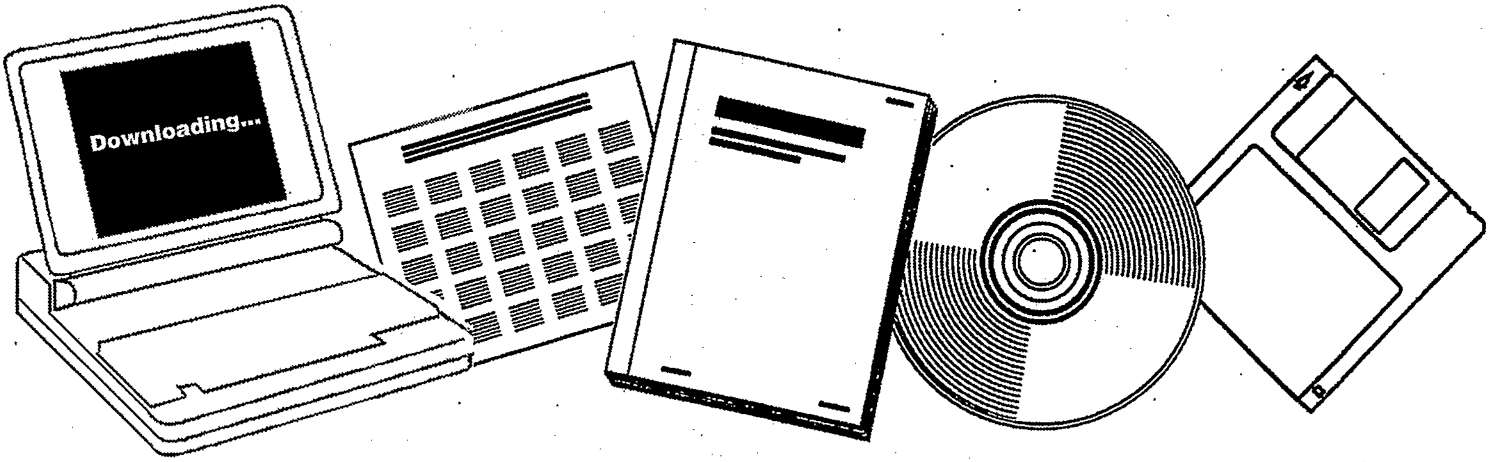
# STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES. PROGRESS REPORT, AUGUST 1, 1985-JANUARY 31, 1986

TEXAS UNIV. AT AUSTIN

1986



DOE/ER/10720--20

DE86 013118

# STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES

## Progress Report

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

August 1, 1985 - January 31, 1986

## DISCLAIMER

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. DE-AS05-80ER10720

## 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 has been selected for study because it catalyzes the formation of branched hydrocarbons and alcohols and permits one to study the reaction chemistry at elevated and atmospheric pressures. It is also a single metal oxide system which permits one to identify the catalytic properties of the metal cation without interference from a second metal component.

## DESCRIPTION OF THE RESEARCH EFFORT

Research has continued into the mechanisms of propagation and branching during high pressure (35 atm) CO hydrogenation, and into the manner in which CO and $H_2$ are activated over $ZrO_2$ and the nature of the active site. The mechanism has proven to be difficult to sort out using rate studies and will require carbon-13 isotope labeling to test our hypotheses. The active site appears to have been identified and the interaction of CO with the surface of $ZrO_2$ has been thoroughly explored. The results, their significance and research to be conducted through the end of the current contract period will be presented below.

A variety of techniques have been used to study the manner in which CO is activated over $ZrO_2$. These include temperature-programmed techniques, oxygen-18 isotope labeling and infrared spectroscopy. We focused our energy on elucidating the mechanism whereby methanol formed over $ZrO_2$ because the reaction product contained oxygen and we felt we would be able to identify the precursors to methanol by isotope studies. The results of this work are discussed in detail in Appendix 1, a manuscript submitted to the Journal of Catalysis. This study confirmed a mechanism we had proposed earlier on the basis of different techniques [1,2,3]. This mechanism involves CO interacting with $ZrO_2$ to form a surface formate, the formate is reduced to a surface methoxide and the methoxide is hydrolyzed to methanol by water, which is either added in the reactant stream or is formed during the hydrogenation reaction at elevated temperatures. The isotope studies permitted us to propose the nature of the active site and to propose the details of formate formation and conversion.

Figure 8 of Appendix 1 contains the detailed mechanism we proposed. During the course of the isotope studies we found that both methanol and formate incorporated negligible oxygen from water and a significant amount of oxygen from the zirconia surface. The essential aspect of this mechanism is the role played by lattice anion vacancies. The mechanism presented in Figure 8 accounts for the incorporation of lattice oxygen into methanol. The need for such a vacancy needs to be confirmed and we intend to pursue this through the remainder of the contract period and into the start of renewal grant period.

The mechanism also shows that the source of hydrogen in the reduction processes is surface hydroxyl. The contribution of surface hydroxyl versus hydride hydrogen remains unresolved over zirconia. Hydride has been reported by Onishi et al. [4] over zirconia and by Lamotte et al. [5] over thoria. Hydride is required in CO conversion mechanisms which are initiated by CO forming a surface formyl [6]. We have been unable to reproduce the results of Onishi et al. over zirconia prepared according to their methods or any other method we have tried. The reason for this discrepancy is unknown but may be associated with the availability of coordinatively unsaturated Zr cations on the surface. We propose that unsaturated sites are required for the reaction (see Figure 8) and these may become quickly blocked by water which forms during any exposure of zirconia to hydrogen. The need for a formate to account for the oxygen-18 distributions we observed (Appendix 1) and the results of an earlier study [2] are more consistent with hydrogen being supplied by surface hydroxyl. Surface hydroxyl has also been invoked by Edwards and Schrader [7] as the source of hydrogen in CO conversion over a ZnO-based catalyst system which is known to contain surface hydride.

As detailed in Appendix 1, we also found that two kinetically different types of surface hydroxyl groups were present over $ZrO_2$. We found that bicarbonate/carbonate contained a different distribution of labeled-oxygen than did formate. A significant amount of oxygen originating from water was found in the bicarbonate/carbonate species. A series of infrared studies was conducted with CO and $CO_2$ over the zirconia prepared from $ZrCl_4$. Figure 1 presents the spectra observed when CO and $CO_2$ were adsorbed on the surface of zirconia. The bands observed for CO are associated with a formate and the bands observed for $CO_2$ are associated with bicarbonate and carbonate species. We were unable to get the bicarbonate to reduce to the formate in the IR cell. These results combined with additional temperature-programmed results were used to propose that $CO_2$ interacts with a terminal hydroxyl group on the surface of zirconia, that this terminal hydroxyl originates from water, and that $CO_2$ is probably not directly reduced to methane/methanol over zirconia but must be converted into CO via the bicarbonate species.

We plan to document the different interaction of CO and $CO_2$ by conducting a series of oxygen labeling experiments with oxygen-18 $CO_2$. It should be possible to identify the extent to which $CO_2$ reacts with a water-based hydroxyl group and whether or not bicarbonate decomposes to CO (as proposed in Appendix 1), and that this provides an indirect route to the conversion of $CO_2$ into hydrocarbons. The labeled-$CO_2$ and -$H_2O$ needed for these studies has been ordered and we intend to initiate the experiments as soon as the chemicals arrive.

The active site for CO activation (Figure 8 of Appendix 1) is proposed to involve a coordinatively unsaturated Zr cation and an adjacent bridging surface hydroxyl. We intend to study this further by means of adsorption studies conducted with $SO_3$ combined

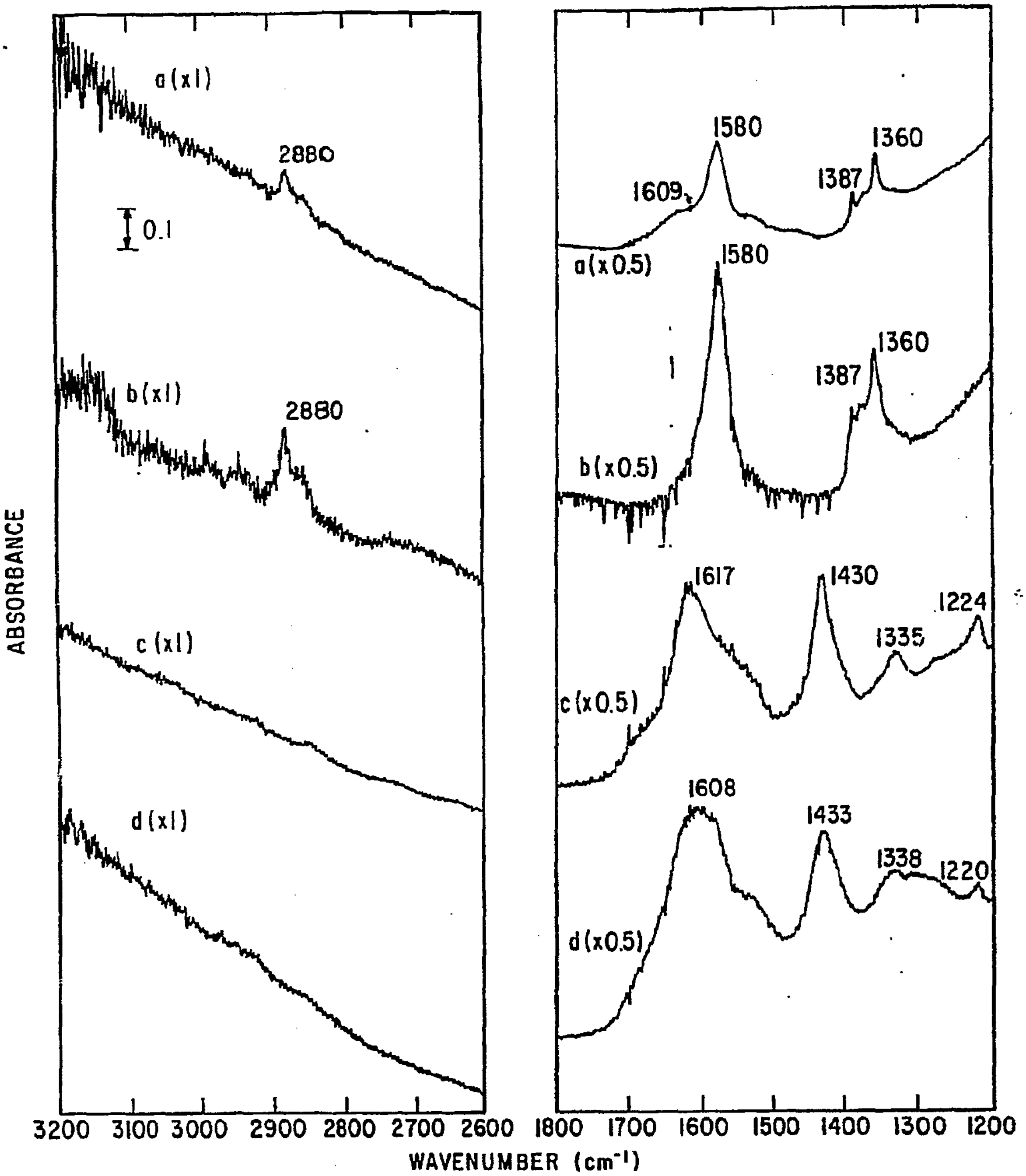


FIGURE 1. IR SPECTRA OF $ZrO_2$ AFTER ADSORPTION OF (A) CO AT 225°C, (B) CO AT 500°C, (C) $CO_2$ AT 225°C, AND (D) $CO_2$ AT 500°C.

with the titration results found in Appendix 1. These experiments will be initiated after we complete the $CO_2$ labeling studies. The details of the approach are discussed in the renewal proposal because the technique is required for additional work we are proposing. Briefly, $SO_3$ is expected to adsorb at the coordinatively unsaturated cation sites and form an $SO_4$ anion with the cation and a lattice oxygen anion [8]. If our mechanism is correct, then there should be agreement between the amount of $SO_4$ formed and the amount of methanol titrated (see Table 3 in Appendix 1).

The work described in Appendix 1 also presents the results of a series of steady-state experiments in which we demonstrated that methanol can be synthesized catalytically at atmospheric pressure without cofeeding water. A temperature in excess of 500 C was required. We feel that this high temperature is in some way associated with the ability of the zirconia to reduce the formate and to generate sufficient water for methoxide hydrolysis. We were unable to reduce preformed formate to methoxide in the static infrared cell used to generate the spectra in Figure 1. We suspect that by the time we raise the cell to a temperature sufficient to cause formate reduction, the formate has decomposed via alternate oxidation paths. The reducibility of the various surface intermediates shown in Figure 8 of Appendix 1 will be investigated. The experiments and their importance are discussed in the renewal proposal. The thrust is to achieve, through the use of a second metal such as copper, a surface which more readily reduces the formate to the intermediates needed in the formation of branched hydrocarbons and alcohols.

The previous Progress Report, DOE/ER/10720-16, described the manner by which we were attempting to define the mechanism responsible for isosynthesis in general and branching in particular. The experimental approach involves measuring the product distribution as a function of synthesis conditions and noting the effect of $C_1$ to $C_4$ oxygenated additives on the products formed. A branching mechanism was suggested which involved the interaction of a propionate anion and a methoxide in an aldol-like condensation reaction. The mechanism is presented in Figure 2. Our continuing efforts remain consistent with such a mechanism. However, the high pressure work also reveals the complex nature of the surface reactions and that more than one mechanism must be responsible for the propagation and branching reactions.

Two general schemes for isosynthesis have been (one is in press) [6,9] proposed. Both involve chain growth by means of CO insertion; however the mechanistic details are appreciably different. Mazanec's scheme (developed using analogies to organometallic chemistry) involves CO insertion into a bound aldehyde, I, to form a cyclic acyl, II, as represented in Figure 3. The substituents of the cyclic acyl influence subsequent transformations, step-wise hydrogenation to the alcohol or 1,2-shift of hydrogen (favored over alkyl [6]) through the second valence bond structure, III, in which the carbonyl carbon is carbenic. The product of the 1,2-shift is ultimately transformed

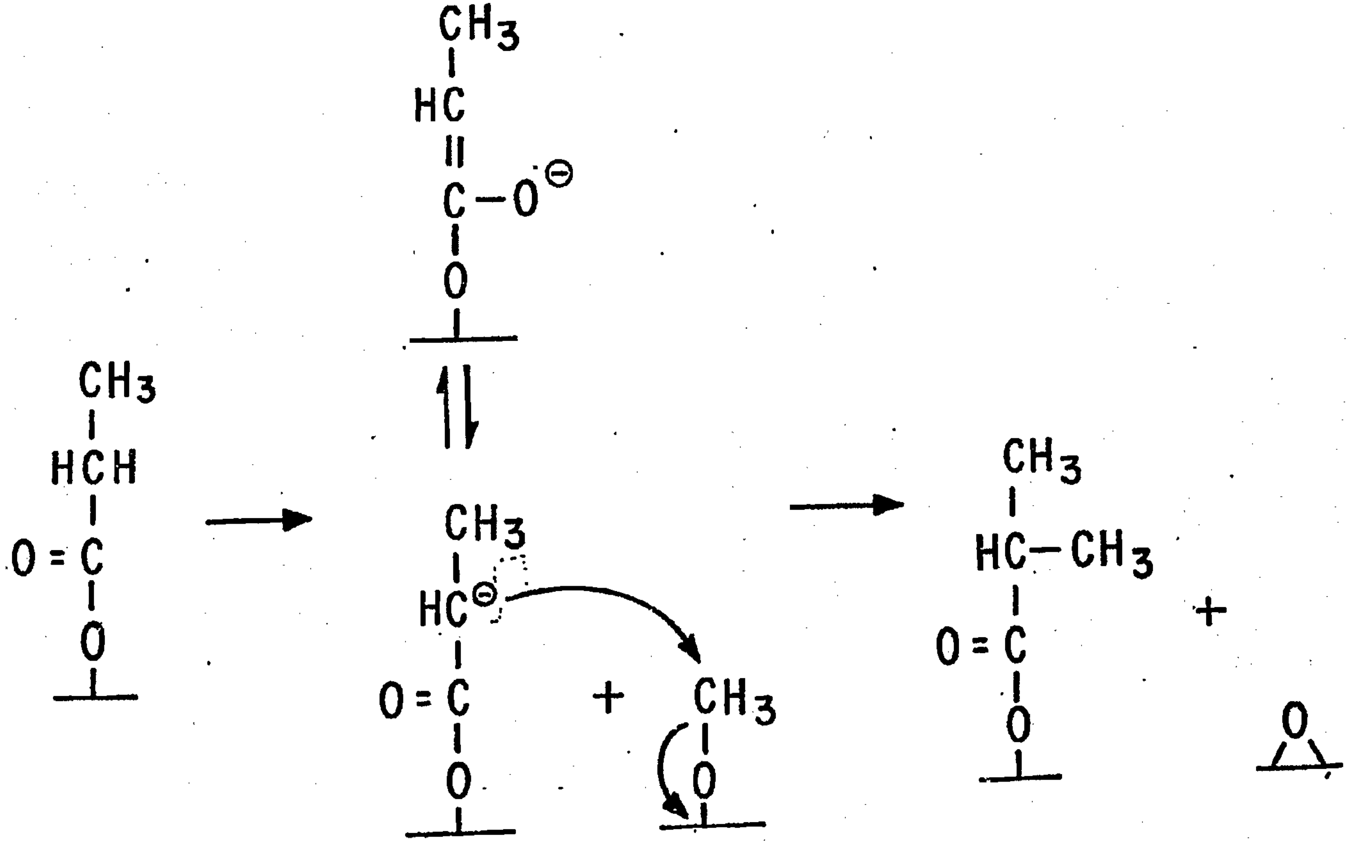


Figure 2. Proposed $C_4$-branching mechanism.

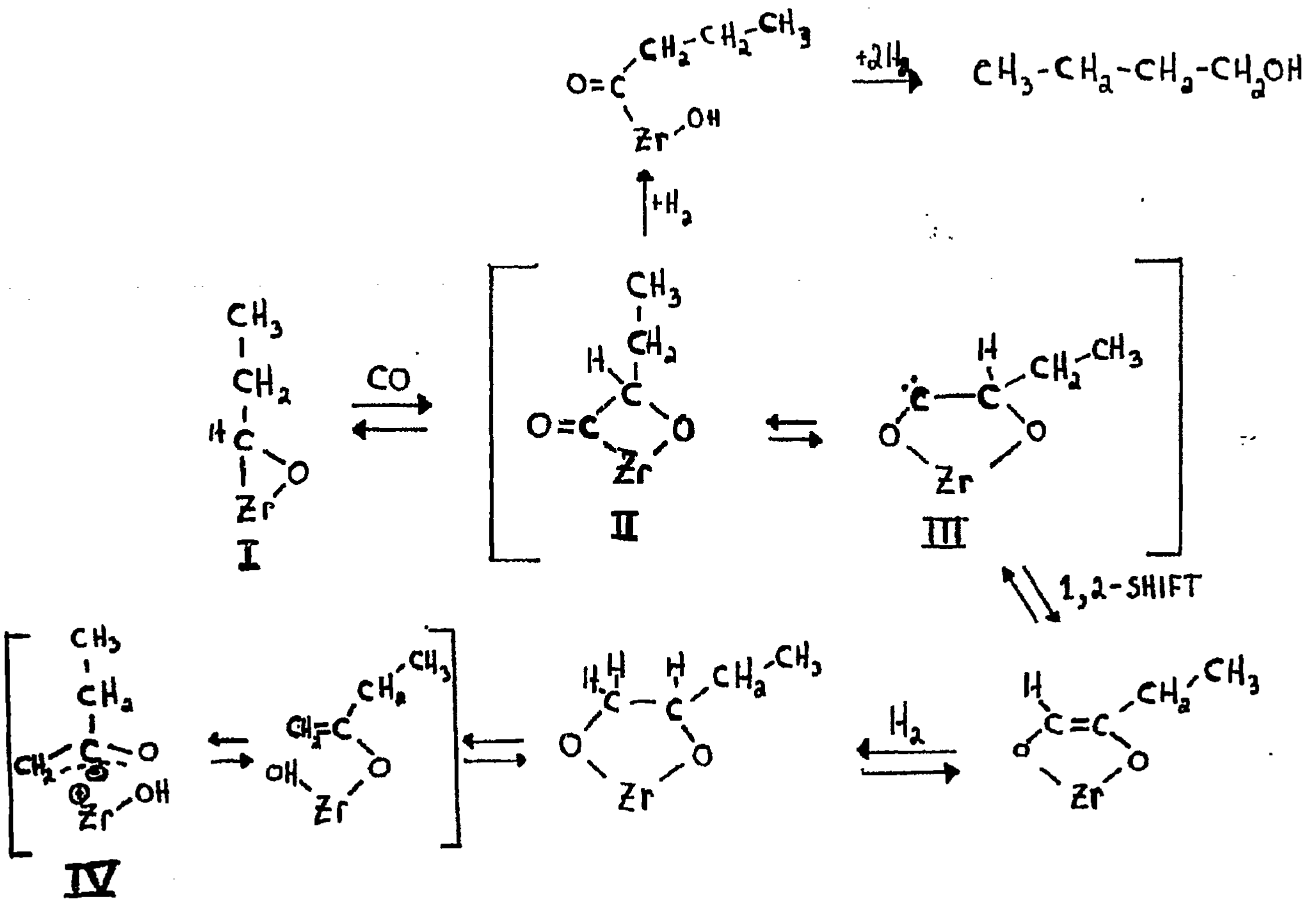


Figure 3. Representative reactions for CO insertion during isosynthesis (adapted from Reference 6).

into enolate anion, IV. The enolate may be converted to an olefin or to a bound aldehyde which would then undergo CO insertion. The nature of the initial bound aldehyde and ease with which it will undergo 1,2-shift are reasoned to account for both linear and branched products [6]. The other CO insertion scheme has been proposed by Klier and co-workers [9] on the basis of extensive studies of alcohol synthesis over a variety of metal oxide systems. Figure 4 presents the Klier's scheme. An alkoxide is proposed to undergo CO insertion to form a formate which is subsequently reduced to the alcohol. There is an important distinction between the two mechanisms in that CO insertion by Klier's mechanism only leads to linear products.

Both mechanisms [6.9] propose that branching proceeds by an aldol-like condensation process and again the details of the reaction differ. Figures 5 and 6 present the two reactions. Both reactions involve an enolate anion, V, which is associated with a cation center. A zirconium cation is presented here however alkali-promoted systems are expected to enhance the formation of V and the alkali cation could be associated with V [9]. Mazanec's scheme involves attack on V by methoxide (Figure 5) and Klier's scheme involves attack on V by a formyl. Mazanec's condensation scheme and our proposed scheme (Figure 2) differ in the structure to which the methoxide adds. A distinction between these intermediates, propionate anion or enolate anion, is probably not possible because they may interconvert via the propionate and bound aldehyde, I.

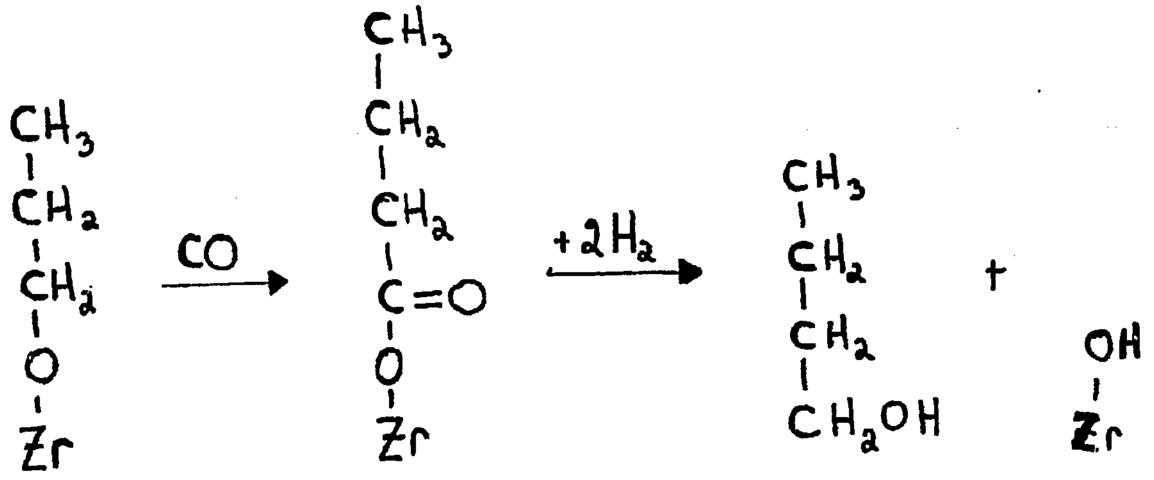


Figure 4. Representative reactions for CO insertion during isosynthesis (adapted from Reference 9).

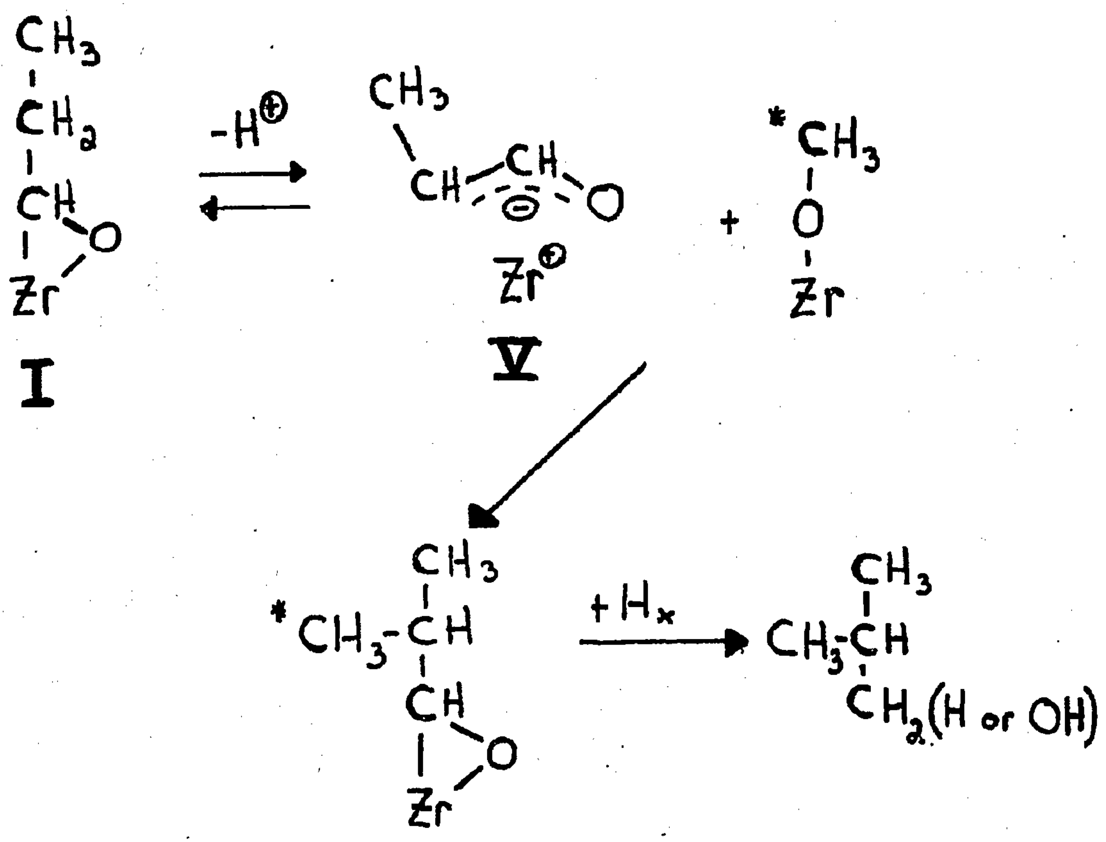


Figure 5. Representative reactions for condensation involving alkoxide (adapted from Reference 6).

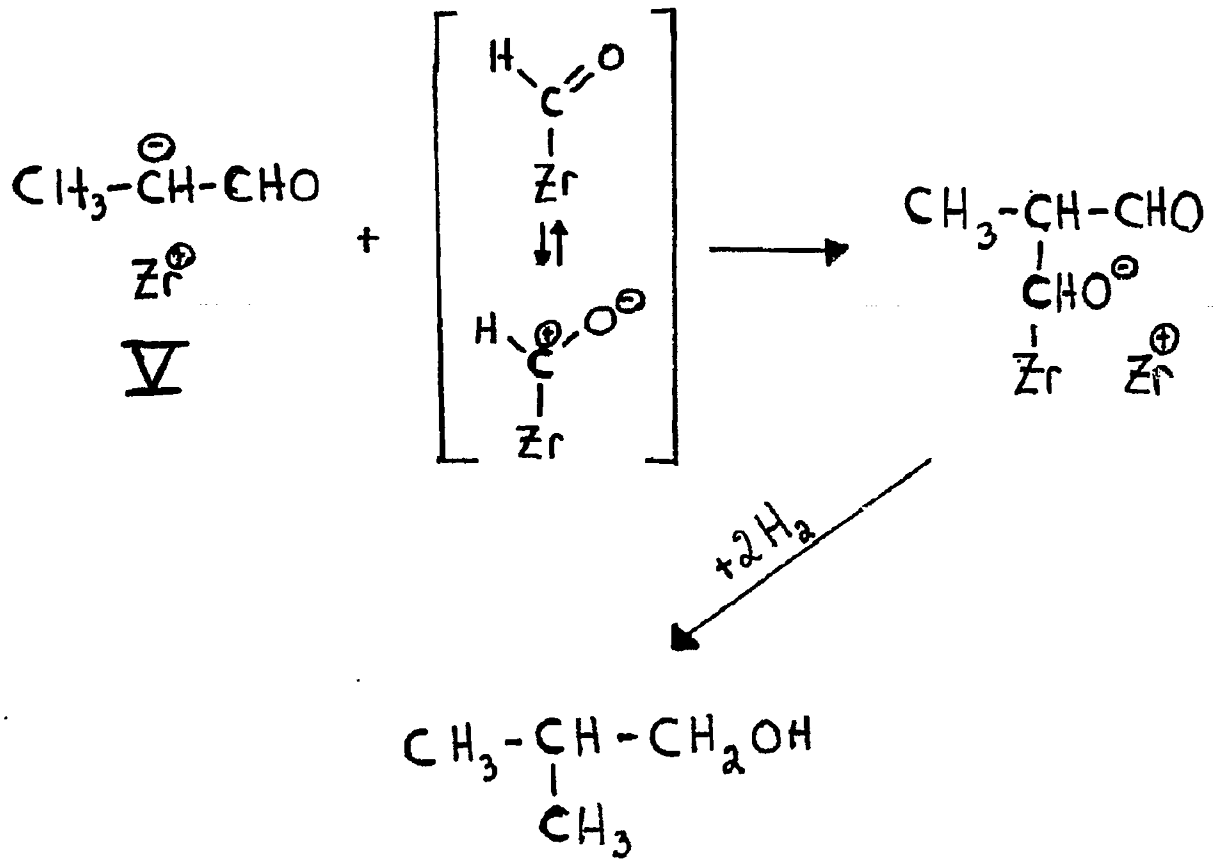


Figure 6. Representative reactions for condensation involving formyl (adapted from Reference 9).

Addition of unlabeled-oxygenated compounds to the feed, to determine if they are incorporated into the products, may not provide a discriminating test between the two mechanisms. We have measured the effect of adding methanol, formaldehyde, acetaldehyde, n-propanol, propionaldehyde, and 2-methylpropionaldehyde. These were added in concentrations ranging from 10 to 1000 times greater than the concentration of the compound resulting from isosynthesis. In many cases the oxygenated additive did not appear to incorporate, in appreciable amounts, into the synthesis products but rather underwent self condensation or reduction. The propionaldehyde additions have provided the most information and support the hypothesis that branching proceeds via an aldollike condensation (Figures 2 and 5) but only suggest the details of this process. Table 1 presents the effect of adding 200 ppm of propionaldehyde to the feed (isosynthesis typically produces 2-4 ppm of propionaldehyde at the reported conditions). Methane, methanol and dimethyl ether decreased, while ethylene, propylene, propane and isobutene increased in concentration. The propionaldehyde appeared to react with the methane and methanol precursor to form isobutene. Our atmospheric studies have demonstrated that the methane/methanol precursor is a methoxide. It is important to note that the amount of propionaldehyde added can be almost totally accounted for from the increase of ethylene, ethane, propylene, and isobutene. Condensation is a termination mechanism and the use of the additives listed above reveal nothing about the propagation process.

Table 1 Isosynthesis Products at 425 C and 35 atm

| Feed Gas | $H_2$/CO/He | $H_2$/CO/He with 200 ppm of $C_2H_5CHO$ |
|---|---|---|
| $CH_4$ | 1312 | 863 |
| $C_2H_4$ | 104 | 123 |
| $C_2H_6$ | 103 | 103 |
| $C_3H_6$ | 67.0 | 204 |
| $C_3H_8$ | 19.0 | 27.0 |
| i-$C_4H_{10}$ | 6.1 | 5.5 |
| i-$C_4H_8$ | 252 | 301 |
| n-$C_4H_{10}$ | 4.0 | 4.7 |
| 1-$C_4H_8$ | 28.5 | 30.7 |
| t-2-$C_4H_8$ | 27.7 | 27.6 |
| c-2-$C_4H_8$ | 26.4 | 26.1 |
| $(CH_3)_2O$ | 486 | 455 |
| $CH_3OH$ | 171 | 155 |
| $C_2H_5CHO$ | 0 | 0 |
| i-$C_4H_8/CH_3OH$ | 1.47 | 1.94 |

---

(a) ppm

A detailed analysis of Mazanec's and Klier's mechanisms suggest that the application of carbon-13 labeled additives should provide the information required to confirm the insertion and condensation mechanisms. We propose to initiate these as soon as the compounds arrive. The labeled studies can then be combined with our extensive rate data to provide a detailed mechanism for isosynthesis and higher alcohol synthesis that is backed up with experimental evidence.

The labeled studies will involve an examination of the effects of adding carbon-13 labeled acetone and carbon-13 labeled methanol to a $^{12}CO/H_2$ reactant stream. Isopropanol is not seen over zirconia suggesting that it is unlikely that acetone can adsorb on the surface of zirconia and transform into the alkoxide required in Klier's CO insertion mechanism. Acetone is expected to form an adsorbed aldehyde by analogy to the previous experience we have with formaldehyde. (This will be tested using IR.) Mazanec's proposed mechanism for CO insertion will lead to isobutane and/or isobutene in which one of the terminal carbons is $^{12}C$ and or isobutanol in which the $-CH_2OH$ group contains $^{12}C$. The acetone is also expected to form an enolate and undergo condensation by either of the routes (Figures 5 and 6) to produce a linear $C_4$ product with $^{12}C$ at one of the ends. The formation of one or more of the branched products listed above will substantiate Mazanec's mechanism. The absence of a branched product combined with appreciable loss of acetone would support Klier's mechanism for CO insertion.

Methanol and methanol co-fed with propionaldehyde should enable us to elucidate the condensation process. We find no evidence in our atmospheric studies to suggest that the methoxide, which will form from methanol, will be oxidized to the formyl structure shown in Figure 6. It is unlikely that much oxidation of any kind will occur under the strongly reducing conditions of isosynthesis. The formation of branched alcohols and hydrocarbons containing a $^{13}CH_3$ as the attached methyl group will substantiate Mazanec's mechanism. We do not expect carbon-13 incorporation into the branched position for Klier's scheme.

These experiments will require the necessary control experiments to verify the assumptions made above. All the analytical instrumentation needed in the control and labeling experiments is in place. We hope to complete these experiments over unpromoted $ZrO_2$ before the end of the current contract period. The carbon-13 techniques will also be used in the research which is proposed in the renewal request.

## References

1. M-Y. He and J. G. Ekerdt, J. Catal. 87, 238 (1984).
2. M-Y. He and J. G. Ekerdt, J. Catal. 87, 381 (1984).
3. M-Y. He and J. G. Ekerdt, J. Catal. 90, 17 (1984).
4. T. Onishi, H. Abe, K-i.Maruya, and K. Domen, J. Chem. Soc., Chem. Commun., 617 (1985).
5. J. Lamotte, J. C. Lavalley, E. Druett, and E. Freund, J. Chem. Soc. Faraday Trans. I 79, 2219 (1983).

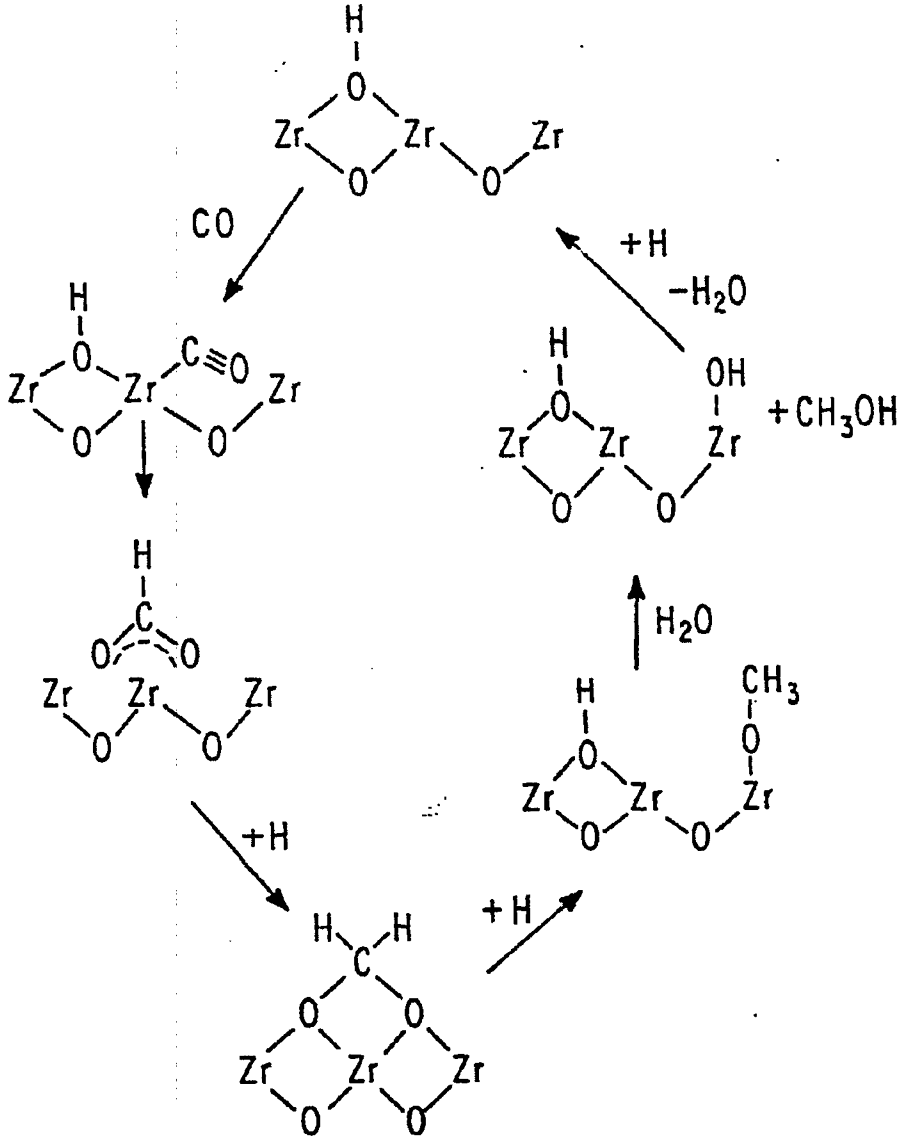
6. T. J. Mazanec, "On the Mechanism of Higher Alcohol Formation Over Metal Oxide Catalysts, Part I: A Rationale for Branching in the Synthesis of Higher Alcohols from Syngas", J. Catal.(in press).

7. J. F. Edwards and G. L. Schrader, J. Phys. Chem. 89, 782 (1985).

8. a) T. Jin personal communication.
   b) T. Yamaguchi, T. Jin, and K. Tanabe, "Structure of Acid Sites on Sulfur Promoted Iron Oxide", (submitted to J. Phys. Chem.).
   c) T. Jin, T. Yamaguchi, and K. Tanabe, "Mechanism of Acidity Generation on Sulfur Promoted Iron Oxide", (submitted to J. Phys. Chem.).

9. G. A. Vedage, P. B. Himelfarb, G. W. Simmons, and K. Klier in "Solid State Chemistry in Catalysis" (eds. R. K. Grasselli and J. F. Brazdil) ACS Symposium Series 279, 1985.

from Appendix I



[Jackson, Ekerdt -- Figure 8]

Appendix I (preprint) removed.
Jsw

# APPENDIX 2

## Publication and Presentations of Work Supported in the Current Contract Period

### Publications

1. Temperature-Programmed Studies of the Adsorption of Synthesis Gas on Zirconium Dioxide (with M-Y. He), J. Catalysis 87, 238 (1984).

2. Infrared Studies of the Adsorption of Synthesis Gas on Zirconium Dioxide (with M-Y. He), J. Catalysis 87, 381 (1984).

3. CO and $CO_2$ Hydrogenation Over $ZrO_2$ (with M-Y. He), Reprints, A.C.S. Div. Petrol. Chem. (1984, St. Louis Meeting) 29, 532 (1984).

4. Methanol Formation on Zirconium Dioxide (with M-Y. He), J. Catalysis 90, 17 (1984).

5. CO and $CO_2$ Hydrogenation Over Metal Oxides: A Comparison of ZnO, $TiO_2$ and $ZrO_2$ (with M-Y. He, and J. M. White), J. Molecular Catalysis 30, 415 (1985).

6. Study of Fischer-Tropsch Synthesis Over $Fe/SiO_2$: Effect of Diethylamine on Hydrocarbon and Alcohol Production (with K. G. Anderson), J. Catalysis 95, 602 (1985).

7. Methanol Synthesis Mechanism Over Zirconium Dioxide (with N. B. Jackson) (submitted).

### Presentations

1. "Isosynthesis Reactions over Zirconia" (with M. A. Barker, and M.-Y. He) 1983 ACS National Meeting, Washington, D.C.

2. "CO and $CO_2$ Hydrogenation over Metal Oxides" (with M.-Y. He, and J. M. White) 1983 Southwest Catalysis Society Fall Symposium, Houston, TX.

3. "Alkyl and Acyl Intermediates in Fischer-Tropsch Synthesis" (with C. J. Wang and K. G. Anderson) 1984 ACS National Meeting, St. Louis, MO.

4. "CO and $CO_2$ Hydrogenation over $ZrO_2$" (with M.-Y. He) 1984 ACS National Meeting, St. Louis, MO.

5. "Isosynthesis over Zirconium Dioxide" (with N. B. Jackson and S. Tseng), Ninth North American Catalysis Society Meeting, 1985, Houston, TX.

6. "Hydrogenation of Carbon Oxides Over Zirconium Dioxide" (with N. B. Jackson) 1985 ACS National Meeting, Miami Beach, FL.

7. "Formate and Methoxide Intermediates in CO and $CO_2$ Hydrogenation Over Metal Oxides" (poster) Second China - U.S. - Japan Symposium on Heterogeneous Catalysis, 1985, Berkeley, CA.

8. "Adsorption and Reaction of Carbon Dioxide on Zirconium Dioxide" (with N.B. Jackson and R.G. Silver) 1986 ACS National Meeting, New York, NY.

9. "Isosynthesis Mechanisms Over Zirconium Dioxide" (with R.G. Silver and S.C. Tseng) 1986 ACS National Meeting, Anaheim, CA.