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# Isosynthesis Reactions of $CO/H_2$ over Zirconium Dioxide

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The reaction of an equimolar mixture of $H_2$ and CO was studied over $ZrO_2$ at 350 to 450°C, 35 atm total pressure, and varying residence times. The isosynthesis reaction mechanisms were studied by monitoring the incorporation of oxygenated compounds into the isosynthesis products. Propionaldehyde and [$^{13}C$]acetone, [$^{13}C$]isopropanol, and [$^{13}C$]methanol were added to the $CO/H_2$ reactant stream. Their effect on the isosynthesis product distributions and on the isotopic distribution of the products was monitored as a function of oxygenate feed rate. Propionaldehyde, acetone, and methanol were found to incorporate into the isosynthesis products. The isotopic distribution of the products was used to support an isosynthesis reaction scheme that involves CO insertion into a bound aldehyde or ketone as the major chain growth step and a second chain growth step that involves condensation between methoxide and a surface bound enolate.

## I. INTRODUCTION

The isosynthesis process refers to the selective conversion of synthesis gas into branched aliphatic hydrocarbons over oxides. Pichler and Ziesecke performed much of the pioneering work on this reaction (*1*, *2*). A historical perspective on the isosynthesis process and a complete discussion of the pioneering research can be found in Refs. (*1–5*). The most active oxide known is $ThO_2$, which catalyzes the formation of hydrocarbons containing four to eight carbons, with 2-methylpropane as the major product (*2*). Isosynthesis activity has also been reported over a number of other metal oxides including $ZrO_2$ (*2*, *6–8*), $UO_2$ (*2*), $La_2O_3$, and $Dy_2O_3$ (*9*). Zirconium dioxide was selected for the studies reported here because it was the second most active oxide studied by Pichler and Ziesecke.

A considerable amount of information is available concerning the effects of synthesis conditions, oxide composition, and alkali dopants on the isosynthesis rates and product selectivity (*2*). The reaction required high pressures (30–600 atm) and high temperatures (375–475°C) over $ThO_2$. Operation of this reaction at temperatures less than 375°C resulted in substantial yields of branched alcohols. Reaction temperatures of 425 to 450°C resulted in the formation of branched hydrocarbons, primarily the branched $C_4$'s. Methane, ethane, and propane were the principal products at reaction temperatures above 500°C.

Although the effects of synthesis conditions on products have been well researched, much less is known about the reaction chemistry involved in the synthesis of $C_2$ and higher ($C_{2+}$) products over the isosynthesis oxides. A number of reaction schemes have been proposed to describe the synthesis of branched hydrocarbons and alcohols over metal oxides (*1*, *5*, *10–12*). The early mechanisms (*1*, *5*) have not been developed to the level of detail found in the more recent mechanisms (*10*, *11*) and are not discussed here. The mechanisms of Vedage *et al.* (*10*) and Mazanec (*11*) both involve two propagation processes, CO insertion and condensation. The species into which CO inserts and the species which undergo condensation are different for the two mechanisms.

The CO insertion scheme of Vedage *et al.* (*10*) was based on alcohol synthesis studies over various Cu/ZnO oxide sys-

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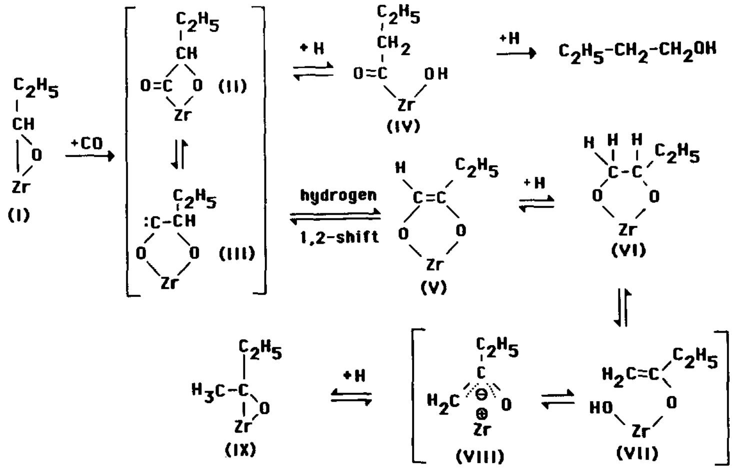

FIG. 1. Proposed scheme for CO insertion into a bound aldehyde (adapted from Ref. (*11*)).

tems. The reaction involves CO insertion into an alkoxide ($RCH_2O$) to generate an alkionate ($RCH_2COO$) that is subsequently reduced to the next higher alkoxide. The alkoxide can continue to grow by CO insertion or can terminate to the alcohol. This mechanism can only lead to linear products if stepwise CO insertion originates with methoxide. To account for the formation of branched products, Vedage *et al.* proposed an aldol-like condensation scheme in which a formyl species reacts with an enolate ($RCH_2C^{-}HCHO$) at the carbon next to the carbonyl carbon.

Mazanec has proposed mechanisms for the formation of higher alcohols over oxide catalysts that involve CO insertion (Fig. 1) and condensation (Fig. 2) (*11*). (Hydrogen is shown to represent reduction; the stoichiometry of a path is not given.) These mechanisms were based on extensive analogies to organometallic chemistry. Mazanec proposed that the primary C–C bond-forming reaction involved CO insertion into bound aldehyde (**I**) to produce a cyclic acyl (**II**), which has a second valance bond structure (**III**) in which the carbonyl carbon has carbenic character. The 1,2-shift of H (favored over alkyl (*11*)) from **III** ultimately leads to the bound ketone, **IX**. If 1,2-shift of H or R from **III** does not occur, the cyclic acyl, **II**, is reduced to an alcohol. This CO insertion scheme can lead to both linear and branched products. The condensation reaction (Fig. 2) between $\eta^3$-enolates (**X**) and alkoxides (**XI**) was proposed to explain deviations from Schulz–Flory distributions.

The possible $C_1$ species that are involved in chain growth over $ZrO_2$ have been identified (*13–19*). Figure 3 summarizes the activation of CO and its conversion into methane and methanol. Formate is shown converting to methoxide via either oxy-

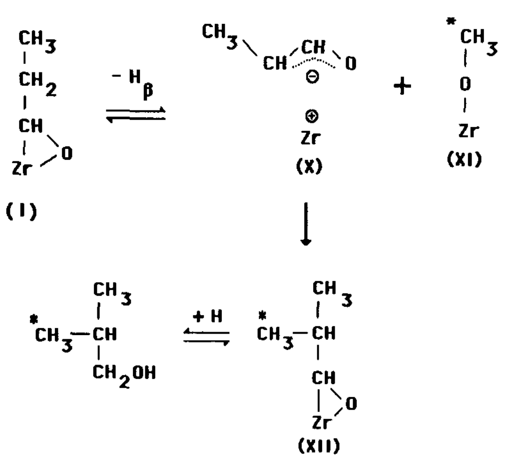

FIG. 2. Proposed scheme for condensation between an enolate and a methoxide (adapted from Ref. (*11*)).

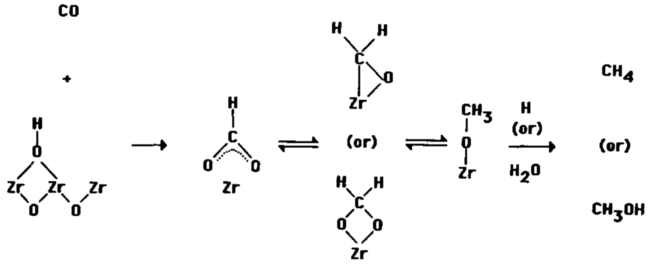

FIG. 3. Proposed scheme for CO activation and $C_I$ synthesis.

methylene, $H_2COO$, or adsorbed formaldehyde, $H_2CO$. The role of formate and methoxide species is well established (*18*). Oxymethylene was originally proposed (*17*) to be the intermediate between formate and methoxide. An IR study of formaldehyde adsorption on $ZrO_2$ was used to investigate this intermediate structure, and the bands in the C–H stretching region could not be assigned positively. Although oxymethylene was suggested in Ref. (*17*), the C–H stretching bands could also be attributed to the adsorbed formaldehyde species shown in Fig. 3. Precedence for the adsorbed formaldehyde structure is found in the zirconocene complexes, $[(Cp)_2ZrX]_2(\mu\text{-}CR_2O)$, where $X$ = halide, H, aryl and $R$ = H, alkyl. These complexes have formaldehyde O bridging the two metal atoms and C bound to either of the two metal atoms (*20–23*).

The studies reported herein examined the proposed mechanisms for isosynthesis reaction by employing $^{13}C$-labeled oxygenates that were expected to adsorb and transform into the intermediates proposed by Vedage *et al.* (*10*) (alkoxides) and Mazanec (*11*) (adsorbed aldehydes/ketones and methoxide). According to these schemes 2-methylpropene can be formed from acetone or isopropanol only by CO insertion. Methanol permits testing of the condensation schemes. The extent to which the various oxygenates incorporated into the isosynthesis products is reported, and isosynthesis mechanisms over $ZrO_2$ are discussed.

## II. METHODS

### *Apparatus*

The apparatus is shown schematically in Fig. 4. The reactions were conducted in a 32-cm-long section of 0.533-cm i.d. 304

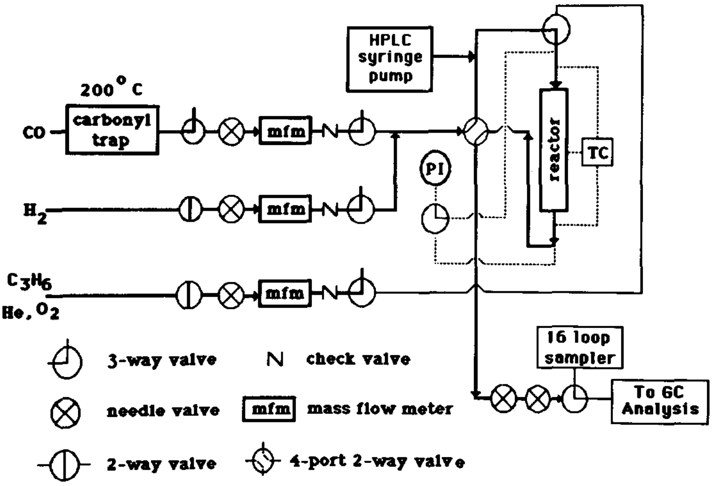

FIG. 4. System schematic.

stainless-steel tubing. Two grams of $ZrO_2$ powder was used, resulting in a catalyst bed length of approximately 5 cm. The entire system, excluding the reactor, was made of 0.318-cm o.d. tubing; stainless steel was used for all but the carbon monoxide inlet line, which was made of copper. The tubing was maintained at 180°C to preheat the gases prior to entering the reactor and to prevent product condensation in the reactor effluent lines. The system pressure was reduced from 35 atm to ambient pressure using the dual metering valves shown.

The reactor effluent was sampled using gas-tight syringes for analysis performed on a Varian 3700 gas chromatograph (GC), using a 16-loop sampling valve for analysis performed on a Finnegan MAT 4000 series GC/MS, or condensing in flasks immersed in liquid nitrogen for GC/MS analysis. Gas composition was established with the Varian 3700 GC and used to determine production rates. The Finnegan MAT 4000 GC/MS was used to determine $^{13}C$-isotope distributions in the products.

The GC/MS was configured to analyze the $C_3$ to $C_5$ products. A 0.318-cm o.d. × 2.74-m stainless-steel column packed with 0.19 wt% picric acid on 80/100 mesh Carbopack C was used to separate 1-butene from 2-methylpropene. The effluent collected with the 16-loop gas sampling valve was injected into the picric acid column. A Supelco SPB-5 capillary column (60 m × 0.32 mm i.d. with a 1-$\mu$m-thick coating) was found to work best for the remaining product separation on the GC/MS because the elution characteristics matched those found for the dimethyl siloxane column used in the Varian GC. *n*-Dodecane was used as a solvent for the products collected in the liquid nitrogen cooled flasks. The product/*n*-dodecane mixture was injected, via syringe, into the SPB-5 column.

Isotopic distributions were computed with a regression analysis program that compared the mass fragmentation pattern for a GC/MS peak to the pattern observed for the same peak in the absence of a $^{13}C$ feed additive. The program and its use are presented elsewhere (*24*). We were able to establish the percentage of a product that contained a certain number of $^{13}C$ atoms but were unable to identify the location of the $^{13}C$ atoms within the molecule. The accuracy of this method was 1–2%; isotope percentages at this level may not signify $^{13}C$ incorporation.

The oven temperature ramping procedure and column switching sequence used to separate the reaction products on the Varian 3700 GC are presented elsewhere (*24*). The Varian 3700 GC was equipped with a Scientific Glass Engineering (SGE) multidimensional column switching system (MDCSS) and dual flame ionization detectors. A 0.318-cm o.d. × 2.74-m stainless-steel column packed with 0.19 wt% picric acid on 80/100 mesh Carbopack C was needed to separate 1-butene from 2-methylpropene. A nonpolar 0.53-mm i.d. × 50-m capillary column (SGE) loaded with a 5-$\mu$m coating of dimethyl siloxane (SGE) was employed as the primary column. The effluent from the primary column could be diverted, using the MDCSS, to a detector or to a second column when product peaks coeluted. A medium polar 0.53-mm i.d. × 50-m capillary column (SGE) loaded with a 3-$\mu$m coating of 7% cyanopropyl and 7% phenyl methyl siloxane was used as the second column. Table 1 lists the products monitored with the Varian GC. Standard mixtures were used to establish the elution times.

### *Procedures*

All synthesis reactions were conducted at 35 atm. Two grams of fresh zirconia was loaded into the reactor for each experiment, purged with oxygen at ambient temperature, and heated at 425°C for at least 30 min in flowing oxygen. The reactor was purged with flowing He for 30 min at 425°C. Hydrogen was then admitted at 425°C and 35 atm, followed 1 hr later by CO. The $H_2$/CO flows were subsequently adjusted to give a constant ratio of 1.

TABLE 1

Products Monitored

$C_1$'s
  Methane
  Methanol
$C_2$'s
  Ethane
  Ethylene
  Dimethyl ether
$C_3$'s
  Propane
  Propylene
  Propionaldehyde
  *n*-Propanol
  Isopropanol
  Acetone
Linear $C_4$'s
  *n*-Butane
  1-Butene
  *trans*-2-Butene
  *cis*-2-Butene
Branched $C_4$'s
  2-Methylpropane
  2-Methylpropene
  2-Methyl-1-propanol
  2-Methylpropionaldehyde
Linear $C_5$'s
  *n*-Pentane
  1-Pentene
  *trans*-2-Pentene
  *cis*-2-Pentene
Branched $C_5$'s
  2-Methylbutane
  2-Methyl-1-butene
  2-Methyl-1,3-butadiene
  2-Methyl-2-butene
  3-Methyl-1-butene

After CO was introduced, a 2-hr waiting period was adopted before gas samples were taken for GC analysis. This period permitted temperature and flows to stabilize and any possible induction in the zirconia activity to occur. A second gas sample was taken to assure steady state had been reached. The zirconia did not exhibit a noticeable decline in activity over the longest period of time monitored, 30 hr.

A HPLC syringe pump (Isco Model μLC-500) was used to meter the oxygenated compounds into the reactor. The pump outlet was heated at 180°C and was connected as closely as possible to the reactor inlet. Oxygenate addition was initiated 3.5 hr after introducing $CO/H_2$ to the reactor and establishing the activity of the $ZrO_2$. Addition rates always started at the lowest flow reported; a hysteresis problem was not found with the order in which the oxygenate addition rate was changed.

### *Materials*

The nonporous zirconium dioxide was made by precipitating $Zr(OH)_4$ from a nitrate solution (Nyacol) using concentrated ammonium hydroxide. A final pH of approximately 10 was reached during the precipitation. The resulting gel was rinsed with distilled water, oven-dried at 120°C for 24 hr in hydrocarbon-free air, and calcined at 600°C for 4 hr in the same air. Approximately 30 g of zirconia was made in each batch. The fresh zirconia $N_2$ BET area ranged from 60 to 65 $m^2/g$ and the X-ray diffraction pattern was characteristic of the monoclinic phase with only a minor peak for the tetragonal form (*24*).

Hydrogen (99.999%), CO (99.8%), and He (99.995%) were purified by passing through oxygen absorbing filters and molecular sieve filters to remove water. The $O_2$ (99.995%) was purified with a molecular sieve filter. Carbon monoxide was also heated to 200°C to remove any carbonyls prior to mixing with any other gases. Acetone-free methanol (Fisher, reagent grade, 99.5+%), propionaldehyde (Aldrich, 99+%), acetone (MCB, reagent grade, 99.5+%), isopropanol (Fisher, certified ACS grade, 99+%), *n*-propanol (Fisher, reagent grade, 99+%), and n-dodecane (Aldrich, 99+%) were used without further purification. [$^{13}$C]Acetone (($^{13}CH_3)_2{}^{13}CO$, Incon Services, Inc., 99% isotopically pure), [$^{13}$C]isopropanol ($(CH_3)_2{}^{13}CH_2OH$, MSD Isotopes, 99.1% isotopically pure), and [$^{13}$C]methanol ($^{13}CH_3OH$, Incon Services, Inc., 99% isotopically pure) were introduced into the syringe pump and diluted with about equal amounts of [$^{12}$C]acetone, isopropanol, and methanol, respectively. Dilution was necessary to ensure a sufficient supply of $^{13}$C during the course of each experiment.

## III. RESULTS

Steady-state activity and selectivity were investigated at different temperatures and different residence times. The results are summarized in Table 2. It was not possible to monitor the concentration of CO, $CO_2$, and $H_2O$ in the reactor effluent. The pressure was always held constant at 35 atm. Pressure selection involved a compromise

TABLE 2

Effect of Residence Time and Temperature on the Product Distributions at 500 psig Total Pressure

| Temperature (°C): | 425 | 425 | 425 | 425 | 400 | 375 | 350 |
|---|---|---|---|---|---|---|---|
| Residence time (min): | 0.237[a] | 0.158[b] | 0.119[c] | 0.237[d] | 0.246[d] | 0.256[d] | 0.266[d] |
| Catalyst batch: | N-06 | N-06 | N-06 | N-01 | N-01 | N-01 | N-01 |
| CO conversion[e] (%): | 0.6 | 0.8 | 0.7 | 0.4 | 0.4 | 0.3 | 0.2 |
| $C_4$ olefin/$C_4$ paraffin (molar ratio) | 16.4 | 18.7 | 21.0 | 20.2 | 23.0 | 21.3 | 30.0 |
| Methane (mole %) | 42.8 | 36.2 | 34.2 | 41.9 | 28.1 | 19.1 | 17.5 |
| Methanol | 4.1 | 6.8 | 8.1 | 5.9 | 9.4 | 12.4 | 18.5 |
| Dimethyl ether | 16.8 | 22.7 | 28.2 | 10.4 | 36.1 | 54.3 | 54.1 |
| Ethane and ethylene | 11.8 | 9.6 | 8.1 | 11.1 | 6.1 | 3.5 | 3.1 |
| Propane and propylene | 3.0 | 3.4 | 2.9 | 4.7 | 2.9 | 2.4 | 2.2 |
| Linear $C_4$'s | 4.6 | 4.1 | 3.4 | 5.9 | 3.5 | 1.7 | 0.6 |
| Branched $C_4$'s[f] | 13.1 | 13.7 | 12.1 | 16.2 | 10.9 | 5.4 | 3.2 |
| Linear $C_5$'s | 0.5 | 0.4 | 0.3 | 0.4 | 0.5 | 0.2 | 0.1 |
| Branched $C_5$'s[g] | 2.3 | 3.2 | 2.7 | 3.5 | 2.4 | 0.8 | 0.5 |

[a] $CO/H_2$ = 50/50 cc/min (STP).

[b] $CO/H_2$ = 75/75 cc/min (STP).

[c] $CO/H_2$ = 150/150 cc/min (STP).

[d] $CO/H_2/He$ = 45/45/12 cc/min (STP).

[e] Based on hydrocarbon and alcohol products.

[f] The ratio of 2-methylpropene/branched $C_4$'s is always greater than 0.93 (except at $T$ = 350°C 2-methylpropene/branched $C_4$'s = 0.78).

[g] Monomethylated $C_5$'s only.

between the need to conduct isosynthesis at high pressures, 50 to 100 atm (*2*), and the desire to maximize the amount of gas that can be delivered from a cylinder of carbon monoxide. The blank activity of the stainless-steel reactor surface and the heated transfer lines was measured and found to be insignificant (less than 0.008% CO conversion at 425°C). Methane was the primary product formed and no branched hydrocarbons or oxygenated products were detected in the blank experiments.

Table 2 reveals several interesting trends. Among the $C_4$ hydrocarbons, the selectivity toward 2-methylpropene was at least 70% in the isosynthesis temperature range (350–425°C). The selectivity toward monomethylated $C_5$ hydrocarbons was much higher, at least 80%. Experiments (not shown) below 325°C revealed that methanol, dimethyl ether, and $C_1$ to $C_3$ hydrocarbons were the principal products (*24*). These observations are consistent with selectivities over $ThO_2$ where the isosynthesis reaction is reported to start at 375°C (*2*).

A previous study in our group (*8*) over a commercial grade of nonporous $ZrO_2$ revealed that the isosynthesis reaction became externally diffusion controlled at temperatures greater than 450°C with activation energies for CO hydrogenation on the order of 2–4 kcal/mole. A maximum temperature of 425°C was used for the majority of the experiments reported herein to maximize yields of isosynthesis products and still operate in a kinetically controlled reaction regime. Arrhenius activation energies were determined for the rates of formation of the products listed in Table 1. The energies ranged from 20 to 50 kcal/mole. No correlations between the activation energy and the structure of the product were found.

Residence time was changed to gain insight into the reactions leading to $C_4$ products. The residence time data are not sufficient to identify primary products. The

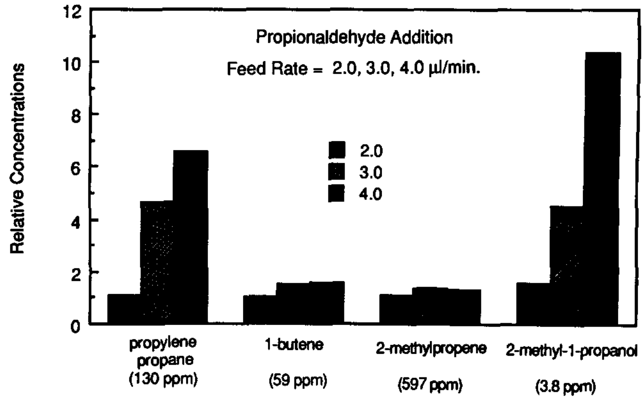

FIG. 5. Concentration of specific products relative to the amount of each product formed in the absence of propionaldehyde versus the propionaldehyde addition rate. The concentrations in parentheses refer to the amounts formed prior to propionaldehyde addition.

ratio of the branched to linear $C_4$'s increased with decreasing residence time suggesting competing paths to branched and linear products. The ratio of $C_4$ olefins to paraffins also increased with decreased residence time suggesting that olefins form before paraffins during the isosynthesis reaction.

Possible surface reactions were discussed in the Introduction and suggest that oxygenated intermediates are involved in CO hydrogenation over zirconia. A series of experiments was performed in which propionaldehyde, acetone, isopropanol, *n*-propanol, and methanol were added to the $CO/H_2$ feed to determine if they adsorbed to form surface intermediates and were incorporated into the synthesis products. The experiments were conducted at 425°C, 100 $cm^3$/min (STP) of 1/1 $H_2/CO$, and 35 atm total pressure. The activity of each loading of catalyst charged to the reactor was established prior to adding the oxygenated reactant because the initial activity, under the standard conditions listed above, was found to vary. The cause for this variation was not determined.

### *Propionaldehyde*

Propionaldehyde was added at flow rates up to 4 μl/min. Additives such as propionaldehyde should be fed at the lowest rates possible, so that the normal synthesis process is not significantly affected, yet permit one to detect the presence or absence of incorporation. Changes in the effluent concentrations of selected products are presented in Fig. 5. The concentrations in parentheses refer to the respective product concentration prior to propionaldehyde addition. There was no apparent effect of propionaldehyde on the isosynthesis products at feed rates less than 1.0 μl/min. Significant changes in the isosynthesis products occurred at a feed rate of 3.0 μl/min. The amount of 2-methyl-1-propanol, 2-methylpropene, 2-methylpropane, 1-butene, *t*-2-butene, and some of the $C_5$'s increased, propionaldehyde hydrogenation to propylene increased significantly, and the amount of methane, methanol, and dimethyl ether (DME) decreased. The ratio of branched to linear $C_4$'s did not change appreciably in the presence of propionaldehyde suggesting that propionaldehyde did not alter the reaction mechanisms on the catalyst surface.

Propionaldehyde cofeeding experiments were also conducted at 425, 400, and 375°C at a constant feed rate of 3.5 μl/min. The amounts of 2-methylpropionaldehyde and 2-methyl-1-propanol increased with decreasing temperature. Comparison of the oxygenated product yields in the presence

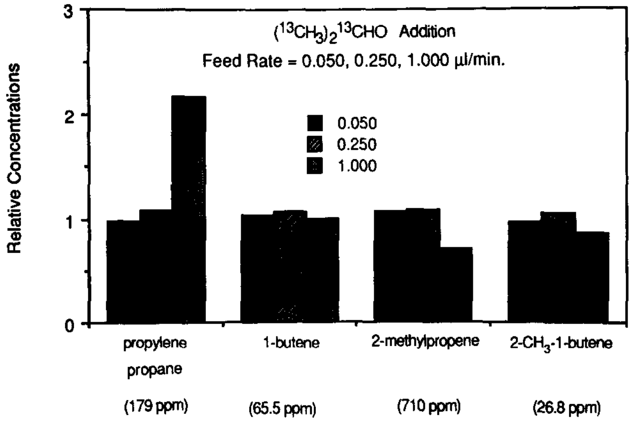

FIG. 6. Concentration of specific products relative to the amount of each product formed in the absence of acetone versus the acetone addition rate. The concentrations in parentheses refer to the amounts formed prior to acetone addition.

of propionaldehyde with the steady-state temperature data revealed that the increase was associated with the propionaldehyde fed.

All of the propionaldehyde fed to the reactor cannot be accounted for in the products listed in Table 1. Similar observations were made for the other oxygenate studies that are presented below. This was not investigated. We do note that $C_{6+}$ products were also formed but were not analyzed.

### *Acetone*

Experiments were conducted with a mixture of 52.6% [$^{12}$C]acetone and 47.4% [$^{13}$C] acetone, in which all three carbons were labeled. (An extensive series of experiments was conducted with unlabeled acetone to identify feed rates at which acetone did not significantly inhibit the isosynthesis surface reactions, yet either showed incorporation into the $C_4$ products or underwent reduction to propylene.) Selected results obtained during cofeeding of the labeled mixture are presented in Fig. 6. No obvious incorporation pattern of acetone was seen in the $C_{4+}$ products that were analyzed on the Varian GC.

The products were also analyzed on a GC/MS and the mass fragmentation data were used to compute the percentage of $^{13}$C enrichment. Acetone did not undergo significant scission of the C–C bond. The linear $C_4$ and $C_5$ olefins, 2-methylpropene, 2-methylbutane, 2-methyl-1-butene and 2-methyl-2-butene, and 3-methyl-1-butene displayed $^{13}$C enrichment. These products contained either no atoms or three atoms of $^{13}$C, insignificant amounts contained one or two $^{13}$C atoms. No $^{13}$C enrichment was found for 2-methylpropane, *n*-butane, isopentane, and *n*-pentane. It was not possible to separate 2-methylpropionaldehyde and 2-methyl-1-propanol from $C_6$ hydrocarbons under the conditions at which the GC/MS was operated. Figure 7 presents the percentage of a specific product that contained three $^{13}$C atoms. (All of the products listed above as containing $^{13}$C displayed increasing incorporation with increasing acetone feed rate.) These results demonstrate that acetone did incorporate into the isosynthesis products and that the incorporation increased with feed rate. It is interesting to note that acetone converted into both branched and linear olefins suggesting that two different mechanisms occur on the zirconia surface to consume an acetone-induced species, one leading to branched and the other to linear compounds.

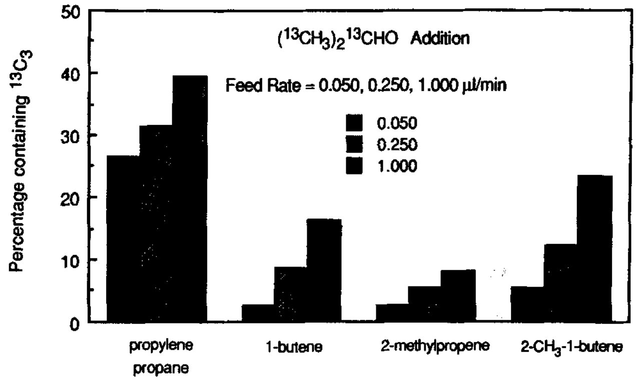

FIG. 7. Percentage of specific reaction products containing $^{13}C_3$ versus the acetone addition rate. The acetone mixture contained 47.4% [$^{13}C_3$]acetone.

## *Isopropanol*

Experiments were conducted with a mixture of 47.3% [$^{12}$C]isopropanol and 52.7% [$^{13}$C]isopropanol, $(CH_3)_2{}^{13}CHOH$. The GC results were similar to the acetone results in that no significant shifts in the product distributions were observed except for an increase in propylene and propane at and above isopropanol feed rates of 0.250 µl/min. Figure 8 presents the percentage of a specific product that contained $^{13}$C. No $^{13}$C enrichment was found for *n*-butane, 2-methylpropane, or $C_5$ hydrocarbons. The percentage of labeled propylene at 1.0 µl/min was equivalent to the percentage in the isopropanol mixture revealing appreciable reduction of isopropanol to propylene.

Incorporation of [$^{13}$C] isopropanolol into the butenes was significantly less than that observed using [$^{13}$C]acetone under equivalent synthesis conditions and oxygenate feed rates. For example, at 1.0 µl/min of acetone the reactor effluent contained 500 ppm of 2-methylpropene with 7.9% containing three $^{13}$C atoms whereas at 1.0 µl/min of isopropanol the reactor effluent contained 352 ppm of 2-methylpropene with 1.2% containing one $^{13}$C atom. (Isotope distributions have an accuracy of 1–2%). Similarly, the acetone experiment resulted in 65 ppm (16.4% enrichment) of 1-butene and 54 ppm (19.9% enrichment) of *t*-2-butene while the isopropanol experiment resulted in 46 ppm (2.7% enrichment) of 1-butene and 47 ppm (3.4% enrichment) of *t*-2-butene.

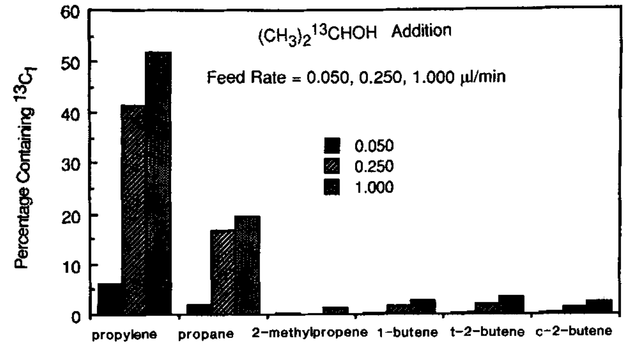

FIG. 8. Percentage of specific reaction products containing $^{13}$C versus the isopropanol addition rate. The isopropanol mixture contained 52.7% $(CH_3)_2{}^{13}CHOH$.

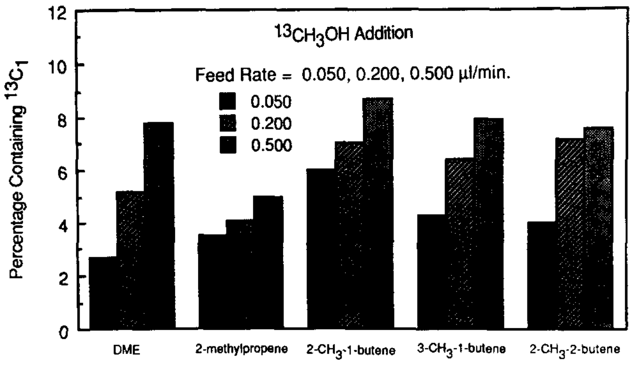

FIG. 9. Percentage of specific reaction products containing $^{13}C$ versus the methanol addition rate. The methanol mixture contained 46.6% [$^{13}C$]methanol. No $^{13}C$ incorporation was found in any of the linear $C_4$ or linear $C_5$ compounds.

### *n-Propanol*

*n*-Propanol was fed at 0.25, 0.50, and 1.00 µl/min. No evidence of incorporation or changes in the product distribution with feed rate were observed except for reduction of *n*-propanol to propylene and propane at flows of 0.50 and 1.00 µl/min.

### *Methanol*

Experiments were conducted with a mixture of 53.4% [$^{12}C$]methanol and 46.6% [$^{13}C$]methanol. No significant changes were observed in the isosynthesis products at feed rates up to 0.50 µl/min, which approximately corresponds to the maximum molar addition rate used for acetone and isopropanol. Figure 9 presents the percentage of a specific product that contained $^{13}C$ as a function of methanol feed rate. These products contained one $^{13}C$ atom. No $^{13}C$ enrichment was found for 2-methylpropane, isopentane, *n*-butane, *n*-pentane, and the linear butenes and pentenes. The $^{13}CH_3OH$ results show that methoxide is only involved in a chain growth mechanism that leads to branching.

## IV. DISCUSSION

The propionaldehyde studies provide insight into the reaction processes occurring during isosynthesis, specifically that chain growth proceeds by more than one path and involves oxygenated intermediates and that the primary isosynthesis products are oxygenated. 2-Methylpropene was the major $C_4$ product formed under the conditions employed in this study. A significant and somewhat parallel increase in 2-methylpropene and propylene was observed as the flow of propionaldehyde was increased. An increase in propylene was also observed when isopropanol was cofed, but 2-methylpropene showed no increase. Even in the presence of a significant amount of [$^{13}C$]propylene (Fig. 8) there was negligible $^{13}C$ enrichment of 2-methylpropene. More enrichment would be expected if olefins were involved in chain growth steps. Propionaldehyde-induced surface species appear to have undergone chain growth to linear and branched $C_4$ products (Fig. 5). The nature of the $C_3$ oxygenated species that underwent chain growth is suggested by the $^{13}C$ isotope studies and is discussed below.

Isosynthesis studies show that methanol, DME, and 2-methylpropionaldehyde increased in absolute concentration and as a percentage of the isosynthesis products as the residence time of the reactor was decreased. The propionaldehyde studies showed that (i) 2-methyl-1-propanol and 2-methylpropionaldehyde increased in parallel with 2-methylpropene when propionaldehyde was fed to the reactor, and (ii) 2-methyl-1-propanol and 2-methylpropionaldehyde also increased substantially with decreasing temperature, at a constant propionaldehyde addition rate. These observations are consistent with isosynthesis forming oxygenated hydrocarbons as the primary products, which are subsequently converted through dehydration and hydrogenation into olefins and alkanes. The exact nature of the oxygenated primary products was not revealed in these studies.

In accordance with the possible chain growth mechanisms, which were discussed in the Introduction, the linear products formed via CO insertion into either adsorbed *n*-propionaldehyde or *n*-propoxide, and the branched products formed, in part, via a condensation reaction between either methoxide or formyl and a $C_3$ surface species. The CO insertion mechanisms were studied using [$^{13}$C]acetone and [$^{13}$C]isopropanol. The condensation mechanisms were explored using [$^{13}$C]methanol.

Methanol was found to incorporate into 2-methylpropene and monomethylated $C_5$ olefins and did not incorporate into the $C_4$ and $C_5$ linear products (Fig. 9). An extensive series of studies over $ZrO_2$ at 1 atm has shown the $C_1$ surface species that form from CO, formic acid, formaldehyde, and methanol, and how they interconvert (*15–17*). Methanol adsorbed as methoxide. A recent isotope study of CO hydrogenation to methanol has demonstrated that formate and methoxide interconvert, probably via oxymethylene or formaldehyde, that methoxide is the immediate precursor to methanol, and that formyl species are not involved in $C_1$ synthesis reactions over $ZrO_2$ (*18*). We propose that a [$^{13}$C]methoxide species was involved in the formation of the $^{13}$C-labeled monomethylated olefins because there is no basis for assuming that formyl species were formed over $ZrO_2$. The [$^{13}$C]methanol and the propionaldehyde results provide experimental evidence to support the condensation mechanism shown in Fig. 2 that was proposed by Mazanec (*11*).

The two schemes for CO insertion involve either the alkoxide or the bound aldehyde species. The aldehyde route (Fig. 1) can produce both branched and linear products (*11*). Discriminating tests for the CO insertion mechanisms are feasible with isooxygenates, acetone, and isopropanol, because 2-methylpropene can only be produced from either of these reactants by CO insertion.

Nearly equal amounts of [$^{13}$C]acetone and [$^{13}$C]isopropanol were employed. [$^{13}$C] Acetone was seen to incorporate into 2-methylpropene (Fig. 7). [$^{13}$C]2-Methylpropene formed in the presence of isopropanol (Fig. 8); however, the level of incorporation was significantly less than was found with acetone.

The identity of adsorbed $C_3$ species following adsorption of acetone and isopropanol, under the reaction conditions, could not be determined, although the $C_3$ species are suggested by comparison to $C_1$ species. Alkoxide formation from alcohols and zirconium tetrachloride is well documented (*25–30*). Methanol has been reported to form the methoxide over $ZrO_2$ (*16, 19*). Formaldehyde was found to form a species on the $ZrO_2$ surface that could have been either adsorbed formaldehyde or oxymethylene (see Introduction) (*17*). Oxymethylene/adsorbed formaldehyde was reduced reversibly to methoxide. If a parallel set of reactions was present for the iso-$C_3$ oxygenates, then acetone adsorbed as acetone and isopropanol adsorbed as isopropoxide. The formation of [$^{13}$C]propylene from acetone (Fig. 7) and isopropanol (Fig. 8) suggests that adsorbed acetone could be reduced to isopropoxide, with isopropoxide ultimately reacting to propylene. The ketone to alkoxide conversion is probably reversible enabling both adsorbed acetone and isopropoxide to be present for either $^{13}$C-labeled reactant. However, a much higher concentration of adsorbed acetone is expected when acetone is fed.

The formation of 2-methylpropene from acetone and the negligible incorporation of isopropanol into 2-methylpropane provide

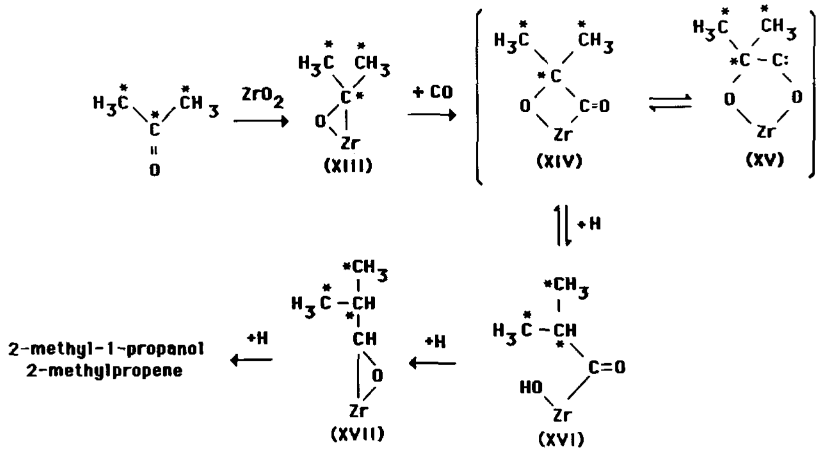

FIG. 10. Proposed scheme for CO insertion into bound acetone.

experimental evidence to support the CO insertion mechanism proposed by Mazanec (*11*). This mechanism is shown in Fig. 10. The data do not support a CO insertion reaction into alkoxides because greater levels of incorporation of $^{13}C$ should have been observed for isopropanol than for acetone. The low level of $^{13}C$ incorporation with isopropanol is consistent with the scheme shown in Fig. 10 if some of the isopropoxide was converted to adsorbed acetone during the experiments reported in Fig. 8. Oxidation of isopropoxide is supported by Yamaguchi *et al.* (*31*) who reported a 100/1 propylene/acetone ratio in the products desorbed from a $ZrO_2$ surface that was doped with isopropanol-$d_8$.

Figure 10 was adapted from the scheme proposed by Mazanec (*11*). Insertion of CO into the zirconium–carbon bond of adsorbed acetone, **XIII**, leads to the formation of branched $C_4$ species **XIV** and **XV**. Since a 1,2-shift of methyl is unlikely (*11*), the preferred reaction is hydrogenation of **XIV** to adsorbed 2-methylpropionaldehyde, **XVII**, via **XVI**. The means by which **XVII** converts to products was not revealed in our studies. One route to products could involve hydrolysis of **XVII** to 2-methyl-1-propanol, which then dehydrates to 2-methylpropene.

[$^{13}C$]Acetone also incorporated into the linear butenes (Fig. 7). The condensation scheme for **XIII** that accounts for the linear products is shown in Fig. 11. [$^{12}C$]Methoxide, **XIX**, which is synthesized from CO/$H_2$, reacts with the $\eta^3$-enolate **XVIII** to form adsorbed methyl ethyl ketone, **XX**. Abstraction of a methyl hydrogen from **XIII** is supported by H–D exchange studies of adsorbed acetone-$d_6$ over $ZrO_2$ (*31*). Bound ketone **XX** is expected to be reduced and then hydrolyzed to 2-butanol,

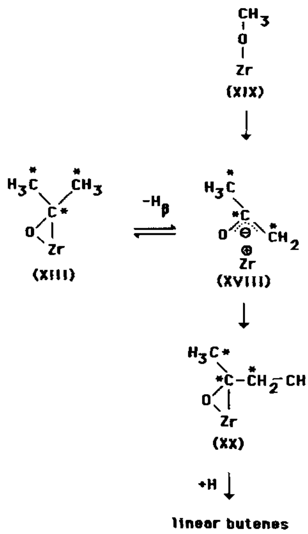

FIG. 11. Proposed condensation reaction for bound acetone.

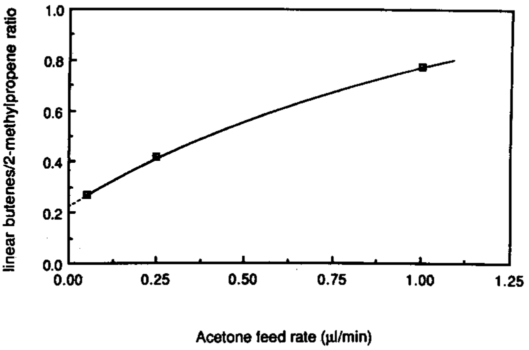

FIG. 12. Ratio of the total amount of the $^{13}C_3$-enriched linear butenes to the $^{13}C_3$-enriched 2-methylpropene versus the acetone addition rate.

which can, in turn, undergo dehydration to form the linear butenes. Dehydration of 2-butanol and isomerization of the linear butenes over $ZrO_2$ has been reported by Yamaguchi *et al.* (*32*).

The two chain growth reactions, methoxide condensation with an $\eta^3$-enolate and CO insertion into bound aldehydes/ketones, can be used to construct reaction paths to the isosynthesis products reported here. (Mazanec (*11*) presents a more complete discussion of the surface reactions that are possible.) The path shown in Fig. 1 for converting **I** to **IX** can be used to visualize the formation of adsorbed acetaldehyde if the ethyl of **I** is replaced by a hydrogen atom creating adsorbed formaldehyde. Carbon monoxide insertion into adsorbed acetaldehyde followed by a 1,2-hydrogen shift and hydrogenation would produce a 1,2-propanediolate. (This is analogous to the formation of the 1,2-butanediolate, **VI**, that is shown in Fig. 1.) Hydride loss from the 2-position of 1,2-propanediolate would lead to adsorbed acetone, **XIII**, and hydride loss from the 1-position would lead to adsorbed propionaldehyde, **I**. Figures 1, 10, and 11 depict paths to the $C_4$ products.

A variety of reaction paths are available to describe the formation of $C_5$ products. The $^{13}C$-substituted products suggest some of the reactions that lead to $C_5$ products. Acetone reacted to 3-methyl-1-butene, 2-methylbutane, 2-methyl-1-butene, 2-methyl-2-butene, and the linear pentenes. The location of the $^{13}C$ isotopes within these molecules could not be determined. Condensation of **XX** or CO insertion into **XVII** could account for 3-methyl-1-butene, 2-methyl-2-butene, and 2-methylbutane. Condensation of **XX** could also account for the linear pentenes while CO insertion into **XX** could account for 2-methyl-1-butene. [$^{13}C$]Methanol was found to incorporate into 3-methyl-1-butene, 2-methyl-1-butene, and 2-methyl-2-butene indicating condensation's role in the synthesis of these branched $C_5$ species. 3-Methyl-1-butene and 2-methyl-2-butene could also form from the condensation of **IX**, and 2-methyl-1-butene could form from the condensation of *n*-butyraldehyde.

The preceding discussion has identified the chain growth reactions that occur during isosynthesis over $ZrO_2$. Examination of the relative rates of CO insertion and condensation is possible with the [$^{13}C$]acetone data. The absolute amounts of the $^{13}C$-enriched products were determined by multiplying the percentage containing three $^{13}C$ isotopes by the concentration of the product. The ratios of the absolute amount of linear butenes-$^{13}C_3$ to 2-methylpropene-$^{13}C_3$ are plotted in Fig. 12 and represent the ratio of the condensation rate to the CO insertion rate. The zero-feed intercept should represent isosynthesis rates unaffected by a cofed oxygenate. The extrapolated zero-feed value of 0.25 suggests that the CO insertion reaction into **XIII** (Fig. 10) was four times faster than conversion of **XIII** by condensation (Fig. 11).

## V. SUMMARY

This study used $^{13}C$-labeled reactants to probe the mechanisms responsible for chain growth during isosynthesis over $ZrO_2$. The studies focused on two mechanisms that had been proposed for branched alcohol synthesis over metal oxides (*10, 11*). Both mechanisms proposed chain growth by CO insertion and chain growth by condensation.

The incorporation of methanol into the isosynthesis products and previous studies of CO activation over $ZrO_2$ (*15–18*) were used to argue in favor of the condensation scheme involving methoxide and an $\eta^3$-enolate. The incorporation of acetone and the negligible incorporation of isopropanol were used to argue in favor of CO insertion into an adsorbed aldehyde/ketone. Carbon monoxide insertion was found to occur four times faster than condensation. The mechanisms were discussed in detail and routes to the synthesis of all the products were given.

## ACKNOWLEDGMENT

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