CATALYSTS AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

by

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ABSTRACT

Trickle bed reactor experiments using precipitated and commercial zirconia resulted in the production of more C_2-C_5 hydrocarbons than the fixed bed gas phase reactor when using a hydrogen to CO ratio of 1. Because of problems associated with solvent cracking the reactor temperature for the trickle bed was limited to 400 °C, whereas temperatures up to 450 °C had been used for the fixed bed reactors.

Co-feeding H_2S with the synthesis gas resulted in reduction of C_1 to C_3 production rates, an increase in C_5 production and an increase in the production of 3-methyl-1-butene. Zirconia prepared with Ce resulted in a highly active and selective catalyst with isobutylene production rates of 4 to 8.5 kg/(m^3 cat. h) for CO conversions of 15 to 34%.

Kinetic models necessary for reactor design are first order for CO and one half order for hydrogen, indicating the dissociation of hydrogen on the catalyst surface. Carbon dioxide was found to be the most abundant specie on the surface of the catalyst and retards the rate of reaction. A modification of the Anderson Schultz Flory distribution resulted in an empirical procedure for estimating product distributions.

INTRODUCTION

Zirconia and thoria are generally recognized as being the most selective catalysts for the synthesis of isoalkenes and isoalkanes from synthesis gas (1-11). Thoria is the most active and selective of the two catalysts, but because it is an alpha emitter, it is desired to develop non radioactive catalytic materials. This study has focused on the use of additives and different methods of preparation to increase the catalytic activities and selectivities for producing isobutylene. We have also examined the effect of reactor type on the selectivity and activity of a commercial zirconia.

Stoichiometry, kinetics and thermodynamics of isosynthesis limits the maximum yield of isobutylene. Only 7 g of hydrocarbon per 28 g (1 mole) of CO consumed is theoretically feasible when the oxygen is rejected on CO_2. The stoichiometry limit is readily observed by examining the following stoichiometric equations.

- Paraffins: $2nCO + (n+1)H_2 \text{-->} C_nH_{2n+2} + nCO_2$

  $nCO + (2n+1)H_2 \text{-->} C_nH_{2n+2} + nH_2O$
- Olefins: $2nCO + nH_2 \text{-->} C_nH_{2n} + nCO_2$

  $nCO + 2nH_2 \text{-->} C_nH_{2n} + nH_2O$
- Alcohols: $(2n-1)CO + (n+1)H_2 \text{-->} C_nH_{2n+1}OH + (n-1)CO_2$

  $nCO + 2nH_2 \text{-->} C_nH_{2n+1}OH + (n-1)H_2O$
- Water-Gas Shift: $CO + H_2O \text{<-->} CO_2 + H_2$
- Dimethyl Ether: $3CO + 3H_2 \text{-->} CH_3OCH_3 + CO_2$

Since one desires an excellent water gas shift reaction, the majority of the oxygen in CO will be rejected as carbon dioxide, even when one considers that the water gas shift reaction is probably in equilibrium. The kinetic and thermodynamic limit is inherent in the fact that isosynthesis involves chain growth and condensation reactions. Therefore, even though a higher limit of isobutylene is produced relative to Fischer-Tropsch synthesis, once isobutylene is produced the catalyst has the capacity to promote the chain growth to the C_5s and higher molecular weight olefins. Equilibrium calculations with only the CO, hydrogen, ethylene, propylene, isobutylene and 2-methyl-2-butene yield an equilibrium distribution of 1.73 wt.% ethylene, 15.6 wt.% propylene, 30.79 wt.% isobutylene and 51.89 wt.% 2-methyl-2-butene for a reaction temperature and pressure of 700 K and 7 MPa, respectively.

Equilibrium conversion of CO for the system is 98.9% with equilibrium carbon conversion to each of the olefins is 1.71%, 15.43%, 30.45%, and 51.31%, respectively. When normalized to 100 moles of CO, converted carbon conversions are the same as weight percents of the hydrocarbon distribution. The thermodynamic limit of isobutylene production with no paraffin production is 2.1553 grams of isobutylene produced per 28 g (1 mole) of CO consumed. Because isobutylene is formed by a combination of chain growth and condensation reactions, a yield greater than 2.1553 g/mole of CO consumed is feasible, and might be obtained at low CO conversions. But at high CO conversions the thermodynamic limits will be approached, and at higher conversions more paraffins will be produced, because they are more favorable thermodynamically than the olefins.

Rate equations for use in reactor design have been developed using classical techniques (12), i.e. by the use of a plug flow reactor model and curve-fitting techniques. A Hougen-Watson-

Langmuir-Henselwood rate equation first order in CO, half order in hydrogen and retardation of CO_2 was found to fit the data over all of the catalysts evaluated. The kinetics for the Anderson Schulz Flory distribution were modified to allow for condensation reactions to obtain a complete model for use in reactor design.

CATALYSTS SYNTHESIS

Zirconia has been prepared by precipitation with ammonium hydroxide or sodium hydroxide using zirconyl nitrate and by a modified sol gel method (13). Several other methods were investigated but the catalytic activities were low relative to the "precipitated and hydrogel" catalysts. The precipitation and sol gel procedures were used to prepare a series of catalysts with dopants to explore their effect on the catalysts' activities and selectivities. Catalysts prepared by these procedures are listed in Table 1. One might note that the catalysts prepared by sol gel were all tetragonal and the surface area changed very little before and after reaction. The reasons the catalyst prepared by precipitation had such large changes in surface areas are unknown.

Table 1. Properties of Isobutylene Synthesis Catalysts.

Catalyst	XRD Pattern		S.A., m^2/g		ρ_b
	B.R.	A.R.	B.R.	A.R.	g/cm^3
ZrO_2 (ppt)†	C/M	C/M	89	n/a	2.14
ZrO_2 (comm)	M	M	27	25	1.98
ZrO_2 (sol gel)	T	T	24	24	2.11
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
7% Ce, ZrO_2 (ppt)†	C	C	98	49	2.28
0.5% K, ZrO_2 (sol gel)	T	T	32	29	2.30
0.5% Ca, ZrO_2 (sol gel)	T	T	26	25	2.32

B.R.: After calcination at 500°C († 450 °C) for 2.5 hours, but before reaction;
A.R.: After CO/H_2 reaction;
M: Monoclinic; C: Cubic; T: Tetragonal.

EXPERIMENTAL UNITS USED FOR CATALYST EVALUATION

Three bench scale units, two of which were operated as gas-phase fixed bed reactors and one as a trickle bed reactor, with on-line analysis were used for evaluation of the catalysts. Intralaboratory and interlaboratory reproducibility was illustrated in last year's meeting (14,15). Similar results were obtained from all three units when operated as gas phase fixed bed reactors. Only one of the units could be operated as a trickle bed reactor, and a schematic of the trickle bed and slurry reactor system is presented in Figure 1.

For the trickle bed reactor, decalin was used as the solvent since no decomposition of the solvent was observed when hydrogen and decalin were passed over the catalyst. Alkane solvents were found to be unacceptable because zirconia catalyzed their decomposition presumably by hydrocracking and cracking reactions.

RESULTS AND DISCUSSION

Trickle Bed Reactor:

Figures 2 and 3 illustrate the product distributions obtained when using a trickle bed and a fixed bed reactor operated at 396 °C. The major effect of using a trickle bed reactor is the increase in conversion of CO to C_3 compared to conversion to C_4s and C_5s. Figure 3 indicates the decrease in isobutylene selectivity. Figure 4 illustrates the decline in CO conversions with increasing oil flow rate at a constant gas flow rate. Figure 5 shows that as oil flow rate increases propylene decreases and C_4s and C_5s production increases. In addition to the resistance to mass transfer from the gas to the liquid and possibly interparticle and intraparticle resistances to diffusion, an accumulation of water droplets was observed in the recycle oil. In the fixed bed gas phase reactors no water in the gas stream was detected by the gas chromatographs. If one desires to increase the propylene content of the hydrocarbon stream the use of a trickle bed reactor might be attractive.

Catalyst Synthesis and Evaluation Using Fixed Bed Reactors:

Three primary methods have been used to prepare zirconia and zirconia doped catalysts. These have been precipitation/coprecipitation using zirconyl nitrate, a modified sol gel method using the alkoxides, and hydrothermal synthesis.

Hydrothermal synthesis was used in an attempt to produce a zirconate which might have a higher activity than the zirconias. Several zirconates were produced, but they were unstable and converted to cubic zirconias on calcination. These zirconias were not as active as the zirconias prepared by the sol gel and precipitation methods, therefore, the work on hydrothermal synthesis was discontinued.

Catalysts prepared by the three different methods produced zirconia with monoclinic, tetragonal and cubic zirconias. The pH of the solution after precipitation as well as the dopant appeared to control the type of structure obtained. However, the catalysts prepared by the sol gel procedure were all tetragonal. In this report only results for catalysts prepared by the precipitation and sol gel procedures are presented.

Catalyst Synthesis Using Precipitation:

The most active catalysts were prepared by using precipitation of the metal nitrates with ammonium hydroxide. These were 7% Ce on zirconia, 1.6% sodium on zirconia, 3.2%Ti, 2%Th/ZrO_2 and undoped zirconia. After calcination the Na and undoped zirconia were monoclinic. The Ce doped zirconia was cubic, and the 3.2%,2%Th/ZrO_2 was a combination of the tetragonal and monoclinic zirconia. Figures 6 through 10 illustrate the variation of CO conversion and isobutylene, C_4, methane and C_{5+} production rates. As indicated in Figure 6 the activities are very close as measured by the extent of conversion. Figures 7 through 10 demonstrate substantially different rates of production for each component with the most striking difference being the rate of production of methane compared to the rate of production of C_{5+}.

The Na doped zirconia has the lowest production rates of methane and the highest production rates of C_{5+} and oxygenates. But the 7% Ce/ZrO_2 and the Ti, Th/ZrO_2 have much higher production rates of isobutylene. Another difference in the preparation of these materials is with the exception of the 1.65 Na/ZrO_2; the pH of the solution with precipitate was decreased from about 10 to 6 or 7 prior to drying and calcining. This treatment resulted in reducing the amount of oxygenates produced compared to the 1.6% Na/ZrO_2 catalyst. The percent of oxygenates produced for this catalyst was in the range of 20 to 25% of the hydrocarbons produced. Figure 11 presents a comparison of the hydrocarbon distributions for the most active precipitated catalysts. A penalty in increasing the activity and reducing the production of the oxygenates is the increase in production of methane.

Catalysts Prepared by Sol Gel Procedure:

The procedure used for preparing these catalysts is a variation of the method developed by Dosch et al. (13) at the Sandia National Laboratories in Albuquerque, New Mexico. Instead of using an alkali to form the soluble intermediate, tetramethyl ammonium hydroxide is used. When a catalyst with a dopant is prepared the dopant in the form of the hydroxide is added to the methanol solution containing the tetramethyl ammonium hydroxide.

Figures 12 through 18 illustrate the production rates, CO conversion and product distributions of the catalysts listed in Table 1. Precipitated zirconia is used as a common zirconia relative to the earlier data presented at 400 °C. Higher temperatures were used with these catalysts to increase the production rates and to minimize alcohol formation. However, experiments conducted at 400 °C with the catalysts prepared by the sol gel procedure produced substantially less oxygenates than were obtained with precipitated zirconia, apparently because of the increased acidity of these catalysts relative to the precipitated catalysts. It is apparently this acidity that results in the formation of the tetragonal phase instead of the monoclinic phase obtained by precipitation. These catalysts, as shown in Figure 16, are less active than the precipitated catalyst. However, as demonstrated in Figure 17, less methane and less C_{5+} is produced by the sol gel prepared zirconia at approximately the same CO conversion. Doping with K or Ca also reduces the methane productivity with no decrease the activity of the catalysts, as illustrated in Figure 18.

Effect of Co-Feeding H_2S:

Experiments feeding H_2S with hydrogen and CO were conducted to determine the effect of H_2S on the hydrocarbon distribution. The objective was to reduce the formation of methane by poisoning the methane producing sites, which might be on the catalyst or the walls of the reactor.

The first experiments were conducted on the 7% Ce/ZrO_2 which had been cooled to room temperature and reheated. We had observed that if the undoped zirconia or doped zirconia were cooled and reheated to reaction temperature the production of methane substantially increased. An increase in methane production also occurred if the catalyst was subjected to temperature cycles with time on stream. These effects are demonstrated in Figure 19, which shows the product distribution for a fresh catalyst, a cycled catalyst, a reheated catalyst, and after reheating with H_2S. The temperature for the cycled catalyst started at 400 °C, was increased to 425 °C, then 450 °C, and finally decreased to 400 °C. When H_2S was co-fed with the hydrogen, methane production substantially decreased, as illustrated in Figure 19, and substantially increased the C_{5+} fraction.

A fresh catalyst was prepared; Figure 20 illustrates the effect of co-feeding H_2S on the product distribution. For the fresh catalyst the dramatic decrease in methane formation was not observed, but the C_2+C_3 productivity decreased, and the C_{5+} content increased. The most drastic change occurred in the C_5s, where a substantial increase in production of 3-methyl-1-butene occurred, as Figure 21 shows. The role of H_2S in these reactions requires further investigation as to its meaning in the mechanism of isosynthesis. An interesting fact is that 3-methyl-1-butene is the least thermodynamically favored of the branched C_5 olefins.

Kinetic Modelling:

The following rate equation was valid for predicting the rate of CO conversion, as illustrated in Figure 22:

$$r_{CO} = \frac{k_p p_{CO} p_{H_2}^{0.5}}{\left(1 + K_{CO_2} p_{CO_2}\right)} \qquad \left[\frac{mol}{kg_{cat}\ sec}\right]$$

The parameters obtained for the catalysts presented in Table 1 are tabulated in Table 2. The activation energies, enthalpies of adsorption for CO_2 for the 7% Ce-ZrO_2 without and with H_2S were 7.39 kcal/mol, 17.91 kcal/mol and 12.14 kcal/mol, 14.22 kcal/mol, respectively. The low activation energy for the Ce-doped zirconia without H_2S suggests that intraparticle or interparticle diffusion resistances were significant.

Table 2. Rate Constants, Adsorption Equilibrium Constants, and Isosynthesis Parameters Obtained from SimuSolv®.

Catalyst	$k_p \times 10^6$ $\left(\frac{mol}{kg_{cat}\,atm^{1.5}\,sec}\right)$	K_{CO_2} (atm^{-1})	Parameters	
			α	γ
ZrO_2 (ppt.)*	6.90	0.330	n/a	n/a
ZrO_2 (comm.)†	10.0	2.75	0.550	2.25
ZrO_2 (sol gel)†	5.88	0.331	0.358	3.84
1.6% Na-ZrO_2 (ppt.)*	11.55	1.001	n/a	n/a
3.2% Ti, 2% Th, ZrO_2 (ppt.)*	8.79	0.641	n/a	n/a
7% Ce-ZrO_2 (ppt.)*	10.52	0.596	n/a	n/a
7% Ce-ZrO_2 (ppt.)* {H_2S}	10.97	0.503	n/a	n/a
0.5% K-ZrO_2 (sol gel)†	n/a	n/a	0.464	3.98
0.5% Ca-ZRO_2 (sol gel)†	n/a	n/a	0.481	5.17

* Parameters obtained for 400 °C, 50 atm, and 1/1 CO/H_2 Ratio.
† Parameters obtained for 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

To predict the hydrocarbon distribution, we used a variation of the Anderson Schulz Flory distribution (16) and added a condensation step to produce C_4s from C_2. This mechanism is illustrated as follows:

$$\begin{tikzcd}
{[C_1]} \arrow[r, "k_{p_1}"] \arrow[d, "k_{t_1}"] & {[C_2]} \arrow[r, "k_{p_2}"] \arrow[d, "k_{t_2}"] \arrow[rr, bend left, "k_d"] & {[C_3]} \arrow[r, "k_{p_3}"] \arrow[d, "k_{t_3}"] & {[C_4]} \arrow[r, "k_{p_4}"] \arrow[d, "k_{t_4}"] & {[C_5]} \arrow[d, "k_{t_5}"] \\
P_1 & P_2 & P_3 & P_4 & P_5
\end{tikzcd}$$

$$\frac{d[C_2]}{dt} = k_{p_1}[C_1] - k_{t_2}[C_2] - k_{p_2}[C_2] - k_d[C_2]$$

$$\frac{d[C_3]}{dt} = k_{p_2}[C_2] - k_{t_3}[C_3] - k_{p_3}[C_3]$$

$$\frac{d[C_4]}{dt} = k_{p_3}[C_3] + k_d[C_2] - k_{t_4}[C_4] - k_{p_4}[C_4]$$

$$\frac{d[C_{i+1}]}{dt} = k_{p_i}[C_i] - \left(k_{t_{i+1}} + k_{p_{i+1}}\right)[C_{i+1}] \quad for\ i \geq 4 \quad .$$

By using the pseudo steady state assumption and constant k_p/k_t the following series of equations were developed:

$$\frac{P_2}{P_1} = \frac{\alpha}{1 + \alpha + \alpha\gamma}$$

$$\frac{P_3}{P_2} = \alpha$$

$$\frac{P_4}{P_3} = \alpha + \gamma$$

$$\frac{P_{i+1}}{P_i} = \alpha \quad for\ i \geq 4 \quad .$$

where

$$\alpha = \frac{k_p}{k_t + k_p}$$

$$\gamma = \frac{k_d}{k_{p_2}} \quad .$$

The alpha parameter is the traditional Fischer Tropsch parameter, whereas the gamma parameter (Figure 23) is defined as the ratio of the rate of condensation to the rate of chain growth. This value was determined from the slope of the line between C_3 and C_4. By using the summation of mole fractions to be 1, a carbon balance and the predicted amount of CO consumed, the rate of production of each hydrocarbon specie can be predicted. A comparison of the predicted production of methane and C_4s are illustrated in Figure 24, and the C_1 to C_5 product distributions are illustrated in Figure 25. The predicted C_4 production is greater than the experimental values for low space velocities. Therefore, an effort will be made to improve the model.

An alternate way to develop the kinetic model is to develop the rate equation for the rate of production of each specie up through C_4, and then use the Fischer Tropsch prediction for the remaining portion of the distribution. We will be investigating the use of this procedure in the next few months. Nevertheless, a kinetic model has been developed that can be used to predict product distributions, production and consumption rates. Such a model had previously been unavailable.

CONCLUSIONS

Substantial progress has been made in developing the data base for evaluating commercialization of isosynthesis. The kinetic model can be used to predict performance of a fixed bed reactor. The dependence of alpha and gamma on the reaction temperature needs to be evaluated. Even though activity decreased with the sol gel procedure, isosynthesis was achieved with low oxygenates production at 400 °C because of acidity of the zirconia. However, a need still exists to develop a catalyst with high activity at a low temperature.

The use of H_2S will eliminate the need for total sulfur removal from a synthesis gas stream from a coal gasification plant. However, further work is needed to assess the role H_2S plays in the mechanism of the reaction since an increase in 3-methyl-1-butene was observed.

Propylene production in the trickle bed reactor increased over that of the fixed bed reactor; there was also a substantial decrease in the isobutylene selectivity. Experiments in a slurry reactor are planned to eliminate possible effects due to hydrodynamics and resistances to mass transfer between the gas and liquid. By using small particles and excellent mixing, no resistance to mass transfer should be observed.

A kinetic model, which can be used to predict reactor performance has been developed for one temperature. The temperature dependence of alpha and gamma will be determined over the next four months. A reactor model for isosynthesis had been unavailable prior to this work.

FUTURE PLANS

To bring the project to completion the following work is planned:

1. Slurry reactor experiments will be conducted in the absence of mass transfer resistances.
2. Experiments will be conducted to determine the effect of temperature on alpha and gamma.
3. An effort will be made to improve the kinetic model.
4. Utilizing the kinetic model fixed bed reactor, slurry reactor and trickle bed reactor performance will be simulated.
5. A limited number of experiments will be conducted to examine the eff . of acidity and oxygen vacancies on catalytic activity.

RECOMMENDATIONS FOR FUTURE PROJECTS

Since the basis for synthesizing isobutylene is to provide a feedstock for producing methyl t-butyl ether, an additive for gasoline, we recommend a study to consider the routes from synthesis gas to produce MTBE and other ethers for blending with gasoline. The scope of such a study should also consider oxygenate blends for diesel and jet fuels.

Since the thermodynamics and kinetics indicate that a distribution of products will be produced in the isosynthesis reactions, and since the experimental work reported herein shows that approximately 60 to 65 wt% of the hydrocarbons produced are C_4s, C_5s, and C_6s, a study should be conducted to determine if ethers suitable for blending with gasoline, diesel or jet fuels could be produced. Since a major fraction, 8 to 30 % of CO is converted to methane, and since this is probably due to the high temperature and low pressure of the reaction, a more active catalyst is needed for conversion of synthesis gas to isobutylene at lower temperatures. We, therefore, recommend a study to develop a new catalyst to produce isobutylene in the temperature range of 250 to 350 °C, or lower and at pressures less than 70 atm.

Because of the observed effect of hydrogen sulfide co-fed with synthesis gas on the product distributions, we recommend further studies to determine the role that H_2S plays in the synthesis procedure. The fact that production of 3-methyl-1-butene, the least favorable compound in the C_5 olefins, increased with H_2S in the feed, information on the mechanism of chain growth or condensation reactions might be inferred. Further work might elucidate this mechanism and lead to development of improved isosynthesis catalysts.

Molecular or microkinetic modelling is a fundamental approach towards understanding the reactions which occur on the surface of a catalyst. We have performed a limited number of calculations in this study and believe further work in this area related to isosynthesis is warranted.

The role of catalytic acidity/basisity and oxygen vacancies in producing an isosynthesis catalyst is not clearly understood. In the current study we have shown that zirconias prepared by sol gel procedures which require acid washing are not very active catalysts. On the other hand, zirconia, which was prepared by the sol gel procedure by use of tetramethyl ammonium hydroxide, was active and more selective for isobutylene than zirconia prepared by precipitation from zirconyl nitrate or zirconyl chloride. We recommend further work on the role of acidity on the isosynthesis, since the acidity of the zirconias by proper treatment can be varied over the range of super acids to strongly basic. Such treatment also affects the structure produced, i.e. monoclinic, tetragonal or cubic.

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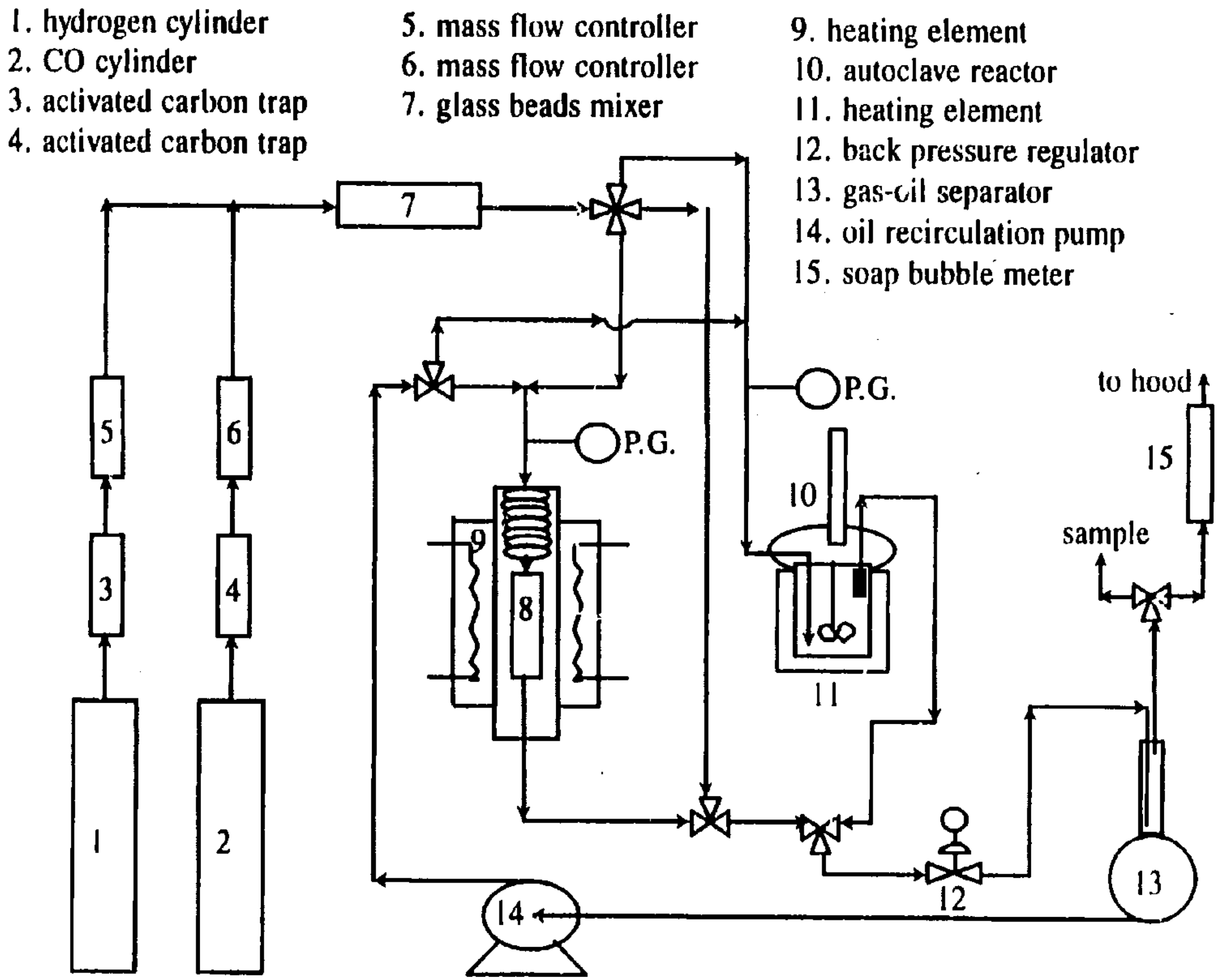

Figure 1. Schematic of trickle bed and slurry reactor systems.

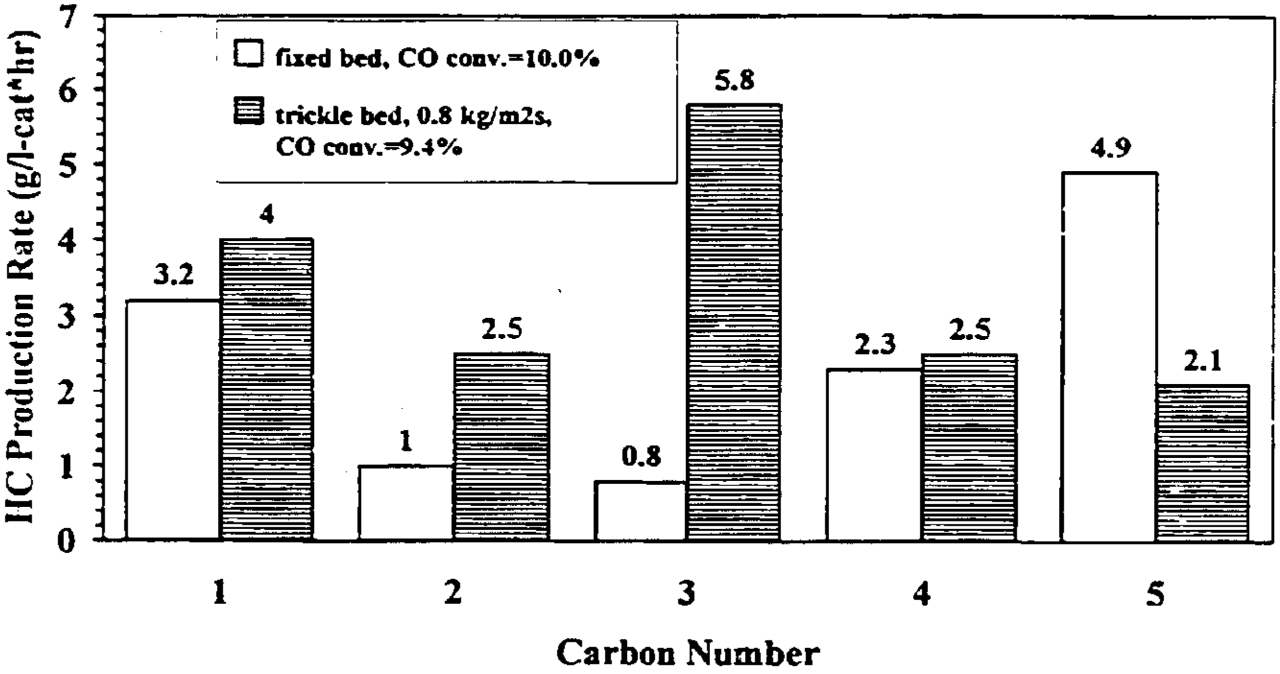

Figure 2. Comparison of Hydrocarbon Distribution for Fixed and Trickle Bed Reactors at 396 °C, 51 atm, 1/1 CO/H2, and Space Velocity=842 (1/hr).

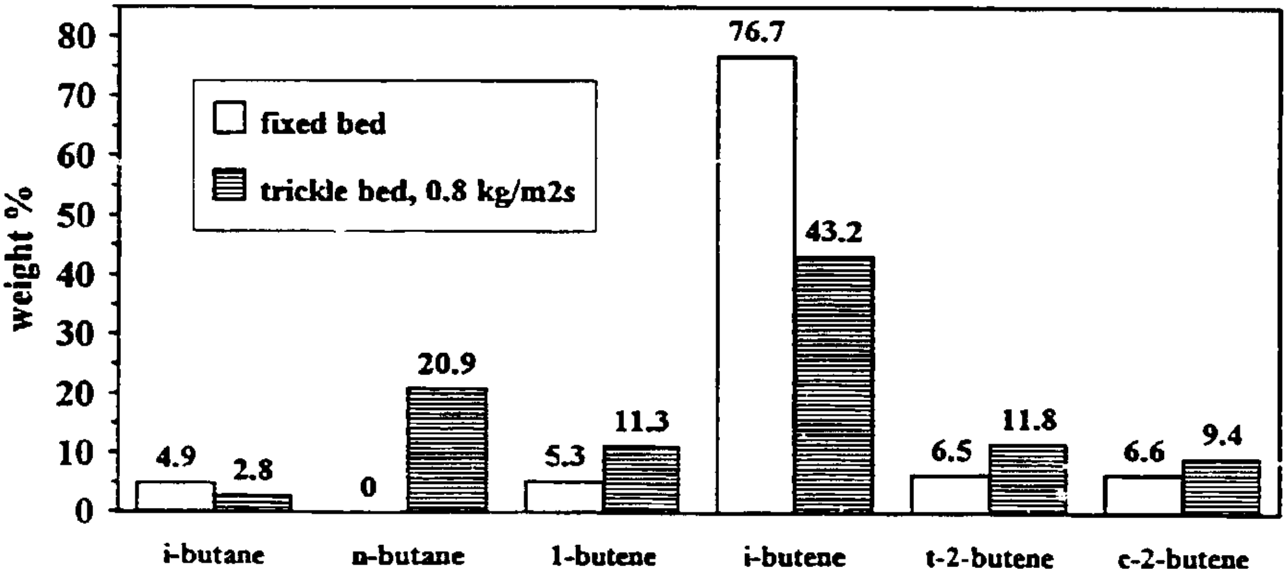

Figure 3. Comparison of C4 Distribution for Fixed and Trickle Bed Reactors at 396 °C, 51 atm, 1/1 CO/H2, and Space Velocity=842 (1/hr).

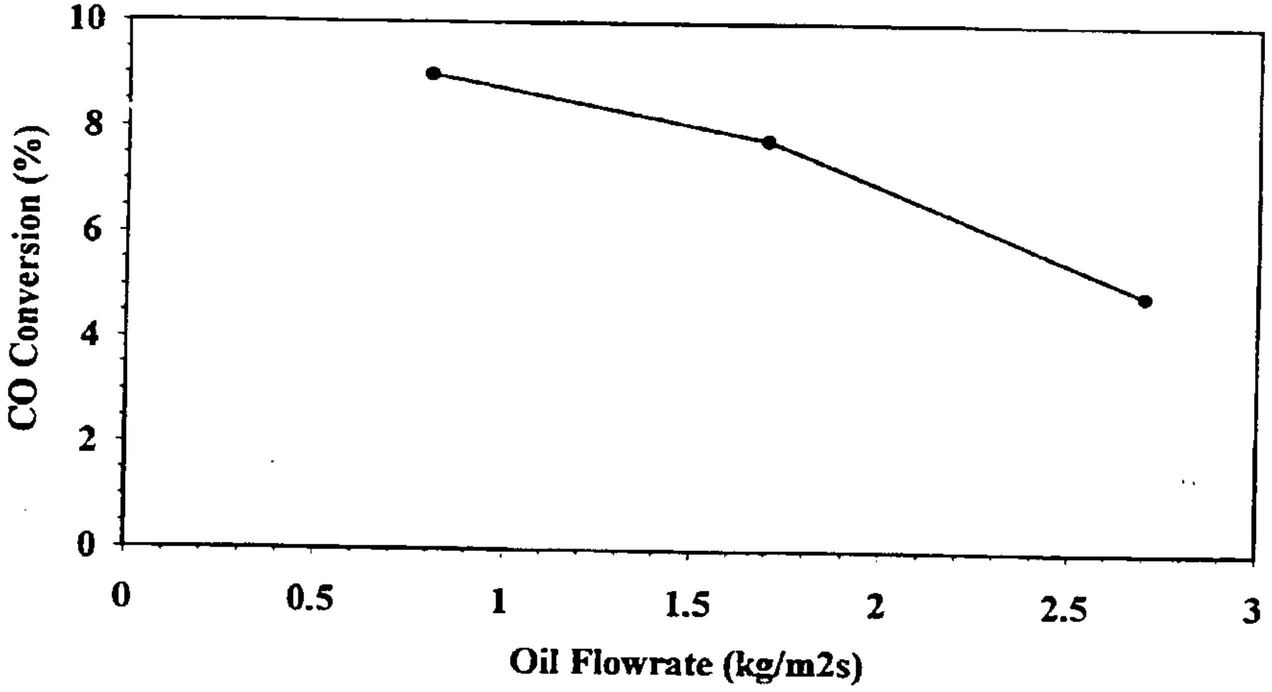

Figure 4. Variation of CO Conversion with Oil Flow Rate at 396 °C, 51 atm, 1/1 CO/H2, and Space Velocity=668 (1/hr).

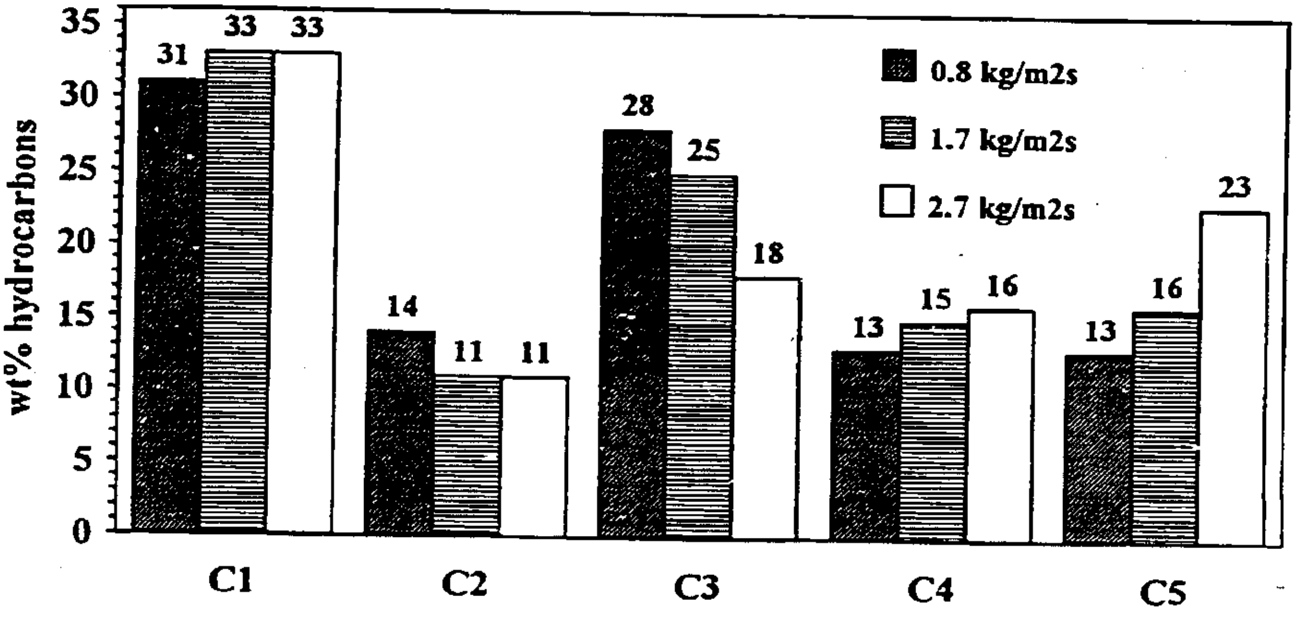

Figure 5. Change in Hydrocarbon Distribution with Oil Flow Rate at 396 °C, 51 atm, 1/1 CO/H2, and Space Velocity=668 (1/hr).

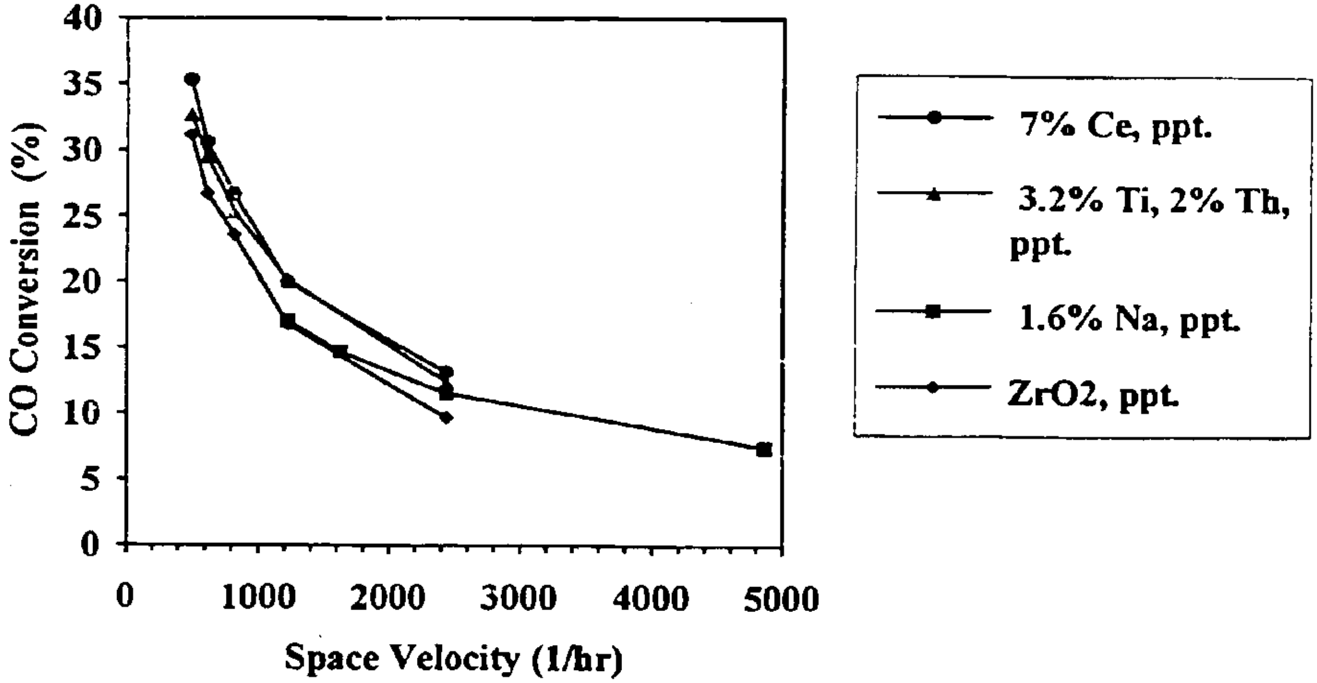

Figure 6. Catalytic Activity at 400 °C, 50 atm, and 1/1 CO/H2 Ratio.

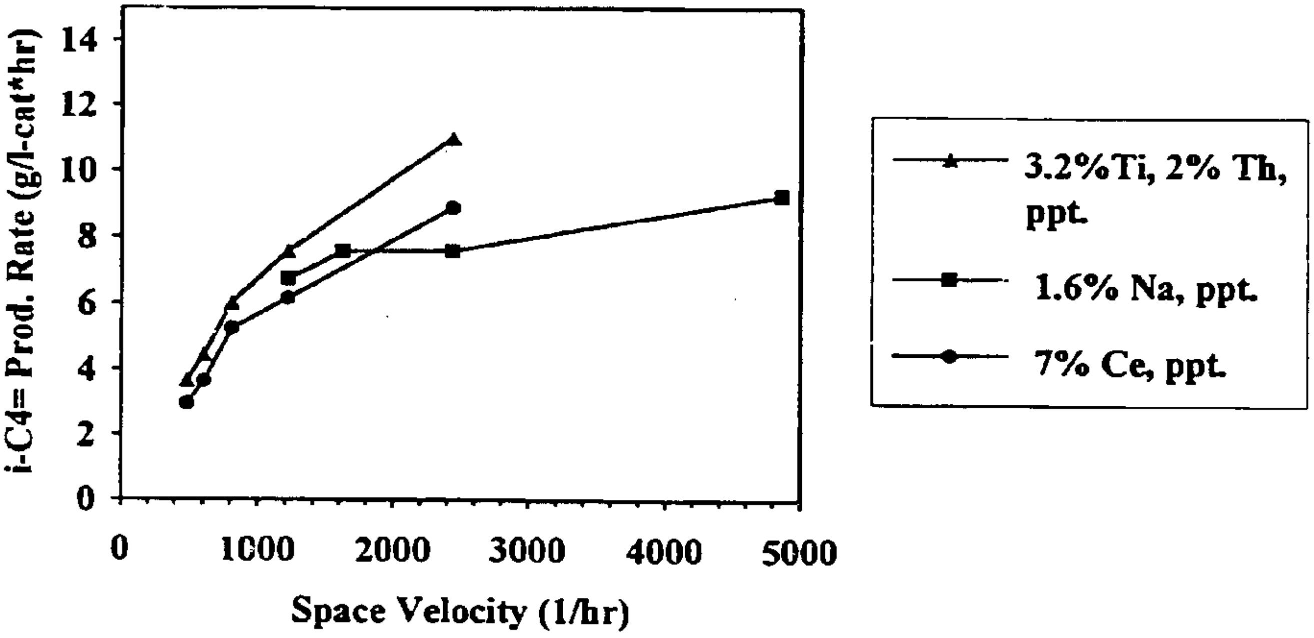

Figure 7. Isobutylene Production Rate at 400 °C, 50 atm, and 1/1 CO/H2 Ratio.

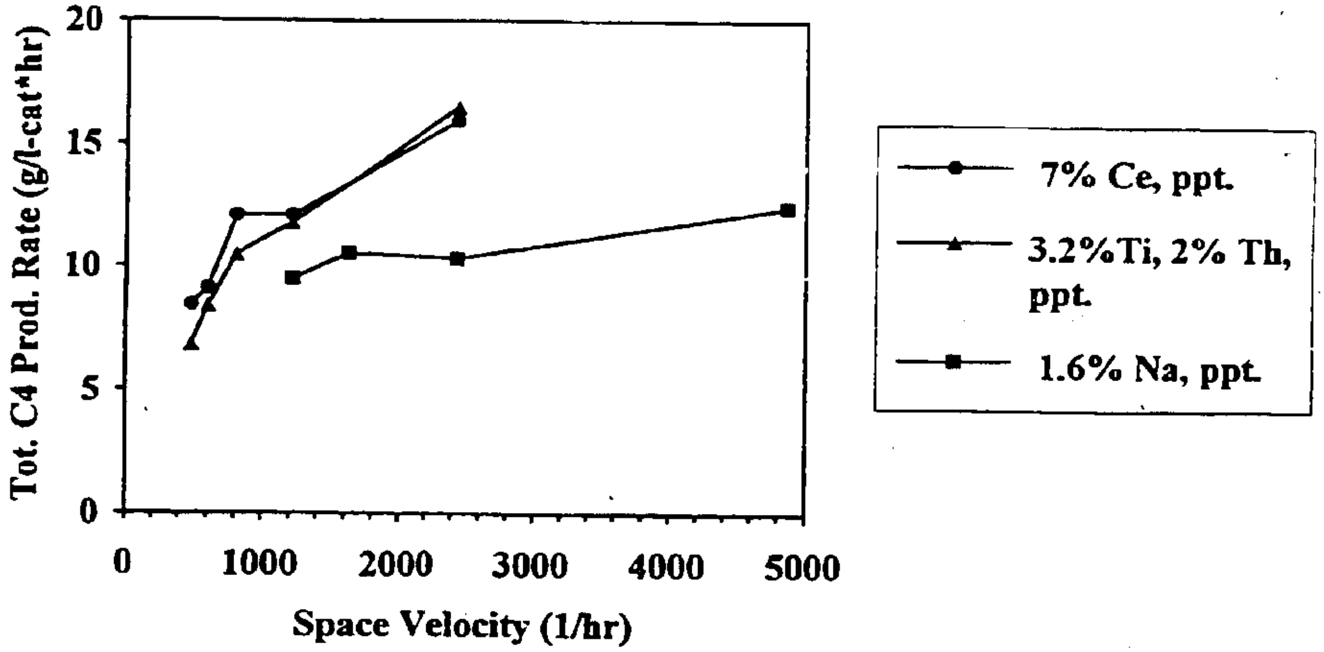

Figure 8. Total C4 Production Rate at 400 °C, 50 atm, and 1/1 CO/H2 Ratio.

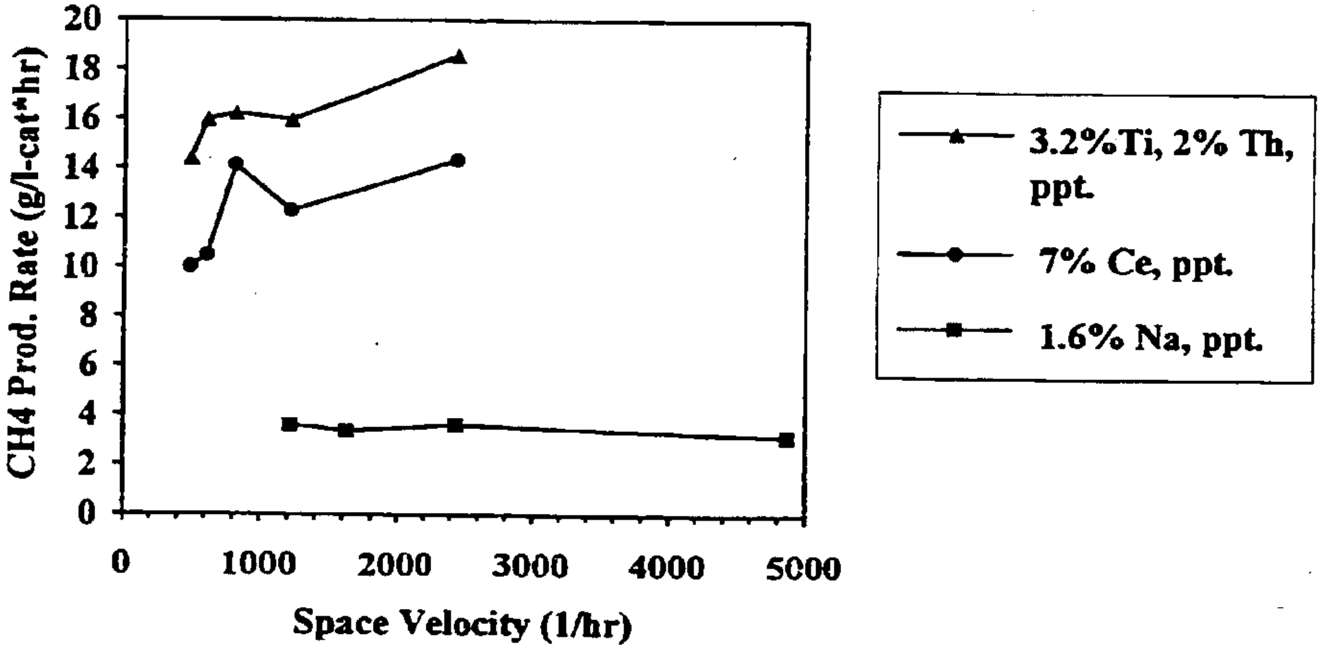

Figure 9. Methane Production Rate at 400 °C, 50 atm, and 1/1 CO/H2 Ratio.

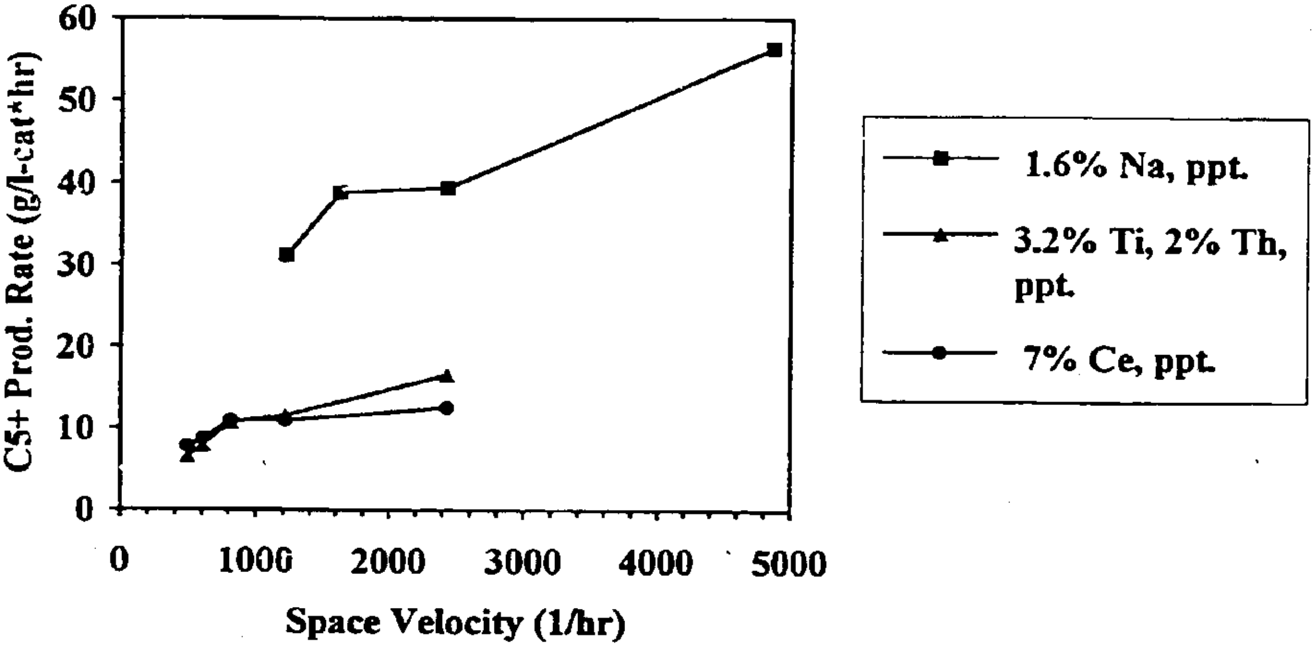

Figure 10. C5+ Production Rate at 400 °C, 50 atm, and 1/1 CO/H2 Ratio.

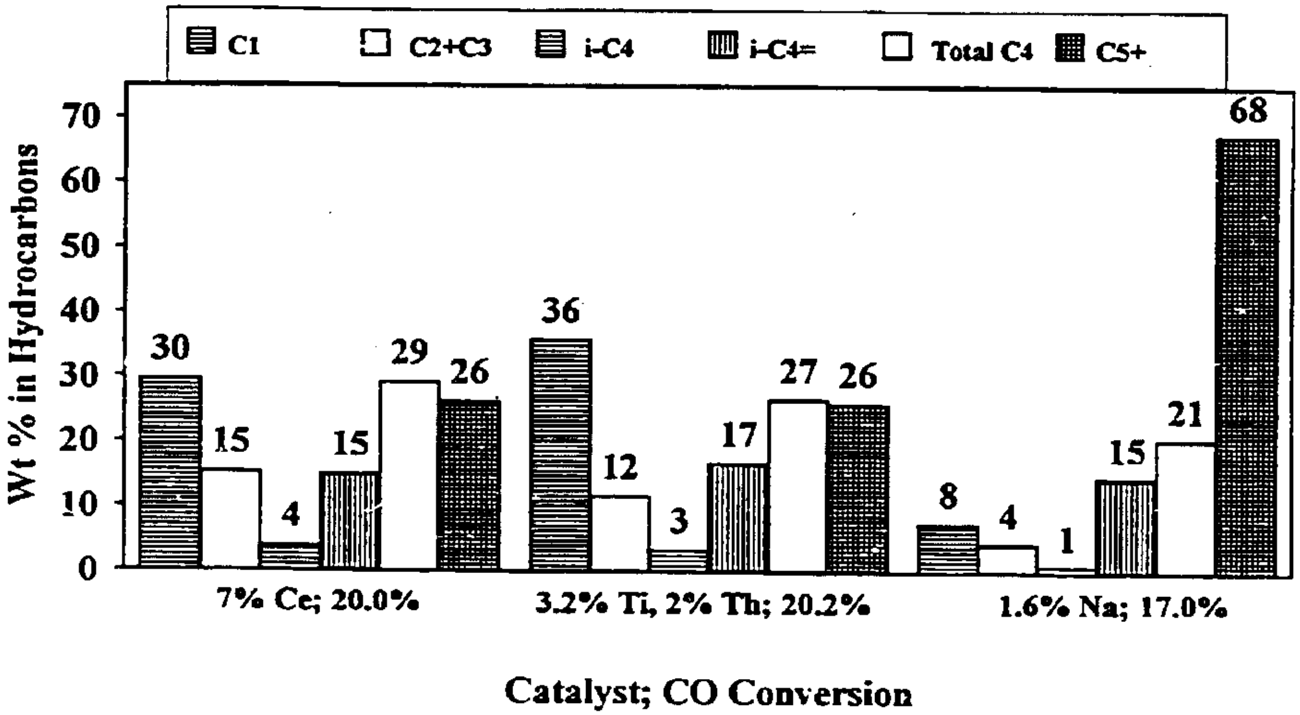

Figure 11. Selectivity in Hydrocarbon Distribution for the Most Active Catalysts at 400 °C, 50 atm, 1/1 CO/H2 Ratio, and Space Velocity 1220 (1/hr).

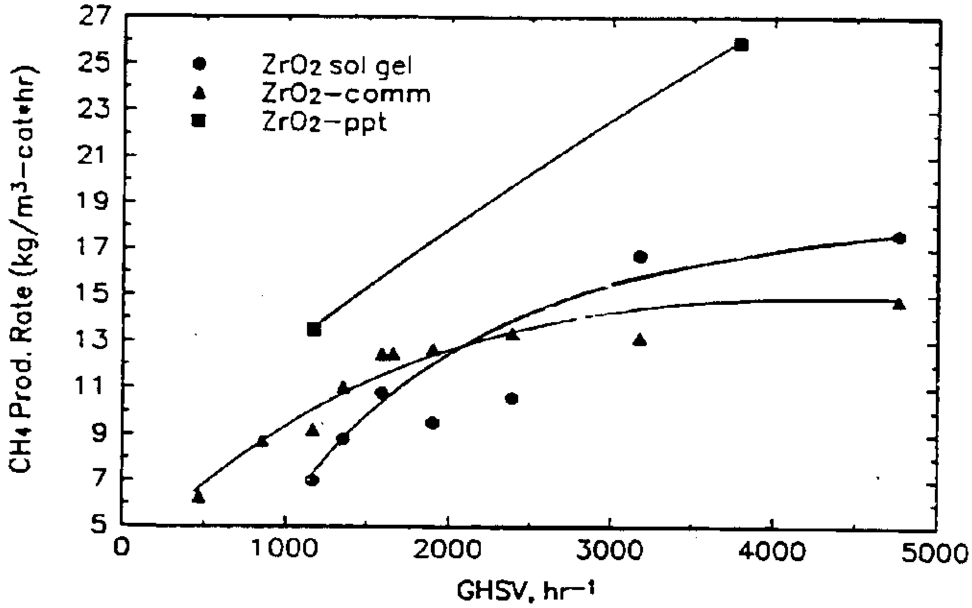

Figure 12. Methane Production Rate at 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

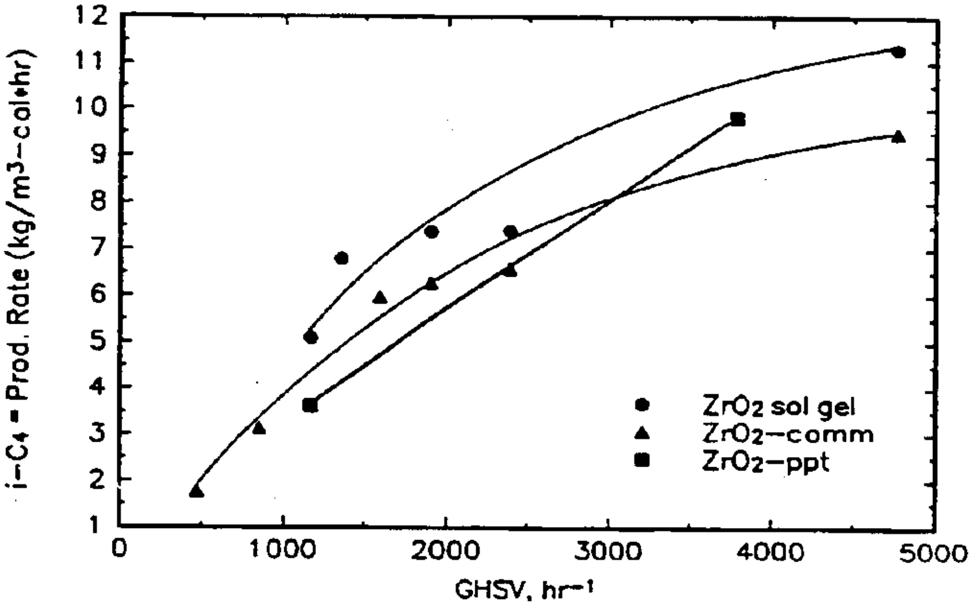

Figure 13. Isobutylene Production Rate at 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

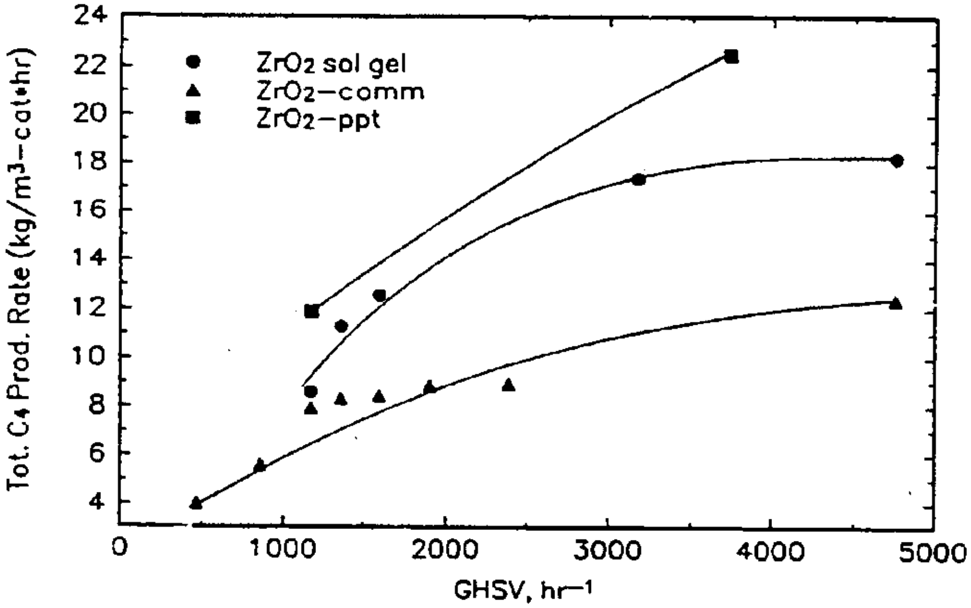

Figure 14. Total C_4 Production Rate at 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

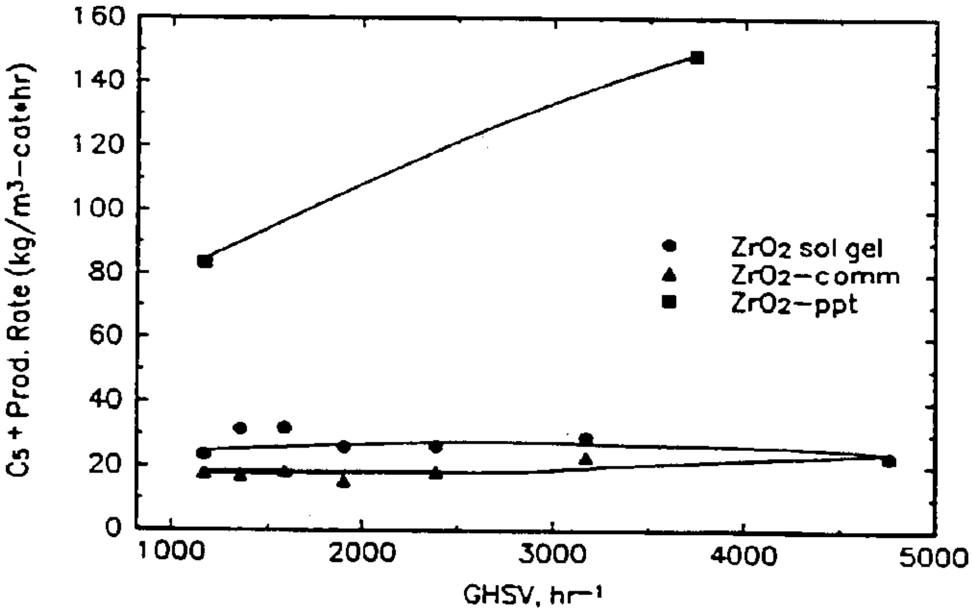

Figure 15. C_5^+ Production Rate at 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

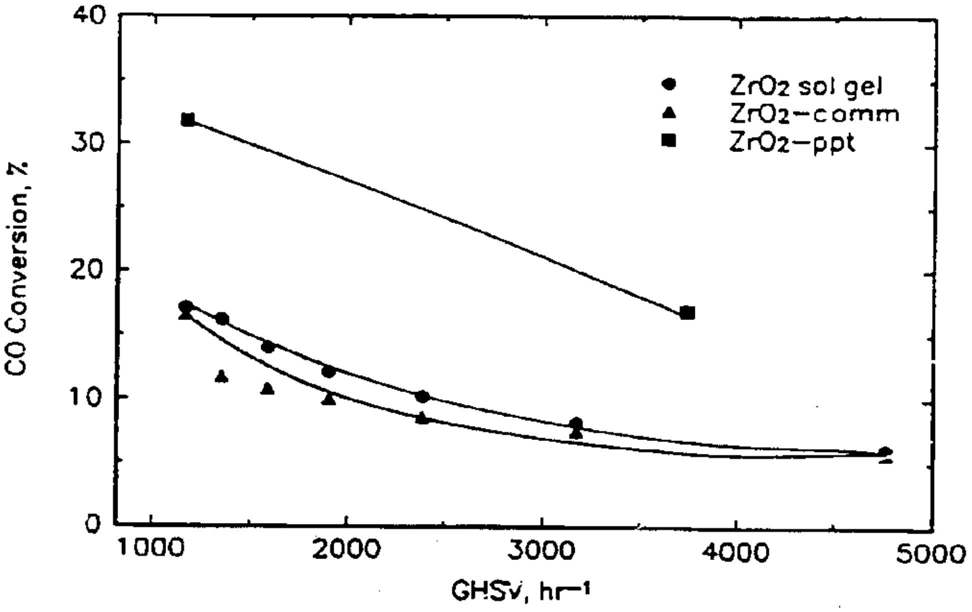

Figure 16. CO Conversion at 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

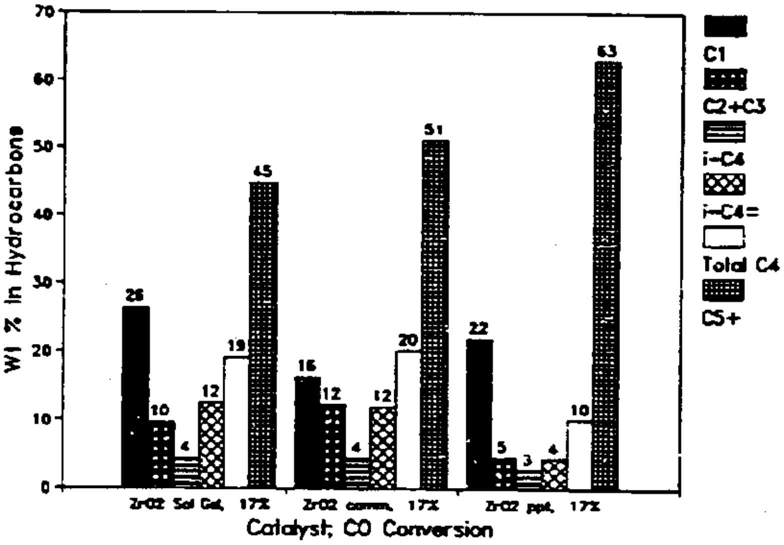

Figure 17. Effect of Preparation on Hydrocarbon Distribution. 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

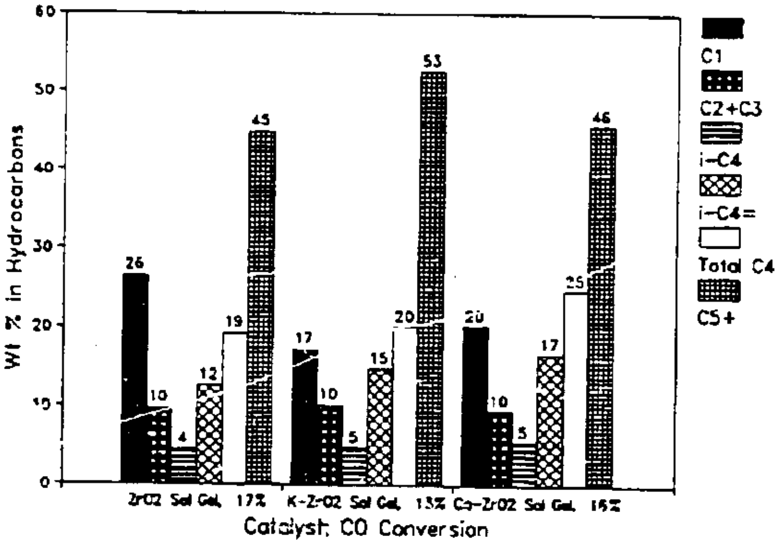

Figure 18. Effect of Dopants on Hydrocarbon Distribution. 450 °C, 70 atm, 1/1 CO/H_2 Ratio, and GHSV of 1200 hr^{-1}.

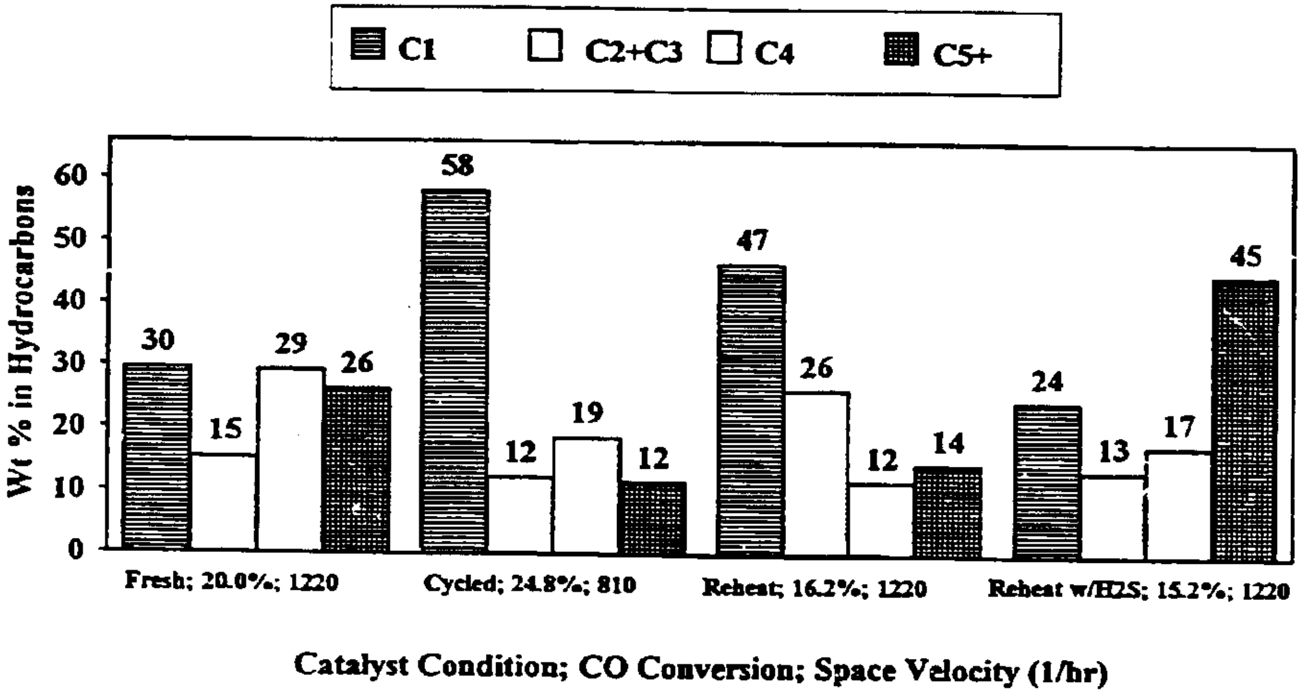

Figure 19. Effect of Temperature Cycles and H2S on Hydrocarbon Selectivity at 400 °C, 50 atm, and 1/1 CO/{H2 or H2+H2S} Ratio.

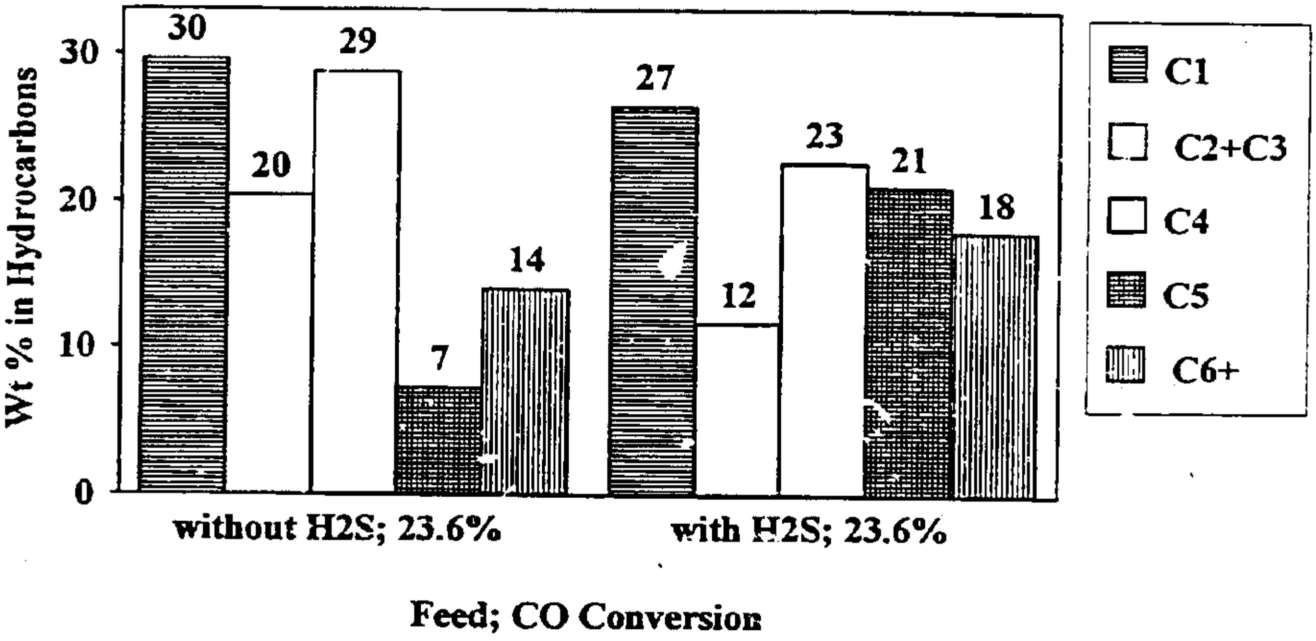

Figure 20. Effect of H2S on Hydrocarbon Selectivity at 400 °C, 50 atm, and 1/1 CO/{H2 or H2+H2S} Feed Ratio and Space Velocity 1220 (1/hr).

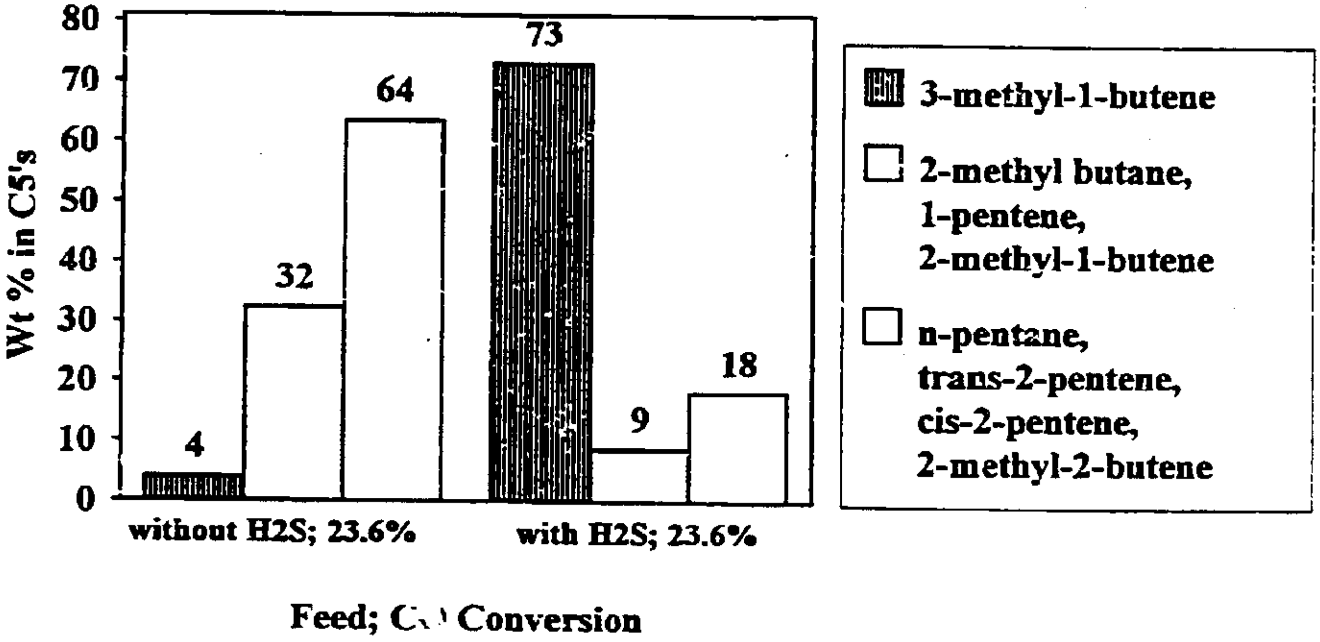

Figure 21. Effect of H2S onC5 Selectivity at 400 °C, 50 atm, and 1/1 CO/{H2 or H2+H2S} Feed Ratio and Space Velocity 1220 (1/hr).

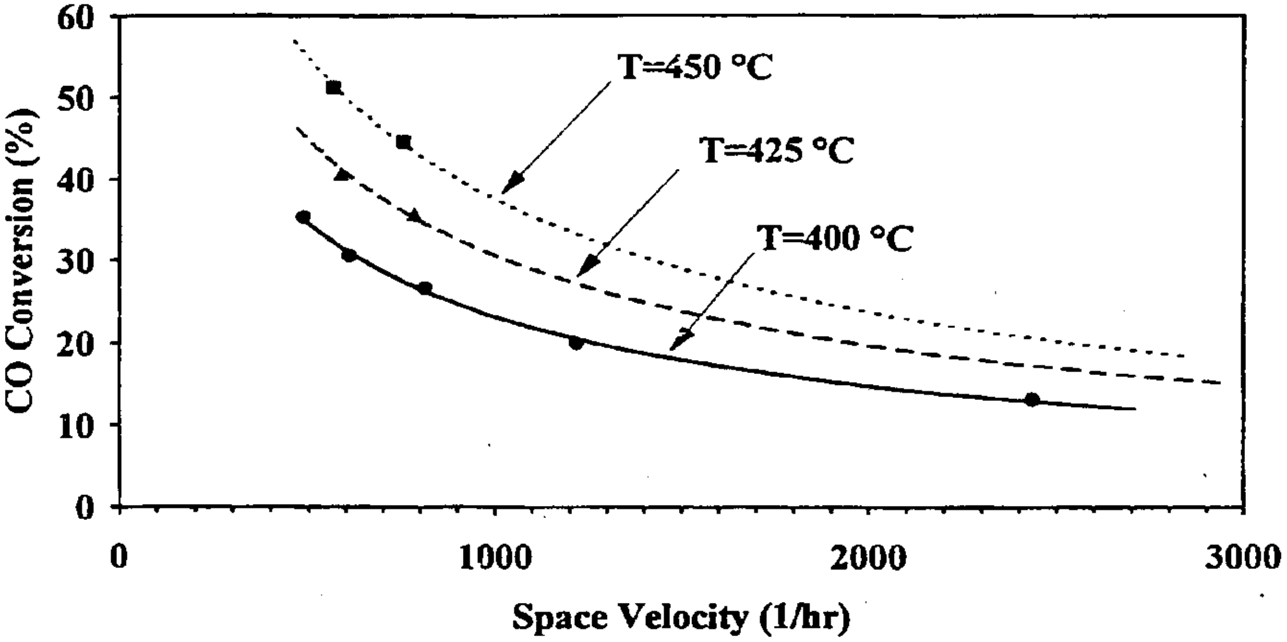

Figure 22. Comparison of Experimental and Predicted Conversion over 7% Ce-ZrO2 (ppt.) at 50 atm and 1/1 CO/H2 Ratio.

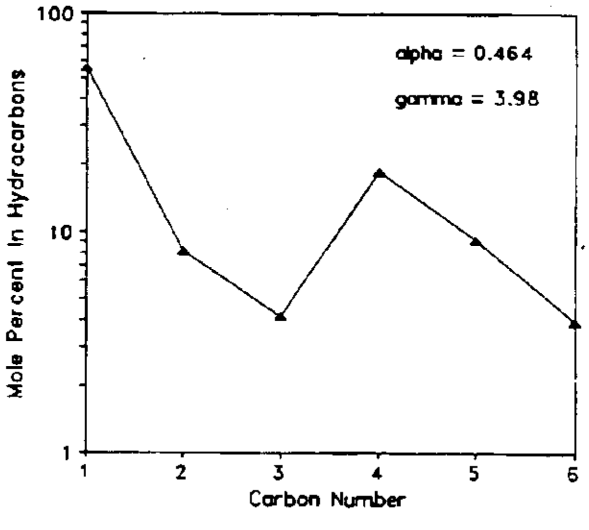

Figure 23. Schulz-Flory Plot for Isosynthesis. K-ZrO_2 Sol Gel, 450 °C, 70 atm, 1/1 CO/H_2 Ratio, and GHSV of 1200 hr^{-1}.

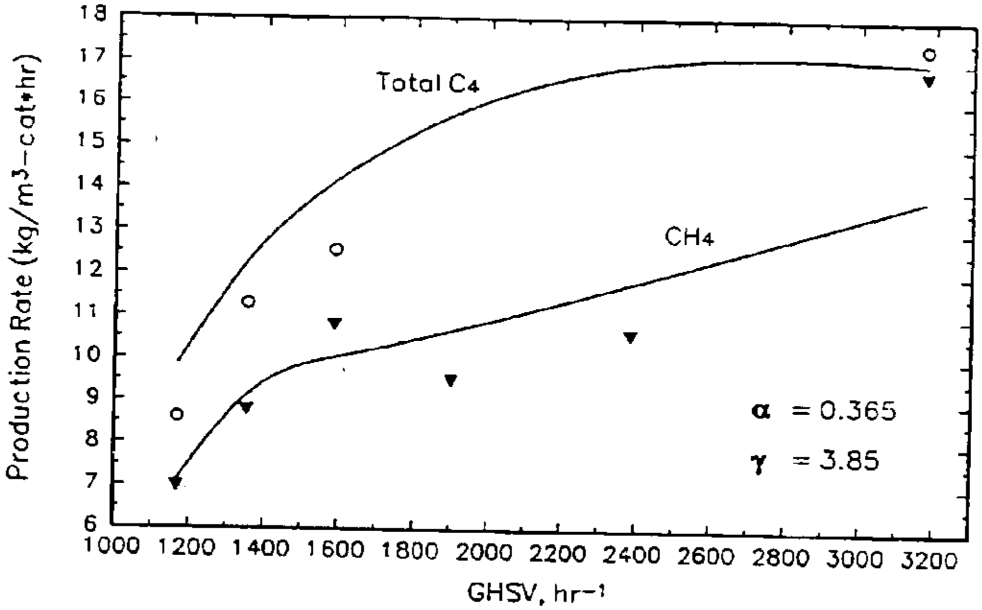

Figure 24. A Comparison of Experimental Values and Calculated Values. ZrO_2 Sol Gel, 450 °C, 70 atm, and 1/1 CO/H_2 Ratio.

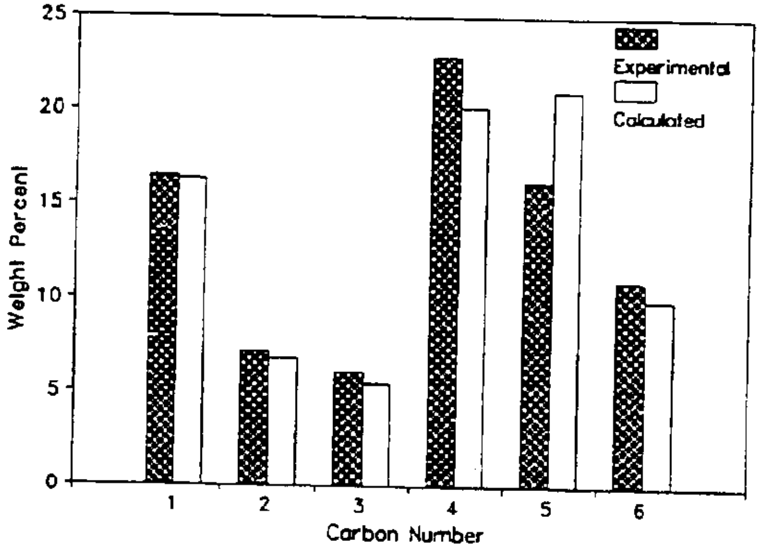

Figure 25. Distribution of Hydrocarbons. ZrO_2 Sol Gel, 450 °C, 70 atm, and GHSV of 1200 hr^{-1}.