

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

Technical Progress Report 3
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by

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SUMMARY

The objective of this research is to elucidate the role of various chemical additives on ethanol synthesis over Rh- and Ni-based catalysts. Chemical additives used for this study will include S, P, Ag, Cu, Mn, and Na which have different electronegativities. The effect of additives on the surface state of the catalysts, heat of adsorption of reactant molecules, reaction intermediates, reaction pathways, reaction kinetics, and product distributions is/will be investigated by a series of experimental studies including temperature programmed desorption, infrared study of NO adsorption, reactive probing, steady state rate measurement, and transient kinetic study.

A better understanding of the role of additive on the synthesis reaction may allow us to use chemical additives to manipulate the catalytic properties of Rh- and Ni-based catalysts for producing high yields of ethanol from syngas.

RESULTS TO DATE

During the third quarter of the project, the effect of sulfur on CO insertion over Rh/SiO_2 was studied in a wide range of reaction conditions to develop a better understanding of the role of sulfur in the oxygenate synthesis.

Sulfur is a notorious poison to various reactions catalyzed by Group VIII metals, especially hydrocarbon synthesis from syngas (1). Several previous studies (2-5) have shown that the sulfur species inhibit chemisorption of hydrogen and dissociative adsorption of carbon monoxide on metal surface leading to suppression of hydrocarbon formation from syngas. Although the effect of sulfur on hydrocarbon synthesis has been well studied, little is known about the influence of sulfur on the oxygenate synthesis from syngas. C_{2+} oxygenated hydrocarbons such as ethanol, ethanal, propanol, etc. can be produced from syngas through carbon monoxide hydrogenation (6-7) and olefin hydroformylation (8,9). Among transition metal, Rh is known to be one of the most active catalysts for the C_{2+} oxygenate synthesis. In a previous paper (10), we reported that sulfur species shows a slight inhibition effect on CO insertion step, the key step to C_{2+} oxygenates, in $CO/H_2/C_2H_4$ over Rh/SiO_2 at 300 °C and 10 atm. In an effort to gain a better understanding of the role of sulfur in oxygenate synthesis, we have investigated the effect of sulfur on Rh/SiO_2 for the C_{2+} oxygenate synthesis in 120-300 °C and 10 atm. Ethylene was used as a probe molecule to study the effect of sulfur on the CO insertion step in the synthesis.

EXPERIMENTAL

Catalyst Preparation

Three wt. % Rh/SiO_2 was prepared by impregnation of SiO_2 (Strem) using Rh chloride (Alfa). Hydrogen flow chemisorption and hydrogen temperature programmed desorption technique were used to determine metal surface area of the catalyst and sulfur coverage on the sulfided Rh/SiO_2. The crystalline size of the catalyst was determined by X-ray line broadening technique.

Reaction Studies

CO hydrogenation was carried out in a differential reactor system under 180 - 300 °C and 10 atm. The product distribution was determined by an HP-5890A gas chromatograph. Ethylene was added to CO/H_2 reactant mixture after steady state CO hydrogenation. The amount of ethylene added ranged from 2-10 %. Added ethylene serves as a probe molecule to determine the effect of sulfur on hydrogenation and CO insertion capabilities of the catalysts. The relative hydrogenation, CO insertion, chain incorporation, and hydrogenolysis activities were estimated by careful determination of the product distribution before, during, and after the addition of ethylene.

Sulfidation

H_2S (1000 ppm of H_2S in H_2) was passed at 15 cc/min. through the catalyst at either 300 or 400 °C for about 30 minutes in order to saturate the catalyst surface with sulfur. Hydrogen was then passed through the catalyst bed for about 1 hour to remove any weakly adsorbed sulfur and also to achieve a uniform distribution of sulfur on the catalyst surface.

RESULTS AND DISCUSSIONS

Table I shows results of hydrogen chemisorption and CO hydrogenation over fresh and sulfided Rh/SiO_2. Sulfidation of Rh/SiO_2 with 1000 ppm or pure H_2S at 300 or 400 °C resulted in a complete loss of hydrogen chemisorption at 25° C. Several previous studies (1,2,11) have suggested that the fraction of metal surface which adsorbs hydrogen is inversely proportional to fractional coverage of sulfur. The complete loss of hydrogen chemisorption capability of S-Rh/SiO_2 indicates that the rhodium surface may be saturated with sulfur. Results of carbon monoxide hydrogenation as presented in Table I show sulfidation by H_2S leads to a significant decrease in CO hydrogenation activity and a dramatic modification of selectivity. Rh/SiO_2 produces mainly methane and acetaldehyde as major products and C_{2+} hydrocarbons and ethanol as minor products over the temperature range of 250 to 300 °C and 10 atm. In contrast, S-Rh/SiO_2 produces only methane at a very low formation rate. The low formation rate of methane on S-Rh/SiO_2 appears to result from the suppression of hydrogen chemisorption as well as dissociative chemisorption of CO brought about by sulfur. The activation energy determined from Arrhenius plot for the unpoisoned reaction is 28.5 kcal/gmol while that for the H_2S poisoned catalyst is only 2.4 kcal/gmol. Sulfidation not only decreases the activation energy of reaction but also reduces the overall reaction rate. The similar behavior for CO hydrogenation has been observed on sulfided Co catalyst (2).

To develop a better understanding of the sulfur effect on CO insertion, the addition of ethylene in CO/H_2 reactant stream was conducted. The addition of ethylene in reactant stream over Rh/SiO_2 leads to an increase in the formation rate of ethane, propionaldehyde, propanol, and methane. This addition, however, did not result in any significant modification of the formation rate of other CO hydrogenation products such as acetaldehyde and higher hydrocarbons. Added ethylene appears to undergo primarily CO insertion to form propionaldehyde and hydrogenation to form ethane. The product selectivity from reaction of added ethylene over Rh/SiO_2 and sulfided Rh/SiO_2 is shown in Table II. Sulfidation of Rh catalyst leads to a decrease in ethane selectivity and an increase in selectivity toward propionaldehyde. The effect of concentration of added ethylene is the same for both catalysts. An increase in the amount of added ethylene increases the rate of ethylene conversion while the product selectivity does not change. Figure 1 and 2 show the Arrhenius plots of propionaldehyde, propanol, and ethane for Rh/SiO_2 and S-Rh/SiO_2 and apparent activation energies determined from these plots are listed in Table III. The apparent activation energies for the formation of propionaldehyde, propanol, and ethane are slightly influenced by sulfidation. Figure 1 and 2 show that the rate of ethane formation and propanol formation decreases by sulfur while the rate of formation of propionaldehyde was essentially unchanged by sulfur over the temperature range of 150 to 300 °C.

Comparison of rates for methanation, ethylene hydrogenation, hydroformylation at 300 °C in Table I and II reveals that sensitivity of these reactions to sulfur poisoning decreases in the order: methanation > ethylene hydrogenation > hydroformylation. The difference in the extent of the sulfur effect on the above reactions indicates the resistance of the various active sites toward sulfur is different. Active sites for methanation have been shown to be ensembles of surface metal atom which could be greatly affected by sulfur species via either transformation to sulfide or blockage of surface atoms. The observation (as shown in Table I) that sulfur causes a significant decrease in rate and activation energy for methanation suggests that sulfur effect on methanation over Rh/SiO_2 may involve both electronic modification and geometric blockage. The less suppression of ethylene hydrogenation than that of methanation by sulfur is not surprising since (i) transition metal sulfide is known to catalyze olefin hydrogenation in the temperature range 120 -400 °C (12) and (ii) olefin hydrogenation is a less demanding reaction than methanation (13). Somorjai (14) has proposed that facile reactions should be less affected by sulfur than demanding reactions.

The incapability of sulfur to affect CO insertion (hydroformylation) suggests that the CO insertion is a facile reaction. The proposition is consistent with a recent study (15) suggesting that CO insertion may be structure insensitive.

The oxidation state of active site for CO insertion over supported Rh catalyst remains a controversial subject (16-18). Both Rh in metallic state (Rh^{o}) and in oxide state (Rh^{+n}) have been suggested as CO insertion site. Although the actual surface state of S-Rh/SiO_2 during reaction in this study is still not clear, examination of results of reaction studies and recent literature concerning sulfided Rh/SiO_2 may shed light on the active site for CO insertion. Konishi et al. (19) have suggested that adsorbed sulfur may result in Rh cation which may have a higher intrinsic activity for hydroformylation than zerovalent Rh atoms. An XPS study of sulfided Rh/SiO_2 (20) has shown that surface sulfidation can be achieved under H_2S/H_2 atmosphere at 300 °C and Rh metal particle at the size of 100 °A can be completely sulfided (RH2S32) at 500 °C. Sulfidation of the Rh under 400 °C in this study may result in surface sulfide. It is also important to note that a consistent low activity for methanation on S-Rh/SiO_2 was observed during the entire course of ethylene addition studies in which the catalyst showed high activity for the formation of propionaldehyde. The above observations and discussions suggest that sulfidation of Rh/SiO_2 may convert Rh metal surface to Rh sulfide which remains active for

CO insertion but inactive for methanation and hydrogen chemisorption.

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Table I
CO Hydrogenation Reaction

	Rh/SiO_2	S-Rh/SiO_2
	300°C	300°C
Selectivity (mol %)		
CH_4	61.26	100
C_2H_4	2.52	
C_2H_6	2.62	
C_3+	2.46	
MeCHO	25.55	
EtOH	5.59	
Overall Rate (gmol/kg-hr)	1.58	0.02
E_A (kcal/gmol)	28.50	2.40

Reaction operated at 10 atm
$CO/H_2 = 1$

S-Rh/SiO_2 denotes presulfided Rh/SiO_2, with 1000 ppm H_2S in H_2 at 400°C.

Table II
$CO/H_2/C_2H_4$ Reaction

	Rh/SiO_2			S-Rh/SiO_2		
		300°C			300°C	
Overall Rate (gmol/kg-hr)	69.17	115.50	187.18	17.67	30.64	62.38
C_2H_4 Added (mol %)	2.8	4.7	7.3	2.3	3.9	5.9
Selectivity (mol %)						
CH_4	5.60	4.08	4.43	0.93	0.54	0.29
C_2H_6	78.97	81.34	80.87	62.42	64.72	68.09
EtCHO	8.30	8.92	9.62	33.29	32.30	29.82
1-Propanol	5.12	4.15	3.60	3.19	2.34	1.72
E_A (kcal/gmol)		17.05				

Reaction operated at 10 atm
$CO/H_2 = 1$ and various amount of C_2H_4 in the reactant stream.

TABLE III
Activation Energies for the $CO/H_2/C_2H_4$ Reaction

	Rh/SiO_2	$S\text{-}Rh/SiO_2$
E_A (kcal/gmol)		
C_2H_6	17.8	14.9
CH_3CH_2CHO	11.0	9.5
$CH_3CH_2CH_2OH$	27.0	27.3

FIGURE 1

CO/H2/C2H4 BEFORE H2S ADDITION

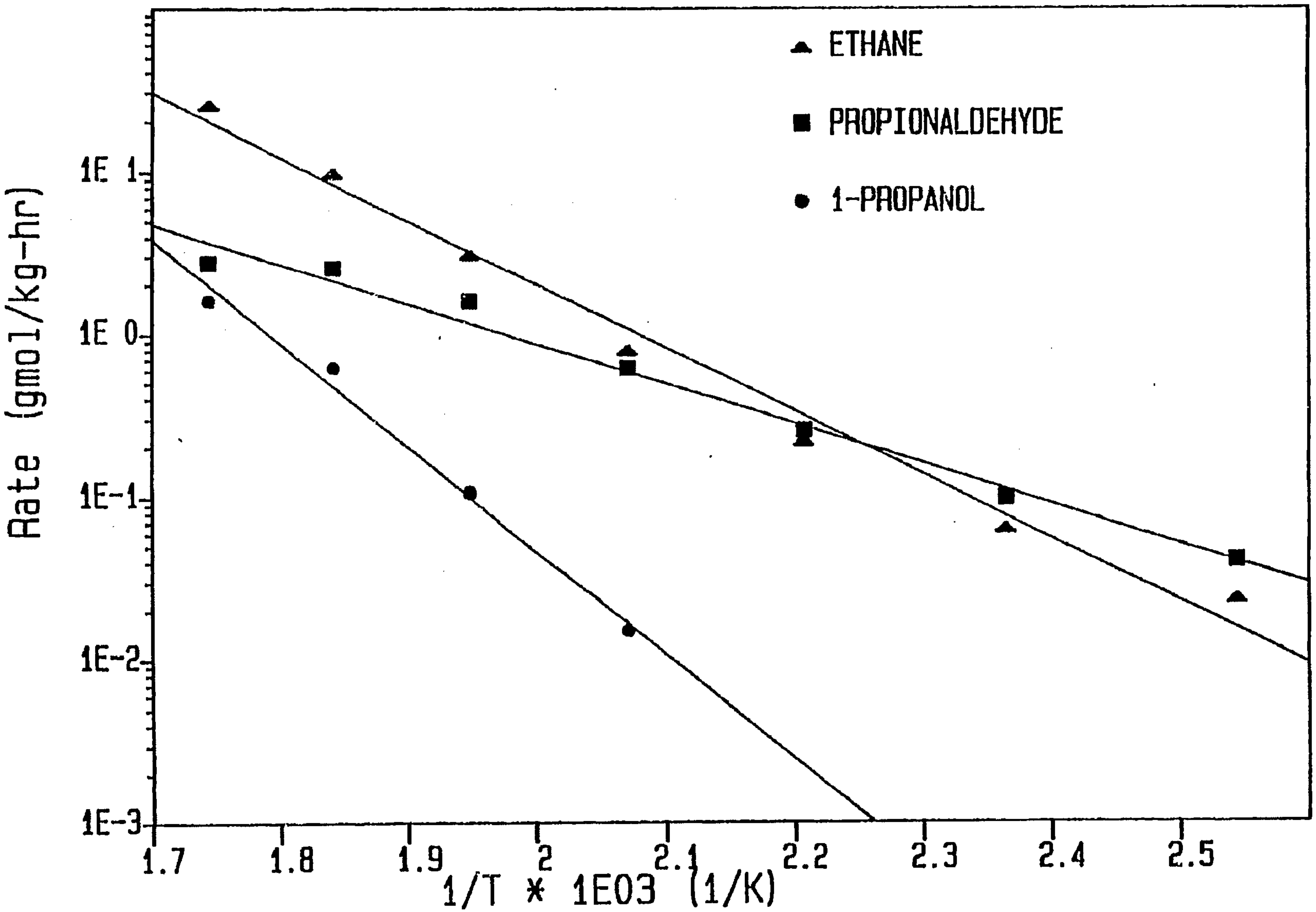
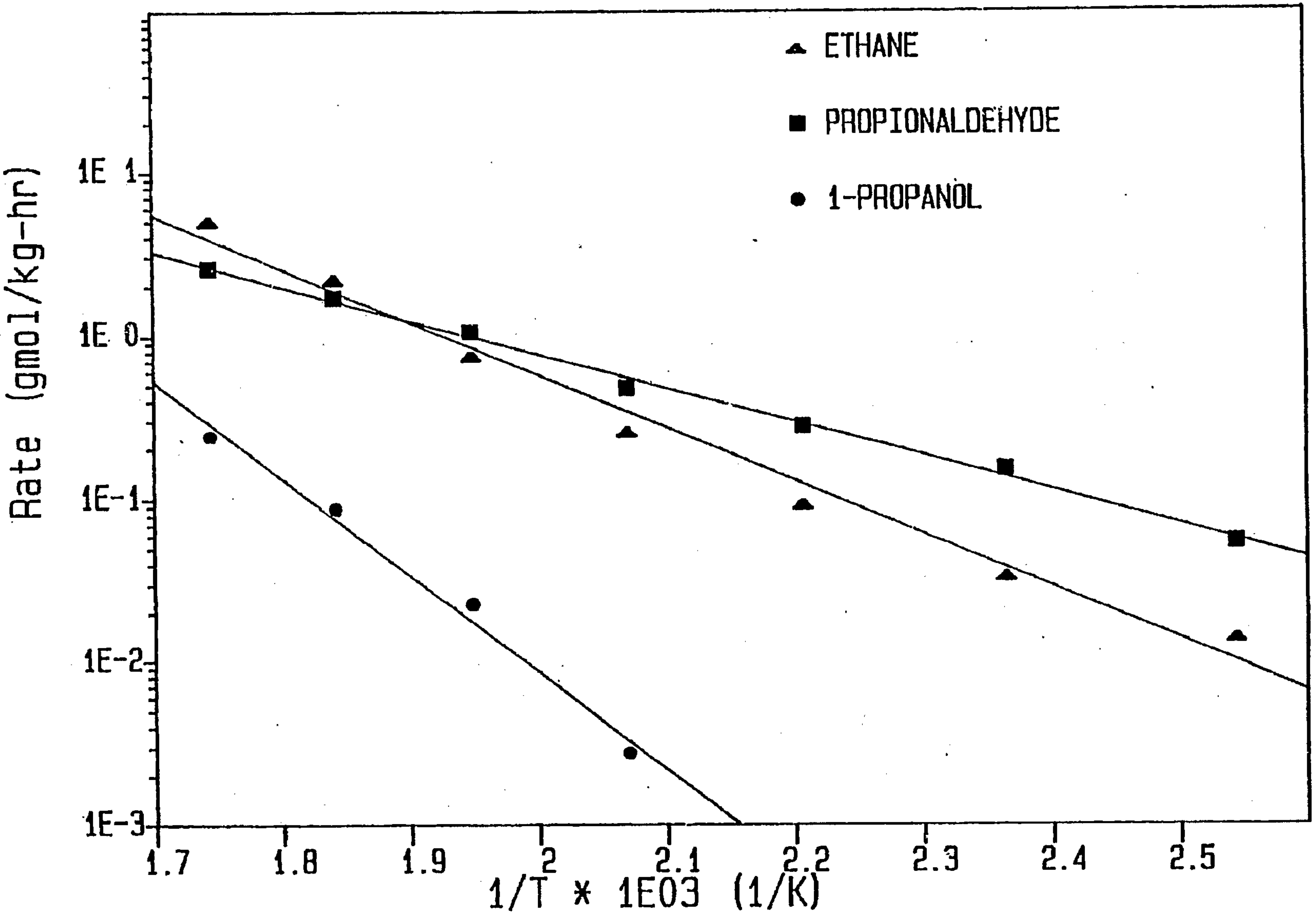


FIGURE 2


CO/H2/C2H4 AFTER H2S ADDITION

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