

DOE/PC/90045-T11

QUARTERLY REPORT

Report Period

July 1, 1992 to September 30, 1992

3Q/92

FOR

CATALYST AND PROCESS DEVELOPMENT FOR
SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

Submitted to

United States Department of Energy
Pittsburgh Energy Technology Center

November 13, 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)

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**CATALYSTS AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS
CONVERSION TO ISOBUTYLENE**

by

R. G. ANTHONY, A. AKGERMAN, W. S. POSTULA, Z. FENG,
C. V. PHILIP, AND C. ERKEY

Kinetics, Catalysis and Reaction Engineering Laboratory
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122

DOE CONTRACT NO: DE-AC22-90PC90045
(Texas A&M Research Foundation Project No. 6722)

ABSTRACT

A series of zirconia catalysts prepared by a modified sol gel procedure, co-precipitation with ammonium hydroxide, and by a hydrothermal method were evaluated for catalytic activity. These catalysts were prepared containing silicon, thorium, titanium, cerium and the alkali metals. A catalyst containing 2% thorium on zirconia was the most active. The isobutylene and isobutane selectivity were 19.4 wt% and 1.82 wt%, respectively.

Macro- and micro-kinetic models indicate that CO₂ formation inhibits the rate of CO conversion, hydrogen is dissociatively adsorbed, and CO is molecularly adsorbed. The microkinetic model indicates the strengthening of the metal-oxygen bond might increase the production rate of isobutylene.

INTRODUCTION

Zirconia and thoria have been reported as being the most selective catalysts for the synthesis of isoalkenes and isoalkanes from synthesis gas (1-10), and a considerable amount of research has been conducted using these catalysts [1-10]. Even though these materials appear to be the best catalysts discovered to date, their activity is still relatively low. This study has focused on the use of additives and different methods of preparation to increase the catalytic activities and selectivities for producing isobutylene.

Rate equations for use in reactor design and microkinetic models have been developed for use in reactor design, interpolation of data, and to provide insight on the effect of various catalytic properties. The rate equations for CO conversion are developed using classical techniques (Holland and Anthony, 1989), a plug flow reactor model and classical curve-fitting techniques. The microkinetic model was developed by utilizing mechanisms published in the literature for CO conversion to isobutylene, bond energy calculations, Polanyi parameters, and classical methods of parameter estimation. For the microkinetic model stiff

differential equations are encountered, but the SimuSolv^{®1} software handles the system very well.

CATALYSTS SYNTHESIS

Zirconia has been prepared by precipitation with ammonium hydroxide or sodium hydroxide from zirconyl nitrate, by a modified sol gel method [11], and by a hydrothermal method. A catalyst with 2% Th on zirconia was prepared by precipitating zirconia followed by impregnating with thorium nitrate, drying and calcining at 500 °C for 5 hours. A 10% Th on zirconia was prepared by a hydrothermal method. Zirconia was prepared with 1.6% Na by using sodium hydroxide and ammonium hydroxide to precipitate zirconyl nitrate. Zirconia and zirconia/silica with a molar ratio of 4 Zr:1 Si were prepared using the modified sol gel procedure, and these catalysts gave a tetragonal XRD pattern after calcination and after reaction. The 1.6%Na/10.3%Ti/ZrO₂ (HT) had a cubic structure, and the remaining catalysts were monoclinic after calcining them at 500 °C for 2.5 hours. Table 1 presents the characterization data obtained for the catalysts used in this study.

EXPERIMENTAL UNITS USED FOR CATALYST EVALUATION

Two bench scale units with tubular reactors and on-line analysis were used for evaluation of the catalysts. The data in Table 2 illustrates intra- and inter-laboratory reproducibility for a zirconia catalyst prepared by precipitation using the two reactor systems and data reported by Gajda et al. [12] of UOP. Essentially the same results are obtained for each of the units and laboratories. This was expected since the units use tubular reactors, but because of different ovens, gc's, and reactor size and configuration the tests were conducted to insure intra- and inter-laboratory reproducibility for our catalyst program. By comparing the results with data reported by Gajda et al., inter-laboratory reproducibility is illustrated. Since the catalyst used by Gajda et al. was prepared by precipitation of zirconyl chloride, the results shows that catalysts of equal reactivity and essentially the same selectivities are obtained for catalysts prepared by precipitating zirconyl nitrate or zirconyl chloride. Because the two units yielded the same results on the same catalyst no reference is made in the manuscript as to which unit was used to collect the data.

RESULTS AND DISCUSSION

Figure 1 shows a comparison at 400 °C of catalytic activities. Zirconia, zirconia with 1.6% sodium, and 3.2%Ti, 2%Th/ZrO₂ were prepared by co-precipitation of zirconyl nitrate with ammonium hydroxide. After calcination the first two catalysts were monoclinic, while the 3.2%Ti,2%Th/ZrO₂ gave a tetragonal structure. Hydrothermal synthesis was used to prepare catalysts with 1.6 wt% Na, 10.3% Ti/zirconia and 0.6%Na, 2%Ti, 2%Th/zirconia which had cubic and tetragonal structures, respectively. The activities of the catalysts are ranked as 3.2% Ti, 2% Th/zirconia > 1.6% Na on zirconia > zirconia > 1.6% Na: 10.3% Ti on zirconia. The product from the latter catalysts contains 31.2% i-C₄s with

¹A registered trademark of Dow Chemical Co. U.S.A.

45 to 60% isobutylene and no linear C_4 s.

Figures 2 through 4 illustrate the expected variation of isobutylene, methane and C_5^+ production rates for the catalysts listed in Figure 1. Figures 5 and 6 illustrate the product distributions obtained for the most active and selective catalysts. The weight percent of isobutylene does not vary significantly with the type of catalyst, but the total C_4 weight fraction is a significant function of the type of catalyst. For the 1.6%Na:10.3%Ti/ ZrO_2 the C_4 s consisted only of isobutylene and isobutane.

Figures 7 through 12 show comparisons at 450 °C of the catalytic activities and product distributions obtained for 2%Th/ ZrO_2 prepared by precipitating the ZrO_2 to form a gel and impregnating with thorium nitrate, a 10%Th/ ZrO_2 prepared hydrothermally, $HZrO_2$ -HCl 0.25Si by sol gel, 0.21% $NaZr_{0.8}Si_{0.2}O_x$, 0.32% $KZr_{0.8}Si_{0.2}O_x$ prepared by ion exchanged of $HZr_{0.8}Si_{0.2}O_x$ and zirconia prepared by precipitation. The catalysts were washed with water and acetone, dried and calcined at 500°C. The XRD of the catalysts prepared by sol gel were all tetragonal. The activities are ranked as 2%Th/ ZrO_2 > ZrO_2 > 10%Th/ ZrO_2 \geq $HZrO_2$ -HCl0.25Si > 0.21% $NaZr_{0.8}Si_{0.2}O_x$ > 0.32% $KZr_{0.8}Si_{0.2}O_x$.

Table 2, in addition to illustrating intra and inter laboratory reproducibility, also illustrates the effect of temperature on the activity and product distributions obtained at 400 °C and 450 °C for a precipitated zirconia catalyst. By using the precipitated zirconia as a reference or tie for catalysts evaluated at either 400 or 450 °C, the relative activities of the catalysts can be determined. Figure 13, which illustrates the effect of temperature on the mean reaction rate of CO for catalysts studied at more than one temperature can also be used as an aid in the overall ranking of the catalysts. This plot indicates the 10%Th/ ZrO_2 -HT is almost as active as zirconia prepared by precipitation.

Isobutylene selectivities were of the order of 10 to 25 wt% of the total hydrocarbons produced. The selectivities were in this range for the active catalysts whether methane or C_5^+ were being produced. The rate of production of isobutylene and hydrocarbons decrease as the CO conversion increases because longer space times are required to increase the CO conversion. A major goal in isosynthesis is to obtain a catalyst of sufficient activity so the reaction can be operated at low temperatures and low pressures with high CO conversions and production rates of isobutylene. Hence, improvement in the activities for converting CO to hydrocarbons and an increase in the selective to isobutylene will result in a higher production rate of isobutylene.

The overall ranking of catalytic activities for CO consumption is 2% Th/ ZrO_2 (ppt.) \approx 3.2% Ti, 2% Th/zirconia (ppt.) > 1.6% Na/ ZrO_2 (ppt.) > ZrO_2 (ppt.) \geq 10% Th/ ZrO_2 (HT) \geq $HZrO_2$ -HCl 0.25Si (sol gel) > 1.6% Na, 10.3% Ti/ ZrO_2 (HT). Differences in these catalysts are due to the method of preparation and the type and amount of additive. The relative catalytic activities for methane, isobutylene, and C_5^+ productivities are illustrated in Figure 14. The catalysts prepared by sol gel and ion exchange were the least active of all of the catalysts evaluated and are not listed in Figure 14.

The fact that methane production remains essentially constant or decreases as the conversion of CO increases is probably due to the formation of methane on sites different than those for formation of the higher hydrocarbons. An alternate possibility is that in the number of ZrOH sites decrease as the conversion increases reducing the rate of formation of methane. However, the production rate decrease may also be a simple function of the space time, because the CO conversion is a function of space time, i.e. at high space times (low space velocities) CO conversions are higher than at lower space times, but the production rates usually decrease.

The low activities of the catalysts prepared by the sol gel procedure may be because they were tetragonal after calcination and reaction. On the other hand, the method of preparation tends to produce catalysts with more acid sites than catalysts prepared by precipitation. Also, HCl was used to acidify the catalysts prepared by sol gel methods, and the type of acid used in the acidification may affect the catalyst activity. Hence, even though the surface area was increased by adding Si using the sol gel method, the catalyst was less active.

Reactor Modelling

Table 3 illustrates the derivation of a rate equation for CO consumption assuming that CO₂ is the most abundant intermediate on the catalyst surface. The inhibition of the rate with CO₂ was also determined empirically from the curve fits of the data. Adsorption characteristics of CO₂ were evaluated using TPD of a zirconia saturated with CO₂. The desorption isotherm is illustrated in Figure 15. The fact that CO₂ is strongly bonded to the surface in the range of 350 to 440 °C is further evidence of the abundance of CO₂ on the catalyst surface.

Figure 16 shows the fit of the data for a 1:2 H₂:CO feed at 95 atm and the rate equations for CO consumption for the 1.6% Na/ZrO₂ and ZrO₂. The inhibition of the rate by CO₂ and the overall effect of pressure of 1.5 order is illustrated. The curves in Figure 16 were generated by integrating the differential equation for a plug flow reactor, which is given in Table 3. Figure 17 shows a scatter plot for CO conversion over ZrO₂ (ppt.), 1.6% Na/ZrO₂, and 1.6% Na 10.3% Ti/ZrO₂ (HT). The parameters used in the rate equation are listed in Table 4. Figure 18 illustrates a plot for determining the activation energy for the 1.6% Na 10.3% Ti/ZrO₂ catalyst. The activation energy was determined to be 19.3 kcal/mol.

Microkinetic Modelling

Figure 19 illustrates the key steps of the microkinetic mechanism used for microkinetic modelling. Adsorption of CO is rate controlling and production of methane is by formation of the methoxide ion and its subsequent hydrogenation. The methoxide ion also is important in the condensation reactions to produce the higher hydrocarbons. Figure 20 illustrates the product distribution calculated using the microkinetic model assuming that C₄ hydrocarbons are the largest molecules produced. As expected the isobutylene weight percent is substantially larger than the experimental value, but the model does a reasonable job of predicting the amount of methane and isobutane produced.

Synthesis of New Zirconate Structures

The activity of zirconia catalysts might be improved by altering the crystalline structure of a zirconium oxide. Hence, preparation of zirconates with layered or three dimensional structures different from monoclinic, tetragonal or cubic is a goal of this project. Using techniques developed for the synthesis of crystalline titanates, we have synthesized zirconates containing two or more phases. The phases are either amorphous or tetragonal with a phase, probably a layered structure, exhibiting an XRD peak at 1.1 to 1.2 nm and 2.3 to 3.2 nm (see Figures 21-23). These new materials when calcined reduce to a mixture of tetragonal and monoclinic phases. Future plans are to use evaluate these materials for catalytic activity after impregnation with active catalytic components.

CONCLUSIONS

A rate equation for carbon monoxide consumption showing first order in CO and 0.5 order in hydrogen indicates the rate controlling step involves dissociated hydrogen. The inhibition of the rate with carbon dioxide is also shown. Examination of the hydrocarbon distributions indicates a see-saw effect with the C_4 s representing the fulcrum and methane and C_5^+ the end points. The shift in the distributions tends to be towards the C_5^+ for high pressures and long residence times. This distribution can be shifted by incorporating Ti into the catalysts, but the optimum amount of Ti needs to be determined. The sol gel method of preparing the catalysts tends to produce a less active catalyst than by precipitation of a zirconyl salt. The most active catalyst contained approximately 2% Th/ZrO₂.

FUTURE PLANS

Work will continue on the reactor modelling, trickle bed reactor experiments and on preparation and evaluation of new catalysts. The new zirconates will be investigated for catalyst activity.

ACKNOWLEDGEMENT

This work was done as a part of the project funded by the U.S. Department of Energy on "Catalysts and Process Development for Synthesis Gas Conversion to Isobutylene," Contract No. DE-AC22-90PC90045, Texas A&M Research Foundation Project No. 6722

REFERENCES

1. Pichler, H., and Ziesecke, K-H., "Uber die bei der Isosynthesis entstehenden sauerstoffhaltigen Verbindungen, unter besonderer Beruckstichtigung der Alkole," *Brennst. Chem.*, **31**, 360 (1950a).
2. Pichler, H., and Ziesecke, K-H., "The Isosynthesis," *Bur. Mines Bull.*, 488 (1950b).
3. Kieffer, R., G. Cherry, and R. E. Bacha, "Carbon Monoxide-Hydrogen Reactions. Mechanism of Isobutane Formation in Isosynthesis," *Mol. Chem.*, **2(1)**, 11- 23 (1983).

4. Maruya, K., T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, and T. Onishi, "The CO-H₂ Reaction over ZrO₂ to Form Isobutene Selectively," *Bull. Chem. Soc. Jpn.*, **61**, 667-671 (1988).
5. Onishi, T., Maruya, K-I, Domen, K., Abe, H., and Kondo, J., "The Mechanism of CO Hydrogenation Over Zirconium Oxide Studied by FT-IR," *Catalysis: Theory to Practice, Vol. 2* (M. J. Phillips and M. Ternan, Editors), Proceedings of the 9th International Congress on Catalysis, Calgary, (1988).
6. Maruya, K., T. Fujisawa, A. Takasawa, K. Domen and T. Onishi, "Effect of Additives on Selective Formation of Isobutene from the CO-H₂ Reaction over ZrO₂," *Bull. Chem. Soc. Jpn.*, **62**, 11-16 (1989).
7. Vedage, G. A., P. G. Himerfarb, G. W. Simmons, and K. Klier, in "Solid State Chemistry in Catalysis" Eds. R. K. Grasselli and J. F. Bradzil, ACS Symposium Series No. 279 (1985).
8. Mazanec, T. J., "On the Mechanism of Higher Alcohol Formation Over Metal Oxide Catalysts" *J. Catal.* **98**, 115 (1986).
9. Tseng, S. C., N. Jackson, and J. G. Ekerdt, "Isosynthesis Reactions of Carbon Monoxide/Hydrogen Over Zirconium Dioxide," *J. Catal.* **109**(2), 284-297 (1988),
10. Jackson, N. B. and Ekerdt, J. G., "The Surface Characteristics Required for Isosynthesis over Zirconium Dioxide and Modified Zirconium Dioxide," *J. of Catal.* **126**, 31-45 (1990).
11. Dosch, R.G., Stephens, H. P., and Stohl, F. V., SAND89-2400, Sandia National Laboratories, 1990.
12. Gajda, G. J., P. T. Barger, and C. A. Piasecki, "Syngas to Isobutylene," Proceedings of the DOE Contractors Meeting, 153-173, September, 1991.

Table 1. Properties of Isobutylene Synthesis Catalysts.

Catalyst	XRD Pattern		S.A., m ² /g		ρ_b g/cm ³
	B.R.	A.R.	B.R.	A.R.	
ZrO ₂ (ppt.)	M	M	52	35	1.88
1.6% Na-ZrO ₂ (ppt.)	M	M	58	45	2.11
3.2% Ti, 2% Th, ZrO ₂ (ppt.)	T	T/M	49	14	2.62
2% Th, ZrO ₂ (ppt)	T/M	T/M		50	1.35
1.6% Na, 10.3% Ti, ZrO ₂ (HT)	C	C	70	68	0.94
0.6% Na, 2% Ti, 2% Th, ZrO ₂ (HT)	T/M		53	50	1.08
10% Th, ZrO ₂ (HT)	M	M		57	1.58
Zr _{0.8} Si _{0.2} O ₂ (sol-gel)	T	T	73	52	1.47
0.32% K, Zr _{0.8} Si _{0.2} O ₂ (sol-gel)	T	T			1.46
0.21% Na, Zr _{0.8} Si _{0.2} O ₂ (sol-gel)	T	T			1.46
10% Cs, Zr _{0.8} Si _{0.2} O ₂ (sol-gel)	T	T		83	1.46
4.3% Ce, Zr _{0.8} Si _{0.2} O ₂ (sol-gel)	T	T		94	1.38

B.R.: After calcination at 500°C for 2.5 hours, but before reaction

A.R.: After CO/H₂ reaction

M: Monoclinic; C: Cubic; T: Tetragonal

Table 2. Intra and Inter Laboratory Reproducibility for Precipitated ZrO₂.

Comparison	Intralab		Interlab	
	CDS 900	BR#1	CDS 900	UOP ¹
T (°C)	400	400	453	450
P (atm, gauge)	69.1	69	78.6	81.7
H ₂ :CO molar ratio	1	1	1	1
Space Time ² (sec)	40.6	45	60.0	63.1
CO Conversion (%)	12.0	13.2	25.5	20.9
Isosynthesis Profile ³ (molar)	6.37	2.96	0.62	1.00
i-C ₄ ⁼ /all C ₄ 's (wt.%)	69.0	67.6	44.1	32.3
CH ₄ /all hydrocarbon (wt.%)	16.2	15.3	24.2	18.6
i-C ₄ ⁼ /all hydrocarbon (wt.%)	18.7	17.1	12.0	12.2
MeOH+DME/hydrocarbons (wt. ratio)	1.99	ND	0.0767	NA

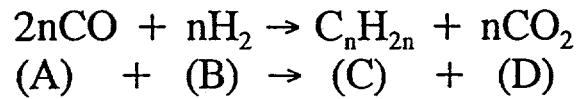
¹The UOP catalyst was prepared by precipitation from zirconyl chloride and ammonium hydroxide.

²Space time is defined as volume of catalyst divided by volumetric feed rate at reaction temperature and pressure.

³Isosynthesis profile is defined as [(moles of C₄'s)/(moles of (C₂'s + C₃'s))].

Table 3. Reactor Modeling.

Assume Predominant Reaction is:



Design Equation:

$$-\frac{dn_A}{dW} = \frac{k_p p_A^a p_B^b}{(q + s p_D)^c}$$

Stoichiometry:

$$n_A = n_A^o (1 - x)$$

$$n_B = n_A^o \left(\beta - \frac{1}{2}x \right) \quad \beta = \frac{n_B^o}{n_A^o}$$

$$n_C = \frac{1}{2n} n_A^o x$$

$$n_D = \frac{1}{2} n_A^o x$$

$$n_T = n_A^o \left[1 + \beta + x \left(\frac{1}{2n} - 1 \right) \right]$$

$$p_i = \frac{n_i}{n_T} P$$

Table 3 (cont.). Reactor Modeling.

Making Substitutions:

$$\frac{dx}{d\tau} = \frac{\rho_b RT_o P^{a+b-1} (1 + \beta) (1 - x)^a \left(\beta - \frac{1}{2}x\right)^b}{M^{a+b-c} N^c}$$

$$M = \left[1 + \beta + x \left(\frac{1}{2n} - 1 \right) \right] \quad q' = \frac{q}{k_p^{1/c}}$$

$$N = \left[q' \left(1 + \beta + x \left(\frac{1}{2n} - 1 \right) \right) + s' \frac{xP}{2} \right] \quad s' = \frac{s}{k_p^{1/c}}$$

Modeling has shown that the following values give a reasonable fit of the data.

$$a \approx 1.0$$

$$b \approx 0.5$$

$$c = 1.0$$

$$n = 4$$

$$K_{CO_2} \Rightarrow 0.25 - 0.50 \text{ for all catalysts}$$

The final form of the rate equation is:

$$r_{CO} = \frac{k_p P_{CO} P_{H_2}^{0.5}}{(1 + K_{CO_2} P_{CO_2})}$$

Table 4. Parameters for Rate Equations in CO Conversion Scatter Plot.

Catalyst	$k_p \times 10^6$ $\left(\frac{\text{mol}}{\text{kg}_{\text{cat}} \text{sec atm}^{1.5}} \right)$	$K_{CO_2} \left(\frac{1}{\text{atm}} \right)$
ZrO ₂ (ppt.)	6.30	0.279
1.6% Na, ZrO ₂ (ppt.)	8.20	0.298
1.6% Na, 10.3% Ti, ZrO ₂ (HT)	6.06	0.275

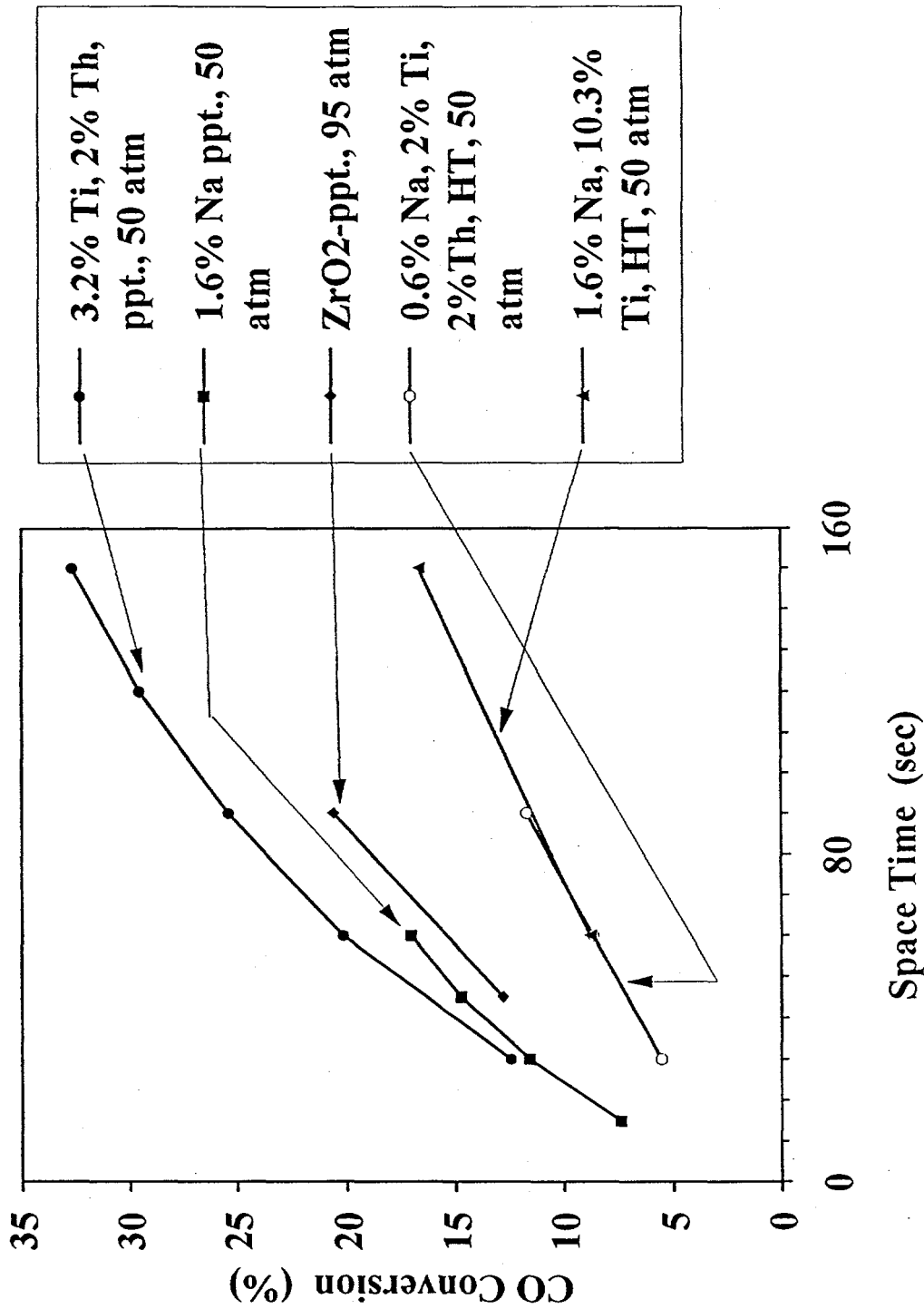


Figure 1. Catalytic Activity at 400 C and 1/1 CO/H₂ Ratio.

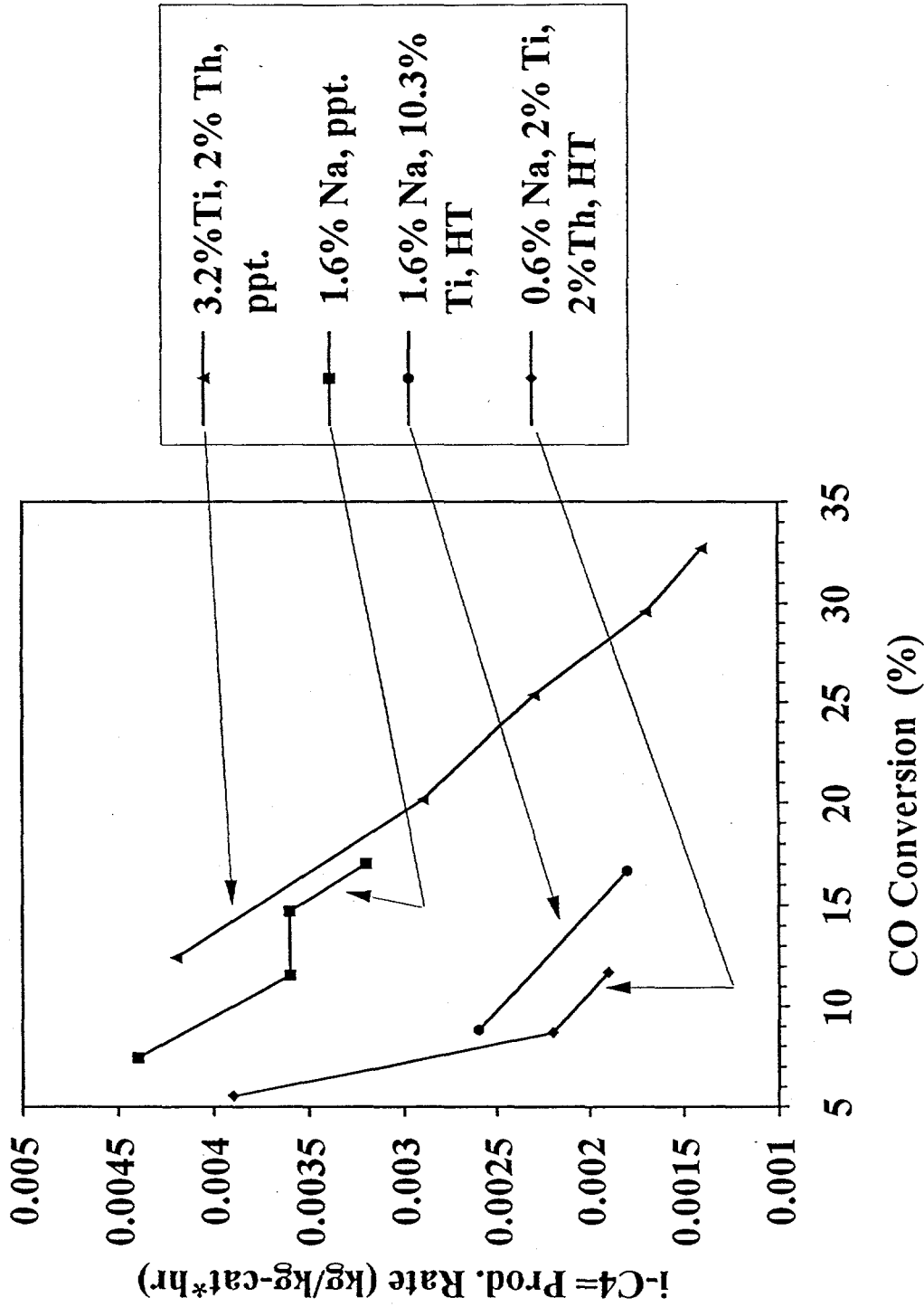


Figure 2. Isobutylene Production Rate at 400 C, 50 atm, and 1/1 CO/H₂ Ratio.

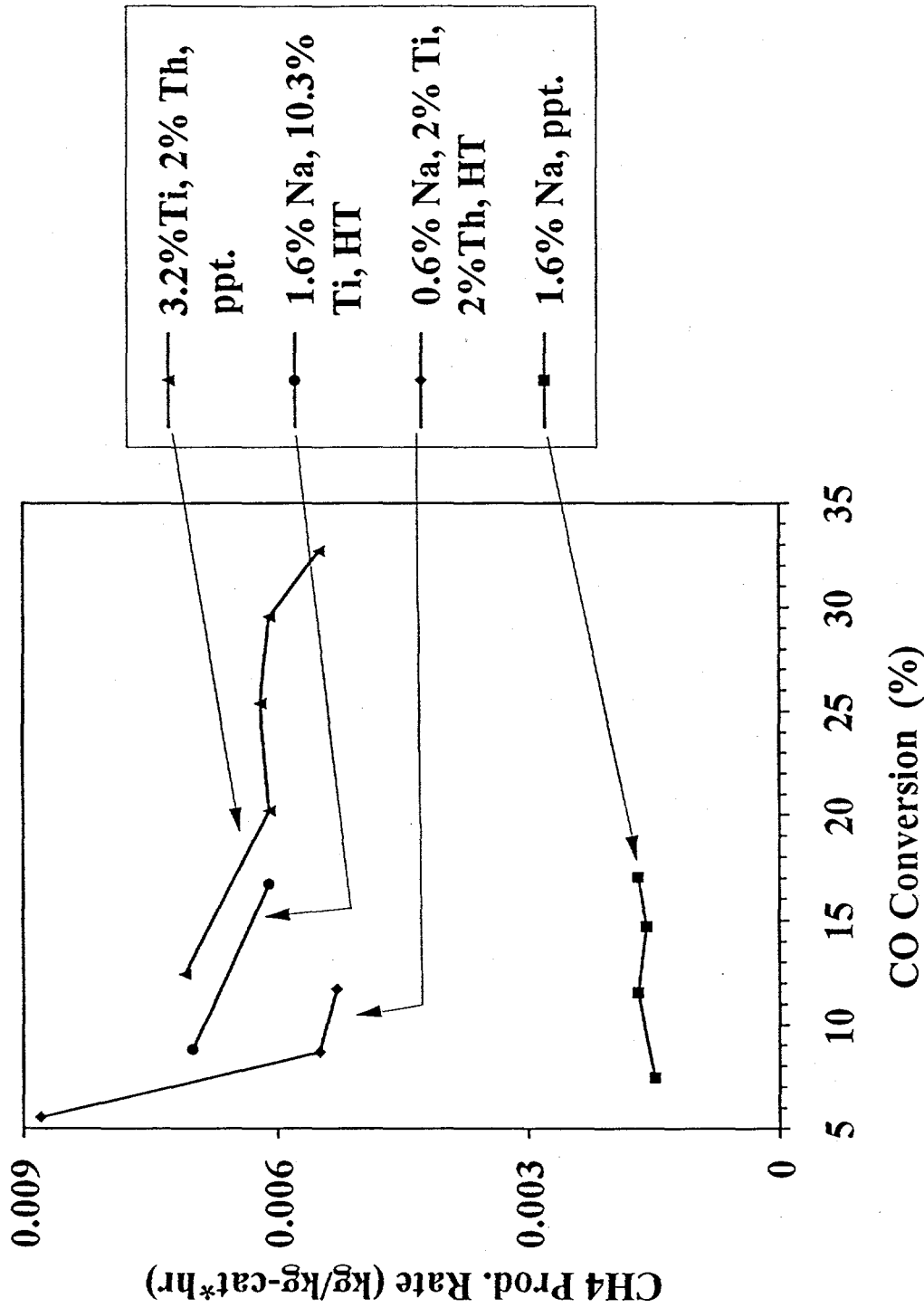


Figure 3. Methane Production Rate at 400 C, 50 atm, and 1/1 CO/H₂ Ratio.

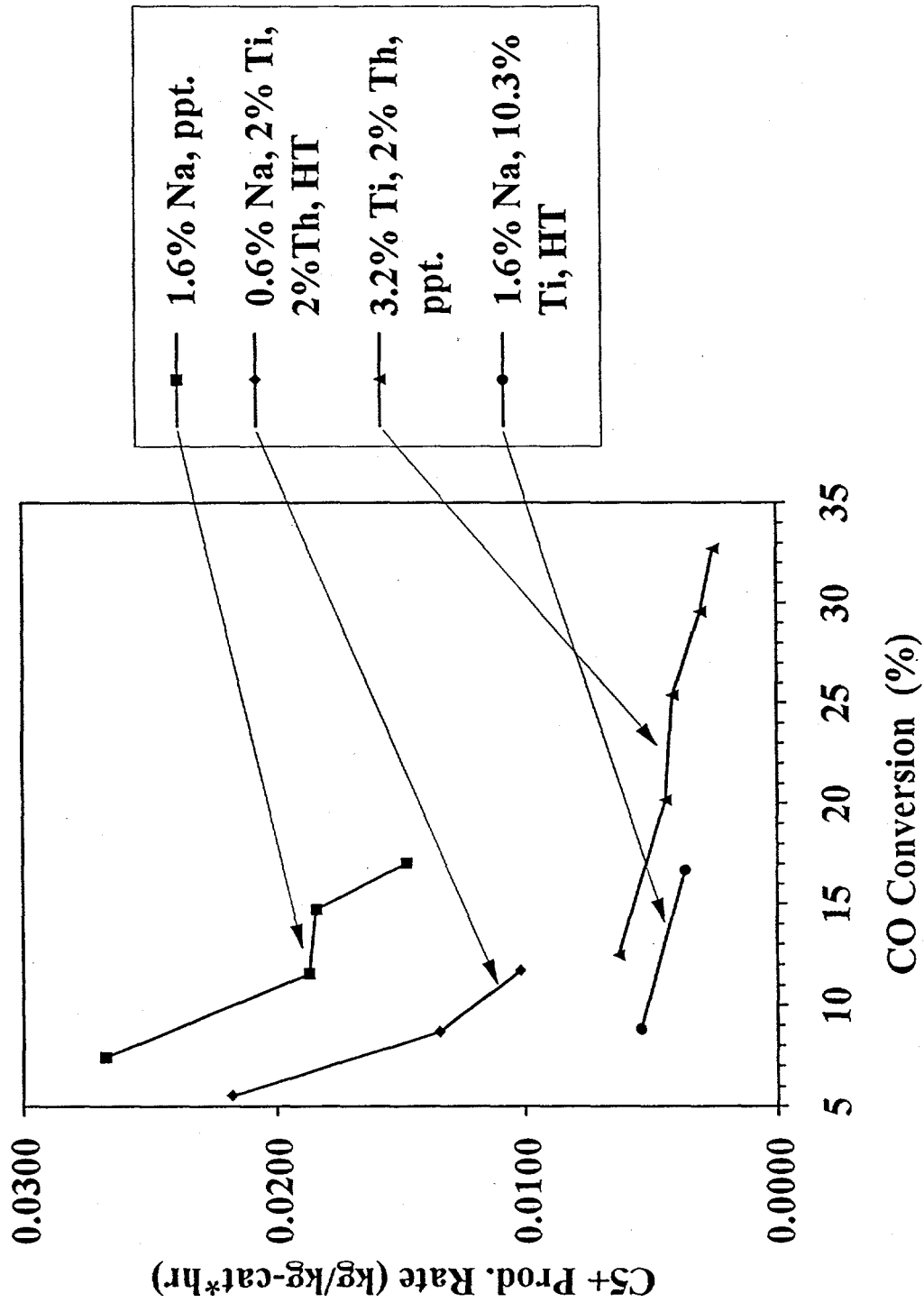


Figure 4. C5+ Production Rate at 400 C, 50 atm, and 1/1 CO/H₂ Ratio.

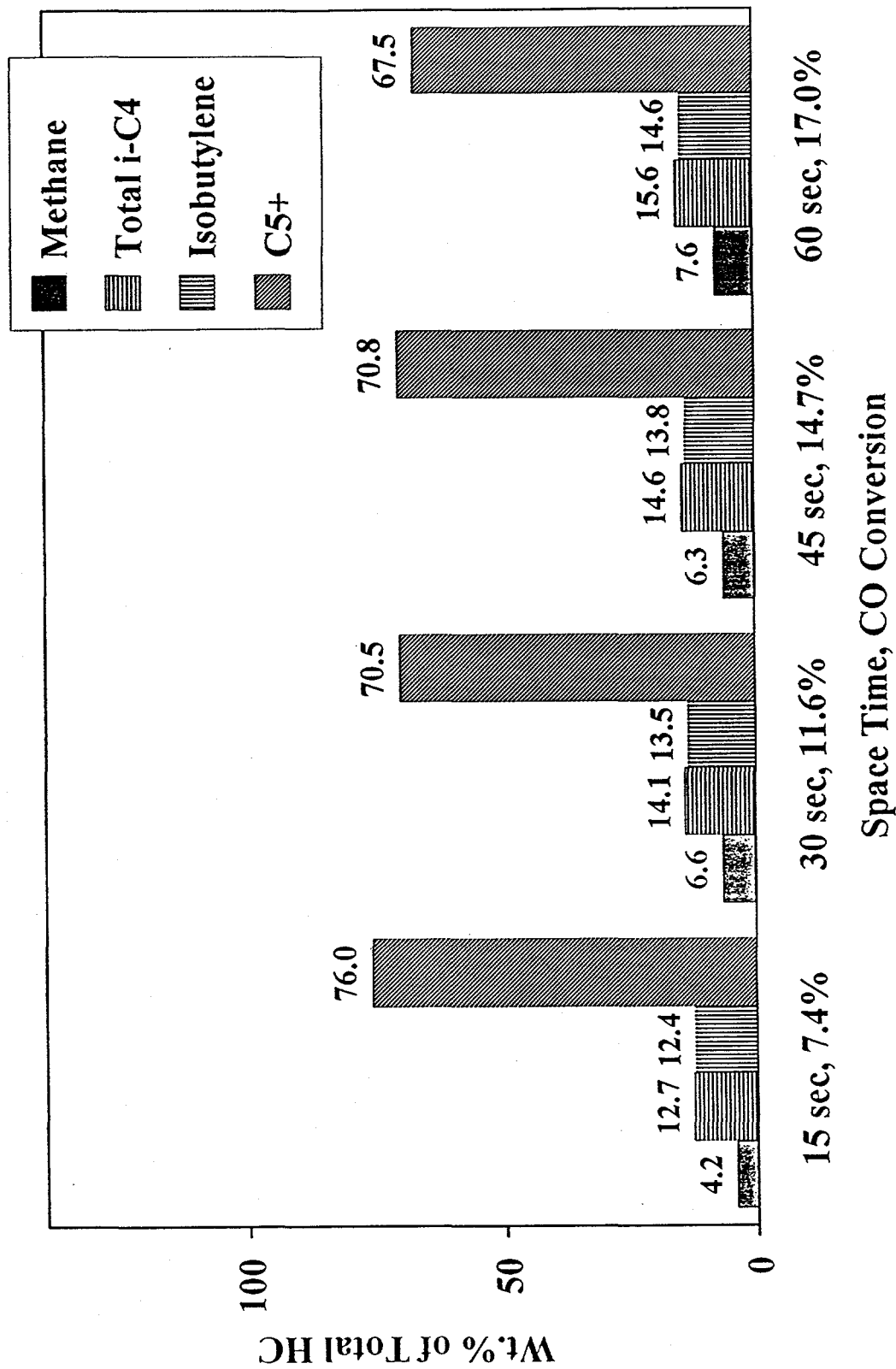


Figure 5. Changes in Hydrocarbon Distribution with Space Time at 400 C, 50 atm, and 1/1 CO/H₂ Ratio over 1.6% Na, ZrO₂ (ppt.)

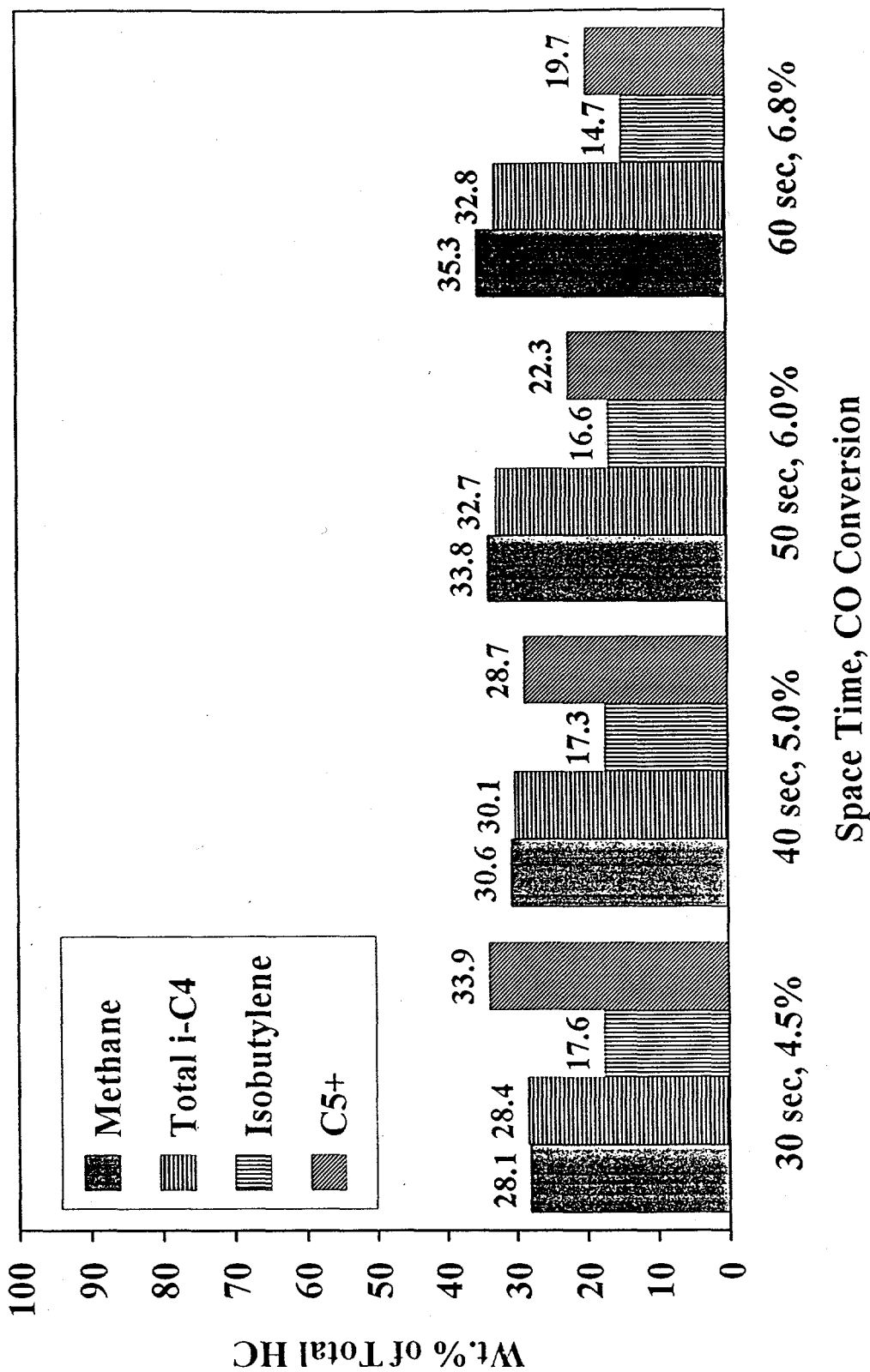


Figure 6. Changes in Hydrocarbon Distribution with Space Time at 400 C, 21 atm, and 1/1 CO/H₂ Ratio over 1.6% Na, 10.3% Ti, ZrO₂ (HT).

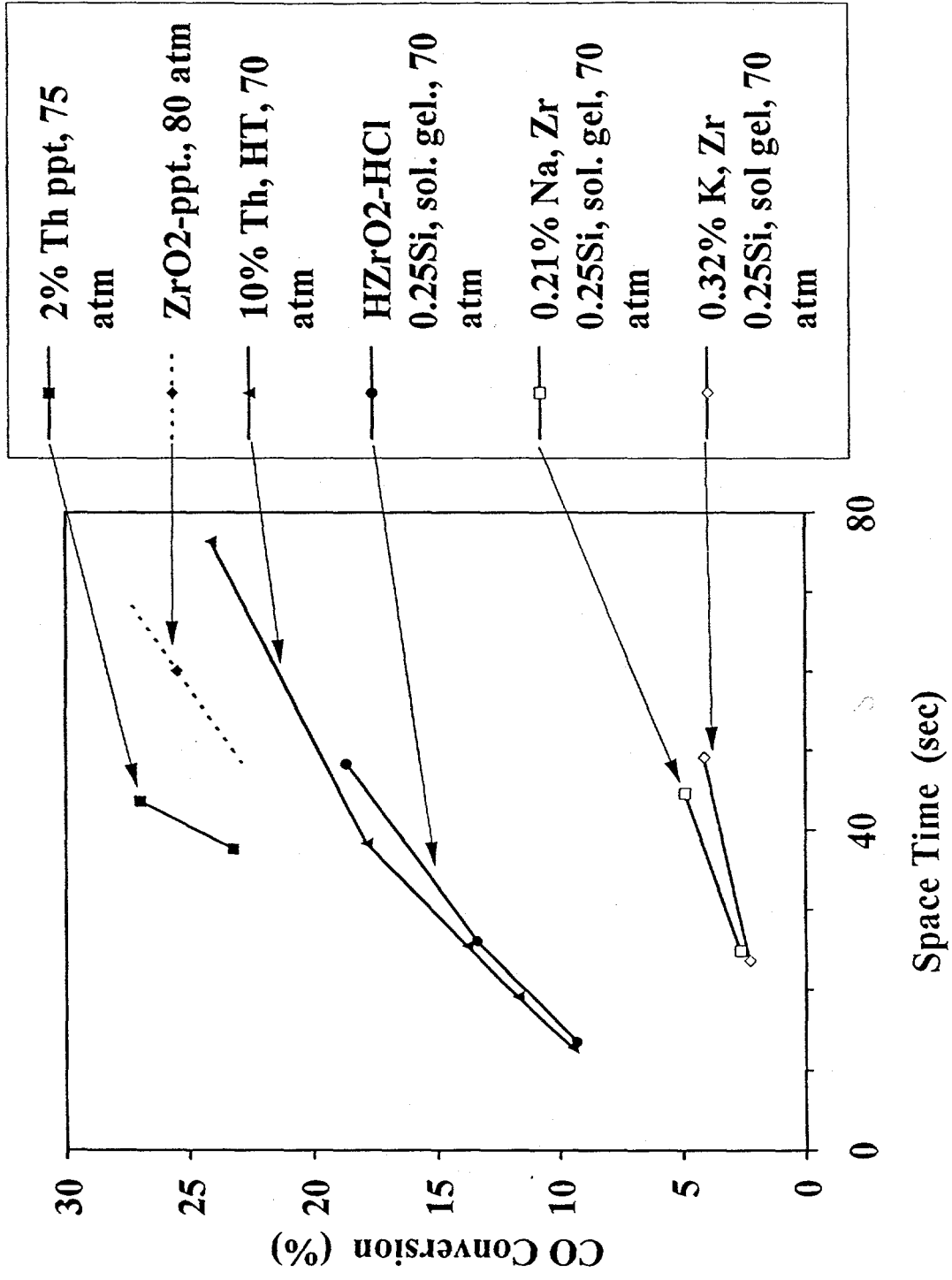


Figure 7. Catalytic Activity at 450 C and 1/1 CO/H₂ Ratio.

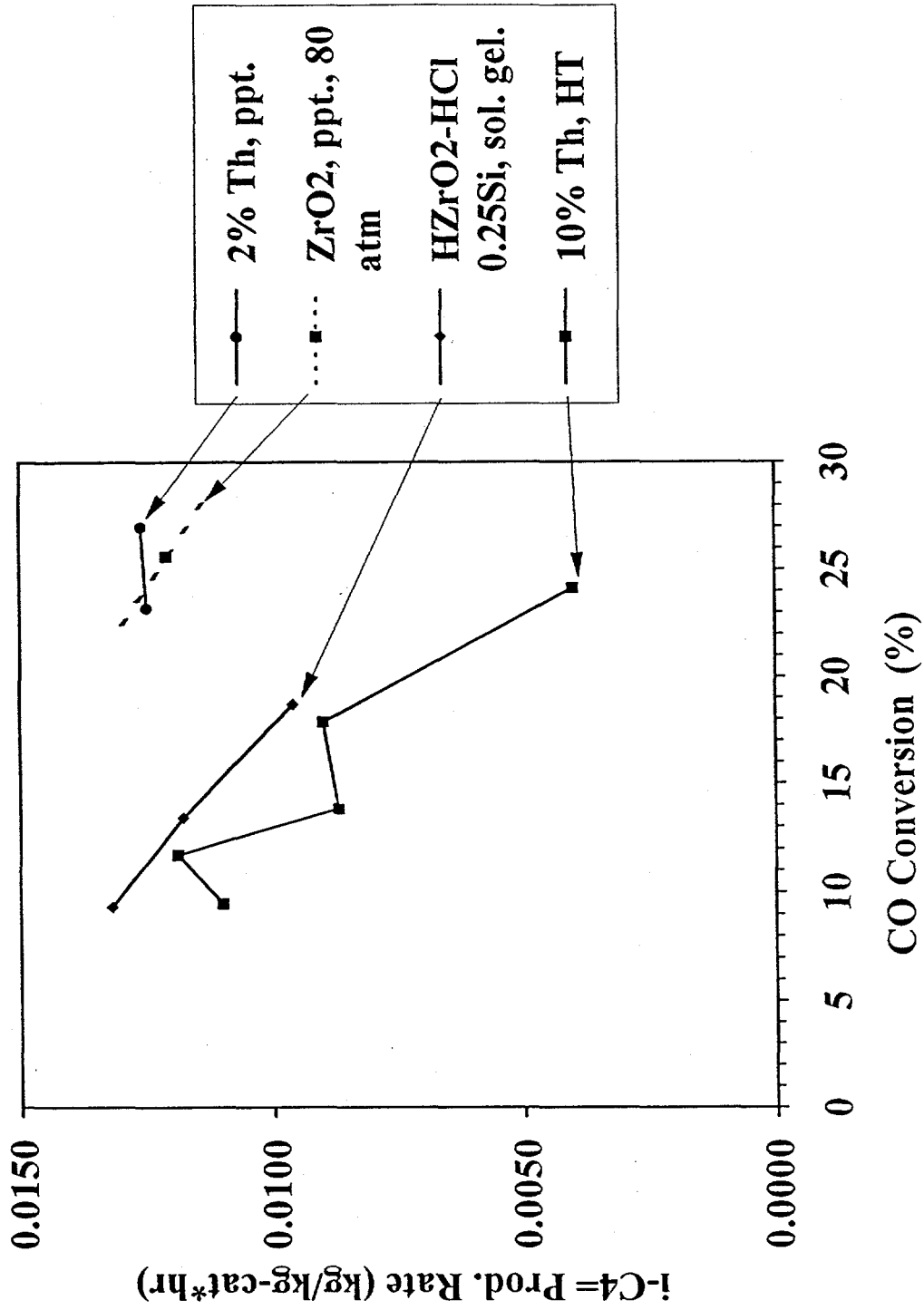


Figure 8. Isobutylene Production Rate at 450 C, 70 atm, and 1/1 CO/H₂ Ratio.

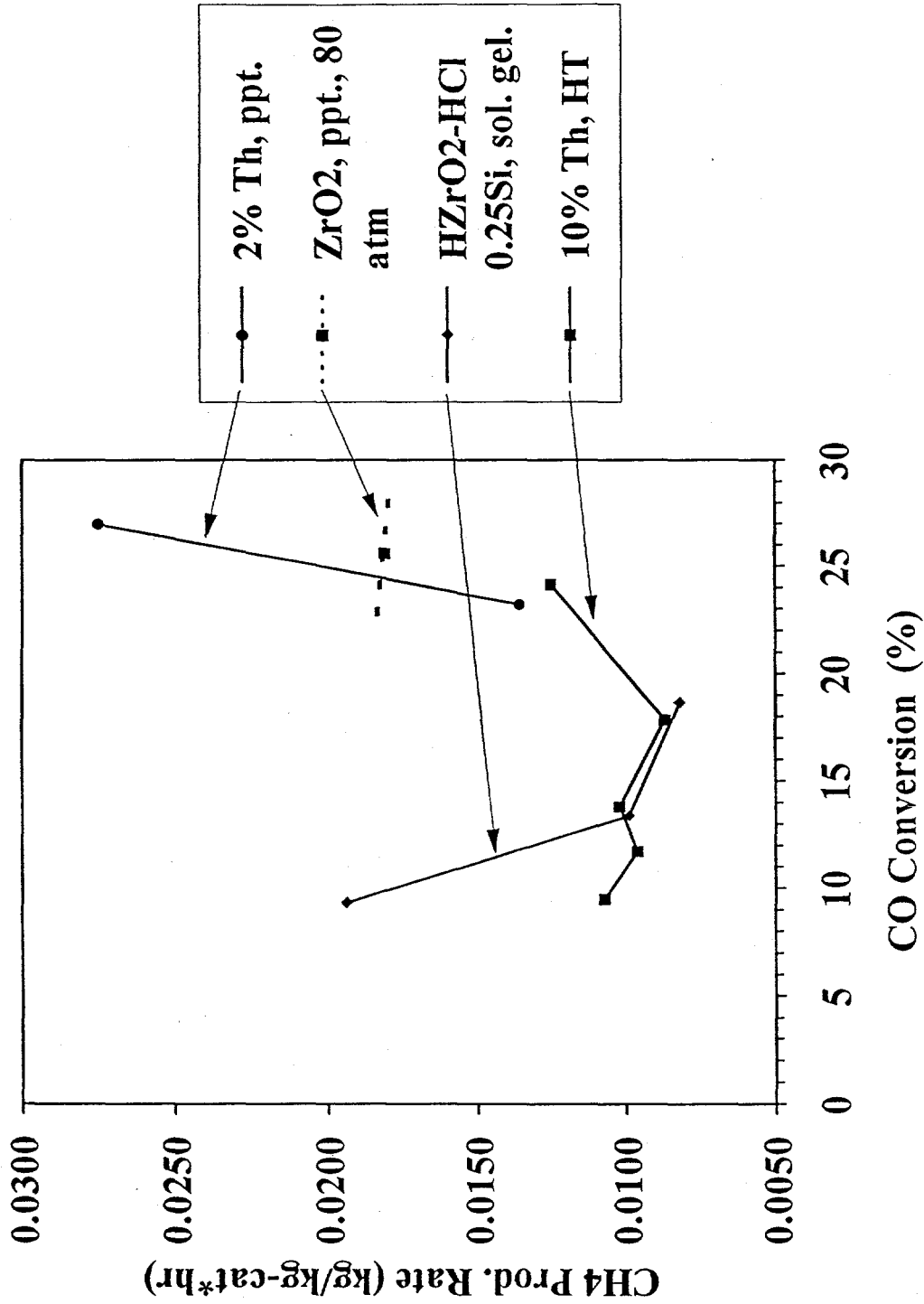


Figure 9. Methane Production Rate at 450 C, 70 atm, and 1/1 CO/H₂ Ratio.

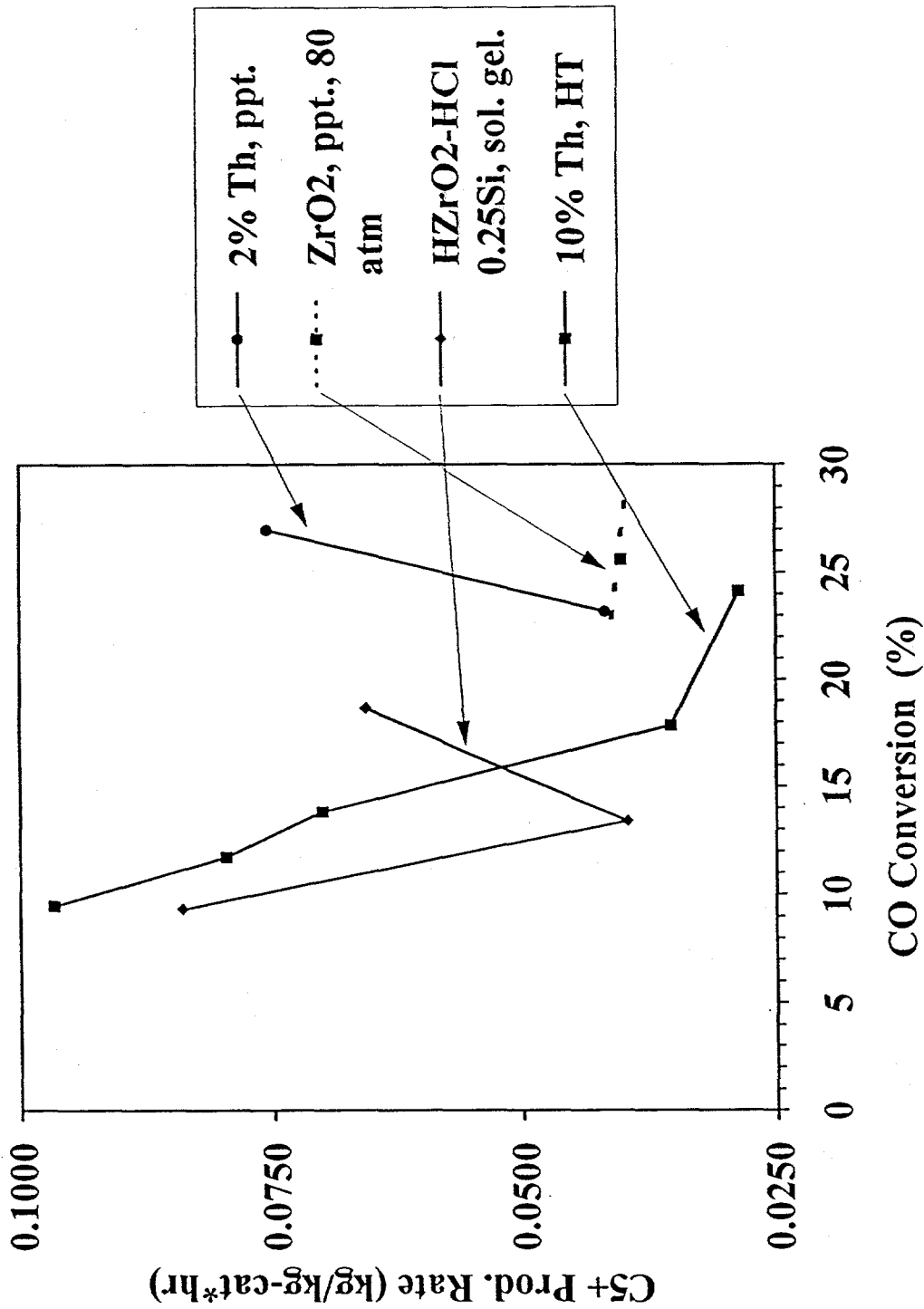


Figure 10. C5+ Production Rate at 450 C, 70 atm, and 1/1 CO/H₂ Ratio.

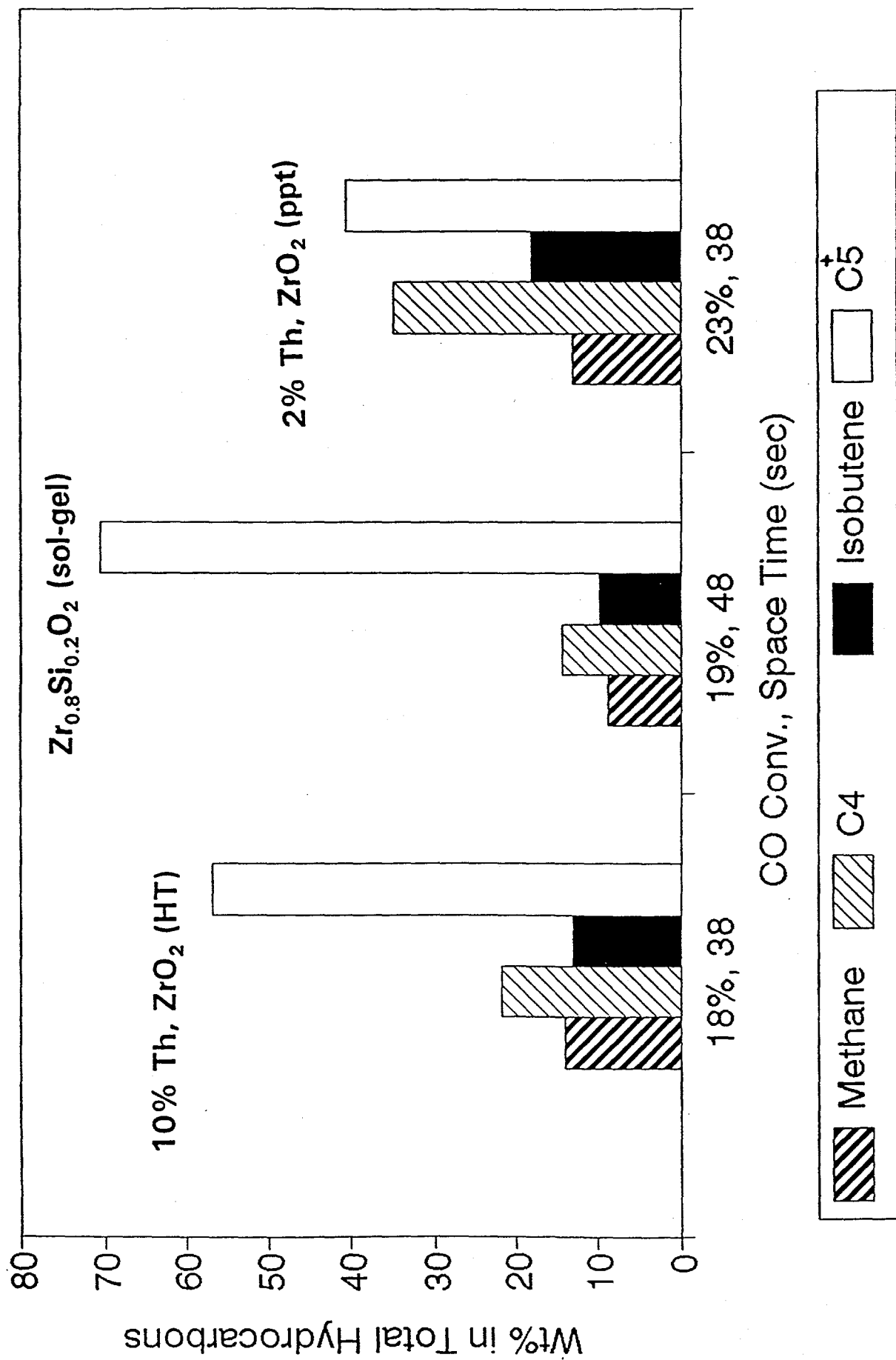


Figure 11. Product Distribution for Different Catalysts at 450 °C and 70 atm.

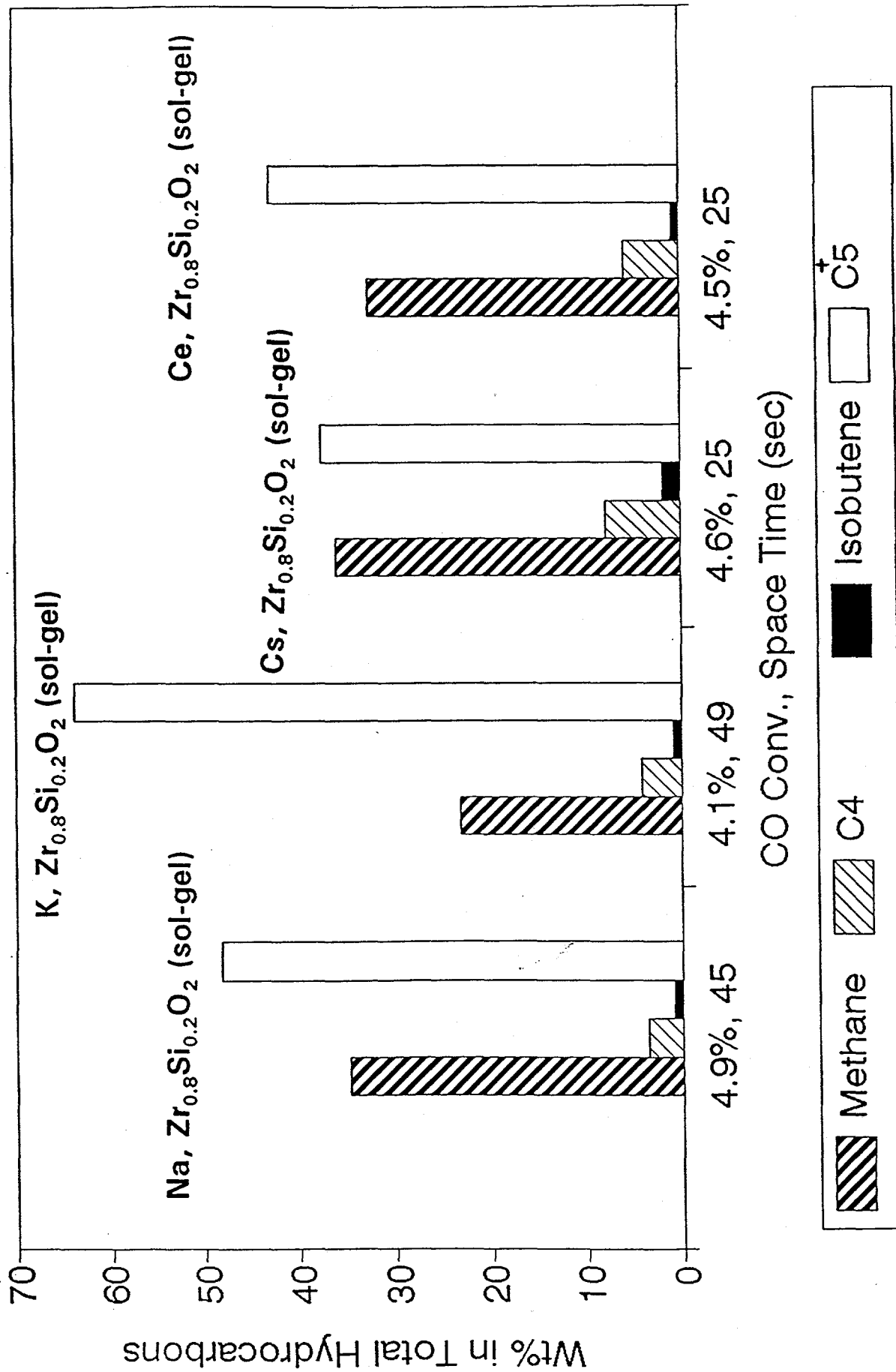


Figure 12. Comparison of Sol-Gel Zirconias

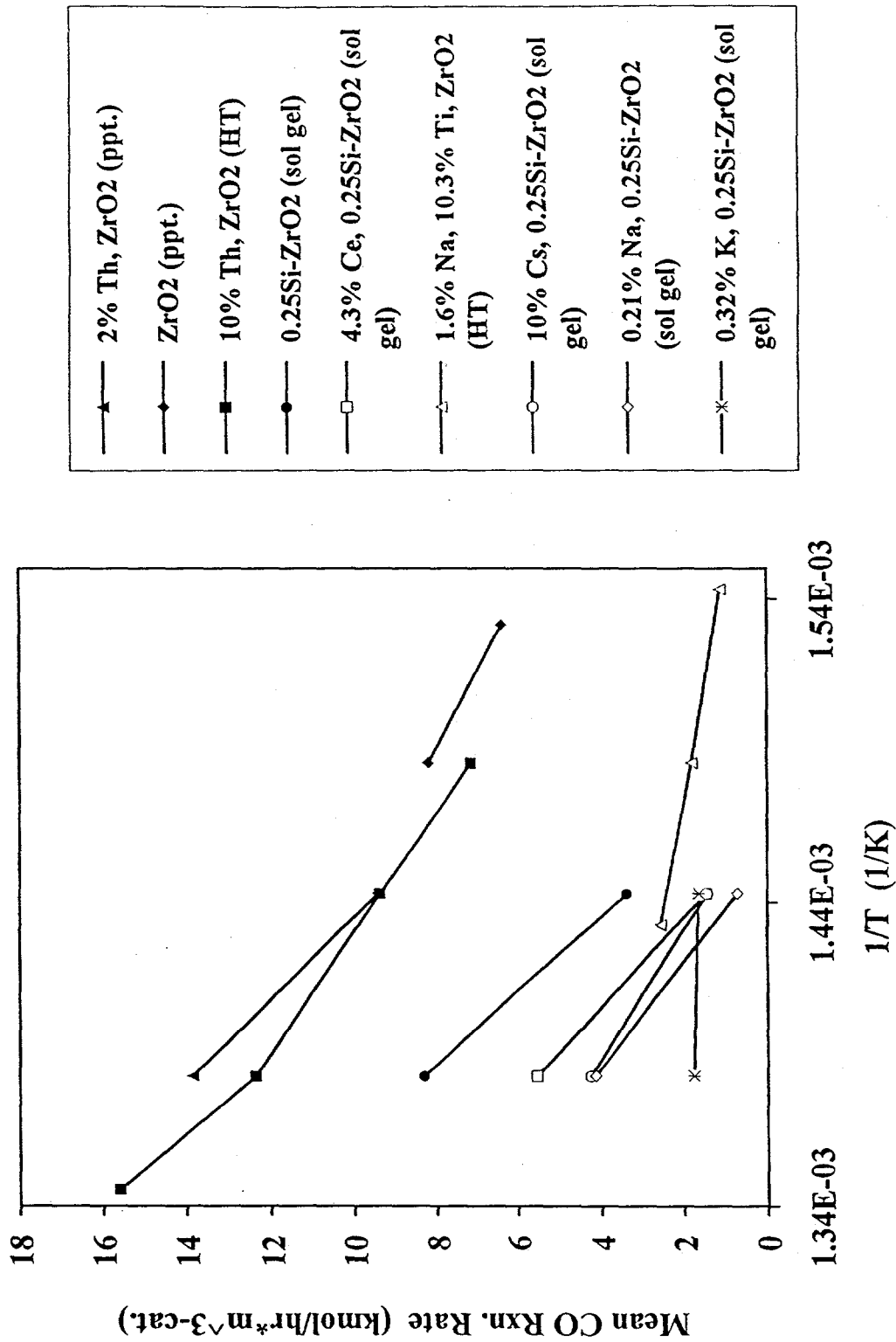


Figure 13. Effect of Temperature on Reaction Rate.

● Activity Based on CO Conversion

2% Th, ZrO₂ (ppt) ≈ 3.2% Ti, 2% Th, ZrO₂ (ppt) > 1.6% Na, ZrO₂ (ppt) > ZrO₂ (ppt) > 10% Th, ZrO₂ (HT)

● Methane Production Rate

3.2% Ti, 2% Th, ZrO₂ (ppt) ≈ 10% Th, ZrO₂ (HT) > 2% Th, ZrO₂ (ppt) > ZrO₂ (ppt) > 1.6% Na, ZrO₂ (ppt)

● Isobutylene Production Rate

2% Th, ZrO₂ (ppt) > ZrO₂ (ppt) ≈ 10% Th, ZrO₂ (HT) > 3.2% Ti, 2% Th, ZrO₂ (ppt) > 1.6% Na, ZrO₂ (ppt)

● C₅⁺ Production Rate

2% Th, ZrO₂ (ppt) ≈ 10% Th, ZrO₂ (HT) > 1.6% Na, ZrO₂ (ppt) > ZrO₂ (ppt) > 3.2% Ti, 2% Th, ZrO₂ (ppt)

Figure 14. Overall Ranking of Catalysts Tested.

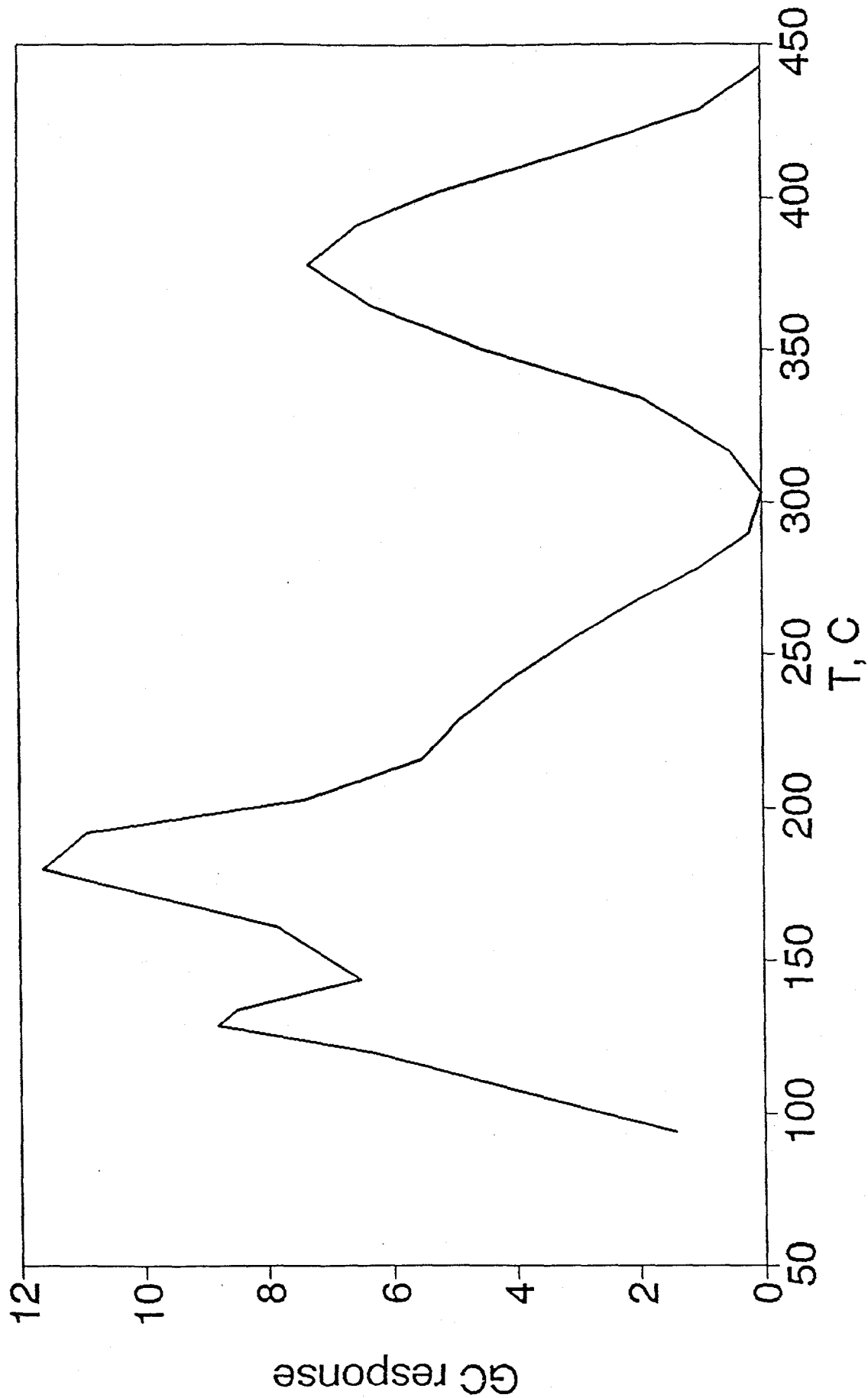


Figure 15. TPD of CO₂ on 2% Th/ZrO₂ (ppt). 75 °C to 450 °C at 5 °C/min.

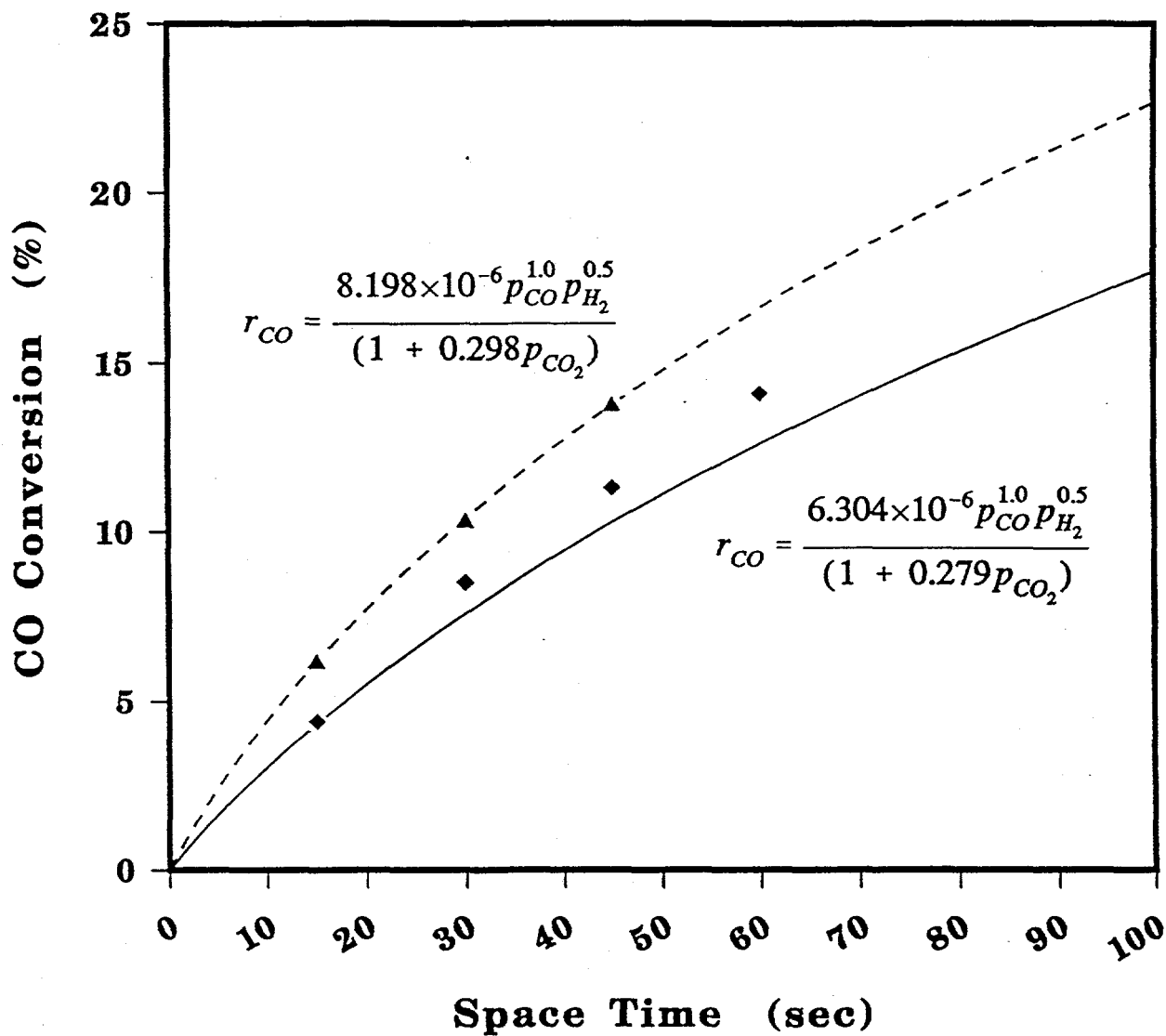


Figure 16. Simulation of 1.6% Na (▲) and ZrO₂ (◆) at 400 °C, 95 atm and 2/1 CO/H₂. Rate is mol/sec*kg_{cat}.

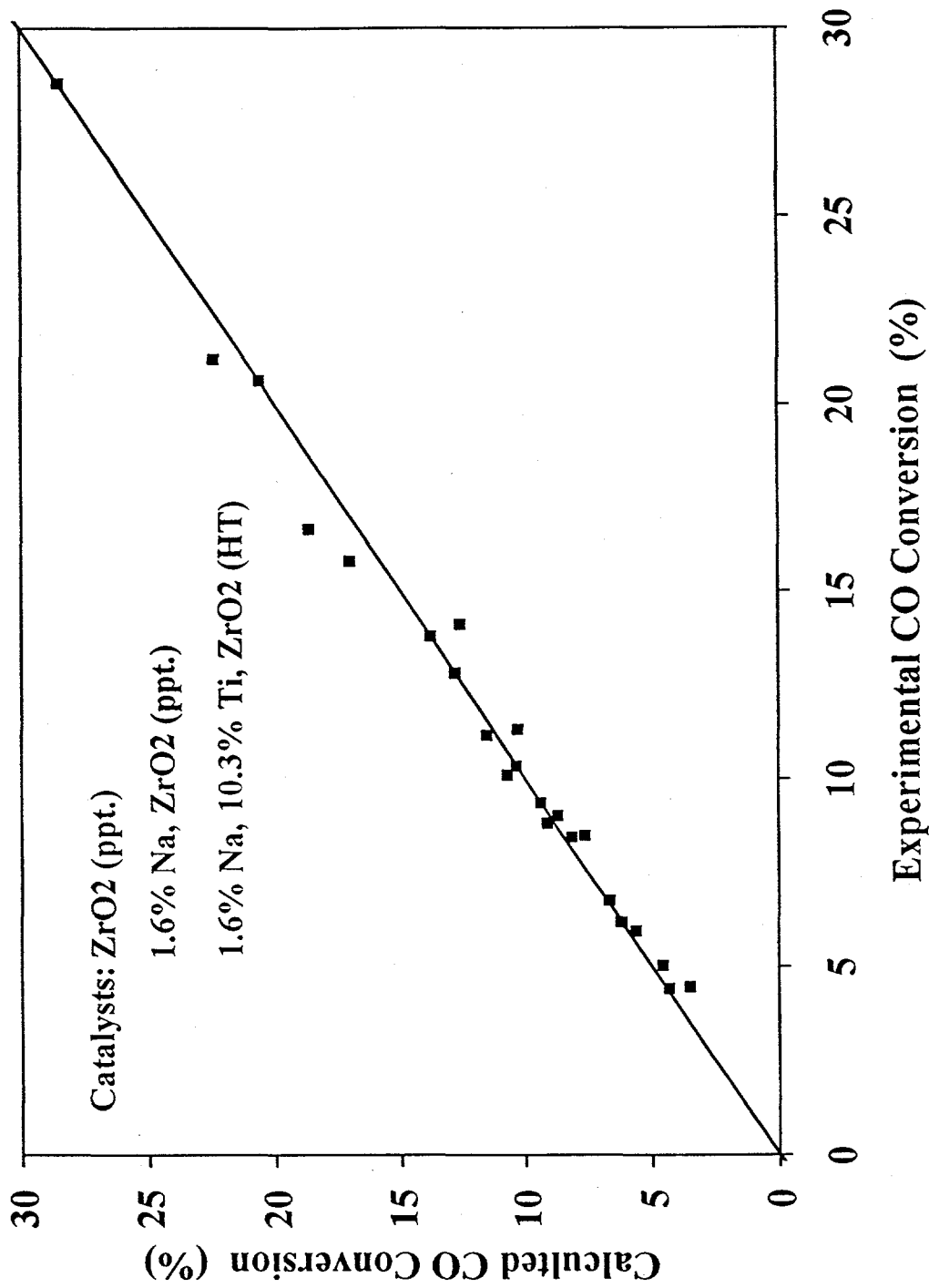


Figure 17. Comparison of Experimental Conversion and Conversion Calculated Using the Rate Equation and SimuSolv.

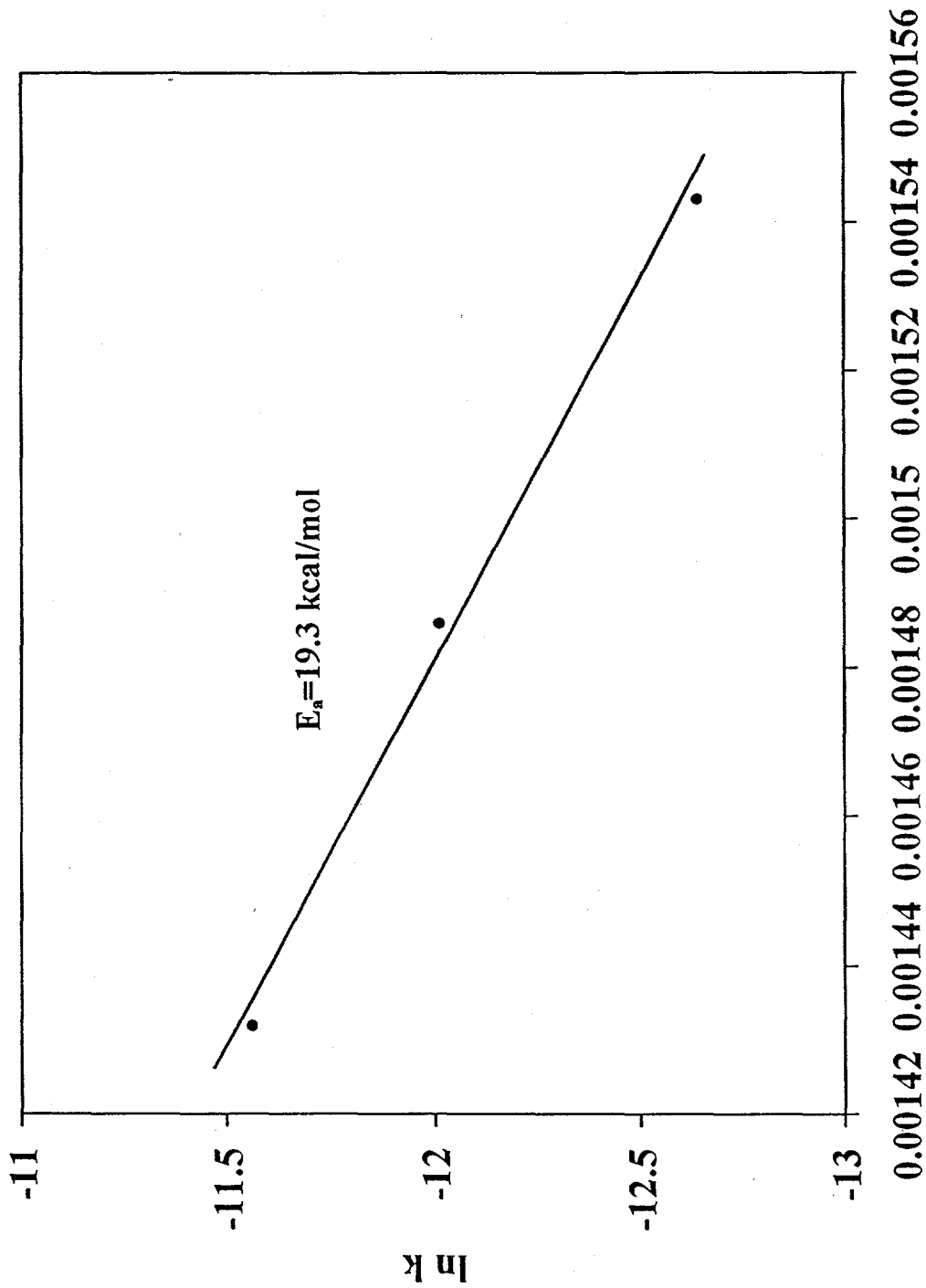


Figure 18. Determination of Activation Energy Using SimuSolv Rate Constants for 1.6% Na, 10.3% Ti, ZrO₂ (HT).

1. $\text{H}_2 + 2\text{ZrO} \rightleftharpoons 2\text{ZrOH}$
2. $\text{CO} + \text{ZrO} \rightleftharpoons \text{ZrOCO}$
3. $\text{ZrOCO} + \text{ZrOH} \rightleftharpoons \text{ZrOCHO} + \text{ZrO}$
4. $2\text{ZrOCHO} \rightleftharpoons \text{CO}_2 + \text{ZrOCH}_2 + \text{ZrO}$

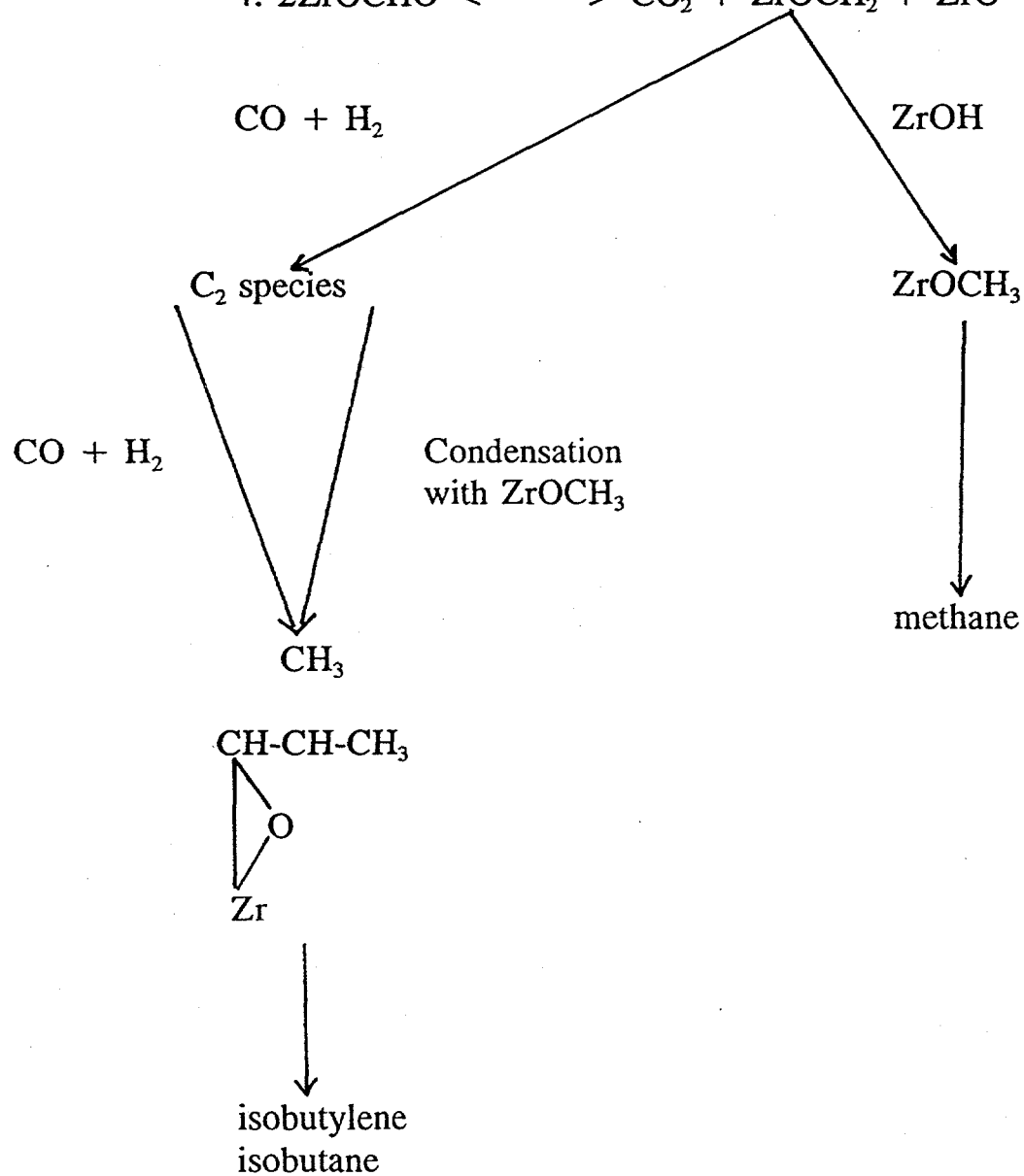


Figure 19. Mechanism for Isobutylene Synthesis.

$T = 425 \text{ C} / P = 50 \text{ atm} / (CO/H_2) = 1 / (CO) \text{ conversion} = 4.8 \%$
 space velocity = 1006 h / space time = 70 s
 catalyst prepared by sol-gel process

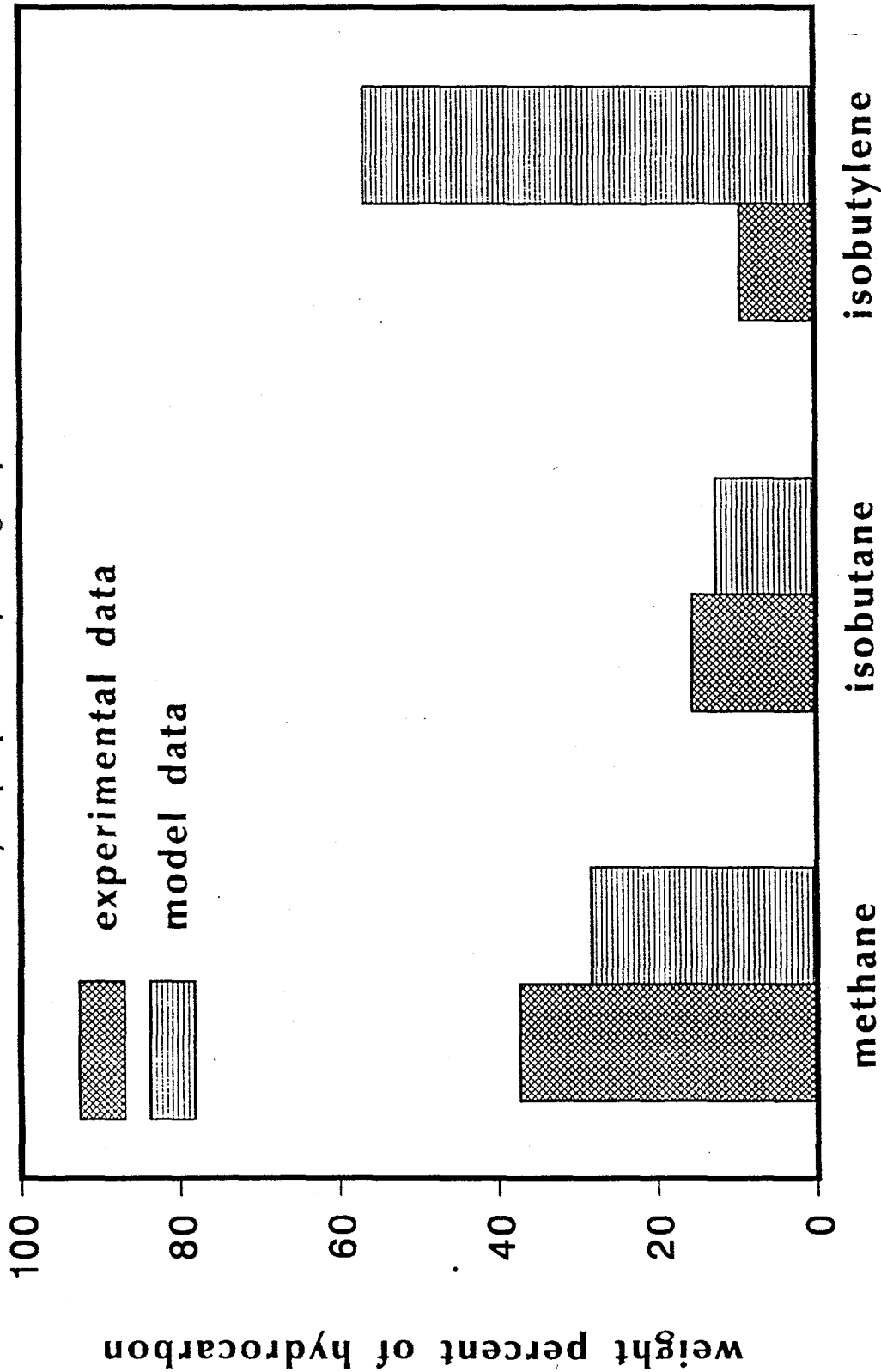


Figure 20. Comparison of Experimental and Microkinetic Model Hydrocarbon Distributions.

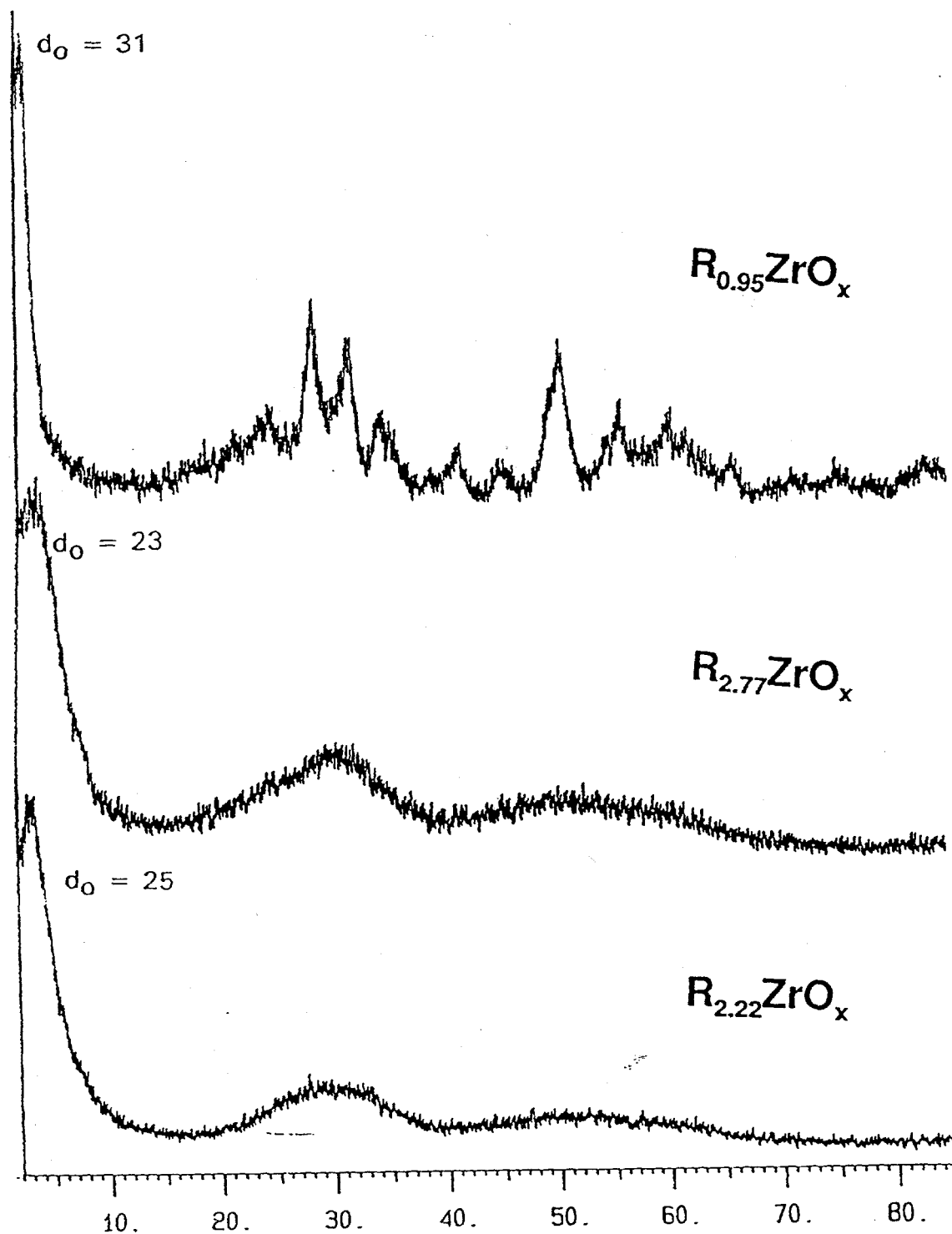


Figure 21. Alkyl-Amine Zirconate with Amorphous and Monoclinic Phases.

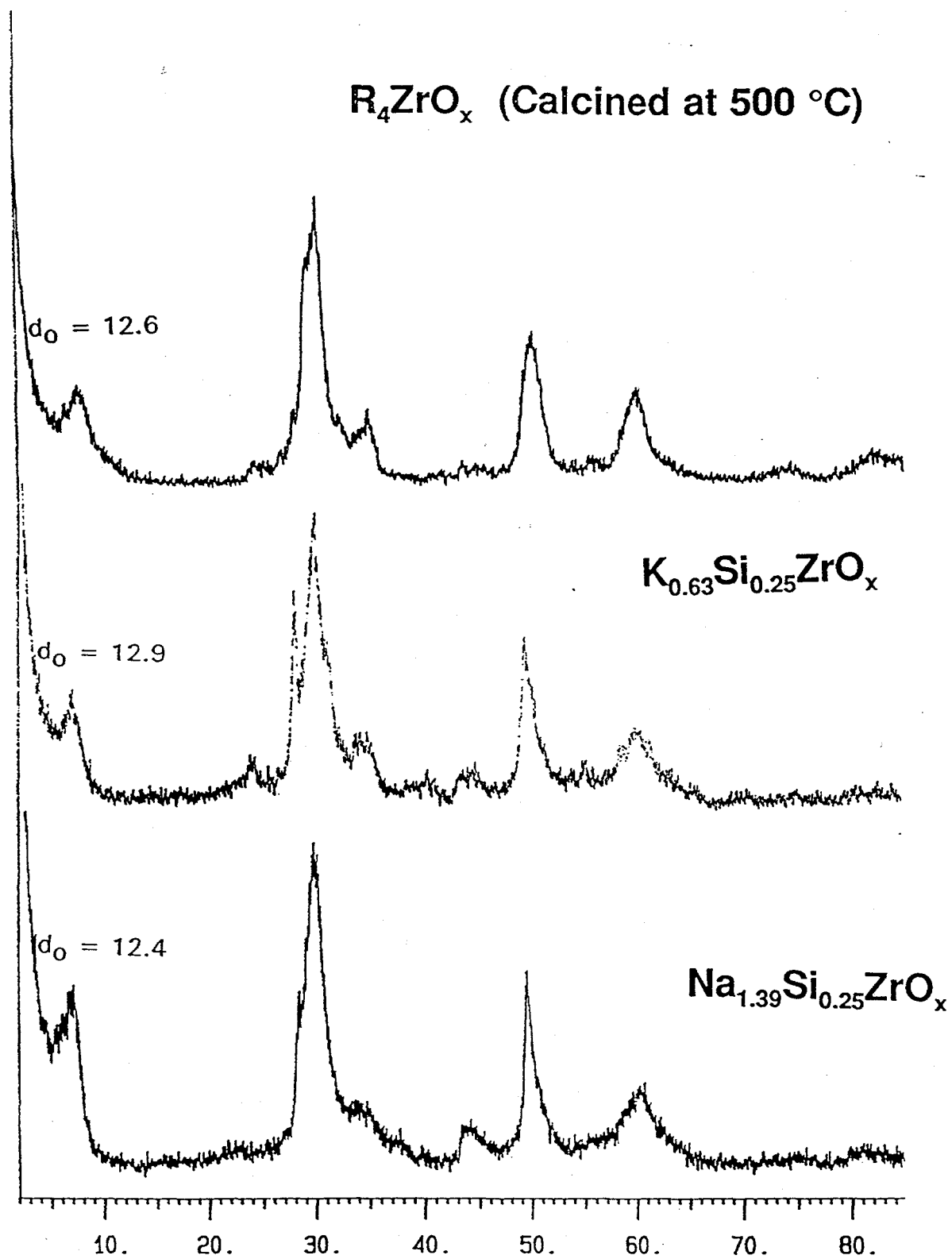


Figure 22. Alkali Silico-Zirconate with Tetragonal Zirconia Prepared by Hydrothermal Synthesis.

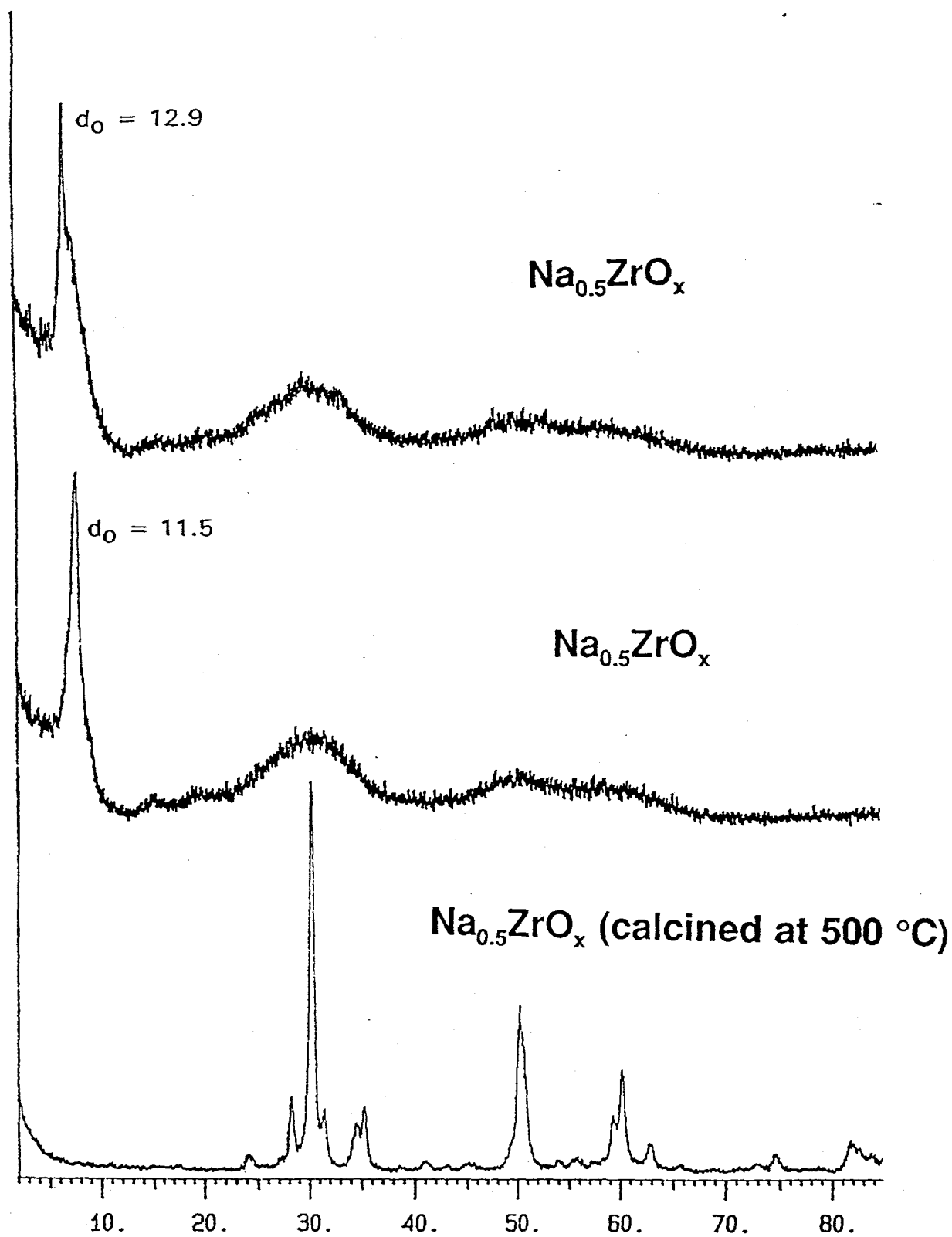


Figure 23. Comparison of a Alkali Zirconate As Prepared Amorphous Sample with a Calcined Sample.