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EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL: TECHNICAL PROGRESS REPORT 2, DECEMBER 16, 1987--MARCH 15, 1988

AKRON UNIV., OH. DEPT. OF CHEMICAL
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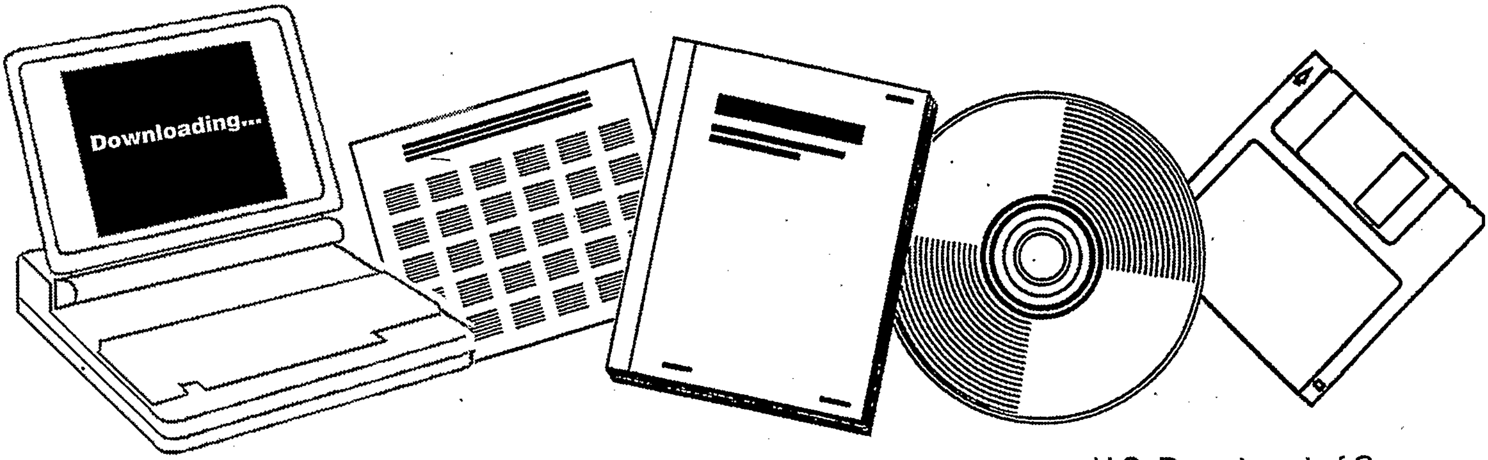

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

DOE/PC/79923--T2

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Technical Progress Report 2
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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 second quarter of the project, the following tasks and research have been completed.

1. A temperature programmed desorption system has been built and the system will be tested in the third quarter.
2. Effect of sulfur on CO insertion over Rh/SiO_2 was studied.
3. A series of $Ag-Rh/SiO_2$ catalysts was prepared for studying the structure sensitivity of CO insertion.

EXPERIMENTAL

Catalyst Preparation

3 wt % Rh/SiO_2 was prepared by impregnation of SiO_2 (Strem) using Rh chloride (Alfa). The $Ag-Rh/SiO_2$ was prepared by using co-impregnation of Ag nitrates and Rh chloride (Alfa). The ratio of Ag to Rh additive is 0.3 - 1.5. Hydrogen temperature programmed desorption technique was used to determine the dispersion of the catalyst and sulfur coverage on the sulfur-poisoned Rh/SiO_2.

Reaction Studies

Ethanol synthesis was carried out in a differential reactor system under 250 - 300 °C and 10 atm. The product distribution was determined by an HP-5890A gas chromatograph.

A small amount of ethylene (3-4 mole %) was added to CO/H_2 reactant mixture after steady state kinetic study. The addition of probe molecules such as ethylene during CO hydrogenation could produce ethyl species which may undergo (a) hydrogenation to form ethane, (b) CO insertion to form propionaldehyde, (c) chain incorporation to form higher hydrocarbons, and (d) hydrogenolysis to form methane. 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 the probe molecule.

Catalyst Poisoning Study

Diluted H_2S (1000 ppm of H_2S in H_2) was passed at 30 cc/min. along with 90 cc/min. of H_2 through the catalyst bed at 300 °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. Hydrogen temperature programmed desorption (TPD) was performed to estimate the coverage of sulfur on the catalyst surface. Followed by TPD study, CO hydrogenation and C_2H_4 addition experiments were carried out at 10 atm and in the temperature range of 250 to 300 °C.

RESULTS AND DISCUSSIONS

Hydrogen temperature programmed desorption profiles for unpoisoned and sulfur-poisoned Rh/SiO_2 are shown in Figure 1. An appreciable H_2 desorption peak was observed for the fresh catalyst. In contrast, no desorption peak was observed for sulfur-poisoned catalyst indicating that hydrogen chemisorption is poisoned by the presence of sulfur on the catalyst surface. The inability of the poisoned catalyst to chemisorb any hydrogen suggests that the catalyst surface is saturated with sulfur.

The rates of product formation from CO hydrogenation over unpoisoned and sulfur-poisoned Rh/SiO_2 are shown in Tables I and II. For unpoisoned catalyst, reaction products include mostly hydrocarbons and a small amount of acetaldehyde in the temperature range of 250 - 300 °C. The catalyst is not active for the synthesis of acetaldehyde and ethanol compared to our previous Rh/SiO_2. The difference in catalyst selectivity between two Rh/SiO_2 could be due to the difference in the property of SiO_2. The property of SiO_2 will be carefully investigated. After sulfur poisoning only a small amount of methane was produced. The significant decrease in rate of product formation indicates that sulfur strongly inhibits an otherwise relatively active reaction.

Figure 2 shows the Arrhenius plot of the CO hydrogenation reactions before and after sulfur addition. Activation energies for the CO hydrogenation reactions are derived from the slopes. The steep slope for the reaction before H_2S addition suggests that the CO hydrogenation reaction is highly temperature sensitive whereas the corresponding reaction after H_2S addition becomes relatively temperature insensitive. The activation energy of the unpoisoned reaction is 28.5 kcal/gmol while that for the H_2S poisoned catalyst is only 2.4 kcal/gmol. However, H_2S not only decreases the activation energy of reaction but also reduces the overall reaction rate. A similar trend was also observed for the activation energy for the rate of formation of methane.

The decrease in activation energy and overall rate of CO hydrogenation brought about by sulfur poisoning has been observed on Ni catalysts. Goodman and Kiskinova (1) have reported that the Arrhenius plot for the reaction on cleaned Ni surface catalyst is usually linear over a wide range of temperature but it flattens out in the high temperature region (> 600°K) resulting in a low value of reaction rate and activation energy when the catalyst is poisoned by H_2S. The divergence of rate from linearity at high temperatures may be due to low concentration of adsorbed hydrogen as a result of sulfur poisoning. Apesteguia et al. (2) observed that most of the H_2S added is adsorbed strongly on the catalyst metal surface resulting in the suppression of H_2 chemisorption. H_2 chemisorption suppression causes a considerable loss of activity and decreases selectivity towards hydrogenation products.

Tables III and IV show the rate of product formation from ethylene in C_2H_4 addition study. Figure 3 shows the Arrhenius plot for the overall conversion of ethylene in $CO/H_2/C_2H_4$ reaction. The activation energies for the overall conversion of ethylene are 20.8 kcal/gmol and 7.2 kcal/gmol, respectively, before and after H_2S poison. Figure 4 shows the Arrhenius plot for the rate of production of hydroformylation products (propionaldehyde). The almost horizontal plot for propionaldehyde formation over sulfur-poisoned catalyst indicates that hydroformylation over sulfur-poisoned catalyst is relatively temperature insensitive. As a result, the rate of propionaldehyde formation on the sulfur-poisoned Rh catalyst is higher than that on the unpoisoned catalyst at low temperature. This observation agrees with the study by Konishi et al. (3). Their study showed that hydroformylation over Rh catalyst is not subject to sulfur poisoning. It is speculated that the active center for CO insertion might be Rh^{n+} (4) which may not be poisoned by sulfur. Sulfur might even enhance the CO insertion.

FUTURE PLAN FOR THE NEXT QUARTER

A temperature programmed desorption system will be completed and tested. Ethanol synthesis over $Ag\text{-}Rh/SiO_2$ catalyst will be performed to determine the structure sensitivity of the synthesis reaction.

REFERENCES

1. Goodman, D.W., and Kiskinova, M., Surf. Sci. 105 (1981), L265-L270.
2. Apesteguia, C.R., Garetto, T.F., and Borgna, A., J. Cat. 106, 73 (1987).
3. Konishi, Y., Ichikawa, M, and Sachtler, W.M.H., J. Phys. Chem. 91, 6286 (1987).
4. van der Lee, G., and Ponec, V., J. Cat. 99, 511 (1986).

TABLE I
CO Hydrogenation Before H_2S Addition

Compound Rate (gmol/kg-hr)	CH_4	C_2+HC	CH_3CHO	C_3OX
300° C	1.964	0.692	0.014	0.0126
275° C	0.672	0.227	*	*
250° C	0.248	0.044	*	*

* A very small quantity is observed
Only a small amount of EtOH is observed

TABLE II
CO Hydrogenation After H_2S Addition

Compound Rate (gmol/kg-hr)	CH_4	C_2+HC	CH_3CHO	C_3OX
300° C	0.036	-	-	-
275° C	0.030	-	-	-
250° C	0.029	-	-	-

\- No product is observed

TABLE III
CO/H_2/C_2H_4 Reaction Before H_2S Addition

Compound Rate (gmol/kg-hr)	OVERALL	C_2+HC	CH_3CHO	C_3OX
300° C	16.75	6.151	0.002	0.666
275° C	7.86	2.754	*	0.478
250° C	2.92	0.936	*	0.248

* A very small quantity is observed
Only a small amount of EtOH is observed

TABLE IV
CO/H_2/C_2H_4 Reaction After H_2S Addition

Compound Rate (gmol/kg-hr)	OVERALL	C_2+HC	CH_3CHO	C_3OX
300° C	2.89	1.079	-	0.217
275° C	2.15	0.685	-	0.234
250° C	1.58	0.412	-	0.225

\- No product is observed.

\- C_3OX includes C_3H_7OH and C_2H_5CHO.

Figure 1

Hydrogen TPD Profile for Rh/SiO_2 and $S\text{-}Rh/SiO_2$

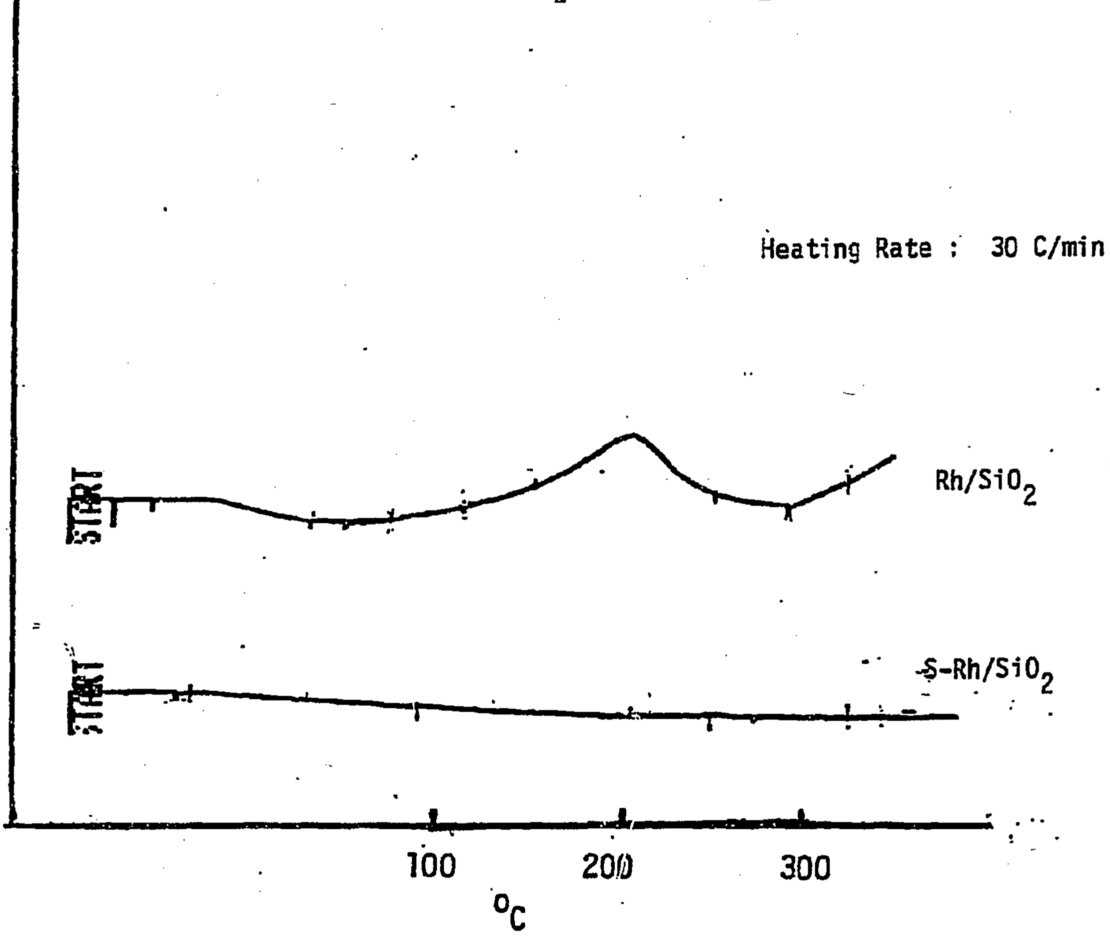


Figure 2

CO HYDROGENATION

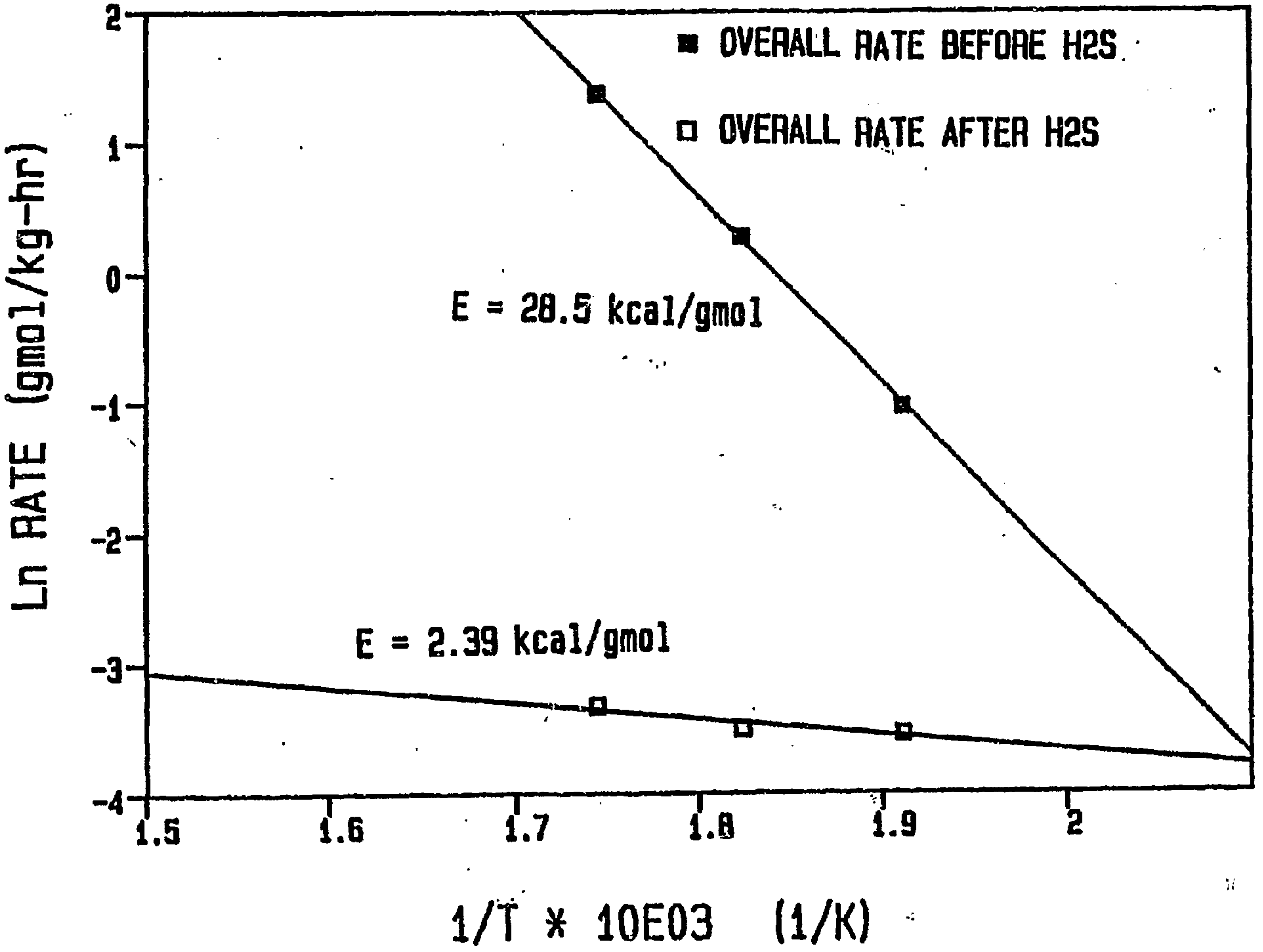


Figure 3

CO/H2/C2H4 REACTION

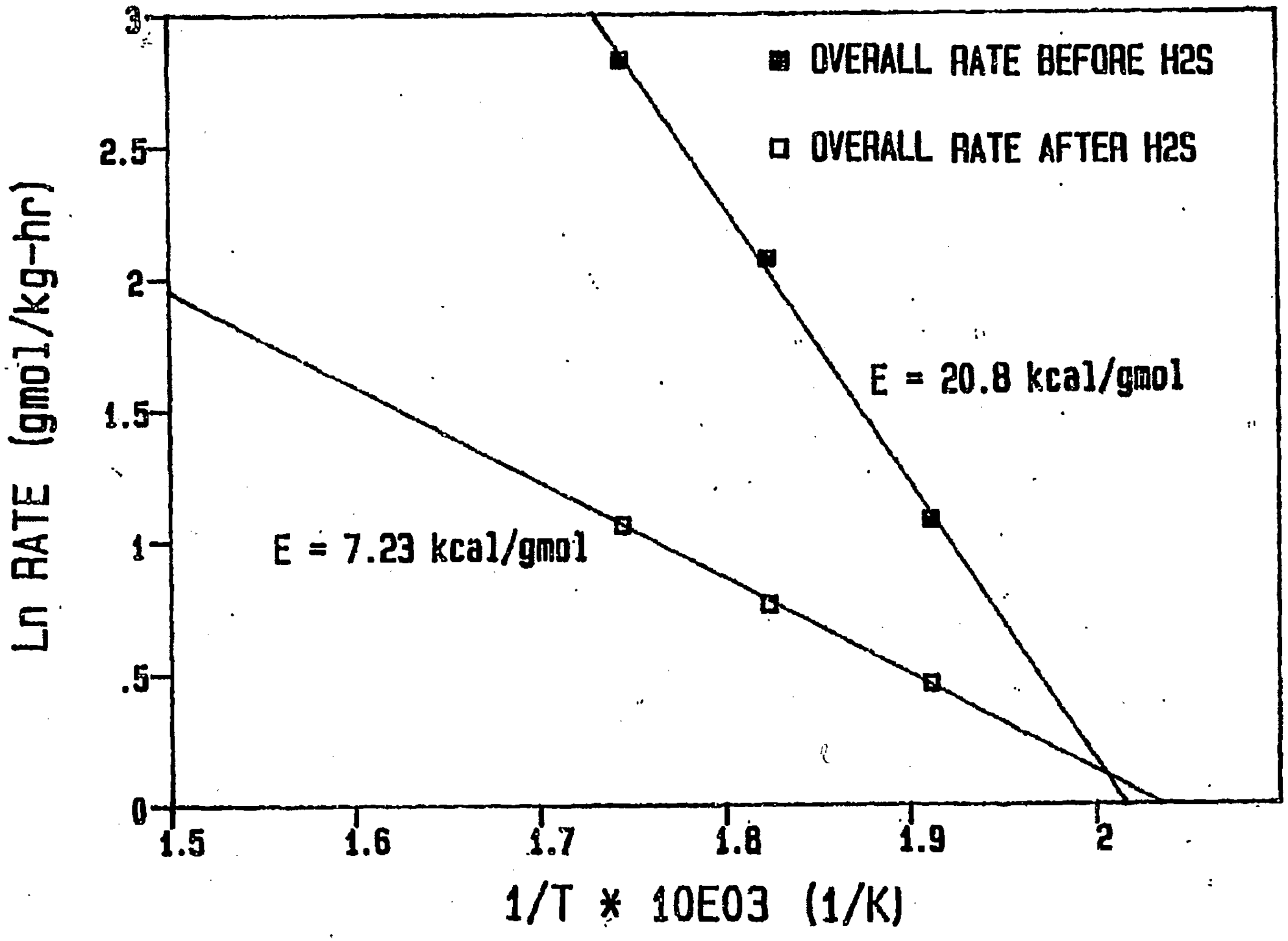
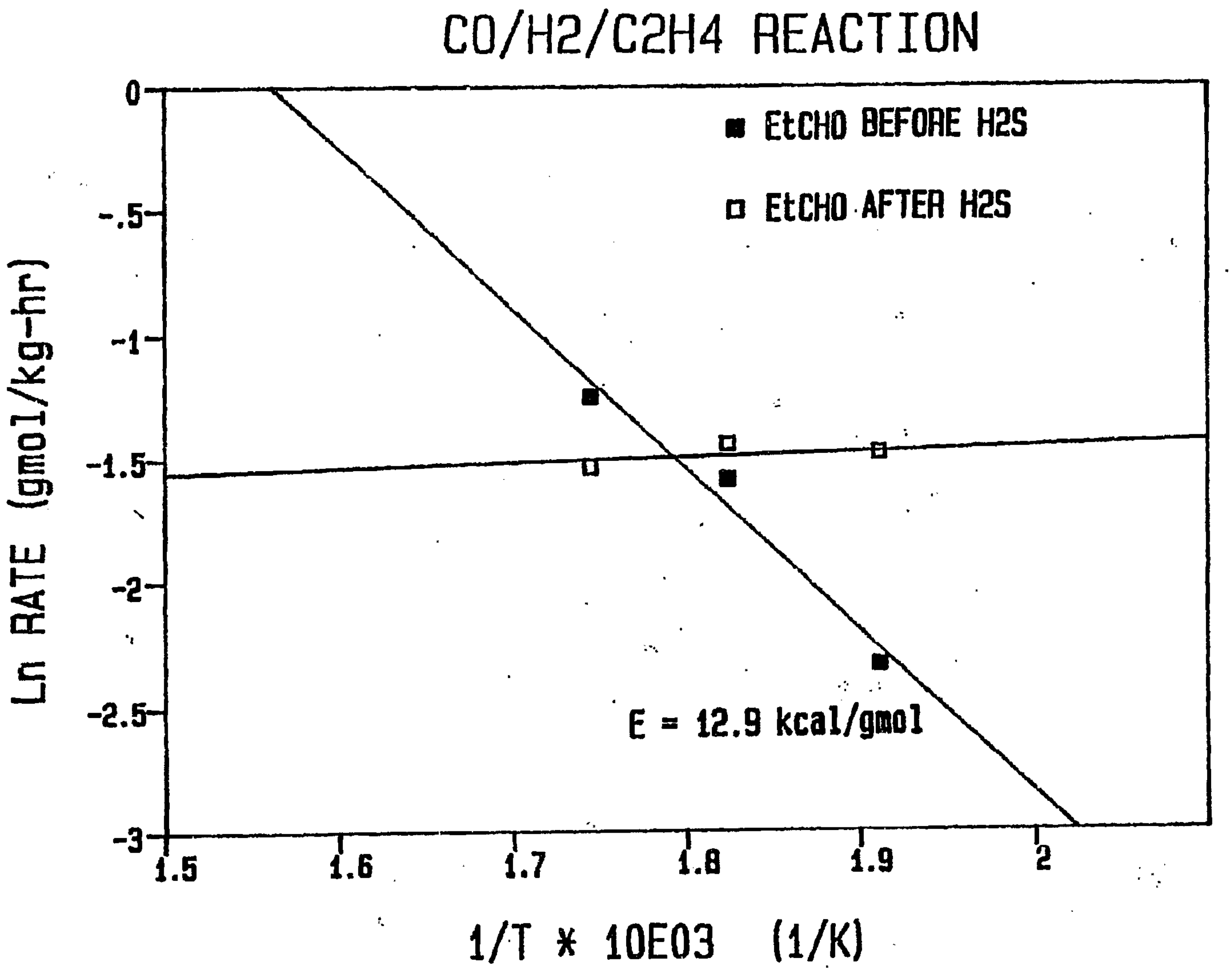


Figure 4


CO/H2/C2H4 REACTION
■ EtCHO BEFORE H2S
□ EtCHO AFTER H2S
E = 12.9 kcal/gmol
Ln RATE (gmol/kg-hr)
0
-.5
-1
-1.5
-2
-2.5
-3
1.5
1.6
1.7
1.8
1.9
2
1/T * 10E03 (1/K)

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