

## CHAPTER I

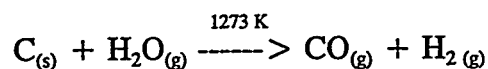
### INTRODUCTION

#### *Project Motivation and Objectives*

Recent amendments to the Clean Air Act will, once again, require reformulation of gasoline. The Environmental Protection Agency has set new standards for fuel vapor pressure, volatile organic compounds (VOCs), aromatic content, and oxygen content (1). The vapor pressure limit (summer 1992) was set at 9 psi while VOCs are to be reduced by 15% by 1995 (compared to 1990). Total aromatics in the gasoline pool are limited to 25 vol% with benzene limited to 1 vol%. Oxygen content will be a minimum of 2-2.7 wt% depending on the area in which the gasoline is used. The purpose of these stricter guidelines is to limit exhaust and evaporative emissions. Carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NO<sub>x</sub>) are the three primary sources of exhaust pollution from today's gasoline, combined with low molecular weight hydrocarbons and aromatics (VOCs) as evaporative sources (2).

Methyl-tertiary-butyl ether (MTBE) is an additive that has received increased attention because of its potential to solve some of the problems associated with current gasoline blends. Addition of MTBE to gasoline can reduce exhaust emissions of CO, HC, and NO<sub>x</sub> and evaporative emissions by replacing VOCs while maintaining the octane rating at an acceptable level. The demand for MTBE is currently the fastest growing of any petrochemical and is likely to continue increasing at a high rate (3). The supply of MTBE is directly linked to the supply of isobutylene, a key reactant.

The demand for reformulated gasoline could result in a shortage of isobutylene on a worldwide basis (4). Isomerization of 1-butene and dehydrogenation of isobutane are two current processes that could supplement the isobutylene pool. These two processes are expensive and are limited by the supply of C<sub>4</sub> feedstocks (2-6). Catalytic cracking can also be utilized to produce a stream with 10-15% isobutylene, but this process is very energy intensive. A process that would take advantage of an ample supply of feed gas is direct conversion of coal derived synthesis gas into isobutylene. Synthesis gas refers to a mixture of carbon monoxide and hydrogen. The reaction for producing synthesis gas from coal is



A process producing isobutylene from synthesis gas could be combined with a methanol synthesis unit and a MTBE synthesis unit since the technology already exists for these two operations.

Previous work on isosynthesis (conversion of synthesis gas to isobutane and isobutylene) was performed at very low conversions or extreme process conditions. No model existed for the prediction of carbon monoxide conversion or product distribution. Such a model would be useful in scale-up to an industrial sized reactor.

The objectives of this research were (1) determine the optimum process conditions for isosynthesis; (2) determine the optimum catalyst preparation method and catalyst composition/properties for isosynthesis; (3) determine the kinetics for the best catalyst; (4) develop reactor models for trickle bed, slurry, and fixed bed reactors; and (5) simulate the

performance of fixed bed trickle flow reactors, slurry flow reactors, and fixed bed gas phase reactors for isosynthesis.

### *Literature Review on Isobutylene Synthesis*

Pichler and Ziesecke (7) were the first to study (and name) the isosynthesis reaction. Isosynthesis refers to the synthesis of *iso*-C<sub>4</sub> hydrocarbons from carbon monoxide and hydrogen. In their study, several single component and multicomponent oxide catalysts were tested for activity toward isosynthesis. Thorium dioxide (ThO<sub>2</sub>) and zirconium dioxide (ZrO<sub>2</sub>) were found to be the most active single component catalysts. Overall, a 20% Al<sub>2</sub>O<sub>3</sub>/ThO<sub>2</sub> catalyst was found to be the most active. Pichler and Ziesecke (7) performed experiments at high temperatures (648-773 K) and high pressures (150-1000 atm) (1 atm =  $1.01325 \times 10^5$  N/m<sup>2</sup>). Although high conversions were obtained, in most cases the isobutylene yield was low. However, isobutylene was the primary C<sub>4</sub> product with ZrO<sub>2</sub> catalyst. Additionally, operation at lower pressures would be desirable because of the cost associated with high pressure equipment.

More recent investigations on the activity and selectivity of zirconium dioxide have been performed (8-14). Kieffer *et al.* (8) investigated CO hydrogenation over rare earth metal oxides (La<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub>) at 400 atm and 683-748 K. They observed ~25% C<sub>4</sub>'s with 80% selectivity to *iso*-C<sub>4</sub>'s at about 20-25% total carbon monoxide conversion. Both hydrocarbons and methanol were formed. Addition of palladium to these oxides resulted in an increase in methane formation. A two step mechanism in which methanol formed first and then transformed into the hydrocarbons was suggested.

Maehashi *et al.* (9) performed isosynthesis using a glass vacuum reactor system with a gas recirculating pump at temperatures from 523-673 K. Also, several tests at 21 atm were conducted in a flow reactor system. They reported a very high selectivity to isobutylene (~80%) among all hydrocarbons at 623 K and 0.68 atm. Conversion for low pressure runs was less than 5%. Carbon monoxide conversion was surprisingly high for the flow system; however, ~80% of the product was carbon dioxide.

Maruya *et al.* (10,11) investigated the effects of various metal promoters. They found that sodium increased the selectivity to C<sub>4</sub>'s while decreasing overall activity. Cerium was found to increase activity while maintaining high C<sub>4</sub> selectivity (~75%). Catalysts doped with niobium were less active and did not give the typical isosynthesis distribution. Instead, the Schulz-Flory plot resembled that of Fischer-Tropsch synthesis. The electronegativity of the dopant oxide was thought to play an important role in selectivity toward C<sub>4</sub>'s, especially isobutylene. An increase in catalyst acidity promoted methane formation and retarded the formation of C<sub>4</sub> hydrocarbons. They concluded that the formation of C<sub>2</sub> species from C<sub>1</sub> species was the rate determining step of the reaction. This work was also performed at very low conversions.

Tseng *et al.* (12) examined the mechanism by the incorporation of <sup>13</sup>C labeled oxygenated compounds into the products. These studies were performed at 623-698 K, 35 atm, and 1/1 CO/H<sub>2</sub> ratio. Methane and methanol were the dominant products even though conversions were low. Two chain growth steps were proposed. One involved CO insertion into a bound aldehyde or ketone and the other involved condensation between methoxide and a surface bound enolate. Maruya *et al.* (11) also found evidence to support this mechanism.

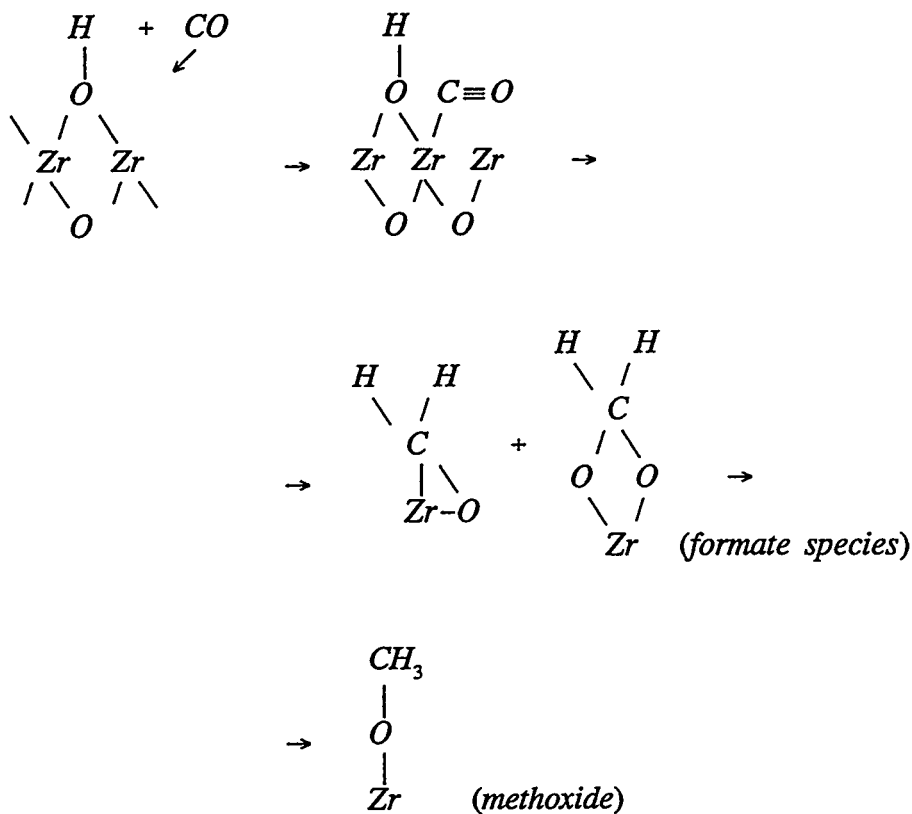
Jackson and Ekerdt (13) doped zirconia with calcium and yttrium oxides in varying concentrations to investigate the effect of oxygen vacancies and acidity on the isosynthesis

reaction carried out at conditions similar to Tseng *et al.* (12). The most active catalysts were those in which ionic conductivity was a maximum, suggesting that vacancies in the crystal lattice play an important role in the reaction. Jackson and Ekerdt (14) also studied the effect of catalyst acidity on  $C_3$  intermediates. They found that more acidic catalysts stabilized the branched  $C_3$  intermediates which led to more  $C_4$  products, but not necessarily the highest branched to linear [ $C_4$ 's and  $C_5$ 's] ratio. A balance of acidic and basic sites on the surface was believed necessary for maximum isobutylene production.

### Reaction Mechanism

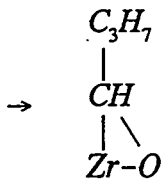
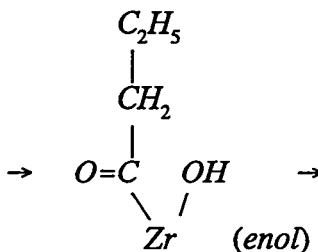
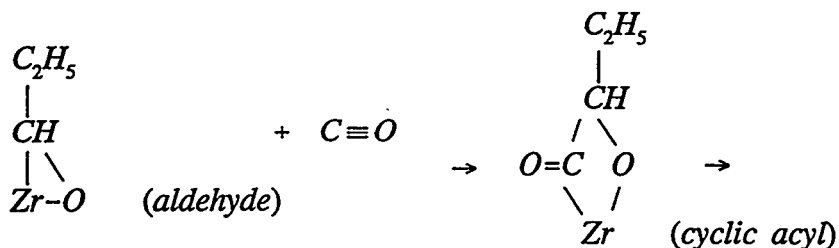
Though there is still controversy regarding the detailed mechanisms, it may be generally agreed that  $C_4$  hydrocarbons are formed by the following steps (12,15):

1. *Chain initiation:* An adsorbed H reacts with carbon monoxide to form an adsorbed formate species for chain initiation.

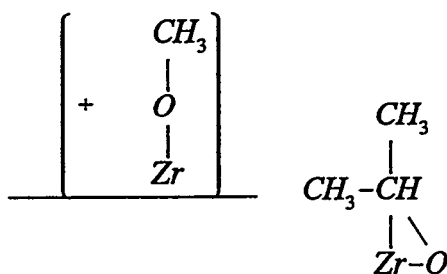
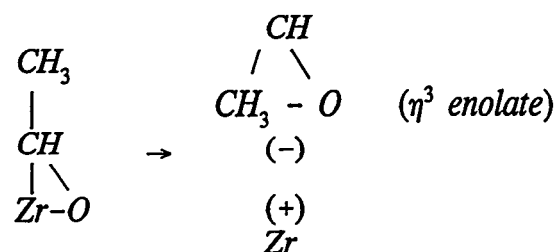


( $\rightarrow CH_3OH$  or  $CH_4$ )

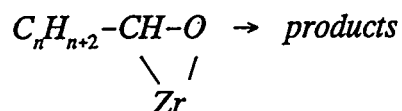
2. Other adsorbed intermediates are formed via *chain propagation by CO insertion*. This reaction is equivalent to the chain growth in F-T synthesis. As can be seen, linear intermediates are formed on the surface. CO attacks the carbon-metal bond.



3. A unique reaction for isosynthesis is the *chain propagation by condensation* of an intermediate with the adsorbed formate. Branched intermediates are formed on the surface and react with an alkoxide. Though condensation reactions are slow compared with CO insertion, they are kinetically significant because of the large surface concentration of adsorbed formate groups on the catalyst.



4. In addition to propagating, intermediates may *terminate* by desorbing into hydrocarbons



Condensation reactions contribute to the deviations in hydrocarbon distribution of isosynthesis from that of an Anderson-Schulz-Flory polymerization scheme, which results in a large amount of iso-C<sub>4</sub> hydrocarbons in the product. Zirconia is one of the active metal oxides for catalyzing condensation reactions (15), and consequently, a large amount of isobutane and isobutene is produced over the catalysts.

An excellent review of isosynthesis has been written by Sofianos (4) and contains more detailed information on proposed mechanisms.

#### *Zirconia Synthesis by Precipitation*

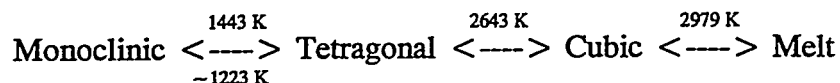
Nearly all work on isobutylene synthesis has been performed using zirconia prepared by co-precipitation. Studies done on the crystal phase (16-20) obtained from precipitation indicate that both pH and the presence of other metal dopant ions play a role in determining the final crystal phase.

Zirconia gels were precipitated from zirconyl nitrate or zirconyl chloride solutions with ammonium hydroxide or sodium hydroxide depending on pH (16-18). When these gels were calcined at 873 K the predominant crystal phase was either monoclinic or tetragonal.

Gels precipitated in the 6.5-10.4 *pH* range resulted in monoclinic zirconia while those precipitated at higher or lower *pH* resulted in tetragonal zirconia. It was observed that the presence of sodium did not stabilize the tetragonal phase when the *pH* was in the range of 6.5 to 10.4.

Benedetti *et al.* (19,20) observed that sodium (3-4 weight %) could stabilize the cubic phase of zirconia up to calcination temperatures of 853 K. The zirconia gel was precipitated from zirconyl chloride solutions using either ammonium hydroxide or sodium hydroxide. Samples precipitated at high *pH* and washed to leave 0.5% sodium were found to give mainly tetragonal phase upon calcination. A sample precipitated at *pH*=8 resulted in a mixture of monoclinic and tetragonal phases. The crystal phase formed was attributed to the presence or absence of sodium, not *pH*.

The three polymorphs of zirconium dioxide mentioned above have been studied extensively. The structure of monoclinic zirconia (21) is the most complicated because it is the least symmetrical. Monoclinic zirconia is the stable phase at room temperature when calcined at high temperature. Tetragonal (22) and cubic (23) zirconia normally exist at higher temperatures, but can be stabilized at lower temperatures by doping the zirconia with other metal cations. The phase transitions of zirconia with temperature at atmospheric pressure are shown below.



### *Kinetics and Thermodynamics*

Isobutane and isobutene are not the only products from the hydrogenation of carbon monoxide under the conditions of this work. As the broad product distribution places severe limitations on the attractiveness of isosynthesis as a commercial operation, the various underlying constraints associated with the synthesis, with respect to the selective formation of isobutane and isobutene, are discussed in detail.

#### *Formation of hydrocarbons*

The reactions of carbon monoxide and hydrogen form a variety of products, including alcohols, ethers, alkanes, alkenes, water, carbon dioxide, and carbon as follows:

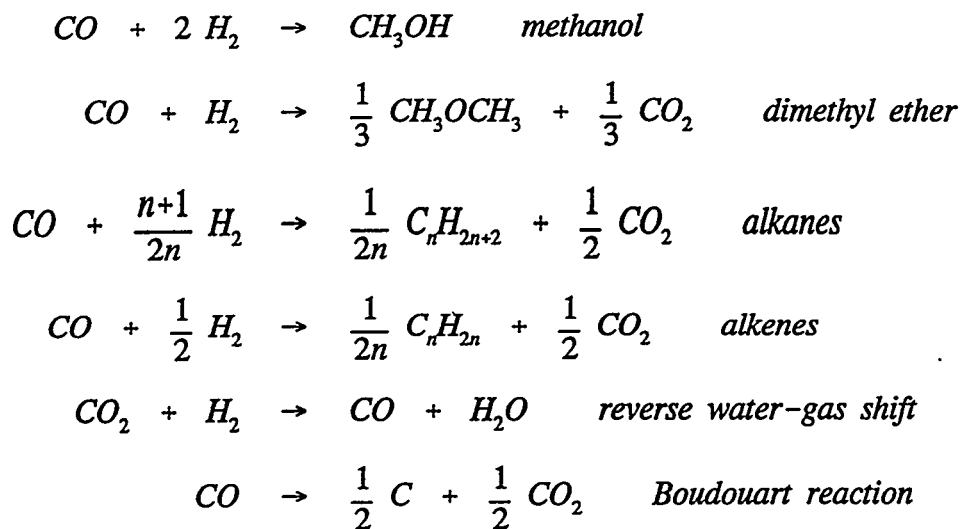
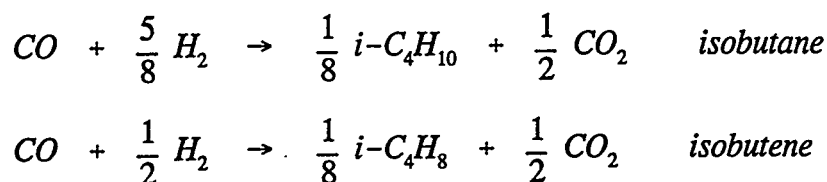


Figure 1.1 shows the equilibrium constants for some of these reactions as a function of temperature. The thermodynamic properties are obtained from Stull *et al.* (24). Of all the hydrogenation reaction to form hydrocarbons, methanation is thermodynamically the most favorable. At equilibria, only methane, carbon dioxide, carbon, and water are found in the products (Table 1.1).

Furthermore, the formation of saturated hydrocarbons is more favorable than that of unsaturated hydrocarbons. For example, consider the following reactions to form isobutane and isobutene:



At 700 K and 70 atm with 1/1 CO/H<sub>2</sub> in the feed, the weight ratio of isobutane to isobutene in the equilibrium mixture is about 3500 to 1.

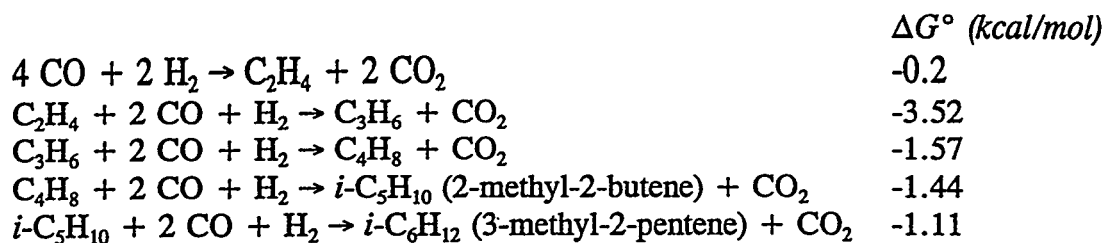
#### *Distribution of isomers*

The Gibbs free energies of formation determine the equilibrium distribution of isomers. At 700 K, the distribution of butenes is 49.22% isobutene, 24.16% *trans*-2-butene, 15.74% *cis*-2-butene and 10.88% 1-butene, and the distribution of butanes is 59.93% *n*-butane and 40.07% isobutane. Therefore, the formation of linear butane and butenes are quite favorable at thermodynamic equilibrium.

#### *Formation of alkenes*

Formation of heavy hydrocarbons (carbon number > 5) is favorable at conditions of

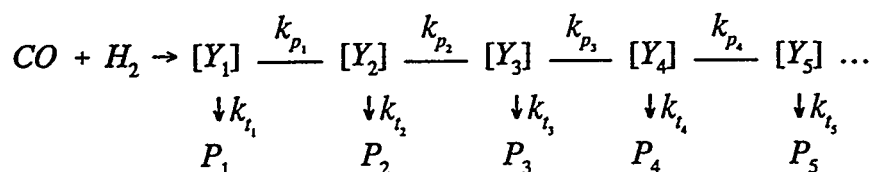
the isosynthesis reaction. To illustrate this, consider the following reactions to form C<sub>2</sub> to C<sub>6</sub> alkenes at 700 K:



Isobutene is not a very favorable product and a large amount of pentene and hexene is formed at equilibrium (Figure 1.2) (It should be pointed out that the distribution is calculated in the absence of alkanes). The limitation on the formation of alkenes caused by the formation of alkanes is more severe for strong hydrogenation catalysts, as reported by Fajula *et al.* (25) and Gadalla *et al.* (26).

### *Kinetic constraints*

CO hydrogenation to form hydrocarbons is seen as starting from a single carbon unit whose size is gradually increased by the repeated addition of other single carbon units, as follows (27-29):



where  $[\text{Y}_i]$  and  $P_i$  denote intermediates and hydrocarbons with carbon number of  $i$ . Further, assume:

1. Starting from initial chain  $\text{Y}_1$ , any chain  $\text{Y}_n$  can be formed by  $n-1$  propagation steps.
2. The chance for any intermediate chain to propagate rather than terminate is given by

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

where  $k_p$  is the rate constant for propagation from  $[\text{Y}_n]$  to  $[\text{Y}_{n+1}]$  and  $k_t$  is the rate constant for termination of  $[\text{Y}_n]$  to product  $P_{n+1}$ .

3.  $\alpha$  is independent of  $n$ , i.e., probabilities of termination and propagation are independent of the length of the carbon chain attached to the surface.

Then, we have:



$$\frac{d[Y_{n+1}]}{dt} = k_p[Y_n] - (k_p + k_t)[Y_{n+1}] = 0$$

$$\frac{d[P_{n+1}]}{dt} = \frac{k_t[Y_{n+1}]}{k_t[Y_n]} = \frac{k_p}{k_p + k_t}$$

$$\frac{[P_{n+1}]}{[P_n]} = \frac{k_p}{k_p + k_t} = \alpha$$

and we obtain a Schulz-Flory-Anderson distribution typical of polymerization reactions:

$$[P_1] = [P_0]\alpha, [P_2] = [P_1]\alpha = [P_0]\alpha^2, \dots, [P_n] = [P_0]\alpha^n.$$

In general,

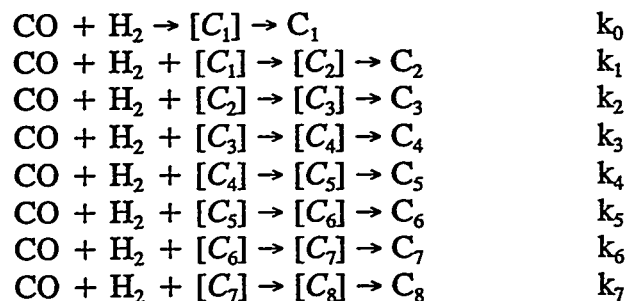
$$C_n = \alpha^n \ln^2 \alpha, \text{ or } \ln C_n = 2 \ln(\ln \alpha) + n \ln \alpha$$

where  $C_n$  is the mole fraction of product  $P_n$ , and  $\ln^2 \alpha$  is obtained from normalizing the distribution by summation over all products. A straight line is obtained by plotting  $\ln C_n$  vs  $n$ .

Even though the above Schulz-Flory-Anderson distribution is obtained for Fischer-Tropsch synthesis, it is not obtained for isosynthesis. Figure 1.3 compares the hydrocarbon distribution for isosynthesis with that for the F-T reaction. A discontinuity at  $C_4$  is observed for isosynthesis. This deviation from the standard polymerization distribution in the F-T synthesis is unique in the forming of  $C_4$  hydrocarbons (15), and cannot be explained by the assumption of equal-reactivity of polymer chains (i.e.,  $\alpha$  is independent of carbon chain).

#### *Constraints on selectivity*

Kinetic constraints also affects product selectivity. Consider the following reactions:



By arbitrarily assuming  $k_1 = k_2 = 0.25k_3 = k_4 = k_5 = k_6 = k_7 = 0.5k_0$ , a selectivity versus space time plot is obtained (Figure 1.4) by applying the procedure presented by Aris (31) and Holland and Anthony (32). The effect of the chain growth mechanism on the selectivity is apparent since the plot indicates that  $C_4$  hydrocarbons cannot be produced with

a selectivity higher than a certain limit which is determined by the ratios of the reaction rate constants. Figure 1.4 also indicates that only  $C_1$  can be produced with a selectivity close to 100%, which places a very severe constraint on the selective production of lower alkenes.

#### *Constraints caused by methanation and Boudouart reaction*

The formations of methane by methanation and carbon by the Boudouart reaction are thermodynamically more favorable than the isosynthesis reaction, and hence restrict the selective production of lower alkenes (30). Methanation can be slightly suppressed by the use of short contact time and low temperatures. Another factor that affects methanation is the hydrogenation strength of the catalyst. For example, catalysts such as nickel and platinum are well known for their strong hydrogenation activity and produce mainly methane. Carbon deposition further causes methanation, since some types of carbon are readily hydrogenated to methane (33). The deposition of carbon in itself causes major problems: it may lead to excessive methane formation, catalyst deactivation, destruction of catalyst pellets, and increased attrition and physical plugging of the reactor (30).

#### *Modeling*

Very few attempts have been made in modeling the conversion or product distribution of the isosynthesis reaction. Such models would be useful in designing an industrial size reactor. Part of the reason for the lack of work on modeling may be the low conversion usually obtained.

Maruya *et al.* (10) calculated activation energies of 79, 84, and 96 kJ/mol for  $C_2$ ,  $C_3$ , and linear  $C_4$  hydrocarbon formation over the temperature range 523-723 K and 210 kJ/mol for branched  $C_4$  hydrocarbons (523-623 K). The rate of  $C_4$  hydrocarbon formation at 673 K was found to be first order in hydrogen and second order in carbon monoxide. Those for  $C_1$ ,  $C_2$ , and  $C_3$  hydrocarbons were written as functions having maximums with carbon monoxide pressure.

Karles and Ekerdt (34) used the mechanism for isosynthesis over zirconia proposed by Tseng *et al.* (12) and Jackson and Ekerdt (13) to model the product distribution using six fitted rate constants. The model utilized several assumptions about the surface species and predicted the wt% distribution among the hydrocarbons through  $C_7$ 's. No  $C_6+$  hydrocarbons were detected in their effluent stream however, and no mention was made of the carbon monoxide conversion levels.

## CHAPTER II

### EXPERIMENTAL

#### *Catalyst Preparation*

In this research catalysts doped with a single component were predominantly used. However, several multicomponent doped zirconias were prepared by both the precipitation and hydrothermal methods. The details of each preparation method are discussed in its respective section.

#### *Zirconia prepared by precipitation (ppt.)*

Single component catalysts included those doped with oxides of lithium, magnesium, manganese, aluminum, cerium, dysprosium, and tantalum. Multicomponent doped catalysts included a sodium-titanium-thorium zirconia and a yttrium-barium-copper zirconia. The following procedure was used in preparing the majority of catalysts. About 41 grams of zirconyl nitrate plus the weight of the source compound required to give the desired molar ratio of dopant to zirconium were dissolved in water (deionized and distilled) in the ratio of 20 ml of water per gram of solid. A 1.5 wt% ammonium hydroxide solution was prepared using 1.3333 ml of ammonium hydroxide stock solution (28-30 wt%) per gram of solid. The gel was precipitated by slowly pouring the metal salts solution into the ammonium hydroxide solution while stirring. Before filtering, the pH of the gel solution was adjusted with nitric acid to 7.00 and allowed to stand for 24 hours. Usually after precipitation the pH of the solution with gel was between 9.5 and 10.5. About 700 ml was poured off the top of each batch before filtering began. The gel was filtered and washed twice with ~1000 ml of water each time. After filtering and washing the gel was dried at 383 K for 24 hours. Final dehydration was accomplished by calcining at 723 K for 2½ hours. The calcined samples were ground and sieved to <250 μm before bulk density was measured. Sodium was included in the zirconia by precipitating with both NaOH and NH<sub>4</sub>OH.

#### *Zirconia prepared hydrothermally (HT)*

Two doped zirconias were prepared by a hydrothermal method. One contained sodium and titanium while the other contained sodium, titanium, and thorium. In the first sample, the molar ratios of Zr/Ti and Na/Ti were 3 and 0.5 and in the second sample the molar ratios of Zr/Ti, Na/Ti, and Th/Ti were 18, 0.6, and 0.2. The first step in this synthesis was preparing two mixtures. In both preparations, mix A contained 25 wt% tetramethylammoniumhydroxide in methanol, 18 wt% NaOH in water, and tetrabutylammoniumbromide. In one case, mix B contained 70 wt% zirconium(IV) propoxide in 1-propanol and 97% titanium(IV) isopropoxide. In the other case mix B also contained thorium nitrate. Mix B was added to mix A while stirring. The gel formed was transferred to a 550 ml stainless steel reactor. Water was added during the washing of the plastic containers used for the two mixtures. The reactor was then sealed and heated in an oven at 443 K. The first preparation was heated for 116 hours while the second was heated for 24 hours. After removal from the reactor the zirconia was filtered, washed with acetone, and

then calcined at 773 K for 2½ hours.

*Zirconia prepared by calcining zirconyl nitrate (CAL)*

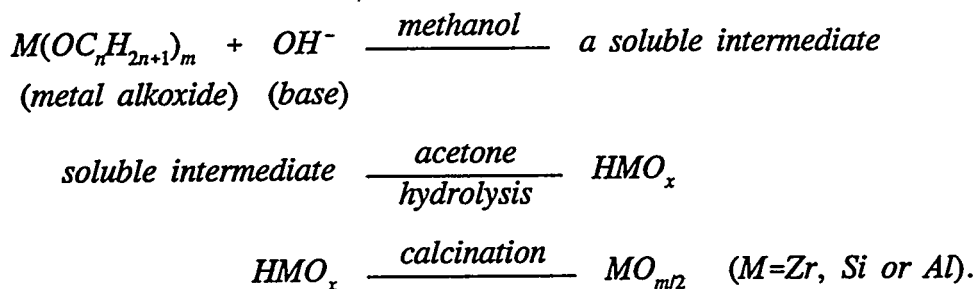
Two zirconias were prepared by this method. The first was a smaller batch to determine the calcination period necessary before no more weight loss occurred in the catalyst. In both cases the zirconyl nitrate was held at 373 K for 2 hours then ramped to 773 K in 1 hour and 20 minutes. The first batch was removed and weighed after 4 hours at 773 K and then again after 7 hours. It was found that no further weight loss had occurred. The second batch was held at 773 K for 4 hours. A similar procedure was used by Evans *et al.* (35) in preparing tetragonal zirconia.

*Zirconia prepared by a conventional sol gel method (CSG)*

A sol gel method was used to prepare zirconia-alumina. To distinguish between this method and the modified sol gel method discussed later, this method is referred to a conventional sol gel method. Zirconium isopropoxide (0.18 moles) was mixed with aluminum butoxide (0.01 moles), and then the mixture of alkoxides was hydrolyzed by adding 190 ml water dropwise. The precipitate was collected by filtering and drying, and was then calcined (773 K for 3 hours). Each batch yielded about 5 grams of material, and is referred to as Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (CSG).

*Zirconia prepared by a modified sol gel method (MSG)*

Zirconium oxides were synthesized using a modified sol gel method proposed by Dosch *et al.* (36) of Sandia National Laboratories. Some modifications of the initial procedure were made in this study, including varying the type of base and using acetone instead of acetone-water for drying and rinsing. The procedure of synthesis is summarized as follows:



Metal alkoxide was slowly added to a methanol solution of a base (inorganic or organic) to form a soluble intermediate. The intermediate was rapidly added to a 1:10 by volume water and acetone solution. The slurry was continuously stirred until the particles were suspended in the solution. Finally, the precipitate was collected by filtering and drying in a vacuum at 353 K overnight. After calcination (773 K for 3 hours), the catalyst was ground and sieved to 250 μm particles.

To synthesize catalysts with different properties, both inorganic (sodium hydroxide) and organic (tetramethylammonium hydroxide) bases were used in the preparation. Mixed

alkoxides were also used in some preparations. Alkali metals, alkaline earth metals, and some transition metals were also added to the catalysts by dissolving the corresponding hydroxides or nitrates in the methanol solution in the first step. The volumes of water, methanol and acetone in the synthesis were 16, 48 and 160 ml, respectively. Two batches of calcium-zirconias, Ca-ZrO<sub>2</sub> (MSG) (0.5 wt% Ca) and Ca(2%)-ZrO<sub>2</sub> (MSG) were prepared with different loadings of calcium.

All the catalysts were prepared by using an organic base (tetramethylammonium hydroxide) except for SiO<sub>2</sub>-ZrO<sub>2</sub>-NaOH (MSG) which was prepared by using an inorganic base (sodium hydroxide). After the preparation and before calcination, SiO<sub>2</sub>-ZrO<sub>2</sub>-NaOH was treated with HCl at a pH of 4 four times to remove over 99.99 wt% of the sodium from the catalyst.

### *Catalyst Characterization*

The surface area of each catalyst and pore volume/pore diameter of several samples were measured using the BET method and a fully automated Micromeritics® Digisorb 2600 apparatus. The catalyst sample is placed in a sample bulb and degassed at 473 K under high vacuum ( $1.3 \times 10^{-8}$  atm) overnight, then the sample bulb is removed and placed in the measurement section of the instrument. The manufacturer's operation manual contains detailed descriptions of the equipment and procedures. The X-ray diffraction (XRD) patterns were obtained using a Scintag XDS-2000 X-ray diffractometer with a Cu anode and a continuous scan of 4° (2θ) per minute.

A Varian atomic absorption spectrometer, model Spectra AA-30, was used to measure the metal composition of some of the catalysts. Hydrofluoric acid was added when necessary to dissolve the catalyst.

The acid-base properties of the modified sol gel catalysts were measured by a temperature programmed desorption (TPD) of ammonia and carbon dioxide. Ammonia and carbon dioxide were stored in gas cylinders. TPD experiments were conducted at atmospheric pressure. Figure 2.1 is the schematic diagram of the TPD apparatus. Typically, a 200 mg sample was loaded in a quartz reactor and activated in a helium stream by heating to 933 K at a rate of 5 K/min and maintaining that temperature for 10 minutes. After the sample was cooled to 343 K, carbon dioxide or ammonia was adsorbed for 30 minutes. The sample was then flushed with helium at a temperature of 343 K and a flowrate of 20 cm<sup>3</sup>/min for 2 hours to remove physisorbed adsorbent. The effluent was monitored by a thermal conductivity detector and an integrator. The detector was calibrated by injecting a known volume of carbon dioxide or ammonia into the injection port.

### *Materials*

Table 2.1 shows the source compounds and their purities for the oxides prepared by the precipitation, hydrothermal, and calcination methods. The majority of starting materials were purchased from Aldrich. The thorium nitrate was purchased from Alfa Products while NH<sub>4</sub>OH (A.C.S. Reagent) and HNO<sub>3</sub> (70.7%) were purchased from Fisher and Mallinckrodt respectively.

Table 2.2 lists the chemicals used in the synthesis of modified sol gel catalysts. Standard solutions for the atomic absorption experiments were purchased from Fisher Scientific and Aldrich Chemical. The water used in all preparations was distilled and

deionized.

Carbon monoxide (C.P. grade, 99.5%) in an aluminum cylinder and  $1.06 \pm 0.02\%$  hydrogen sulfide in hydrogen were purchased from Matheson Gas Products. Carbon monoxide (C.P. grade, 99.5%) in an iron cylinder, hydrogen and nitrogen (reactor purge) gas cylinders were acquired from Bob Smith Corporation. Air (3776 ppm), methane (18 ppm), and water ( $<5$  ppm) were the main impurities in the carbon monoxide. There was also  $<1$  ppm each of carbon dioxide, ethylene, ethane, and propane present. Helium, nitrogen, hydrogen and air cylinders needed to operate the gas chromatographs (GC) were also purchased from Bob Smith.

## *Apparatus and Procedure*

### *Fixed bed reactor 1*

A schematic of the reactor system is shown in Figure 2.2. Carbon monoxide, hydrogen, and nitrogen were passed through molecular sieve (5A) filters to remove water. When the hydrogen sulfide/hydrogen mixture was used it was not passed through a molecular sieve as the hydrogen sulfide would be removed. An aluminum cylinder was used instead of iron in some cases in order to eliminate the formation of iron carbonyls in the cylinder that could poison the catalyst. When the iron carbon monoxide cylinder was used the gas was also passed through an activated charcoal bed and in some cases also a commercial zirconia guard bed to remove any carbonyls.

The purified reactant gases were fed to the reactor through 15 micron filters and Brooks 5850E mass flow meters controlled by 5896 controllers also from Brooks. The carbon monoxide and hydrogen flow meters were rated at 0-28 and 0-30 standard liters per hour respectively. The flow meters were calibrated by measuring the volumetric flow rate with the soap bubble meters for various controller settings. There was no significant difference in pressure drop between flowing through the reactor or through the bypass. Upstream from the reactor, the reactants were mixed in a  $75 \text{ cm}^3$ , 304 stainless steel container filled with glass beads.

The reactor was made from 304 or 316 stainless steel with an overall length of 29 cm and an internal diameter of 0.493 cm. The reactor was heated in a gas chromatograph oven using a coil-type resistance heater. Air was circulated by a fan located inside the oven. The thermocouple measuring reaction temperature was placed outside the reactor about halfway down the length of the catalyst bed and about 2 cm from the reactor wall. Three to fifteen grams of catalyst were loaded into the reactor depending on the bulk density. All other tubing was 0.318 cm or 0.159 cm 316 stainless steel. The reactor pressure was maintained using a Grove S-91W back pressure regulator. Temperature control was accomplished using an Omega 6100 controller. The lines from the 15 micron filter at the reactor exit up to and including the sampling valve (N) were wrapped with heating tape and held at  $\sim 400 \text{ K}$  to eliminate product condensation in the lines before the liquid trap.

The reactor effluent could be injected into two on-line GCs. An SRI model 8610-30 GC equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors and a  $0.318 \text{ cm} \times 1.83 \text{ m}$  Porapak Q 80/100 column was used to monitor oxygenate production and give a partial separation of the  $\text{C}_5$  hydrocarbon fraction. However, the  $\text{C}_6+$  fraction could not be quantified on this GC. To inject on this GC the sample valve (N) was turned so the sample loop was in-line with the flowing product stream. Thirty seconds were

allowed before the sample valve was switched back to inject the sample into the column. Integration was performed by the Peaksimple® II software (from SRI) on an IBM PC.

Separation of CO, H<sub>2</sub>, CO<sub>2</sub>, and all the C<sub>1</sub>-C<sub>4</sub> hydrocarbons was accomplished using a Carle series S TCD GC controlled by a Hewlett Packard 3385A automation system. This system controlled the valve switching of three different sampling valves contained within the GC. This GC used five separate columns and a palladium hydrogen transfer system. The injection procedure for this GC consisted of turning valve V8 to direct flow to the GC instead of to the vent. Two minutes were allowed to flush the sample loop before the sample was taken. Additionally, a gas tight syringe was used to inject a sample of the reactor effluent into a similar Carle series S TCD/FID GC. Valve V7 was closed to direct flow through the sample port (M) and into the syringe. The syringe was filled in this manner to minimize the amount of air that might contaminate the sample. The syringe was filled and injected into the sample loop three or four times to ensure that the sample loop was completely flushed. The C<sub>5</sub>+ hydrocarbon fraction was given in the column back-flush.

The reactor was filled with catalyst by first plugging one end with glass wool (~ ½ inch) and then funneling the powder in from the other end. Any volume inside the reactor not filled with catalyst was packed with glass wool. After the reactor was installed a leak test was performed. First, the back pressure regulator was set to a pressure ~5 atm larger than would be used in the experiment. Then nitrogen was passed through the system at this pressure. Leaks were detected using a soap solution. The three-way valves on either side of the mass flow meters were used to bring the pressure up on both sides of the meter without flowing gas through them. This allowed a faster build-up to the desired pressure without the problem of sticking the mass flow meter closed because of a large pressure drop. Nitrogen could be accurately controlled with the carbon monoxide flow meter because the correction factor between these two gases is approximately one.

During heat-up of the reactor, the system was pressurized to 35 atm and nitrogen was passed over the catalyst at 100 sccm. Heat-up of the reactor from room temperature to 673 K required about 17 minutes.

The catalyst was pretreated at 673 K and 35 atm in flowing nitrogen for 18 hours. After pretreatment the pressure was adjusted to the desired reaction pressure, the reactor was bypassed using valves V3 and V4, and the CO and H<sub>2</sub> or (H<sub>2</sub>+H<sub>2</sub>S) flows were started. Once the composition and flowrate of the feed was measured the reactor was brought on-line. Between experiments, nitrogen was passed over the catalyst (at reaction temperature) at 100 sccm.

A minimum of 2 hours (17 hours for most runs) were allowed for the reaction to come to steady state before effluent analysis began. An experiment consisted of four injections to each of the GC's over a 4-5 hour period. The effluent flow rate was measured at both the beginning and end of this period while noting room temperature and pressure. The GC output was used to determine carbon monoxide and hydrogen conversions as well as product distributions and mass balances.

### *Fixed bed reactor 2*

The CDS 900 reactor system (Figure 2.3) was designed and manufactured by Chemical Data Systems, a subsidiary of Autoclave Engineering. It was a complete gas/liquid phase reaction system designed to facilitate studies of catalytic and non-catalytic processes. The system's modular design permitted a degree of flexibility in both design and operation.

It was comprised of three basic modules: Reactor System, Control System, and Analytical System.

The reactor system was designed to be entirely housed within a temperature-controlled oven. Reactant preparation consisted of receiving, metering, and selectively mixing up to four gases or a combination of two gases and two liquids. In this study, four gas inlets were used for hydrogen, carbon monoxide, nitrogen, and a standard gas mixture (containing nitrogen with roughly 1 vol% of C<sub>1</sub> to C<sub>4</sub> hydrocarbons, carbon dioxide and carbon monoxide: for GC calibration). After the mixer/vaporizer, the mixture passed through a reactor status valve. The setting of this valve determined the inlet stream to the reactor. Either reactants or a failsafe purge gas (nitrogen) was flowing into the system depending on the position of the valve. When the reactor status valve was "on", the reactants entered a 1.27 cm ID stainless steel reactor.

The reactor was heated by a three-zone stainless steel annular heater. The temperature of each heating zone was controlled individually and simultaneously. The pressure inside the reactor was controlled by an automatic back pressure regulator located at the outlet of the reactor. Both the inlet and outlet pressures of the reactor were monitored by pressure transducers and gauges. Two rupture disks were connected to the inlet and outlet of the reactor to ensure safety.

After the back pressure regulator, the product stream, now at atmospheric pressure, exited the reactor module cabinet through a heated transfer line and entered the analytical system. The analytical system consisted of a gas chromatograph equipped with parallel FID and TCD systems. The TCD system included two Porapak Q columns, a Molecular Sieve 5A column, and a palladium hydrogen transfer tube, while the FID system was equipped with a 50 meter BP-1 capillary column. The component separation was complete, except for 1-butene and isobutene, which were separated by the previously described off-line Carle TCD/FID GC. The exhaust stream from the GC was vented to a fume hood.

Molecular sieve (5A) beds were installed in both carbon monoxide and hydrogen feed lines to remove residual moisture. Additionally, a zirconium oxide filter and an activated charcoal filter were installed in the carbon monoxide line to remove carbonyls.

Carbon monoxide and hydrogen were stored in gas cylinders located in a ventilation hood. Roughly 20 grams of catalysts were charged to the reactor. The reactor was pressured to reaction condition at room temperature by flowing nitrogen, and then heated to reaction temperature at a rate of 5 K/min and maintained at that temperature for four hours before reactants were continuously fed into the system and nitrogen feed was discontinued.

#### *Trickle bed reactor*

A schematic diagram of the trickle bed reactor system is shown in Figure 2.4. The feed gases are purified by flow through a guard bed consisting of activated carbon and molecular sieves with particle size of 0.16 cm. Hydrogen and carbon monoxide flowrates are controlled with Brooks model 5850E mass flow meters which have flow ranges of 0-2 and 0-1.5 standard liters per hour, respectively. The flow meters were calibrated by checking the controller set point versus the volumetric flowrate determined by the bubble meter.

The feed gas streams are combined at a predetermined CO/H<sub>2</sub> ratio. To enhance mixing, the gases are passed through a bed of glass beads prior to the reactor. Decalin was fed to the unit using a Milton Roy pump. A relief valve, which is set at 106 atm, was



placed before the reactor to prevent uncontrolled pressure rises in the system. The reactor is a 316 stainless steel tube, 25 cm long, 0.96 cm ID, and 1.2 cm OD. It was mounted vertically in a bed of aluminum pellets. The reactor is divided into three sections. Prior to and after the 7 cm catalyst bed are 6 and 12 cm supporting sections filled with 0.2 cm diameter glass beads.

The reactor was heated by the heating block and controlled by a Omega model 6100 temperature controller. A thermocouple inserted through the middle of the catalyst bed was used to measure the temperature of the bed. The reactor pressure was maintained with a Grove model 91W back pressure regulator. The reactor effluent passed through the back pressure regulator where the pressure was reduced to atmospheric pressure prior to the gas oil separator. The decalin collected at the bottom of the separator was recycled to the reactor. After the gas oil separator a sampling port was used to take gas samples for analysis. The effluent gas was passed through a soap bubble meter to measure the volumetric flow rate before it was vented to a fume hood. The decalin used in this study was obtained from Sigma Chemical and exists as *cis* and *trans* isomers of decahydronaphthalene with a minimum purity of 98% as determined by gas chromatography.

### *Slurry reactor*

A schematic diagram of the slurry reactor system is given in Figure 2.5. The apparatus before and after the reactor is the same as that described for the trickle bed. Decalin was also used as the oil for the slurry experiments.

The reactor was a stirred 100 cm<sup>3</sup> Autoclave model EZ seal with six ports and one thermowell. The feed was introduced to the bottom of the reactor through a dip tube. A 50 micron porous metal filter was connected to the effluent port to prevent the entrainment of catalyst particles. A baffle bar and impeller were connected to the stainless steel reactor cover. The impeller was driven by a Magnadrive II stirrer. Cooling water was passed through the Magnadrive assembly to keep the temperature of the assembly in the permissible range. The reactor was heated using a furnace supplied by the manufacturer which was controlled by a Thermolyne Furnatrol I furnace controller.