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STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES. PROGRESS REPORT, AUGUST 1, 1984-JULY 31, 1985

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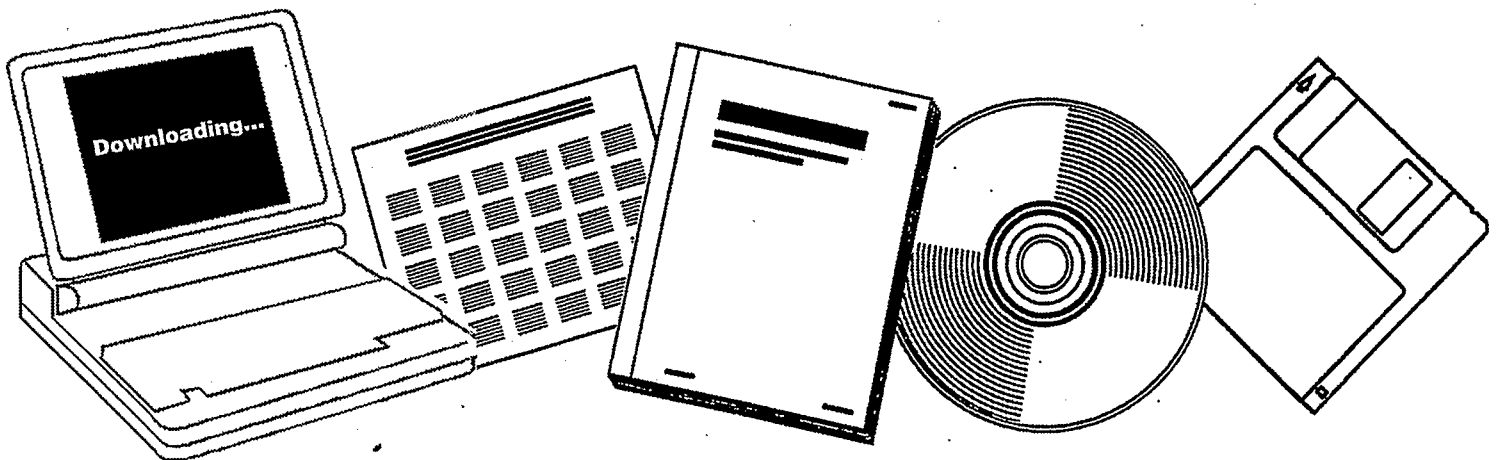
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STUDY OF SYNTHESIS GAS CONVERSION   DOE/ER/10720--16

OVER METAL OXIDES   DE85 010136

Progress Report

John G. Ekerdt
The University of Texas
Austin, TX 78712 $620 3003$

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DISCLAIMER

RESEARCH SCOPE AND OBJECTIVES

The objectives of the research are identification of the reaction intermediates present during CO hydrogenation over metal oxides, determination of the reaction mechanisms, and a description of the active site and how the metal cations and lattice oxygens participate in the CO hydrogenation reactions. Zirconium dioxide was selected for study because it catalyzes the formation of aromatics and highly branched alkanes in a process referred to as isosynthesis. It is a single metal oxide which also permits the role of one cation type to be studied in detail.

DESCRIPTION OF THE RESEARCH EFFORT

The research has continued at atmospheric and at high pressures during the past year. The atmospheric work concentrated on methanol synthesis mechanisms and surface reactions. The high pressure work has been directed toward an identification of the carbon-carbon chain growth step during isosynthesis.

Previous studies at one atmosphere (1-3) have revealed that CO and H_2 interact with ZrO_2 to form the formate, oxymethylene, and methoxide structures indicated in Fig. 1. Methoxide reacted to methane in the presence of gas phase H_2 and to methanol in the presence of gas phase H_2O. We continued to investigate the process whereby methanol was formed. The role of water in methanol formation was addressed using oxygen-18 labeled H_2O and CO. These labeling studies have also provided insight into the manner by which formate is formed at a ZrO_2 surface.

The methanol work is best summarized by making use of Figs. 2-4. Figures 2 and 3 represent the masses detected during temperature-programmed heating of the ZrO_2 in a gas stream of $CO/H_2/H_2O$. The ZrO_2 was pretreated
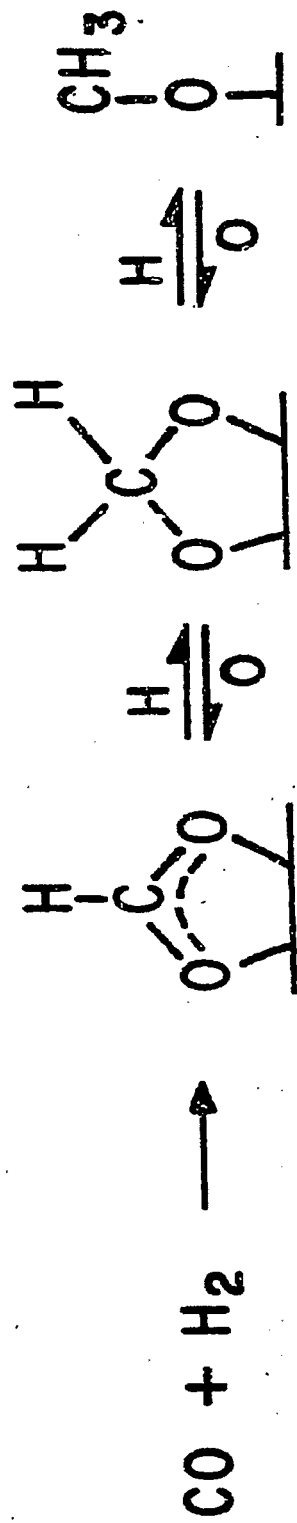
Figure 1. Interaction of CO and H₂ over ZrO₂.

Figure 2. Temperature-programmed study of a surface pretreated with $C^{16}O$ into a flowing stream of $H_2/C^{16}O/H_2^{18}O$.

INTENSITY (arbitrary units)

$C^{18}O_2$ (x0.5)

$C^{16}O^{18}O$ (x0.5)

$C^{16}O_2$ (x0.5)

$CH_3^{16}OH$ (AMU 32)

$CH_3^{18}OH$ (AMU 34)
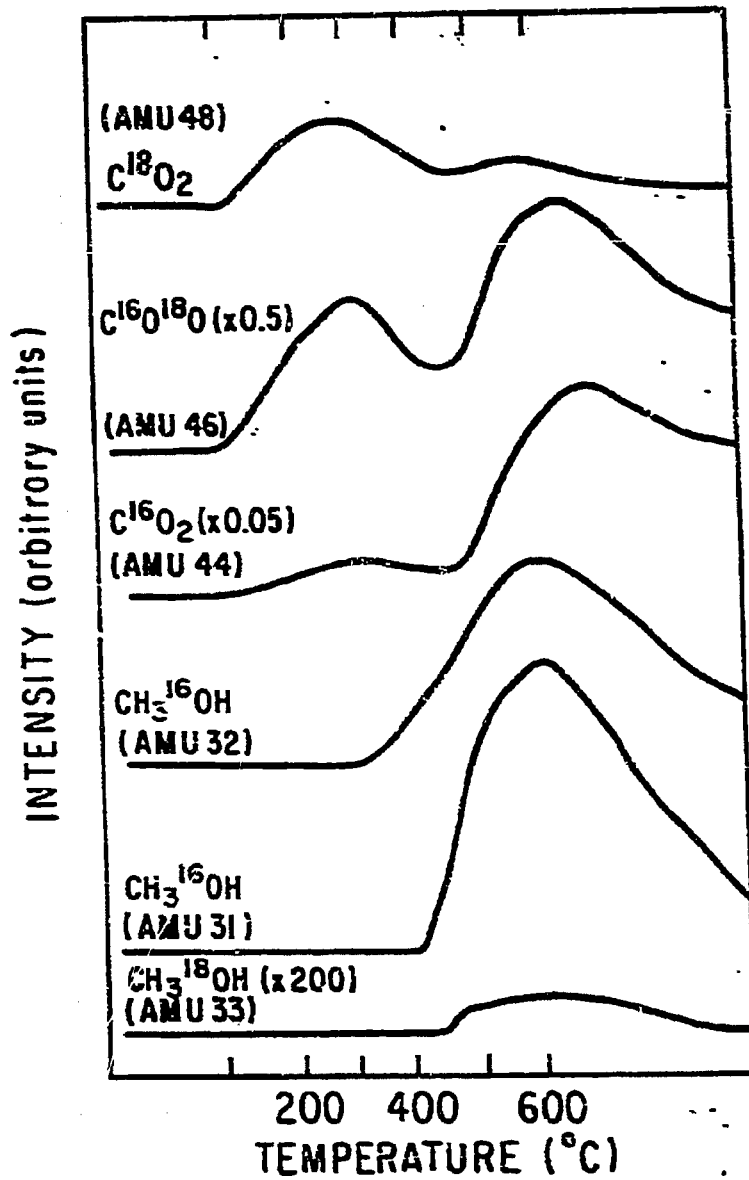
$CH_3^{18}OH$ (AMU 33)
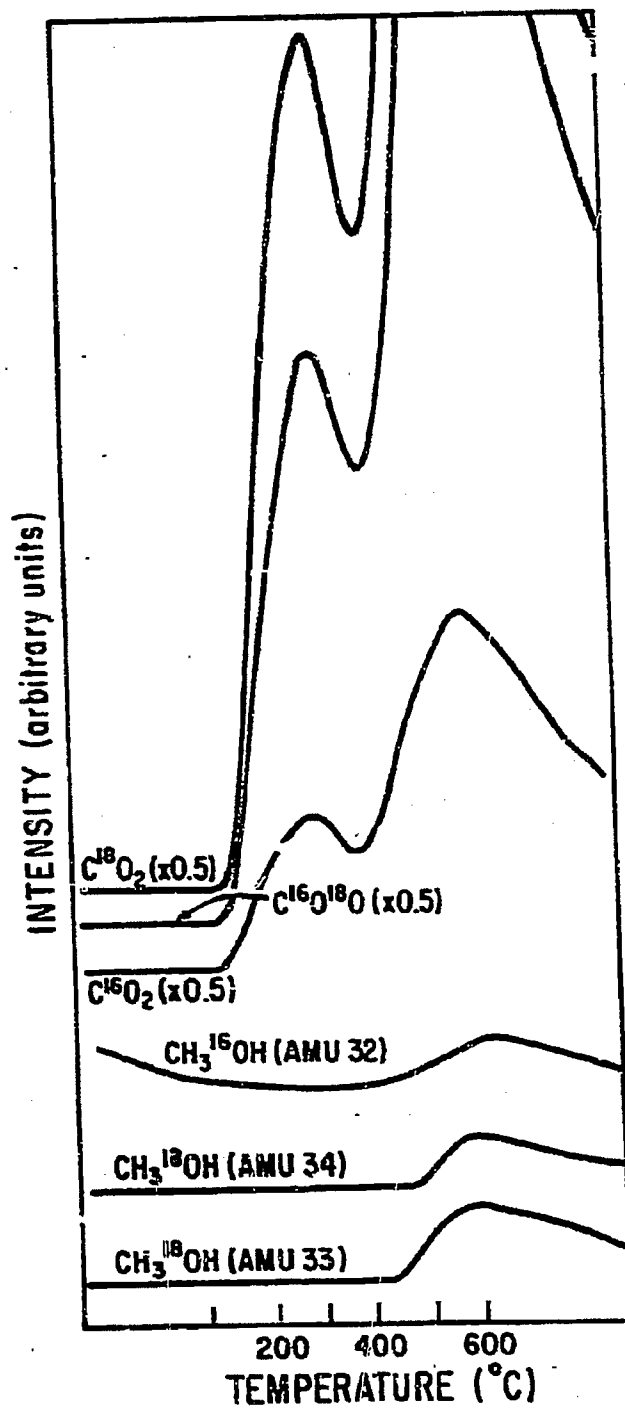
200   400   600

TEMPERATURE (°C)

Figure 3. Temperature-programmed study of a surface pretreated with $C^{18}O$ into a flowing stream of $H_2/C^{18}O/H_2^{16}O$.
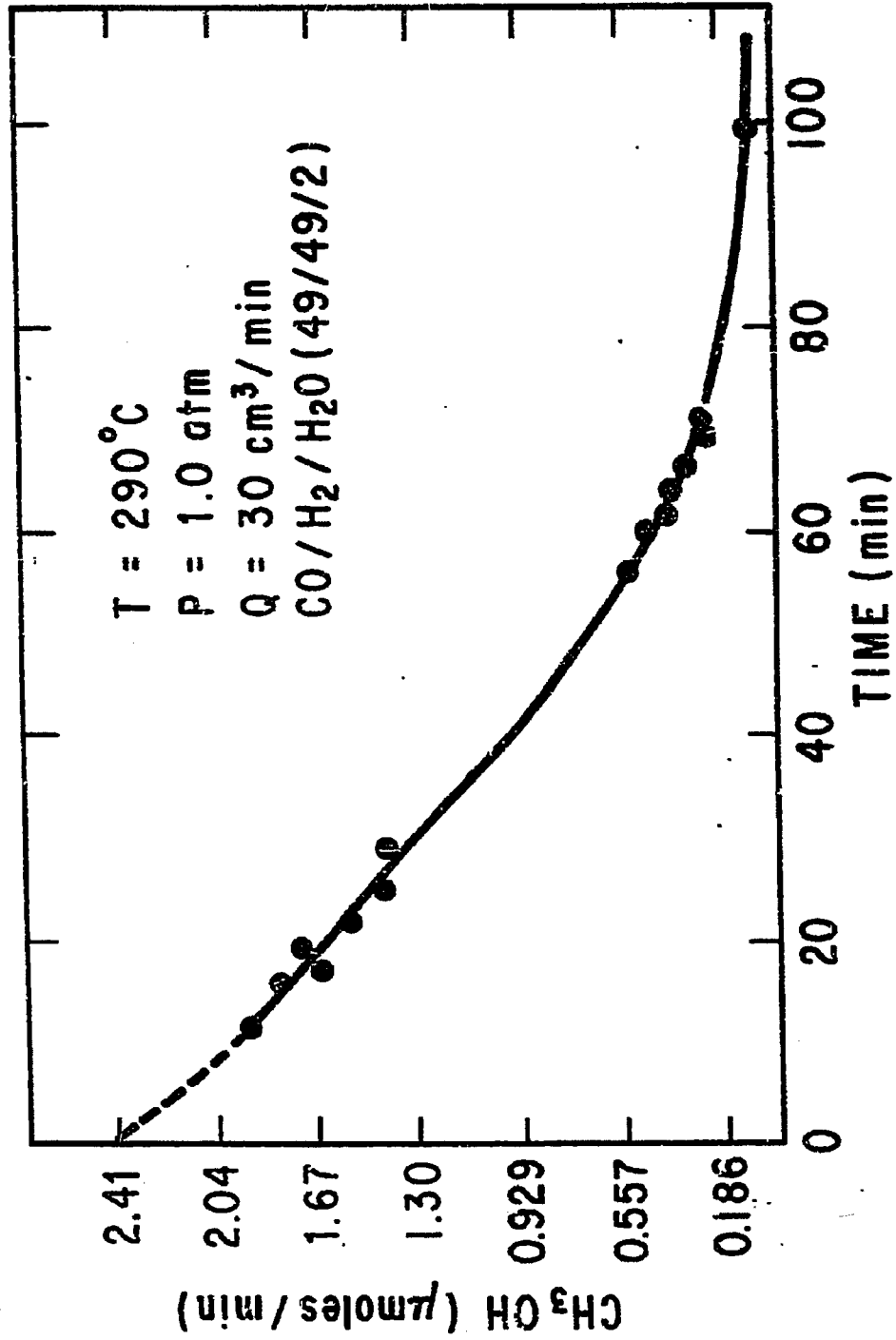
Figure 4. Steady-state production of methanol.

by oxidizing ZrO_2 at 600°C, cooling to 25°C, ramping the ZrO_2 to 620°C and cooling back to 25°C in flowing CO/H_2. Figure 2 presents the products formed following pretreatment with $C^{16}O$, and ramping in $C^{16}O/H_2^{18}O$. Figure 3 presents the products formed following pretreatment with $C^{18}O$, and ramping in $C^{18}O/H_2^{16}O$. Figure 4 represents the amount of methanol formed following a similar pretreatment but only cooling to 290°C at which time $CO/H_2/H_2O$ were caused to flow over the ZrO_2. The temperature was held constant at 290°C until methanol was no longer formed.

The pretreatment enables methoxide to form prior to reacting methoxide with water. The study with $C^{16}O/H_2^{18}O$ (Fig. 2) suggests that the O-Zr bond in the methoxide was cleaved to give 97%-^{16}O methanol. The reaction with $H_2^{18}O$ results in the formation of $Zr^{-18}OH$. This ^{18}O never appeared above 3% in the methanol produced by continuing the cycle of cooling in $C^{16}O/H_2$, ramping in $C^{16}O/H_2/H_2^{18}O$, cooling in $C^{16}O/H_2$, etc. at least ten more times. The carbon dioxide signals in Fig. 2 demonstrate that most of the carbon dioxide was $C^{16}O_2$, however, some $C^{16}O^{18}O$ and $C^{18}O_2$ formed. (This CO_2 is thought to derive from bicarbonate and carbonate species.)

The $H_2^{18}O$ study suggested that the CH_3-O fragment remained intact. Experiments with $C^{18}O/H_2^{16}O$ (Fig. 3) again show scrambling among the carbon dioxides. Examination of the methanol peaks reveals that 47% of the methanol contained ^{16}O. This ^{16}O was lattice oxide which ended up attached to methoxide during the formate to methoxide transformation.

Lattice oxide involvement in methoxide formation along with the absence of increasing amounts of ^{18}O in methanol with repeating cycles provides insight into the nature of sites at which CO is activated over ZrO_2. Figure 5 lists three routes to formate. The first two, reactions 5-1 and 5-2, differ only in the oxygen which is bonded to the zirconium cation in the

$$CO + Zr \overset{\overset{O}{|}}{Zr} \longrightarrow Zr \overset{\overset{C=O}{\underset{|}{\overset{|}{O}}}}{Zr} \overset{H}{\longrightarrow} \underset{Zr \quad Zr}{\underset{|\quad|}{O \diagdown \underset{C}{\overset{H}{|}} \diagup O}} \qquad (5\text{-}1)$$

$$CO + \overset{\overset{O}{|}}{Zr}\; Zr \longrightarrow \overset{\overset{C=O}{\underset{|}{\overset{|}{O}}}}{Zr}\; Zr \overset{H}{\longrightarrow} \underset{Zr \quad Zr}{\underset{|\quad|}{O \diagdown \underset{C}{\overset{H}{|}} \diagup O}} \qquad (5\text{-}2)$$

$$CO + \overset{\overset{OH}{|}}{Zr}\; Zr \longrightarrow \underset{Zr \quad Zr}{\underset{|\quad|}{O \diagdown \underset{C}{\overset{H}{|}} \diagup O}} \qquad (5\text{-}3)$$
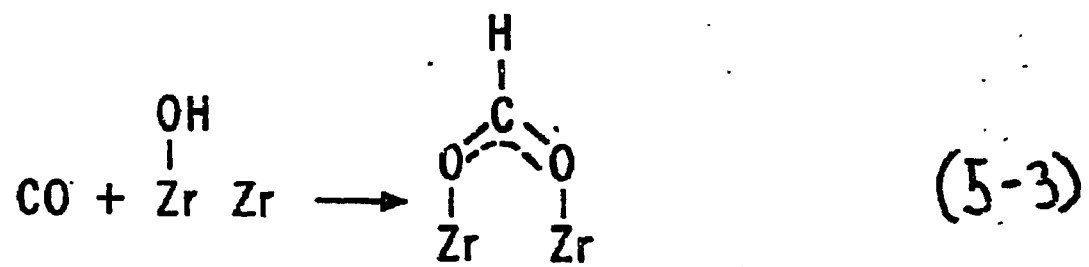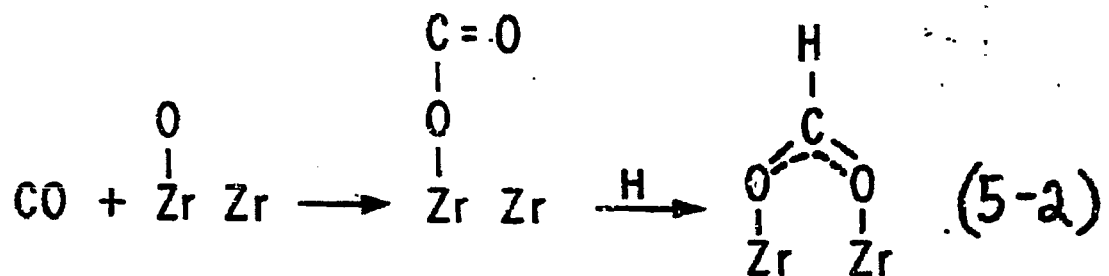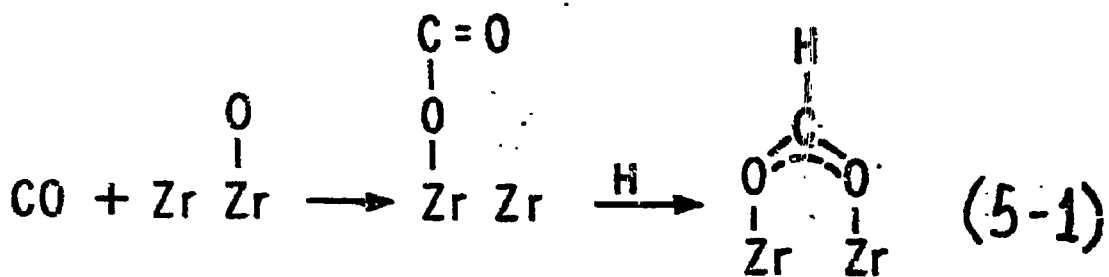
Figure 5. Possible reactions leading to formate species.

intermediate (Zr-O-C=O) Zr. (Lattice oxygen is bonded to Zr in 5-2) Zr-O is meant to represent lattice O^{2-} and Zr is a coordinately unsaturated (CUS) zirconium cation. We propose that these CUS sites are generated at temperatures above 600°C and are available for reaction with CO. The formate ($HCOO^-$) forms by hydrogenation of the COO^- intermediate. We suspect (?) that H comes from adjacent hydroxyl groups. The direct route to formate, reaction 5-3, cannot be disproven, however, it appears unlikely in light of the fact that ^{18}OH is formed from $H_2^{18}O$ and this never became incorporated into methanol to a significant extent. We suspect that CO (and CO_2) interact with Zr-OH to form the bicarbonate and possibly carbonate species. The number of CUS centers in our studies is suggested by the steady-state amount of methanol formed in the experiment represented in Fig. 4. A total of 6.4 x 10^{17} (molecules of CH_3OH)/m^2 was observed. This agrees with studies by Nakano et al. (4) who reported approximately 2 x 10^{16} (molecules of pyridine)/m^2 and 1.6 x 10^{17} (molecules of CO_2)/m^2 adsorbed at the acidic and basic sites of ZrO_2, respectively. They found that the amount of these sites was a function of the calcination temperature.

The atmospheric studies have shown the types of C_1 species which form and have revealed that the active sites may be associated with CUS cations. The studies have also shown that lattice oxygen ions participate in CO hydrogenation. Infrared studies are in progress to determine if Zr-H forms and, if so, if it is involved in the conversion of CO to methoxide. The alternative source of H is hydroxyl hydrogen (2).

The high pressure studies have not been as conclusive as the atmospheric studies but are beginning to show promise and have suggested the appropriate direction we must take. Earlier work (5) had revealed that C_4 products were formed in a step-wise fashion between a C_1 and a C_3 species.

The earlier work had also revealed that isobutene and 1-butene were the primary products at low conversion (<5%) and a pressure of 35 atm and that these primary products were most likely formed from a common intermediate.

We rebuilt our system several times in an effort to obtain better kinetic data on the C_1-C_3 hydrocarbon products and have modified our analytical methods to follow the C_5 and C_6 products. Further modifications are in progress which were suggested by the results discussed below. These modifications include installing a syringe pump to control the rate of addition of intermediate precursors which will enable use to close material balances on the system and purchasing (with local funds) a multidimensional gas chromatograph accessory for our on-line gas chromatograph which will enable us to resolve and measure all the C_1-C_5 hydrocarbon and oxygenated products which are produced.

The carbon-carbon bond forming reaction has been investigated by introducing C_1 and C_3 compounds into the CO/H_2 reactant mixture and noting their effect on the rate of hydrocarbon production and on the branched/normal ratio of the C_4 hydrocarbons. Two such experiments are described below. Table 1 lists the effect of adding 49 ppm of propylene to the feed. Propylene was added at the level at which it was produced and it essentially passed through the reactor unreacted and had a negligible effect on the C_4 products. Propylene was added to test for possible carbonium reactions between an olefin and methanol (a high pressure product) or between a C_3 carbonium ion and the C_1 species shown in Fig. 1. Table 2 lists the results of adding propionaldehyde to the feed. This experiment was a sequential run in which the middle column was recorded 6.12 to 9.77 hours after starting the experiment. The C_1 and C_2 products appear to increase with time-on-stream. The C_3 products increased dramatically in the presence of

TABLE 1

ADDITION OF C_3H_6

T = 425°C

P = 515 PSIA

	AVERAGE CONCENTRATIONS (PPM)	
FEED FLOWRATES	CO/H_2/HE 44/44/12	CO/H_2/HE+C_3H_6 45/45/10 (49 PPM)
C_3H_6	41	92
1-C_4H_8	48	54

TABLE 2

ADDITION OF C_2H_5CHO

FEED TIME (HR)	AVERAGE CONCENTRATIONS (PPM)		
	$CO/H_2/HE$ 2.82-3.58	HE + $CO/H_2/C_2H_5CHO$ 6.12-9.77 (1.32-4.97)	$CO/H_2/HE$ 11.10-13.82 (1.25-3.97)
CH_4	1,029	1,045	1,407
C_2's	217	266	273
C_3H_6	49	243	92
C_3H_8	22	190	
i-BUTANE	5	9	6
i-BUTENE	77	118	78
n-BUTANE	6	7	6
1-BUTENE	10	18	11
t-2-BUTENE	14	19	12
c-2-BUTENE	12	17	11
i-BUTENE/1-BUTENE	7.7	6.6	7.1
BRANCHED/LINEAR	2.0	2.1	2.1
2-CH_3-1-BUTENE	3	5	3
2-CH_3-2-BUTENE	7	11	6

propionaldehyde and nearly returned to the initial condition after propionaldehyde was no longer fed (92 ppm represents the sum of propylene and propane). The C_4's went up an average of a factor of 1.5 and most importantly returned to the initial levels. The major C_5 products are shown and their response was similar to that displayed by the C_4's. The C_4 branched/linear ratio was unaffected while the absolute rates increased when propionaldehyde was present in the feed. These and other studies we have conducted suggest that oxygenated intermediates are present in the C_4 forming reactions.

The proposed reaction mechanism to the iso-C_4 products is presented in Fig. 6. This is an aldol-type process in which the carbon β to a carbonyl carbon is activated for hydride-abstraction by a base as a consequence of the resonance structures shown. We propose that propionaldehyde fed with CO/H_2 adsorbed and was oxidized to propionate. The carbanion is proposed to attack a methoxide carbon producing the methyl-substituted propionate and a lattice oxygen ion. The methyl propionate is expected to be reduced to a methyl-substituted propoxide in a manner analogous to formate to methoxide (1-3). We cannot address the fate of this propoxide, 2-methyl-1-propanol or isobutene. The alcohol is expected to dehydrate to isobutene (5). The similar product distribution in the presence of propionaldehyde (Table 2) strongly suggests that the mechanism in Fig. 6 is responsible for the production of highly branched products during isosynthesis.

Linear C_4 products may form in a related manner. In this case the hydride may be abstracted from the propoxide which would not favor α- over β-abstraction. The α-carbanion would again react with methoxide and the hydrogenated form would be a linear C_4.
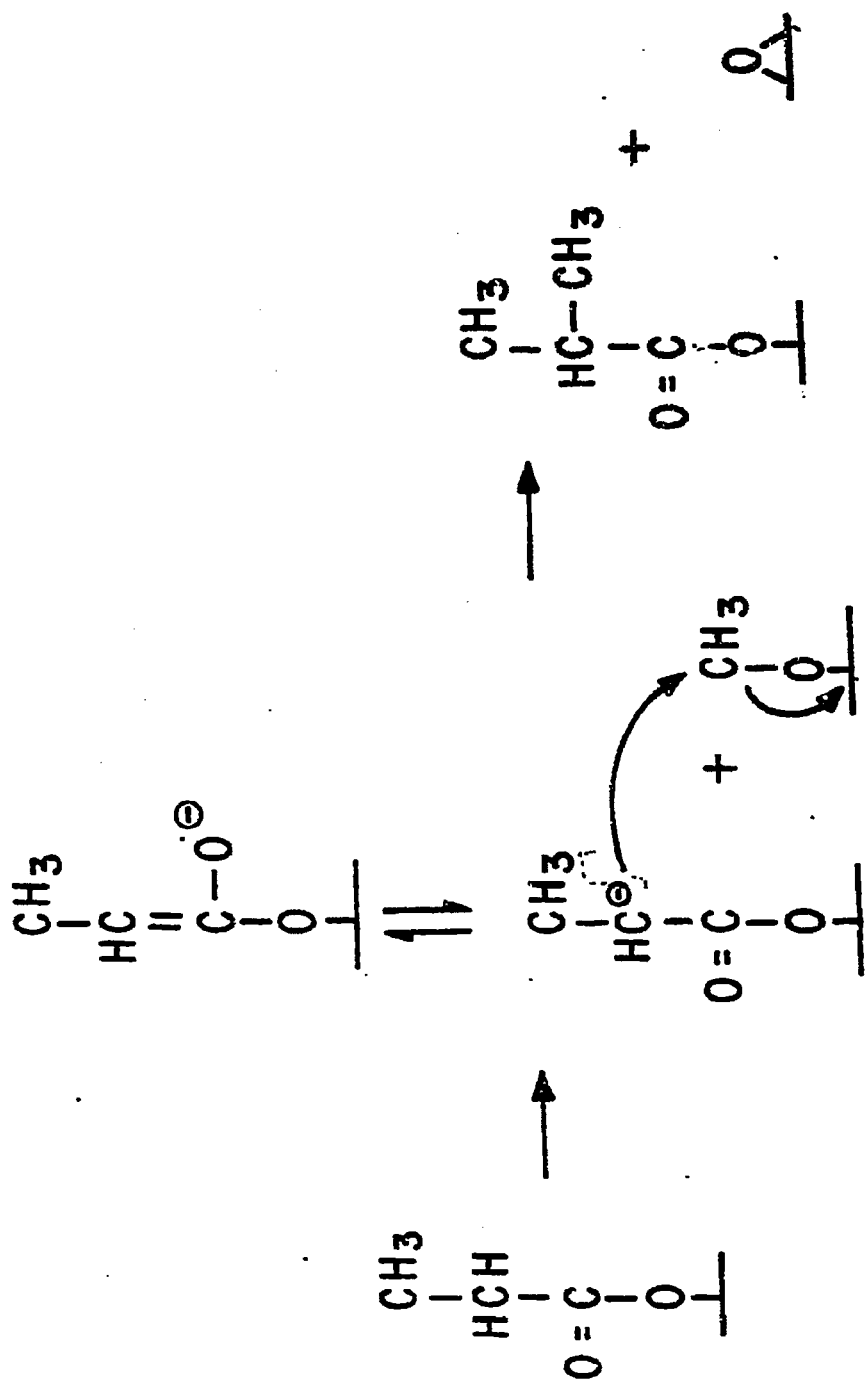
Figure 6. Proposed C₄-branching mechanism.

FUTURE RESEARCH

The high pressure studies will continue over ZrO_2. The studies will determine if oxygenated compounds are the primary products and if the hydrocarbons are formed in secondary reactions. A complete analysis of all oxygenated and nonoxygenated products will permit us to develop the complete mechanism for CO hydrogenation over ZrO_2.

Aldol condensation is base catalyzed. The role of alkali additives (6) will be reexamined to determine if they enhance the production of isoproducts and how they alter the interaction of CO with the zirconia surface. We are interested in their effect on the rates and on the selectivity to proposed intermediates.

These future studies will involve injecting suspected intermediate precursors into the feed and measuring the rates of all products and infrared investigations of the possible rearrangements of C_{2+}-oxygenates on ZrO_2 and alkali-promoted ZrO_2.

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