

# ISOBUTYLENE SYNTHESIS OVER ZIRCONIA AND MODIFIED ZIRCONIA USING HYDROGEN LEAN SYNTHESIS GAS

by

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## INTRODUCTION

Early work on isobutylene and isobutane synthesis employed thoria based catalysts. Later isoalkenes were produced when zirconia was used at lower pressures and temperatures of 623 to 773 K. The difficultly reducible oxide catalysts such as  $\text{ThO}_2$  (1,2) and  $\text{Dy}_2\text{O}_3$ , (3) were used under very severe conditions. A  $\text{CdO}$  catalyst combined with acid supports was used under mild conditions. Recently, Maruya, et al.(4) and Onishi et al. (5) reported the use of  $\text{ZrO}_2$  at mild conditions, and methoxide species and formate ions have been observed on the surface of the  $\text{ZrO}_2$  catalysts. Maruya, et al. (6) also produced a  $\text{C}_4$  fraction with 99% isobutylene with carbon  $\text{C}_4$  selectivities in the range of 77 to 85%. The latter value was obtained when zirconia was impregnated with  $\text{NaOH}$ . The mechanism for formation of the branched alkanes has been postulated to be different than the mechanism for formation of linear alkanes.

Vedage et al. (7) postulated that linear products are produced by  $\text{CO}$  insertion into an alkoxide instead of an aldol-like condensation scheme in which a formyl species reacts with an enolate ( $\text{RCH}_2\text{-HCHO}$ ) at the carbon next to the carbonyl carbon. Mazanec (8) proposed a  $\text{CO}$  insertion scheme involving a bound aldehyde to produce a cyclic acyl which has two valence structures and the carbonyl carbon in one has carbenic character. Subsequent 1,2 shifts of hydrogen or R can lead to linear or branched products. Condensations reactions between eta-enolates and alkoxides were proposed to account for deviations from the Schulz-Flory distribution. Tseng et al. (9) and Jackson and Ekerdt (10) present the results of a comprehensive study and discuss proposed mechanisms on isosynthesis using zirconia. The formation of  $\text{C}_4\text{s}$  is postulated to be by addition and condensation reactions (4,6,9,10).

This manuscript reports data on isobutylene synthesis using zirconia prepared by coprecipitation and modified sol gel procedures.

## CATALYSTS SYNTHESIS AND CHARACTERIZATION

**Synthesis:** The two procedures used for synthesizing the catalysts presented herein were as follows: [1] Reaction of zirconyl nitrate with ammonium hydroxide which precipitates as zirconium hydroxide and is then dried and calcined at 500 °C for 2.5 hours. This catalyst is labelled Cat 1. [2] The sol gel procedures developed by Dosch et al. (11) were used to produce a sodium hydrous zirconium oxide, which was ion exchanged with  $\text{HCl}$  to remove the sodium, washed with acetone, dried and calcined at 500 °C for 4 hours. This catalyst is referred to as Cat 2.

**Characterization:** Differentiation between cubic zirconia and tetragonal zirconia by use of XRD has been reported to be very difficult to impossible. Cubic zirconia is normally formed at temperatures above 1200 °C except in the presence of alkali or alkaline salts. The cubic form can then be stabilized at lower temperatures. Inspection of XRD powder patterns suggests that one should be able to distinguish between the cubic and tetragonal forms. However, this is very difficult to accomplish except for highly crystalline zirconia. Catalysts prepared by procedure 1 could be made as tetragonal or monoclinic depending on the procedure used in calcination. Only the zirconia which had a monoclinic structure as indicated by an XRD powder pattern was used in this study.

The hydrous sodium zirconium oxide prepared by Dosch's method had an ion exchange capacity of approximately 4.5 meq/g. For the catalytic evaluations the sodium content was decreased to less than 0.3% using HCl exchange and then calcined at 500 °C for 4 hours. After calcination Catalyst #2 appeared to be monoclinic. Zirconia formed by this method should be more acidic than the zirconia prepared according to procedure #1.

## CATALYSTS EVALUATION

Two reactor systems, one constructed by us referred to as BR1 and an AE MSBTR 900 purchased from Autoclave Engineers, were used in the evaluation of the catalysts. For both systems the catalysts were loaded and purged with nitrogen at 400 °C for 4 hours prior to conducting the activity studies. Catalytic activity data reported herein for the precipitated catalysts, Cat. #1 batches 3 and 4, were obtained in the BR1 and AE MSBTR 900, and catalytic activity data reported for Cat. #2 were obtained using the AE MSBTR 900, only. Methanol and higher alcohols were detected as product from Cat. 1 when using the AE MSBTR 900, which had on-line analysis of the products. The analysis of the product for BR1 was off-line, and no alcohols were detected in the product stream. Figure 1 illustrates the activity and effect of pressure on CO conversion for zirconia using catalysts CAT 1&2. The space time,  $\tau$ , is defined as the bulk volume of the catalysts divided by the volumetric feed rate calculated at reaction conditions. The actual residence time is greater than the space time because of the decrease in the number of moles with reaction. However, at low conversions space time is a close approximation to residence time, which is dependent on the extent of reaction. Figure 1 shows that pressure does not have a significant effect on conversion at equal space times for a 1:3 or a 1:1 CO:H<sub>2</sub> ratio. Similarly results were obtained by Pichler and Ziesecke (1,2) for thoria catalysts. The data also indicate that Cat. #2 is not as active as Cat. #1. Figure 2 illustrates the expected trend for change in conversion with space time at 95 atm. and 400 °C and 50 atm and 425 °C. A space time of 90 seconds is required to obtain 20% CO conversion. Figure 3 illustrates the expected increase in conversion with increasing temperature for the two catalysts. The trends are the same indicating essentially the same reaction mechanism and activation energy.

In order to gain some insight into the type of reactions occurring several ratios were calculated, and are presented in Table 1. Table 1 illustrates the average values obtained for the isosynthesis profile, the branched to linear C<sub>4</sub>s and the isobutylene selectivity within the C<sub>4</sub> fraction. The isosynthesis profile was defined by Jackson and Ekerdt (10) as the ratio of C<sub>4</sub>s to (C<sub>2</sub>s + C<sub>3</sub>s), and is a measure of the relative importance of the condensation reactions. Ratios obtained in this study are comparable with the values reported by Jackson and Ekerdt (10).

Figures 4, 5, and 6 illustrate the effect of pressure, space time, and CO:H<sub>2</sub> ratio on the molar ratio of isobutylene to methane and the weight ratio of isobutylene to C<sub>2</sub>\* for Cat. #1. Figure 4 shows that for a 1:3 CO:H<sub>2</sub> ratio and low CO conversions (<5%) the isobutylene to

$C_5^+$  decreases as the pressure is increased, but the molar ratio of isobutylene to methane is essentially constant at 0.3. However, Figure 5 shows that for 95 atm and a 2:1 CO:H<sub>2</sub> ratio, the isobutylene to methane molar ratio varies from 0.5 to 0.75 as the CO conversion is increased with an increase in residence time. Figure 6 shows the effect of temperature and pressure on the ratio of isobutylene to  $C_5^+$ . Low pressures and high temperatures increases the ratio.

### CONCLUSIONS

The bench scale reactor systems have been successfully operated for a period of approximately one month with the collection of a substantial amount of data. The data reported above are for batches 3 and 4, Cat. 1. Data were also obtained on a catalyst prepared by catalyst preparation #2. Batches 3 and 4 for preparation of Cat. 1 were chosen because the XRD patterns and Raman spectra indicated they were predominately monoclinic, unlike the result obtained for other batches. Cat 2 was used to study the effect of acidity, and the effect of using a the modified sol gel method for preparing the catalyst. Experiments on Cat #1 in both reactor systems demonstrated the reproducibility of our experimental techniques. The activity of the zirconia catalysts are low and long residence times are required to obtain high CO conversions.

### ACKNOWLEDGEMENT

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Table 1. Isothesis Characteristics of Catalyst 1 and Catalyst 2

Weight Ratios	Catalyst 1	Catalyst 2	Jackson & Ekerdt(10)
Isosynthesis Profile <sup>1</sup>	4.55 ± 1.28	2.29 ± 0.79	2.30
Branched C <sub>4</sub> /Linear C <sub>4</sub>	2.71 ± 0.67	2.97 ± 0.33	5.67
i-C <sub>4</sub> H <sub>9</sub> /All C <sub>4</sub> s	0.63 ± 0.06	0.37 ± 0.15	0.84

<sup>1</sup> Defined as (total weight of C<sub>4</sub> hydrocarbons)/(total weight of C<sub>2</sub>s and C<sub>3</sub>s).

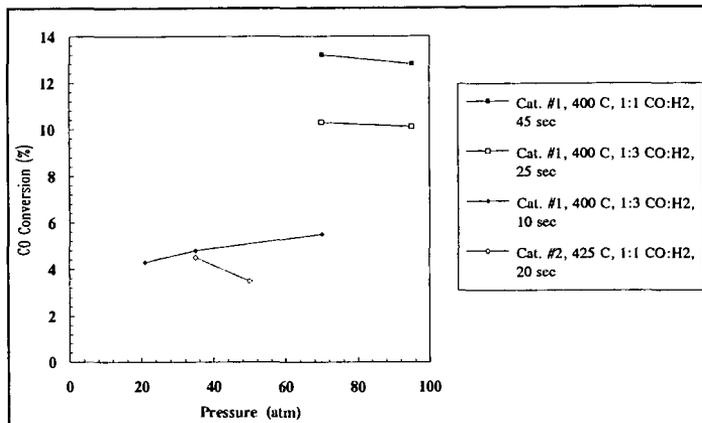


Figure 1. Effect of Pressure on Activity for Catalysts #1 and #2.

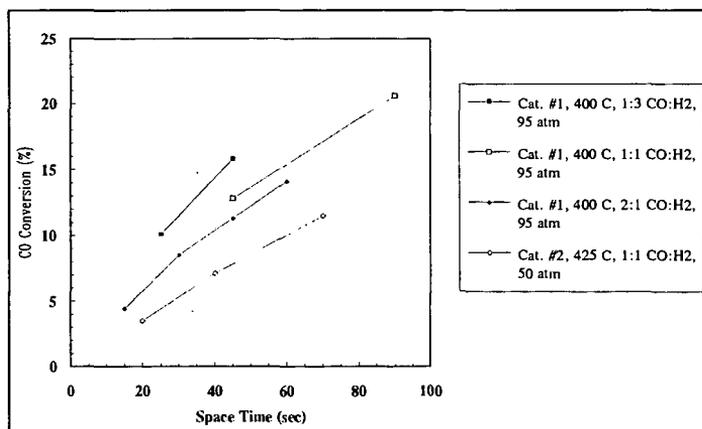


Figure 2. Effect of Space Time on Activity for Catalysts #1 and #2.

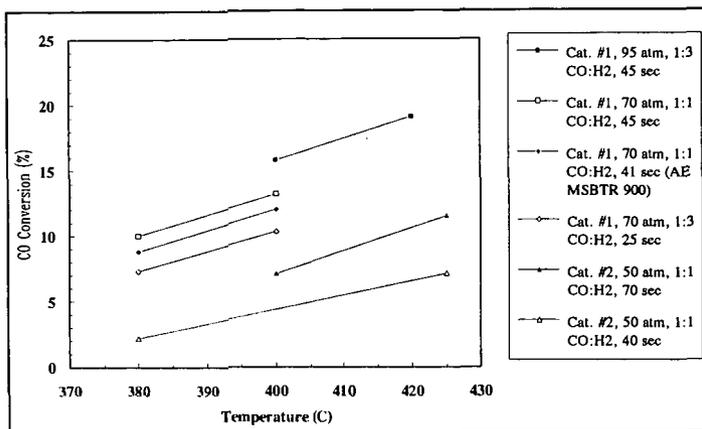


Figure 3. Effect of Temperature on Activity for Catalysts #1 and #2.

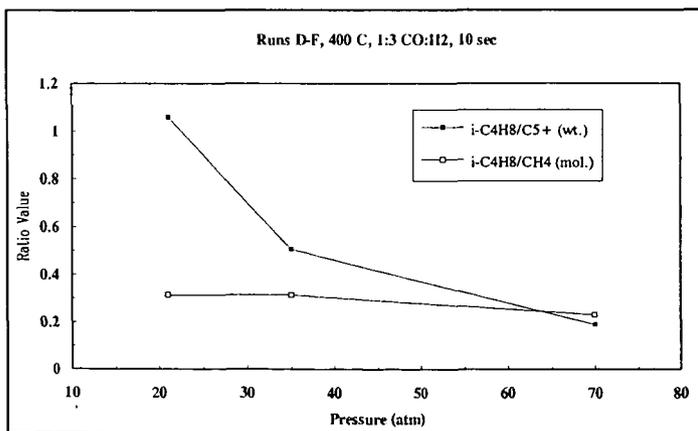


Figure 4. Effect of Pressure on Selectivities for Catalyst #1.

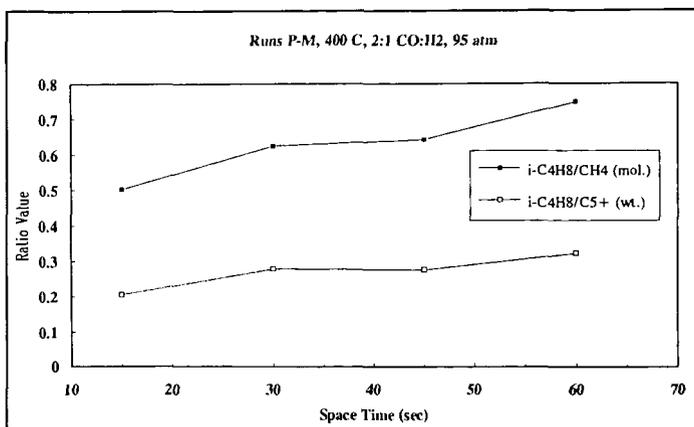


Figure 5. Effect of Space Time on Selectivities for Catalyst #1.

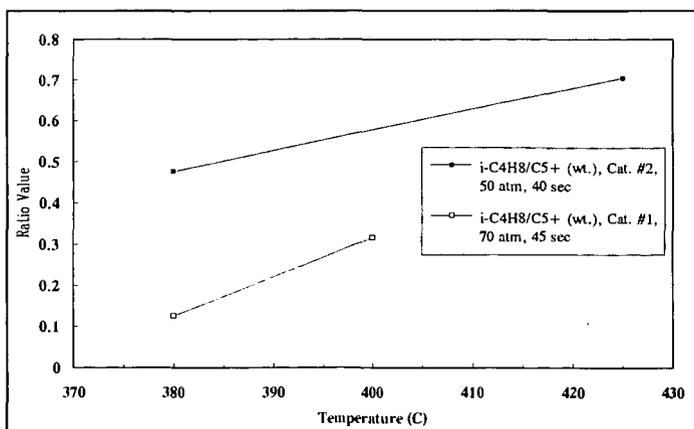


Figure 6. Wt. ratio of isobutylene/C<sub>5</sub>+ increases with temperature for Cat. #1 and #2.