DOE/PC/90045--T5

QUARTERLY REPORT

Report Period

January 1, 1992 to March 31, 1992

DOE/PC/90045--T5

DE92 018483

FOR

CATALYST AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

Submitted to

United States Department of Energy
Pittsburgh Energy Technology Center

May 26, 1992

AUG 06 1992

by

Rayford G. Anthony and Aydin Akgerman
Kinetics, Catalysis and Reaction Engineering Laboratory
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122

UNDER DOE CONTRACT NO. DE-AC22-90PC90045

(Texas A&M Research Foundation Project No. 6722)

CATALYST AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

DOE CONTRACT NO. 90PC90045

TEXAS A&M RESEARCH FOUNDATION PROJECT NO. 6722

Quarterly Report

Report Period: 1/1/92 to 3/31/92

PROJECT OBJECTIVES

The objectives of this project are to develop a new catalyst, the kinetics for this catalyst, reactor models for trickle bed, slurry and fixed bed, and simulate the performance of fixed bed trickle flow reactors, slurry flow reactors, and fixed bed gas phase reactors for conversion of a hydrogen lean synthesis gas to isobutylene.

JUSTIFICATION FOR THE PROJECT

Isobutylene is a key reactant in the synthesis of methyl tertiary butyl ether (MTBE) and of isooctanes. MTBE and isooctanes are high octane fuels used to blend with low octane gasolines to raise the octane number required for modern automobiles. The production of these two key octane boosters is limited by the supply of isobutylene. MTBE when used as an octane enhancer also decreases the amount of pollutants emitted from the exhaust of an automobile engine.

Hydrogen-rich synthesis gas has been converted to isobutylene using a zirconia based catalyst. However, the productivity and yields are low, and the ability of the catalyst to convert a hydrogen-lean synthesis gas to isobutylene with high productivity and yields, and without excessive deactivation is unknown.

PROPOSED PROCESS

A hydrogen-lean synthesis gas with a ratio of H_2/CO of 0.5 to 1.0 is produced from the gasification of coal, lignite, or biomass. This hydrogen-lean synthesis gas can be processed in a "shift reactor" with steam to convert the hydrogen-lean synthesis gas to a hydrogen-rich synthesis gas. But, this processing step is inefficient and consumes considerable energy. If the hydrogen-lean synthesis gas could be converted directly to isobutylene, a significant increase in process efficiency will be the result. We envision a reactor system and catalyst that will selectively and efficiently convert hydrogen-lean synthesis gas to isobutylene. The catalyst, based on past work published in the literature, will most likely be zirconia or thoria based, and will contain components to promote the water-gas shift reaction and increase the selectivity of isobutylene.

GOALS FOR THE QUARTER

The goals for the quarter include 1) file necessary reports. 2) Obtain data on methanol synthesis for use in the microkinetic model. 3) Continue to evaluate the performance of zirconia based catalysts. 4) Evaluate parameters for the macrokinetic model for data presented at the DOE contractors meeting using SimuSolv.

ACCOMPLISHMENTS FOR THE QUARTER

Filing of necessary reports

The quarterly report for the period of October 1, 1991 to December 31, 1991 was filed and approved. Monthly reports for January, February and March were also filed.

Microkinetic Model

Table 1 presents a proposed reaction sequence using a microkinetic model approach. We believe that we will be able to estimate the parameters for this mechanism by using the metal oxygen bond strength, the number of active sites and the Polanyi constant. Aldol condensation and CO insertion are the two routes used to make isobutylene. Additional work is required prior to making a simulation to estimate isobutylene production.

Macrokinetic Classical Mechanism Approach

The following is the derivation of a Hougen-Watson rate equation based on microkinetics. The rate controlling step is assumed to be the 1-2 shift reaction of cycliacyl to enediolate. Inhibition of CO_2 is also taken into consideration.

$$H_2 + 2s \rightarrow 2H_s \qquad \theta_H = \sqrt{K_{H_2} p_{H_2}}\,\theta$$

$$CO + s \rightleftharpoons CO_s \qquad \theta_{CO} = K_{CO} p_{CO} \theta$$

$$CO_s + 2H_s \rightleftharpoons CH_2O_s \text{ (methoxide)} + 2s \qquad \theta_{CH_2O} = \frac{K_M \theta_{CO} \theta_H^2}{\theta^2}$$

$$CH_2O_s + CO_s \rightleftharpoons C_2H_2O_{2s}^{(1)} \text{ (cycli acyl)} + s \qquad \theta_{C_2H_2O_{2s}^{(1)}} = K_C \theta_{CH_2O} \theta_{CO} = \frac{K_C K_M \theta_{CO}^2 \theta_H^2}{\theta^2}$$

$$C_2H_2O_{2s}^{(1)} \rightarrow C_2H_2O_{2s}^{(2)} \text{ (enediolate)} \qquad r_1 = k_s \theta_{C_2H_2O_{2s}^{(1)}} = k_s K_C K_M K_{H_2} K_{CO}^2 p_H P_{CO}^2$$

$$C_2H_2O_{2s}^{(2)} + CO_s + 2H_s \rightleftharpoons C_2H_4O_s \text{ (aldehyde)} + CO_{2s} + 2s \qquad \theta_{C_2H_2O_{2s}^{(2)}} = \frac{\theta_{C_2H_4O} \theta_{CO_2} \theta^2}{K_A \theta_{CO} \theta_H^2}$$

$$C_2H_4O_s + 2CO_s + 2H_s \rightleftharpoons C_3H_6O_s + CO_{2s} + 3s \qquad \theta_{C_2H_4O} = \frac{\theta_{CO_2} \theta^3}{K_2 \theta_{CO}^2 \theta_H^2} \theta_{C_3H_6O}$$

$$C_3H_6O_s + 2CO_s + 2H_s \rightleftharpoons C_4H_8O_s + CO_{2s} + 3s \qquad \theta_{C_3H_6O} = \frac{\theta_{CO_2} \theta^3}{K_3 \theta_{CO}^2 \theta_H^2} \theta_{C_4H_8O}$$

$$C_4H_8O_s + 2CO_s + 2H_s \rightleftharpoons C_5H_{10}O_s + CO_{2s} + 3s \qquad \theta_{C_5H_{10}O} = \frac{K_4\theta^2_{CO}\theta^2_H}{\theta_{CO_2}\theta^3}\theta_{C_4H_8O}$$

$$C_{n-1}H_{2(n-1)}O_s + 2CO_s + 2H_s \rightleftharpoons C_5H_{10}O_s + CO_{2s} + 3s \qquad \theta_{C_nH_{2n}O} = \frac{K_{n-1}\theta^2_{CO}\theta^2_H}{\theta_{CO_2}\theta^3}\theta_{C_{n-1}H_{2(n-1)}O}$$

$$C_4H_8O_s + CO_s \rightleftharpoons C_4H_8 + CO_{2s} + s \qquad \theta_{C_4H_8O} = \frac{K_{C_4H_8}\theta_{CO_2}\theta p_{C_4H_8}}{\theta_{CO}}$$

$$CO_{2s} \rightleftharpoons CO_2 + s \qquad \theta_{CO_2} = K_{CO_2}p_{CO_2}\theta$$

$$CH_2O_s + CO_s \rightarrow CH_{2s} + CO_{2s} \qquad r_2 = k_{CH_4}\theta_{CH_2O}\theta_{CO} = k_{CH_4}K_MK_{H_2}K^2_{CO}p_{H_2}p^2_{CO}\theta^2$$

$$1 = \sum\theta_i = \theta + \theta_{CO} + \theta_H + \theta_{CO_2} + \theta_{CH_2O} + \theta_{C_2H_2O_2^{(1)}} + \theta_{C_2H_2O_2^{(2)}} + \theta_{C_2H_4O} + \theta_{C_3H_6O} + \sum_{i=4}^{\infty}\theta_{C_iH_{2i}O}$$

Assume $K_4 = K_5 = \ldots = K_n$

$$\sum_{i=4}^{\infty}\theta_{C_iH_{2i}O} = \frac{\theta_{C_4H_8O}}{1 - \dfrac{K_n\theta^2_{CO}\theta^2_H}{\theta_{CO_2}\theta^3}} = \theta_{C_4H_8O}[1 + \frac{K_n\theta^2_{CO}\theta^2_H}{\theta_{CO_2}\theta^3}]$$

Relative abundance of CH_2O on the surface -> Negligible amounts of $C_2H_2O_2^{(1)}$, $C_2H_2O_2^{(2)}$, C_2H_4O and C_3H_6O.

$$\theta = \frac{1}{1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}} + K_{CO_2}p_{CO_2} + (K_M K_{H_2} K_{CO})p_{H_2}p_{CO} + K_n K_{CO} K_{H_2} K_{C_4H_8} p_{CO} p_{H_2} p_{C_4H_8} + \dfrac{K_{C_4H_8}K_{CO_2}p_{C_4H_8}}{K_{CO}p_{CO}}}$$

$$r = r_1 + r_2 = k_s K_C K_M K_{H_2} K_{CO}^2 p_{H_2} p_{CO}^2 \theta^2 + k_{CH_4} K_M K_{CO}^2 K_{H_2} p_{H_2} p_{CO}^2 \theta^2$$

$$r = \frac{k p_{H_2} p_{CO}^2}{\left[1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}} + K_{CO_2}p_{CO_2} + (K_M K_{H_2} K_{CO})p_{H_2}p_{CO} + K_n K_{CO} K_{H_2} K_{C_4H_8} p_{CO} p_{H_2} p_{C_4H_8} + \dfrac{K_{C_4H_8}K_{CO_2}p_{C_4H_8}}{K_{CO}p_{CO}}\right]^2}$$

This mechanism gives a rate equation with 2nd order in CO and 1st order in H_2. By assuming a different rate controlling step, one could obtain first order in CO and 1/2 order in hydrogen for an order for the numerator of 1.5. For example, if we assume $CO_s + H_s \rightarrow CHO_s \rightleftharpoons CH_2O_s \rightleftharpoons CH_3O_s$ as the rate controlling step, the rate equation will be first order for CO and 1/2 for H_2. Such a mechanism would correspond with the observed empirical rate equation developed from the conversion data. Based on the empirical model the major term in the denominator of the last equation is the K_{CO2} P_{CO2}, and all other terms are small compared to this term. This procedure differs from that discussed above in that rate controlling assumptions are used and kinetic parameters are estimated from the experimental data. In the non classical microkinetic approach related to Table 1 the rates are estimated using adsorption data, heats of formation and bond energy calculations. The pseudo steady state and rate controlling assumptions are not used. We have a considerable amount of work yet to do on the modelling effort, but the combination of the empirical developed models, the Hougen-Watson approach, and the microkinetic mechanism as exemplified in Table 1 should result in an excellent model for predicting product distributions and conversions for the new catalysts.

Empirical Modelling

Simulation of reactor performance using SimuSolv was conducted using a macrokinetic reaction rate equation. The data used for this modelling have been previously reported. When using a power law model the fit was poor for the larger space times. When a term for inhibition by the product, CO_2, was included the fit improved. Figure 1 illustrates the goodness of fit. The model predicted data at a single pressure and different feed compositions better than it predicted data at different pressures. The points labelled X1, X2, and X3 are at 95 atm, while X4 is at 70 atm. The hydrogen to CO ratio for these 4 sets of data are 0.5, 1, 3 and 3, respectively. The rate equation is as follows:

$$r_{CO} = \frac{9.43 * 10^{-6}\, p_{CO}^{1.28}\, p_{H_2}^{0.29}}{(1 + 1.036\, p_{CO_2})}$$

The constants presented are the optimized constants for these sets of data. The sum of the powers in the numerator is slightly greater than 1.5, and in all of the fits the over all pressure dependance in the numerator was approximately 1.5. Therefore, hydrogen is probably adsorbing dissociatively as the H atom and CO is probably adsorbing as the molecule. The reverse situation could be the case, but it is unlikely. The next step in the empirical modelling approach is to relate product distributions to the conversion of CO or extent of reaction.

Experimental Program:

We have had major equipment problems this quarterly, and were unable to conduct very many experiments to evaluate catalysts activities. After spending about $7000.00 for equipment repairs, we took some data on a monoclinic zirconia at low temperatures and at the higher temperatures. The low temperature work was for the purpose of gaining insight into the mechanisms which may also be occurring very rapidly at the higher temperatures. Hence, intermediate products produced at low temperatures would not appear in the products at the higher temperatures. Because of the small amounts of intermediates produced and difficulties with the analytical equipment, we only obtain qualitative data at the low temperatures. At 250 °C and 60 space time very little product was formed. The product however consisted of methanol and dimethyl ether. At 300 °C the product still consisted of methanol and dimethyl either with the ratio of dimethyl either to methanol increasing. This ratio also increased with increasing space times (space time is proportional to the residence time). At 325 °C the products consisted of methanol, ethanol, and isobutylene. Similar trends in methanol to ethanol and methanol to isobutylene were obtained with increasing space times. These experiments were conducted with a 1:1 CO:H_2 feed and a pressure of 50 atm. Conversions were less than 2%. These results suggest that the intermediate for alcohol formation, may also be the intermediate at higher temperatures for isobutylene formation. The microkinetic model also predicts the formation of the alcohols from the same intermediates that isobutylene is produced.

Experiments were conducted using a sodium impregregnated zirconia. The catalyst preparation is presented in the last quarterly report. Based on analysis for Na by atomic absorption the sodium content of the catalyst is 1.6%. Preliminary results indicate that the catalyst is as active as the pure zirconia and appears to be more selective to isobutylene. Figure 2 compares the activities of the zirconia and the Na impregnated zirconia at 35 atm. Batch #7 is the sodium impregnated zirconia. At 95 atmospheres as illustrated by Figure 3, the activity of the sodium impregnated zirconia is slightly more active than zirconia. Figure 4 shows the effect of pressure and space time (space time is proportional to residence time).

Tables 2 and 3 illustrated the conversions and selectivities obtained for the sodium impregnated catalyst at 400 °C, 21 and 50 atm, and CO:H_2 ratios of 1:3 and 1:1. The second line in each row for each experiment represents the estimated error in the number above it. For convenience weight ratios and mole ratios are presented. In Table 3, the large amount of C_5^+ should be recognized. The number of moles of the C_5^+ will be small but because of the increase in the molecular weight, the weight fraction is high.

Catalysts were also prepared using the modified sol gel procedure developed at Sandia. Hydrous potassium and hydrous sodium zirconium titanium oxide and zirconium silicon oxide were prepared. The use of potassium versus sodium has been found to produce materials with significantly different surface areas. We have also prepared these same type of catalysts using hydrothermal techniques. In the latter case the materials are crystalline, whereas for the former case they are amorphous. The results for these catalysts will be reported next quarter.

GOALS FOR THE NEXT QUARTER

The goals for the next quarter include: 1) Filing the necessary reports, 2) Completing the experiments on the sodium impregnated zirconia. 3) Conduct experiments with the AE

MSBTR 900 on a thoria-zirconia prepared hydrothermally. 4) Continue work to synthesize a zirconate with a layered structure. The objective is to determine if changing the crystal structure will affect the catalysts activity and selectivity. 5) Continue the microkinetic modelling. This approach is finally beginning to produce some useful results. 6) Continue the empirical modelling.

WORK SCHEDULE STATUS REPORT

The work schedule status report is attached. Significant progress is shown on Tasks 1,2 and 3 with some progress on Tasks 4 and 5.

Table 1. Mechanism for Isobutylene Synthesis

(1) $H_2 + 2MO = 2MOH$

(2) $H_2 + 2M = 2MH$

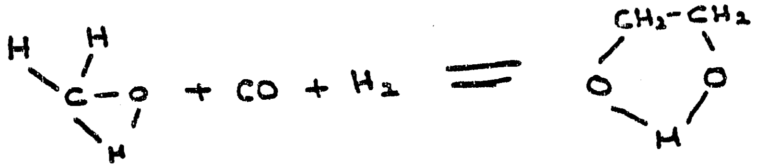
(3) $MOH + CO = MOCHO$

(4) $MOCHO = CO_2 + MH$

(5) $MOCHO + MH = MOCH_2 + MO$

(6) $MOCH_2 + MOH = MOCH_3 + MO$

(7)



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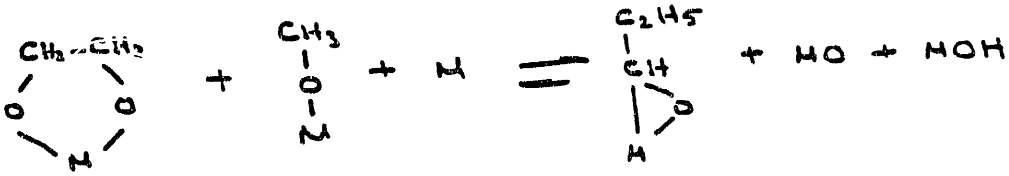

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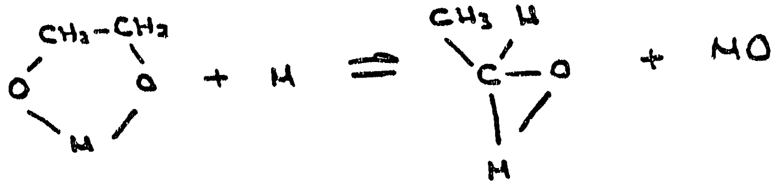

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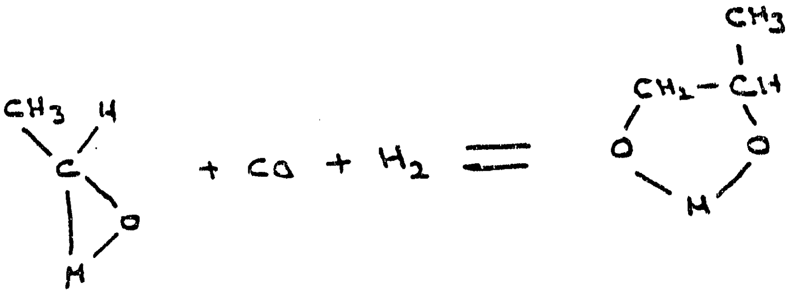

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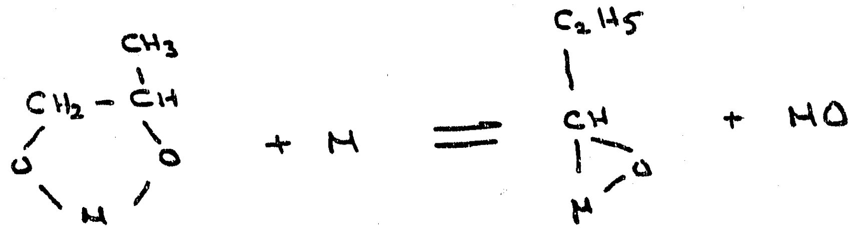

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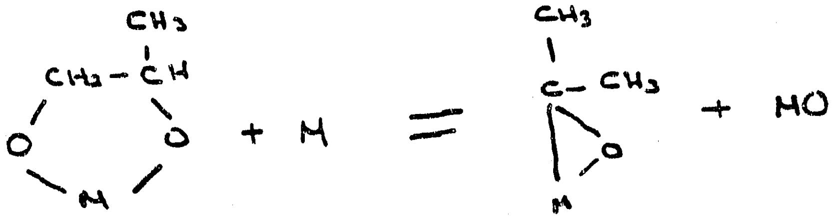

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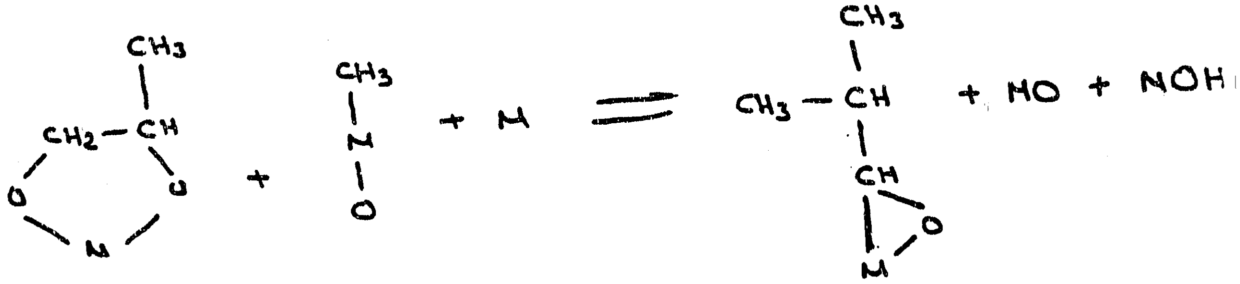

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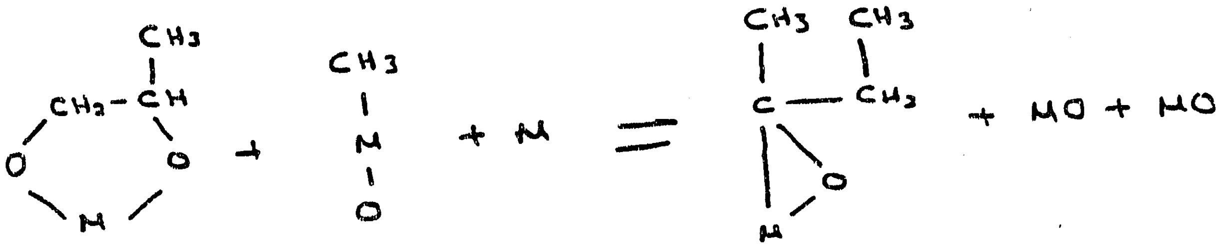

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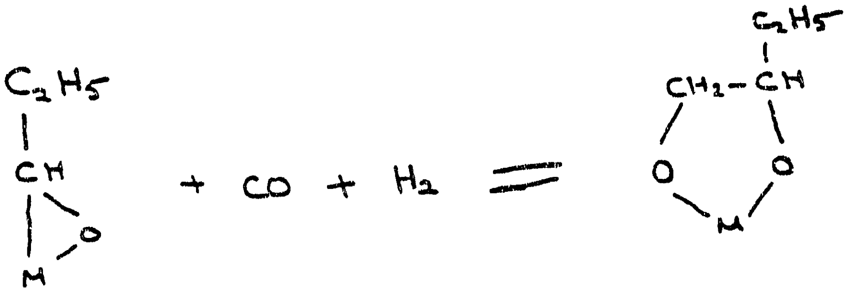

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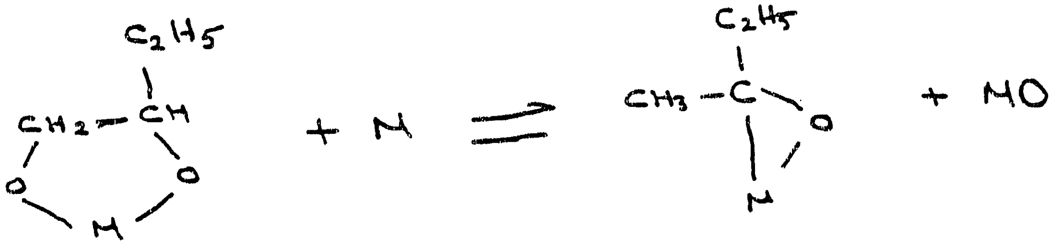

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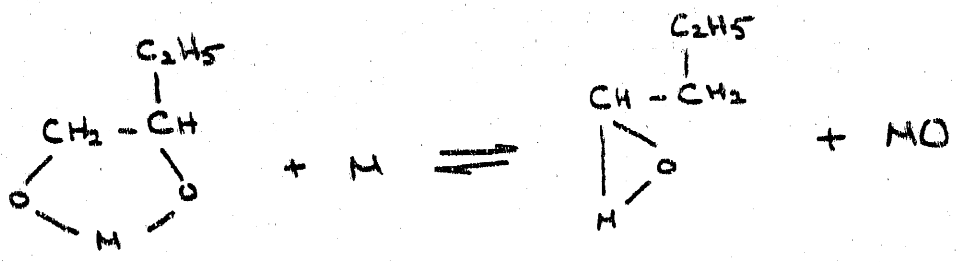

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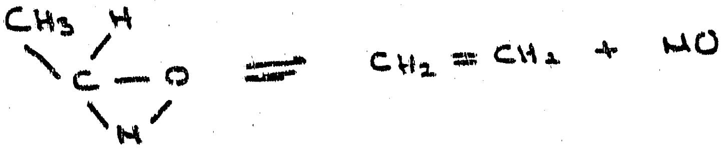

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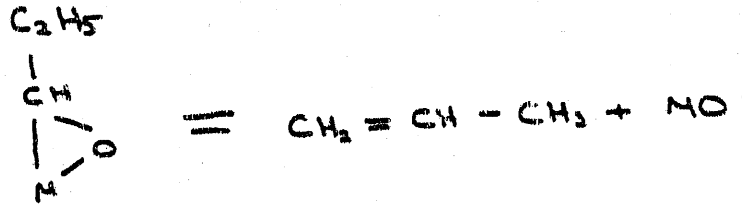

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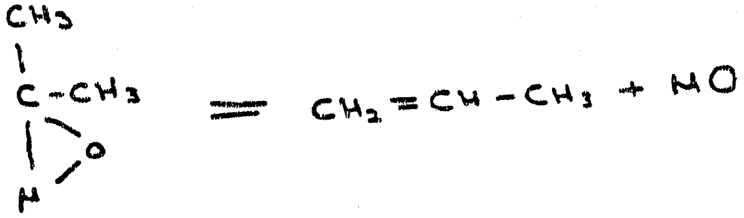

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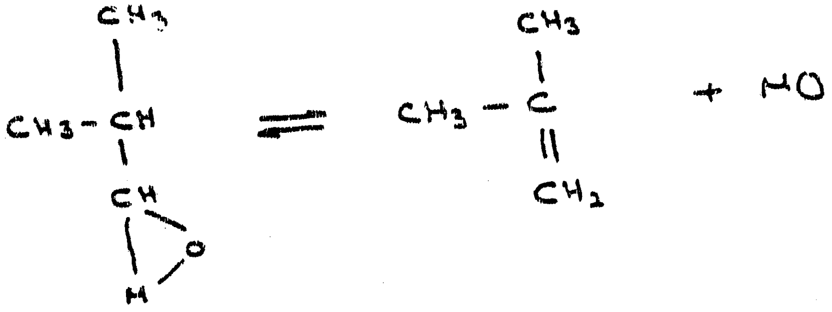

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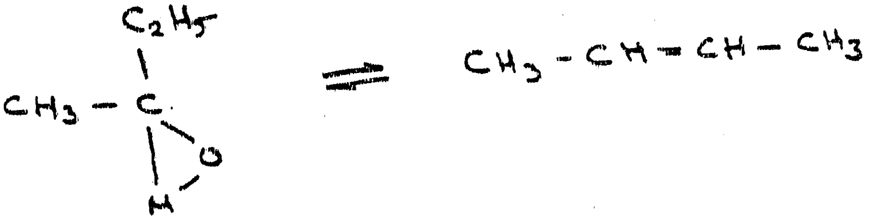

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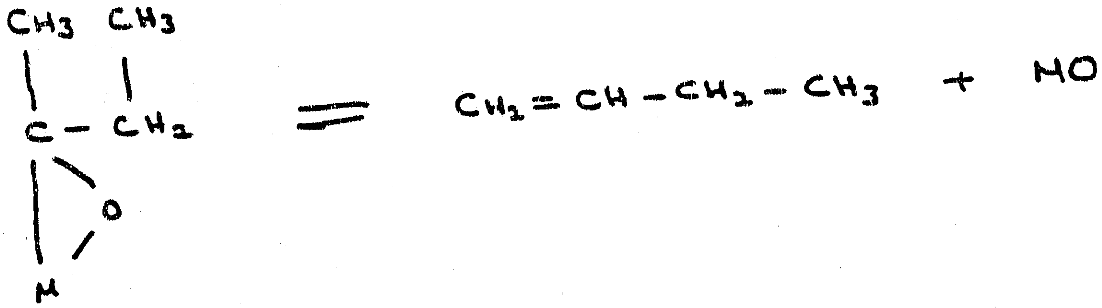

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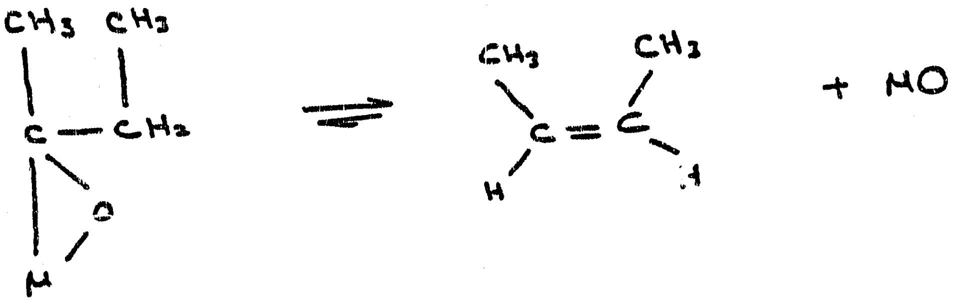

(25) $MOCH_3 + MOH \rightleftharpoons CH_4 + 2MO$

Table 2. Activity and Selectivity Data for 1.6%Na on ZrO_2 Results

Run	T (°C)	P (atm)	CO/H_2 Ratio	Space Time (sec)	CO_2/CO Conversion	Isosynthesis Profile		Branched/Linear C4		$i\text{-}C_4H_8/CH_4$		$i\text{-}C_4H_8/C5^+$	$i\text{-}C_4H_8$/ All C4's		$i\text{-}C_4H_8/i\text{-}C_4H_{10}$
						wt.	mol.	wt.	mol.	wt.	mol.	wt.	wt.	mol.	wt. mol.
SA	400	21	1/3	10	0.0516	4.382	2.434	2.623	2.623	3.242	0.927	0.375	0.724	0.724	very large
					0.0011*	0.518	0.271	0.678	0.678	0.469	0.134	0.025	0.051	0.051	
SB	400	50	1/1	15	0.0744	6.226	3.591	3.469	3.465	4.817	1.377	0.169	0.751	0.752	~30
					0.0003	0.283	0.170	0.265	0.265	0.123	0.035	0.010	0.010	0.010	2
SC	400	50	1/1	30	0.1157	5.024	2.865	3.415	3.408	3.381	0.967	0.199	0.730	0.731	16.7
					0.0022	0.491	0.296	0.090	0.090	0.653	0.187	0.007	0.005	0.005	2.0
SD	400	50	1/1	45	0.1473	6.008	3.411	3.574	3.565	3.605	1.031	0.203	0.726	0.727	13.4
					0.0016	0.199	0.097	0.270	0.269	0.023	0.007	0.015	0.009	0.009	1.5
SE	400	50	1/1	60	0.1704	5.720	3.238	3.306	3.299	3.168	0.906	0.224	0.705	0.707	11.1
					0.0019	0.210	0.111	0.085	0.085	0.174	0.050	0.002	0.007	0.006	1.5

*The second line in the Tables is the estimated error in the number reported.

Table 3. Hydrocarbon Distributions (wt. frac.) for 1.6%Na on ZrO_2

Run	SA	SB	SC	SD	SE
Methane	0.066	0.027	0.042	0.041	0.049
Ethane	0.005	0.003	0.008	0.006	0.008
Ethylene	0.043	0.015	0.018	0.017	0.018
Propane	0.000	0.002	0.003	0.003	0.004
Propylene	0.019	0.008	0.010	0.008	0.008
Isobutane	0.000	0.004	0.009	0.011	0.014
n-Butane	0.000	0.000	0.000	0.000	0.001
1-butene	0.032	0.015	0.021	0.019	0.021
Isobutylene	0.214	0.131	0.143	0.147	0.155
trans-2-butene	0.028	0.012	0.010	0.011	0.013
cis-2-butane	0.021	0.012	0.013	0.014	0.017
C5+'s	0.571	0.771	0.722	0.723	0.692

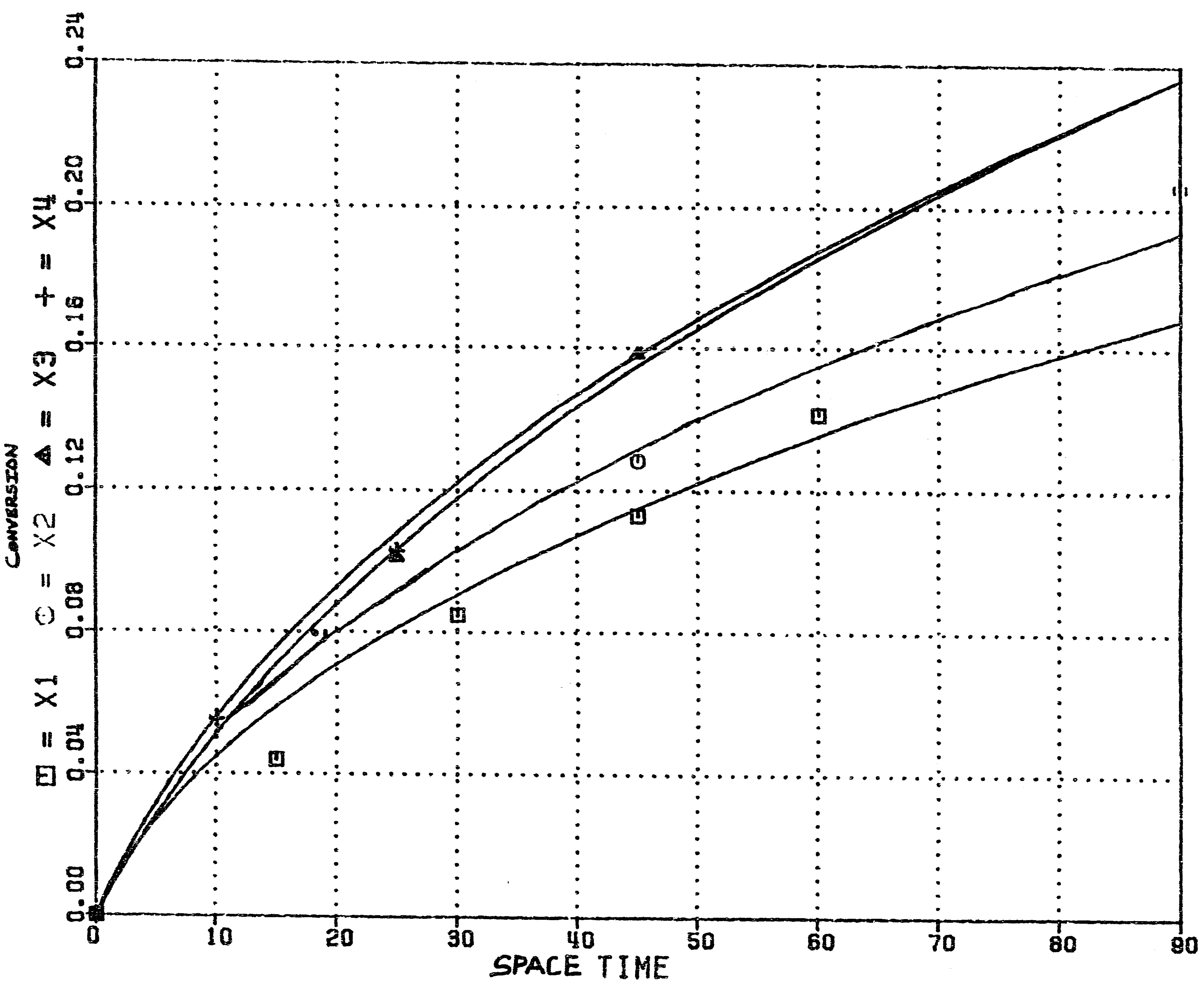

Figure 1. Comparison of Experimental Conversions with Calculated Conversions Using the Plug Flow Reactor Model and the Rate Equation (1). X1, X2, X3, and X4 are data for H_2/CO feed ratios of 0.5. 1, 3, and 3. Reactor Pressures are 95 for X1, X2, and X3 data and 70 atm for the X4 Data. The lines are the calculated conversions.

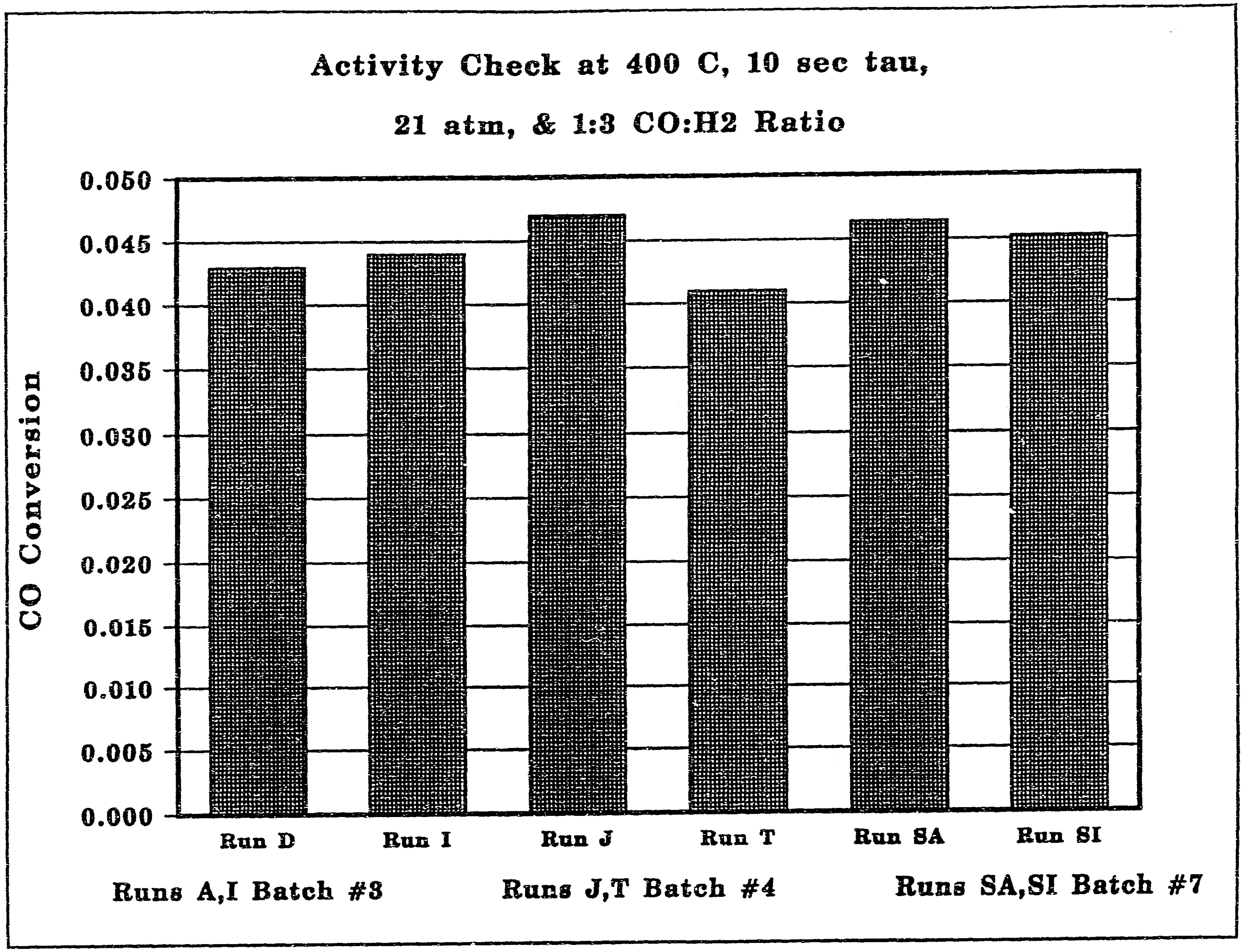

Figure 2. Relative activity of 2 different batches (#3 & #4) with ZrO_2 with 1.6 wt.% Na on ZrO_2 (Batch #7).

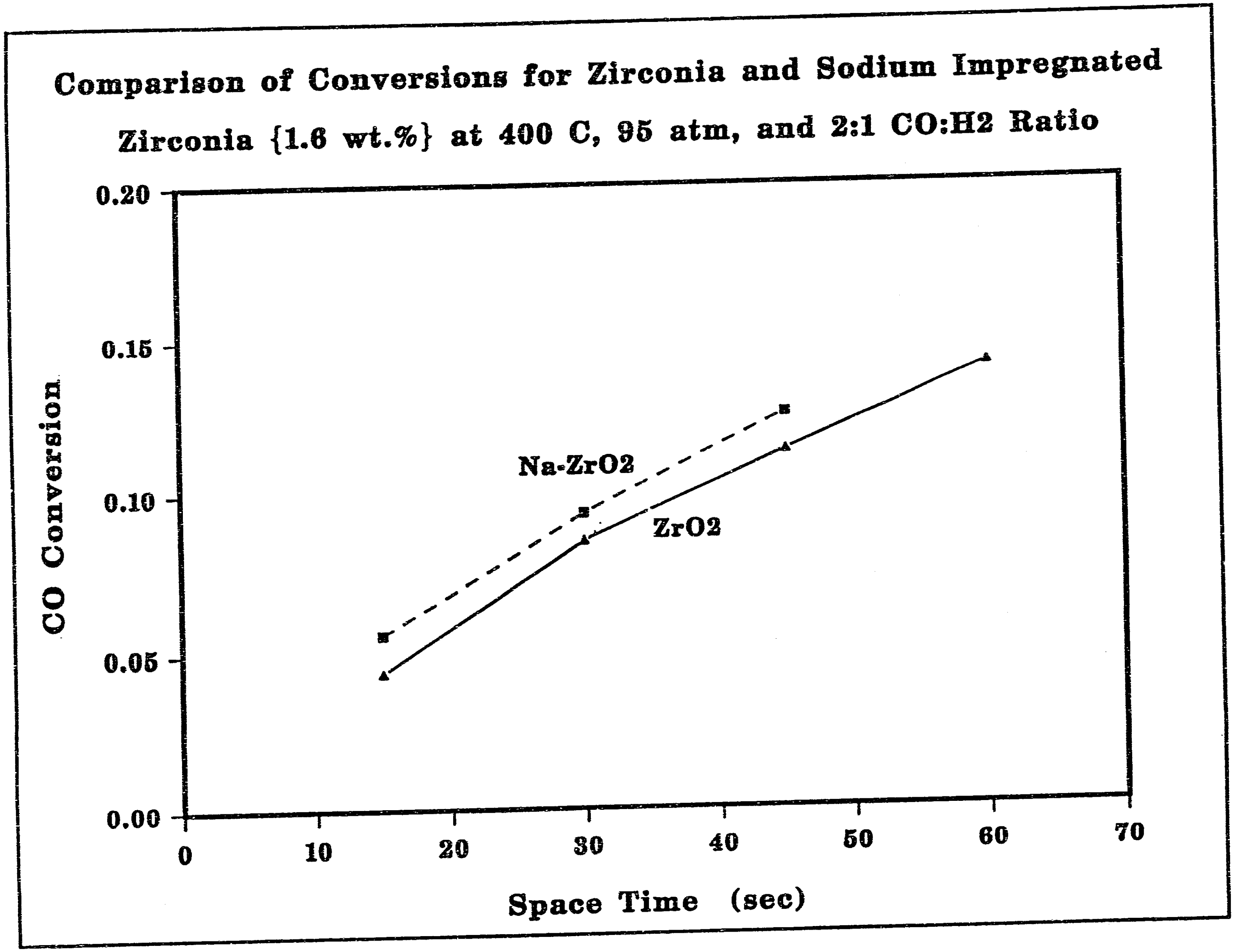

Figure 3. Relative Activity of monoclinic ZrO_2 with and without Na.

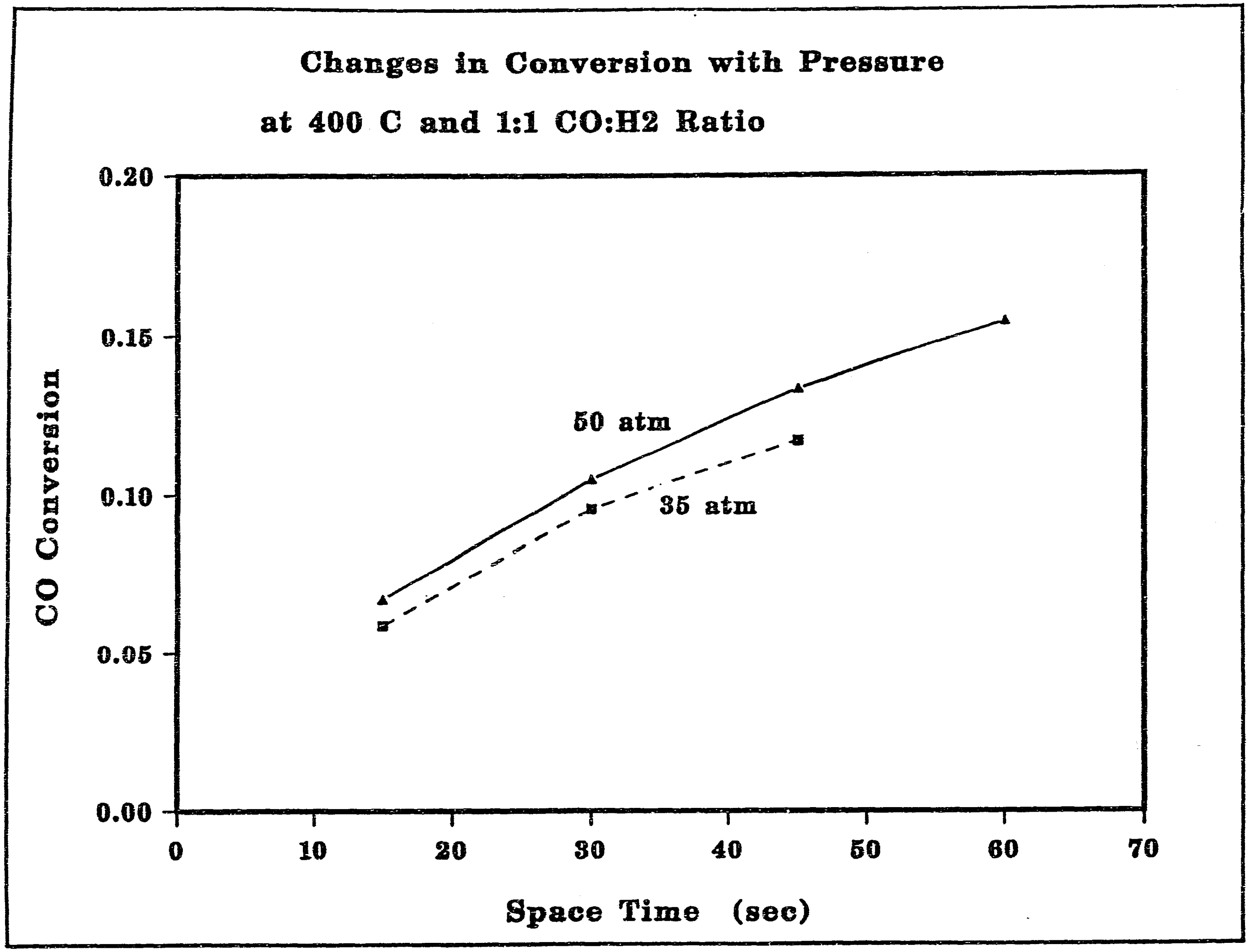

Figure 4. Effect of Pressure on Activity for 1.6 wt% Na on ZrO_2.

Milestones removed.

END

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9/14/92