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QUARTERLY REPORT

Report Period

April 1, 1993 to June 30, 1993

FOR

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

Submitted to

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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 04/01/93 to 06/30/93

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 reactors; to 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.

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. However, this processing step is inefficient and consumes a considerable amount of 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 thorium-based, and will contain components to promote the water-gas shift reaction and increase the selectivity of isobutylene.

GOALS FOR THE QUARTER

Perform experiments using 1.06% H_2S in H_2 over 7% Ce-ZrO₂ prepared by the precipitation method, evaluate the activity of catalysts prepared by calcination of zircony nitrate, synthesize catalysts to test the oxygen vacancy/zirconium vacancy theory of activity, evaluate the activity of catalysts prepared by a modified sol gel method, characterize the acid-base properties of the sol gel catalysts, and continue the modelling work. The details for each task are given in its respective sections below.

ACCOMPLISHMENTS FOR THE QUARTER

1. Filing of Necessary Reports

The quarterly report for the period of January 1, 1993 to March 31, 1993 was filed and approved. Monthly reports for the same period were also filed.

1.1. Synthesis and Testing of 7% Ce-ZrO₂ Using 1.06% H₂S in H₂

Two 7% Ce zirconias were prepared by the precipitation method according to the following procedure. The first batch will be referred to as 7% Ce-ZrO₂ (b) and the second will be 7% Ce-ZrO₂ (c). The solutions used in these preparations are shown in Table 1.

The zirconyl nitrate/cerium nitrate solution was poured into the ammonium hydroxide solution on a stir plate. The usual voluminous precipitate formed, and the solution with ppt. had a pH of 10.05 [9.65]. Nitric acid was then added to bring the pH down to 6.00, and stirring continued for fifteen minutes. The stirrer was then shut off and the precipitate was allowed to sit in this solution for 17 [26] hours. The precipitate was filtered (using vacuum pump), washed twice with water (~1000 ml each time), and dried in the oven at ~115 °C for 24 [23.5] hours. Calcination was carried out in the usual manner (except for final temperature), heating from room temperature to 450 °C and leaving for 2 ½ hours. Also the material was calcined in larger chunks (>3 mm) instead of being ground into a powder (<250 µm) before calcination. The average heating rate was about 3.16 [3.21] °C/min. Table 2 shows a comparison of all three 7% Ce-ZrO₂ batches. Similar characteristics between batches show (again) the repeatability of catalyst synthesis.

The reactor was packed with 12.1587 g of 7% Ce-ZrO₂ (b) and pretreatment, according to the usual procedure, was begun. The temperature controller failed during pretreatment; however, and the catalyst was subjected to three cycles of room temperature to 400 °C before the problem was repaired. We have found that any temperature variations cause the catalyst

product distribution to shift toward methane. Even though this catalyst would now produce predominantly methane, two experiments were conducted to determine if it would be beneficial to synthesize another batch to continue H₂S experiments.

The results of these runs are shown in Tables 3 and 4. The first was an activity check to compare this batch with the previous one. Conversion was lower (16% as compared with 20%) and methane was the dominant (~46 wt.%) product (as expected). When the H₂S (1.06% in H₂) was used the conversion dropped slightly (down to ~15%) but the methane was reduced to almost half. There was also an increase in isobutylene production among the C₄'s. The C₅+ product increase was mainly a C₅ increase, but further analysis was necessary in order to determine which C₅ was being produced. During the run, very little H₂S came out of the reactor (0.023 mol.% compared with 0.47 mol.% fed). There were not any new peaks on the GC that would indicate sulfur containing compounds. If the H₂S was completely adsorbing on the catalyst then the amount coming would be equal to the amount fed (after adsorption was complete), but the small amount eluting was constant over ~6 hours. Possibly, this was still not long enough for the bed to become saturated. These two experiments show that H₂S does have a beneficial effect, thus another batch {7% Ce-ZrO₂ (c)} of catalyst was synthesized to continue testing.

Because the addition of H₂S shifted the product distribution toward C₅+ the boiling points of some of the C₄ and C₅ olefins and paraffins were examined to see if a more quantitative analysis of the C₅+ fraction could be obtained. Table 5 shows these boiling points.

The on-line GC to which all components of the effluent stream are fed is only equipped with a 6 foot Porapak Q column that is used mainly for oxygenate analysis. However, this column, combined with temperature programming, also separates some of the hydrocarbons. The C₁-C₃ hydrocarbons are all separated and elute according to increasing boiling point. The C₄ hydrocarbons elute in three or four peaks, depending on the amount of the 2-butenes formed. The four peaks normally seen on the GC are isobutane, isobutylene + 1-butene, n-butane, and cis- and trans-2-butene. From their boiling points, the C₅ compounds should appear in three groups: 3-methyl-1-butene, 2-methyl butane + 1-pentene + 2-methyl-1-butene, and n-pentane + cis- and trans-2-pentene + 2-methyl-2-butene. The only C₅ that elutes completely separate from the others is 3-methyl-1-butene. The preliminary runs showed that the C₅ fraction is over 80% 3-methyl-1-butene when H₂S is included in the feed stream.

With the knowledge of which products were being formed, further experiments using H₂S

could now be conducted. The reactor was packed with 12.2091 g of 7% Ce-ZrO₂ (c) and pretreated according to the normal procedure. Runs C7CACH and C7CH2SA-C7CH2SK were performed. The results are shown in Tables 6 and 7. Run C7CACH was carried out using pure hydrogen to check the activity of this catalyst with that of previous batches. All of these runs used carbon monoxide from the aluminum cylinder and the comparisons are made relative to the three runs (ACOC7A-ACOC7C) made previously. The activity check run compared well with other non-H₂S data in both conversion and product distribution. When H₂S (1.06% in H₂) was added to the feed, the conversion was almost unaffected (Figure 1), but the product distribution shifted significantly. Table 7 (run C7CH2SA) shows that the C₅+ fraction almost doubles when H₂S is included. The C₂ and C₃ weight fractions are reduced by 50%, while the methane and C₄ fractions showed smaller reductions. The on-line GC showed that the C₅ fraction was ~75% 3-methyl-1-butene in the case of H₂S addition and only ~4% when pure H₂ was fed. In the non-H₂S case the second group (based on boiling points) of C₅'s composed about 33% of the fraction and the third group about 67%. Thermodynamics show that 3-methyl-1-butene is the least favorable of the branched C₅ olefins. Table 8 gives the Gibbs free energy of formation for the C₅ paraffins and olefins.

Overall, 1-pentene is the least favorable C₅ compound but has a very similar ΔG_f° to 3-methyl-1-butene. Perhaps the addition of H₂S reduces the amount of cracking of C₅'s into C₂'s and C₃'s. When H₂S is added the only significant changes in mole percent of products are the C₂'s and C₃'s. In a study (Nakajo *et al.*¹) of the synthesis of acetic acid from CO and H₂ over Rh-Ir-Mn-Li/SiO₂, it was suggested that chain propagation of surface CH_x species are suppressed by H₂S treatment.

Run C7CH2SB was performed at a lower pressure (35 atm) to determine if lowering the pressure would cause the dramatic increase in branched olefin production to shift from C₅ to C₄ hydrocarbons. The product distribution did shift slightly; however, methane was the only component to show a significant increase (26.5% to 30.9%). The remainder of the runs were carried out at the usual pressure of 50 atm.

At all temperatures methane and C₄ fractions increased slightly with space time and C₅+ fraction decreased slightly while the C₂ and C₃ fractions remained almost unchanged. As

¹ Nakajo, T., Arakawa, H., Sano, K-I., and Matsuhira, S., *Chem. Lett.*, Vol. 1987, Iss. 4, 593-596.

temperature was increased, more H_2S was present in the effluent because less was adsorbed and the product distribution began resembling that of non- H_2S runs. Although methane weight fraction never reached the same magnitude. The ratio of isobutane to isobutylene increased as temperature increased. Also, the C_3 fraction containing 2-methyl butane (isopentane) increased to 70%, while the 3-methyl-1-butene fraction decreased to 18% at 450 °C. These results are expected because the paraffins are thermodynamically favored. The same reasoning can be used to explain the decrease in oxygenate production at higher temperatures. Run C7CH2SK was performed at the same conditions as C7CH2SA. Once again, methane production increased and conversion slightly decreased with temperature cycling.

Figures 2-4 show the effect of co-feeding H_2S on the production rates of methane, isobutylene, and total hydrocarbons. In these figures, runs with H_2S are compared with earlier non- H_2S runs over another batch of 7% Ce-ZrO₂. Methane production shows a substantial decrease, while isobutylene production remains almost unchanged. The decrease in total hydrocarbon production with H_2S can be attributed to the decrease in methane production. Figures 5 and 6 show Schulz-Flory plots for both non- H_2S and H_2S runs performed at similar conditions. Although these are not true Schulz-Flory distributions because all the C_5+ fraction is included in the approximated mole percent for carbon number five, the usual characteristics of the isosynthesis reaction can be seen. For the case of co-feeding H_2S the C_5+ mole fraction is actually greater than that of the C_4 's. This increase is the result of the marked increase in 3-methyl-1-butene selectivity.

Finally, during run C7CH2SK, an ice bath was used to try and condense the C_5+ fraction. Although most of the C_5 's were not trapped, some liquid was collected. Calculations show this product to be about 3% of the total hydrocarbon product produced. The liquid sample was analyzed and was found to mainly contain C_{11} - C_{20} hydrocarbons. Figure 7 shows a Schulz-Flory distribution. There are no points for C_6 - C_{10} hydrocarbons because of the lumping of C_5+ and loss of these compounds during liquid analysis because of their vapor pressures (also could account for the reduced amount of C_{11} - C_{13}). These factors cause the deviation of the plot from that of a typical Fischer-Tropsch distribution past C_8 . On comparison of the GC output with that of an analysis of a Fischer-Tropsch product, we found that isosynthesis gives a broader product distribution (all of the isomers formed) where as Fischer-Tropsch gives the n-alkane and the 1-olefin as the major products with other isomers being formed to a much lesser degree.

1.2. Synthesis and Testing of ZrO_2 Prepared by Calcining Zirconyl Nitrate

Zirconia was prepared by heating zirconyl nitrate to 100 °C for two hours then increasing the temperature to 500 °C and holding for four hours. The surface area and bulk density of this sample were 39 m²/g and 1.71 g/cm³ respectively. The XRD pattern showed a mixture of tetragonal (77%) and monoclinic.

Two runs were performed using this ZrO_2 (ZrO_2 CAL). These results are shown in Tables 9 and 10. This catalyst was fairly selective to the C_4 's (34%, 62% of C_4 's was isobutylene). Catalytic activity fell in between that of the precipitated zirconia and that prepared hydrothermally (Figure 8). A large amount of oxygenates (DME and MeOH) were produced, however, with the (DME+MeOH)/HC ratio being about 0.25. The activity and selectivity might be correlated to the pore size. The precipitated catalysts have the highest activity and a single pore size of around 40 Å. The hydrothermal catalysts have the lowest activity with good C_4 selectivity and a single pore size between 150-200 Å. The pore size distribution of the calcined zirconyl nitrate catalyst was bimodal. It had characteristics of both the precipitated and hydrothermal catalysts and its activity and selectivity fell between the two.

1.3. Synthesis of Catalysts to Test Oxygen Vacancy/Zirconium Vacancy Theory

In order to test the oxygen vacancy/zirconium vacancy theory, eight catalysts were prepared. Jackson and Ekerdt² reported that activity was maximum when ionic conductivity was a maximum and attributed this to oxygen vacancies. The eight catalysts would allow the comparison of constant M/Zr ratio, constant number of oxygen or zirconium vacancies, and changing numbers of oxygen vacancies. When lower valence ions are substituted for zirconium, oxygen vacancies are created. When a higher valence ion is substituted, zirconium vacancies are formed. Examples of these substitutions are given in the following equations:

² Jackson, N.B., and Ekerdt, J.G., *J. Catal.*, 126, 31-45 1990.

In this notation, subscript Zr or O denotes a zirconium or oxygen position in the ZrO_2 lattice, a capital V denotes a vacancy, superscript ($\cdot$) denotes a positive charge, and superscript ($'$) denotes a negative charge. These equations are written so that atoms, charge, and lattice sites are balanced.

Details about the catalyst preparation are given in Table 11. Several aspects were common to all preparations: (a) the solids were dissolved in water (deionized and distilled) in the ratio of 20 mL of water per gram of solid, (b) a 1.5 wt% solution of NH_4OH was used with 1.3333 mL of NH_4OH per gram of solid, (c) the pH of the final solution with precipitate was adjusted to 7.0 with nitric acid, (d) the batches remained in the mother liquor (pH 7.0) for 24 hours, (e) about 700 mL was poured off the top of solid before filtering began, (f) the batches were filtered and washed twice with ~1000 mL of distilled-deionized water each time, (g) dried at 110 °C for 24 hours, (h) calcined at 450 °C for two and a half hours, (i) ground and sieved to <250 μm before bulk density was measured, and (j) are pretreated under nitrogen (100 sccm, 400 °C, 35 atm) for ~18 hours before the reactants are fed.

Some of the catalysts prepared have been tested. The reaction conditions for all of the catalysts are 400 °C, 50 atm, 1/1 CO/H_2 ratio, and 90 second space time. The results of the runs will not yet be discussed because one needs to look at them in context with all of the others.

1.4. Activity of sol gel catalysts

Catalysts were prepared by a modified sol gel method as follows: tetramethylammonium hydroxide was mixed with methanol to get a 10 wt% methanol solution of tetramethylammonium hydroxide. Then slowly add zirconium isopropoxide into the hydroxide solution to get a clear soluble intermediate. The intermediate was hydrolyzed by a solution of 1:10 water and acetone. The slurry was continuously stirred until the particles were suspended in the solution. Finally, the precipitate was collected by filtering and was further dried in a vacuum at 353 K overnight. After calcined in air for four hours, the catalyst was crushed and sieved to 0.25 mm particles, and is referred to as ZrO_2 (SG). Catalysts prepared by the modified sol gel method showed weak acidity, which makes them promising materials as an isosynthesis catalyst since formation of iso- C_4 hydrocarbons is catalyzed by acidic sites on the catalyst.

Alkali and alkaline earth metals were loaded by dissolving lithium hydroxide, potassium

hydroxide, magnesium nitrate or calcium nitrate in the tetramethylammonium hydroxide methanol solution, and followed the above procedure. The catalysts are referred to as Li-ZrO₂ (SG), K-ZrO₂ (SG), Mg-ZrO₂ (SG) and Ca-ZrO₂ (SG), respectively. Previous research on zirconium oxide (prepared by precipitating zirconyl nitrate with an aqueous ammonia solution) showed enhancement on the selectivities to iso-C₄'s by the presence of Groups I and II elements, which motivated us to investigate possible promotion effects of alkali and alkaline earth metals on sol gel zirconias.

Table 12 is a summary of the activities. Under the same reaction conditions, mole fractions of isobutane and isobutene in C₄ hydrocarbons are higher for zirconia catalysts prepared by the modified sol gel method than for ZrO₂ (Comm) (a commercial zirconia from Harshaw). The presence of alkali and alkaline earth metals further modifies the performance of the catalysts. An increased isobutane and isobutene production and decreased methane production are observed over potassium, magnesium and calcium promoted catalysts, whereas an increased methane production is observed over lithium doped catalyst. Figure 9 is a Schulz-Flory plot for the catalysts. For Fischer-Tropsch synthesis, the plot will give a straight line, but for isosynthesis in this work, a discontinuity is observed at carbon number of 4. Also worth noting is the parallel lines between carbon numbers of 2 to 3 and 4 to 6. This observation helps the development of kinetics models discussed in following sections of this report.

1.5. Characterization of acid-base properties of sol gel catalysts.

Figure 10 is a temperature programmed desorption (TPD) of carbon dioxide for three different sol gel catalysts: ZrO₂ (SG), SiO₂-ZrO₂ (SG) and Al₂O₃-ZrO₂ (SG). SiO₂-ZrO₂ (SG) and Al₂O₃-ZrO₂ (SG) were prepared by mixing silicon ethyloxide or aluminum propoxide with zirconium isopropoxide in the preparation. Previous work on sol gel catalysts showed that the presence of silicon deactivates the catalysts whereas the presence of aluminum increases the amount of oxygenates in the products. By comparing the basicities of ZrO₂ (SG), SiO₂-ZrO₂ (SG) and Al₂O₃-ZrO₂ (SG), we can conclude that the incorporation of silicon deactivates almost all the basic sites, and consequently, the catalyst showed minimal isosynthesis activity. As for Al₂O₃-ZrO₂ (SG), the presence of aluminum increases the basicity of the material, and results in a larger production of oxygenates. The TPD experiments indicate that optimum basicity is important to achieve a high activity while limiting the amount of oxygenates produced.

1.6. Kinetic model for isosynthesis

1.6.1. Comparison of reaction mechanisms in isosynthesis with those in F-T reaction

There are many similarities between isosynthesis and Fischer-Tropsch reaction: both processes convert synthesis gas to a mixture of hydrocarbons on transition metal oxides under relatively severe conditions. Since F-T synthesis has been studied much more thoroughly in the literature, a brief review of the approach in modeling F-T reaction may provide valuable aid in developing a kinetic model for isosynthesis reaction.

Consider the following reaction series with a stepwise propagation mechanism:

where $[C_i]$'s and P_i 's denote intermediates and hydrocarbons of i carbon numbers, respectively. There is still a debate on whether the chain growth is by CO insertion into the metal-hydrocarbon bond, by condensation of oxygen containing species, or by addition of oxygen free CH_x species, but it is evident that the chain growth involves an intermediate reacting with one carbon atom containing species. A Schulz-Flory distribution is obtained if assuming k_p/k_t as a constant for all the intermediates, as follows:

$$C_{n+1} = \alpha C_n$$

where

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

A straight line is obtained by plotting molar fraction of P_n versus carbon number n in a semilog scale. This approach is also valid for other standard polymerization reactions. However, this linear relation in product distribution will not be obtained for isosynthesis reaction due to the differences in the mechanisms. Instead, a discontinuity in P_n vs n plot is observed at $n=4$ (Figure 9).

Though there is still controversy regarding the detailed mechanisms, it may be generally

agreed that C₄ hydrocarbons are formed over zirconium oxide catalysts by the following steps:

(i) An adsorbed H reacts with carbon monoxide to form an adsorbed formate species for the chain initiation.

(ii) Other adsorbed intermediates are formed via chain propagation by CO insertion. This reaction is equivalent to the chain growth in F-T synthesis. As can be seen, linear intermediates are formed on the surface.

(iii) A unique reaction for isosynthesis is the condensation of an intermediate with the adsorbed formate.

Branched intermediates are formed on the surface. Though condensation reactions are slow compared with CO insertion, they are kinetically significant due to the large surface concentration of adsorbed formate groups on the catalyst.

(iv) In addition to propagating, intermediates may terminate by desorbing into hydrocarbons.

Condensation reactions (iii) contribute to the deviations in hydrocarbon distribution of isosynthesis from that of a Schulz-Flory polymerization scheme, which results in a large amount iso-C₄ hydrocarbons in the product. Zirconium oxide is one of the active metal oxide in catalyzing condensation reactions, and consequently, a much higher amount of isobutane and

isobutene is produced over the catalysts.

1.6.2. Development of a two parameter model for isosynthesis

The discussion on isosynthesis mechanisms indicates that chain growth in isosynthesis reaction is a combination of (i) CO insertions to the C-O bond of the intermediates on the surface, which is analogous to chain growth mechanism in F-T synthesis, and (ii) condensation reactions between intermediates on the surface with adsorbed formate. It can be represented as:

where k_d accounts for the contribution to the C_4 production from condensations of C_2 intermediates. Assuming first order reactions for intermediates,

$$\frac{d[C_2]}{dt} = k_{p_1}[C_1] - k_{t_1}[C_2] - k_{p_2}[C_2] - k_d[C_2]$$

$$\frac{d[C_3]}{dt} = k_{p_2}[C_2] - k_{t_2}[C_3] - k_{p_3}[C_3]$$

$$\frac{d[C_4]}{dt} = k_{p_3}[C_3] + k_d[C_2] - k_{t_3}[C_4] - k_{p_4}[C_4]$$

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

By further assuming steady state for intermediate formation and k_p/k_t to be the same for all the intermediates, the following product distributions are obtained:

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

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

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

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

where

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

$$\beta = \frac{k_d}{k_{p_2}}$$

The model contains two parameters: α , which indicates the probability of chain growth, and β , which is the ratio of condensation rate constant k_d to propagation rate constant k_{p_2} . Table 13 is a summary of the parameters obtained from least square optimization using SimuSolv. Figure 11 is a comparison of calculated hydrocarbon mole fractions from the model with the experimental data. As can be seen, the simulation provides a good fit with the experimental data.

SUMMARY AND CONCLUSIONS

The presence of potassium or calcium in sol gel catalysts increase the production of C_4 hydrocarbon and minimize that of methane while maintaining high activities. Characterization of catalysts using temperature programmed desorption of carbon dioxide indicates that activity and product distribution over an isosynthesis catalyst depend on its acid-base properties. Low activity was observed for catalysts with very weak basicity, and high oxygenate production for catalysts with strong basicity. An optimum strength of basic sites is crucial to achieve high activity while minimizing the amount of oxygenates. A kinetic model was developed based on the reaction mechanisms, and the simulation from the model produces reasonable fit with the experimental data.

GOALS FOR NEXT QUARTER

The goals for the next quarter include the following:

- 1) continue the work on kinetic and reactor modelling;
- 2) evaluate the activity of zeolites for isosynthesis reaction;
- 3) initiate experiments using a slurry reactor to obtain kinetic data; and
- 4) complete experiments to evaluate hypothesis of oxygen vacancy/zirconia vacancy theory.

Table 1. Solutions used in 7% Ce zirconia preparation.

Solution	pH
45.0063 g [45.0033] [†] ZrO(NO ₃) ₂ ·8H ₂ O + 4.0579 g [4.0572] Ce(NO ₃) ₃ ·6H ₂ O in ~980 ml water [‡] { ~15/1 Zr/Ce molar ratio }	1.37 [1.57]
~65 ml of NH ₄ OH stock solution (28-30 wt.%) in 1240 ml water	10.90 [10.25]

[†] Numbers in [] brackets denote values for 7% Ce-ZrO₂ (c).

[‡] All water used in preparation is deionized-distilled water.

Table 2. Properties of 7% Ce-ZrO₂ (ppt.) Catalysts.

Batch	Surface Area (m ² /g)	Bulk Density (g/cm ³)
(a)	103	2.28
(b)	93	2.39
(c)	98	2.32

Table 3 - Run Results for 7.0% Ce-ZrO₂ (b) (ppt.)

Run	T (°C)	P (atm)	CO/H ₂ Ratio	Space Time (sec)	CO ₂ /CO Conversion (%)	Isosynthesis Profile wt. mol.	Branched/Linear r C4 wt. mol.	i-C ₄ H ₈ / CH ₄ wt. mol.	i-C ₄ H ₈ / C5 ⁺ wt.	i-C ₄ H ₈ / All C4's wt. mol.	i-C ₄ H ₈ / i-C ₄ H ₁₀ wt.
C7B ACH	400	50	1/1	60	16.24 0.43*	0.471 0.286 0.122 0.075	0.807 0.807 0.039 0.040	0.090 0.026 0.027 0.008	0.291 0.018	0.332 0.335 0.026 0.026	2.92
C7B H2S	400	50	1/1 [†]	60	15.20 0.07	1.297 0.810 0.097 0.053	1.627 1.619 0.120 0.120	0.346 0.099 0.007 0.002	0.189 0.006	0.487 0.490 0.020 0.020	3.67

* The number below each result indicates the estimated error in that result.

† In this case it actually refers to the CO/(H₂+H₂S) ratio.

Table 4. Distributions (wt%) for Isosynthesis over 7% Ce-ZrO₂ (b) (ppt.)

Run	C7BACH	C7BH2S
Hydrocarbon Distribution		
C ₁	46.5	24.4
C ₂ 's	15.2	6.5
C ₃ 's	11.4	6.9
C ₄ 's	11.6	17.4
C ₅ +s	14.4	44.8
C ₄ Distribution		
Isobutane	11.4	13.2
n-Butane	14.9	2.5
1-butene	9.3	8.5
Iso-butylene	33.2	48.7
trans-2-butene	18.5	16.2
cis-2-butene	12.6	10.9
(DME+MeOH)/HC (%)	0.2	0.5

Table 5. Boiling Points of Various C₄ and C₅ Paraffins and Olefins.

C₄'s	Boiling Point (K)	C₅'s	Boiling Point (K)
isobutane	261.4	3-methyl-1-butene	293.3
isobutylene	266.2	2-methyl butane	301.0
1-butene	266.9	1-pentene	303.1
n-butane	272.7	2-methyl-1-butene	304.3
trans-2-butene	274.0	n-pentane	309.2
cis-2-butene	276.9	trans-2-pentene	309.5
		cis-2-pentene	310.1
		2-methyl-2-butene	311.7

Table 6. Run Results for 7.0 wt% Ce on ZrO₂ (c) (ppt).

Run	T (°C)	P (atm)	CO/ (H ₂ +H ₂ S) Ratio	Space Time (sec)	CO ₂ /CO Conversion (%)	Isosynthesis Profile wt. mol.	Branched/Linear C4 wt. mol.	i-C ₄ H ₁₀ / CH ₄ wt. mol.	i-C ₄ H ₁₀ / C ₅ wt.	i-C ₄ H ₁₀ / All C4's wt. mol.	i-C ₄ H ₁₀ / i-C ₄ H ₁₀ wt. mol.
C7C ACH	400	50	1/1†	60	23.56 0.72*	1.411 0.864 0.112 0.068	1.648 1.643 0.079 0.080	0.510 0.146 0.004 0.001	0.708 0.011	0.521 0.524 0.014 0.014	5.157 5.342 0.288 0.299
C7C H2SA	400	50	1/1	60	23.55 0.13	1.927 1.196 0.041 0.022	2.045 2.037 0.012 0.012	0.457 0.131 0.002 0.001	0.309 0.003	0.532 0.535 0.002 0.002	3.809 3.946 0.030 0.031
C7C H2SB	400	35	1/1	60	22.01 0.01	2.731 1.607 0.028 0.018	2.262 2.251 0.048 0.047	0.385 0.110 0.001 0.000	0.310 0.001	0.523 0.526 0.006 0.006	3.064 3.174 0.071 0.074
C7C H2SC	400	50	1/1	90	27.93 0.11	2.969 1.775 0.058 0.033	2.195 2.179 0.017 0.018	0.384 0.110 0.006 0.002	0.299 0.001	0.461 0.465 0.007 0.007	2.041 2.115 0.075 0.077
C7C H2SD	400	50	1/1	120	33.07 0.02	3.286 1.965 0.056 0.023	2.298 2.275 0.020 0.020	0.322 0.092 0.005 0.002	0.322 0.005	0.387 0.392 0.012 0.012	1.252 1.297 0.079 0.082
C7C H2SE	425	50	1/1	90	38.96 0.12	3.170 1.860 0.019 0.014	2.593 2.559 0.010 0.010	0.195 0.056 0.004 0.001	0.268 0.003	0.267 0.272 0.005 0.005	0.588 0.610 0.017 0.018
C7C H2SF	425	50	1/1	120	44.56 0.05	3.401 2.000 0.037 0.021	2.808 2.769 0.004 0.004	0.143 0.041 0.006 0.002	0.246 0.011	0.201 0.205 0.005 0.005	0.375 0.388 0.013 0.014
C7C H2SG	450	50	1/1	90	52.08 0.10	2.871 1.694 0.028 0.018	3.375 3.335 0.006 0.006	0.052 0.015 0.001 0.000	0.180 0.002	0.102 0.105 0.002 0.002	0.153 0.158 0.003 0.003
C7C H2SH	450	50	1/1	120	57.13 0.01	2.979 1.770 0.031 0.019	3.564 3.529 0.038 0.038	0.032 0.009 0.001 0.000	0.112 0.001	0.063 0.065 0.001 0.001	0.088 0.092 0.002 0.002
C7C H2SI	375	50	1/1	90	14.42 0.00	5.807 3.445 0.062 0.038	3.629 3.608 0.042 0.041	0.369 0.105 0.012 0.003	0.294 0.002	0.598 0.602 0.005 0.005	3.225 3.341 0.151 0.156
C7C H2SJ	375	50	1/1	120	17.17 0.10	5.003 3.058 0.027 0.018	3.594 3.568 0.054 0.053	0.338 0.097 0.005 0.001	0.301 0.000	0.562 0.566 0.001 0.001	2.544 2.635 0.009 0.010
C7C H2SK	400	50	1/1	60	18.33 0.16	4.220 2.508 0.058 0.025	3.232 3.202 0.032 0.031	0.256 0.073 0.001 0.000	0.456 0.003	0.456 0.461 0.003 0.003	1.482 1.535 0.027 0.028

† Denotes CO/H₂ ratio in this case.

* The number below each result indicates the estimated error in that result.

Table 7. Distributions (wt%) for Isosynthesis over 7.0 wt% Ce on ZrO₂ (c) (ppt).

Run	C7C ACH	C7C H2SA	C7C H2SB	C7C H2SC	C7C H2SD	C7C H2SE	C7C H2SF	C7C H2SG	C7C H2SH	C7C H2SI	C7C H2SJ	C7C H2SK
Hydrocarbon Distribution												
C ₁	29.61	26.46	30.87	29.40	32.33	37.21	40.04	50.68	51.28	33.55	35.14	38.03
C ₂ 's	10.95	5.93	5.26	4.83	4.73	5.33	5.09	5.38	4.97	2.09	2.15	2.95
C ₃ 's	9.38	5.82	3.05	3.43	3.47	3.24	3.24	3.59	3.62	1.47	2.07	2.17
C ₄ 's	28.84	22.71	22.65	24.51	26.91	27.14	28.42	25.70	25.61	20.64	21.13	21.46
C ₅ +s	21.23	39.09	38.17	37.83	32.57	27.08	23.22	14.64	14.52	42.25	39.51	35.38
C ₄ Distribution												
Isobutane	10.12	13.97	17.07	22.60	30.98	45.43	53.64	66.93	71.75	18.57	22.08	30.77
n-Butane	3.13	3.03	3.16	3.64	4.53	7.38	8.88	12.17	14.03	1.64	1.62	3.32
1-butene	8.36	7.26	6.82	6.72	6.23	5.14	4.34	2.82	2.06	6.36	6.00	5.63
Iso-butylene	52.11	53.20	52.28	46.10	38.70	26.73	20.10	10.22	6.34	59.83	56.16	45.60
trans-2-butene	15.82	13.41	12.38	12.41	11.57	9.09	7.77	4.75	3.50	6.78	7.33	8.07
cis-2-butene	10.47	9.15	8.30	8.54	7.99	6.22	5.28	3.12	2.32	6.83	6.82	6.61
(DME+MeOH)/HC (%)	1.60	2.05	1.28	2.34	1.56	0.19	0.14	0.00	0.00	26.09	18.92	3.71

Table 8. Gibbs Free Energy of Formation at 700 K for C₅ Paraffins and Olefins

C ₅ Hydrocarbon	ΔG_f° (kcal/mol)
3-methyl-1-butene	53.96
2-methyl butane	45.18
1-pentene	54.20
2-methyl-1-butene	51.55
n-pentane	46.19
trans-2-pentene	52.60
cis-2-pentene	52.71
2-methyl-2-butene	50.47

Table 9. Run Results for ZrO_2 Prepared by Calcining Zirconyl Nitrate.

Run	T (°C)	P (atm)	CO/H_2 Ratio	Space Time (sec)	CO_2/CO Conversion (%)	Isosynthesis Profile		Branched/Linear C4		$i\text{-C}_4\text{H}_{10}/\text{CH}_4$		$i\text{-C}_4\text{H}_{10}/\text{C}_5^+$		$i\text{-C}_4\text{H}_{10}/\text{All C}_4\text{'s}$		$i\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ wt.
						wt.	mol.	wt.	mol.	wt.	mol.	wt.		wt.	mol.	
CZNA	400	50	1/1	60	11.60 0.44*	2.649 0.296	1.569 0.162	1.987 0.193	1.982 0.193	0.738 0.029	0.211 0.008	0.794 0.062		0.615 0.024	0.616 0.024	12.34
CZNB	400	50	1/1	90	14.10 0.08	3.446 0.129	2.031 0.073	2.180 0.086	2.172 0.086	0.917 0.011	0.262 0.003	0.747 0.047		0.620 0.009	0.621 0.009	9.47

* The number below each result indicates the estimated error in that result.

Table 10. Distributions (wt%) for Isosynthesis over ZrO_2 Prepared by Calcining Zirconyl Nitrate.

Run	CZNA	CZNB
Hydrocarbon Distribution		
C_1	27.91	24.19
C_2 's	7.53	6.35
C_3 's	5.11	4.02
C_4 's	33.49	35.76
C_5 's	25.96	29.67
C_4 Distribution		
Isobutane	4.98	6.55
n-Butane	0.00	0.00
1-butene	8.15	7.98
Iso-butylene	61.54	62.00
trans-2-butene	14.85	13.75
cis-2-butene	10.47	9.72
(DME+MeOH)/HC (%)	23.77	27.97

Table 11. Details of Oxygen Vacancy/Zirconium Vacancy Catalyst Preparation

Catalyst	Metal wt%	Weight of Metal Compound [†] (g)	Weight of Zirconyl Nitrate [‡] (g)	mL of NH ₄ OH	pH of Metals Solution	pH of Ammonia Solution	pH of Solution with Precipitate	Heating Rate (°C/min)	Bulk Density (g/cm ³)
Li/Zr = 0.04	0.22	0.3574	41.6404	56.0	1.71	10.33	9.72	3.16	2.18
Mg/Zr = 0.04	0.79	1.3154	41.2090	56.7	2.04	10.49	9.93	3.16	2.18
Mg/Zr = 0.06	1.16	1.9688	41.1201	57.5	1.73	10.37	9.72	3.08	2.18
Mg/Zr = 0.12	2.28	3.9231	40.9674	59.9	1.44	10.35	9.82	3.23	2.20
Dy/Zr = 0.04	4.97	2.2415	41.0534	57.7	1.63	10.42	9.78	3.19	2.32
Dy/Zr = 0.12	13.39	6.7178	41.0109	63.6	1.42	11.17	10.55	3.19	2.55
Ta/Zr = 0.04	5.48	1.4094	41.0290	56.6	1.60	10.22	9.63	3.23	1.93
Ta/Zr = 0.24	24.64	8.4627	41.0597	66.0	1.60	10.18	9.47	3.23	1.60

[†] Source compounds for the metals are:

Li: LiNO₃

Mg: Mg(NO₃)₂·6H₂O

Dy: Dy(NO₃)₃·5H₂O

Ta: TaF₅

[‡] Zirconyl nitrate is ZrO(NO₃)₂·5H₂O

Table 12. Conversions and Production Distributions^a

Catalyst	CO/H ₂ GHSV	CO Conv %	H ₂ Conv %	Distribution of Hydrocarbons and Oxygenates, mole%													
				C ₁	C ₂ ^a	C ₂	C ₃ ^a	C ₃	iC ₄ ^a	tC ₄ ^a	cC ₄ ^a	1C ₄ ^a	iC ₄	nC ₄	C ₅ 's	C ₆ 's	Oxy ^b
ZrO ₂ (Comm)	1100	17	15	47	5.2	5.7	2.4	3.5	9.5	1.1	0.91	0.73	3.9	0.44	14	5.5	0.72
	1900	12	11	52	6.6	6.0	4.4	2.6	11	1.1	1.1	0.77	4.0	0.42	7.0	1.8	0.86
	3200	8.5	7.8	58	4.7	4.4	3.5	1.6	10	1.1	1.0	0.76	2.9	0.43	8.4	2.7	1.2
ZrO ₂ (SG)	1100	16	15	62	2.8	5.0	1.5	1.8	10	t	t	0.51	3.5	t	10	2.7	0.35
	1400	13	11	64	2.8	4.7	1.5	1.8	10	t	t	0.50	3.3	t	8.8	2.4	t
	1900	10	9.2	69	2.7	4.2	1.4	1.8	9.8	t	0.38	0.48	3.1	t	6.4	0.82	1.0
Li-ZrO ₂ (SG)	1100	4.4	4.0	77	2.0	8.5	1.4	2.0	4.5	t	t	t	2.5	t	1.8	0.35	2.7
K-ZrO ₂ (SG)	1100	13	12	55	2.9	5.2	1.4	2.8	14	t	t	0.48	4.5	t	9.2	3.9	1.0
Mg-ZrO ₂ (SG)	1100	13	12	60	3.0	4.3	1.5	1.6	9.9	0.50	0.60	0.56	4.1	t	10	2.9	t
Ca-ZrO ₂ (SG)	1100	15	14	55	4.3	4.8	1.8	1.6	13	0.63	0.64	0.69	4.0	t	13	1.3	3.3

a reaction condition 723 K, 7 MPa, CO/H₂ = 1 in the feed

b oxygenates include methanol, isobutanol, dimethylether and water

t: trace, usually < 0.2 mole%

Table 13. Parameters Obtained from Optimization*

Catalyst	ZrO ₂ (Comm)			ZrO ₂ (SG)			Li-ZrO ₂ (SG)	K-ZrO ₂ (SG)	Mg-ZrO ₂ (SG)	Ca-ZrO ₂ (SG)
CO/H ₂ GHSV	1100	1900	3200	1100	1400	1900	1100			
$\alpha=k_p/(k_i+k_p)$	0.54	0.55	0.57	0.358	0.371	0.365	0.233	0.464	0.408	0.481
$\beta=k_d/k_2$	2.25	2.19	2.63	3.84	3.82	3.88	1.76	3.98	4.49	5.17

* 723 K, 7 MPa, CO/H₂=1 in the feed

Figure 1. Effect of Feeding Hydrogen Sulfide on Conversion at 400 °C and 50 atm over 7 wt.% Ce-ZrO₂ (ppt.).

Figure 2. Effect of Feeding Hydrogen Sulfide on Methane Production Rate at 400 °C and 50 atm over 7 wt.% Ce-ZrO₂ (ppt.).

Figure 3. Effect of Feeding Hydrogen Sulfide on Isobutylene Production Rate at 400 °C and 50 atm over 7 wt.% Ce-ZrO₂ (ppt.).

Figure 4. Effect of Feeding Hydrogen Sulfide on Total Hydrocarbon Production Rate at 400 °C and 50 atm over 7 wt.% Ce-ZrO₂ (ppt.).

Figure 5. Schulz-Flory Distribution at 400 °C, 50 atm, and 1/1 CO/H₂.

Figure 6. Schulz-Flory Distribution at 400 °C, 50 atm, and 1/1 CO/(H₂+H₂S).

Figure 7. Schulz Flory Plot of Hydrocarbon Distribution for Run C7CH2SK.

Figure 8. Changes in Conversion with Space Time at 400 °C and 1/1 CO/H₂ Ratio.

Figure 9. Mole fractions of hydrocarbon with different carbon numbers. 450 °C, 70 atm, CO/H₂ GHSV = 1100, CO/H₂ = 1 in the feed.

ZrO_2 (SG)

$\text{SiO}_2\text{-ZrO}_2$ (SG)

$\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SG)

Figure 10. Temperature Programmed Desorption of CO_2 . 70 °C to 460 °C at 5 °C/min.

a. C₁ Hydrocarbon.

b. C₂ Hydrocarbons.

c. C₃ Hydrocarbons.

d. C₄ Hydrocarbons.

e. C₅ Hydrocarbons.

f. C₆ Hydrocarbons.

Figure 11. Comparison of Hydrocarbon Distributions Observed and Those Calculated.

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