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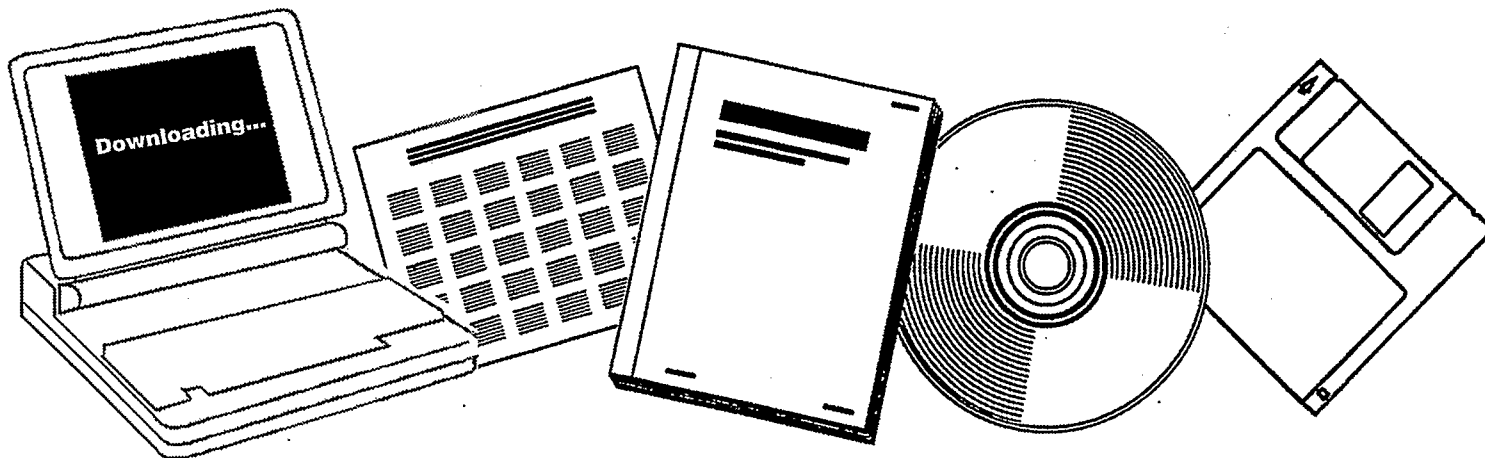
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**STUDY OF SYNTHESIS GAS CONVERSION OVER
METAL OXIDES: PROGRESS REPORT, AUGUST 1,
1986-JULY 31, 1987**

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**STUDY OF SYNTHESIS GAS
CONVERSION OVER METAL OXIDES**

Progress Report

August 1, 1986 - July 31, 1987

John G. Ekerdt

**University of Texas
Austin, Texas 78712**

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RESEARCH SCOPE AND OBJECTIVES

The goals of this program are (1) identification of the reaction intermediates present during CO hydrogenation reactions, (2) determination of the reaction pathways whereby the intermediates are converted into products and (3) the development of an understanding of the causes for catalytic activity and selectivity. Direct CO hydrogenation into branched alkanes and aromatics, isosynthesis, is being investigated over zirconium dioxide and alkali-promoted zirconium dioxide. Reaction mechanisms have been identified by use of infrared spectroscopy, temperature-programmed reaction techniques, and carbon-13 and oxygen-18 isotope labeling. Chain propagation proceeds by CO insertion into adsorbed aldehyde/ketone species and by a condensation reaction between methoxide and enolate species. Current, and future, research is focusing on these chain growth reactions and is directed toward establishing how acid and base promoters affect the absolute rate of these individual reactions. The active site for CO activation was suggested, on the basis of oxygen-18 studies, to be an anion vacancy. The role of anion vacancies in CO hydrogenation is currently under investigation.

DESCRIPTION OF THE RESEARCH EFFORT

Previous work at 1 atm had revealed the C₁ species that form and how they interconvert [1-6]. The key surface reactants for the formation of C₂ and higher products (C₂₊) appear to be methoxide and the species intermediate between formate and methoxide. This intermediate species could be assigned to either oxymethylene or adsorbed formaldehyde as shown in Figure 1 [7].

A recently completed study of C₂₊ product synthesis [7,8] has enabled us to identify the reactions responsible for chain propagation. Chain growth

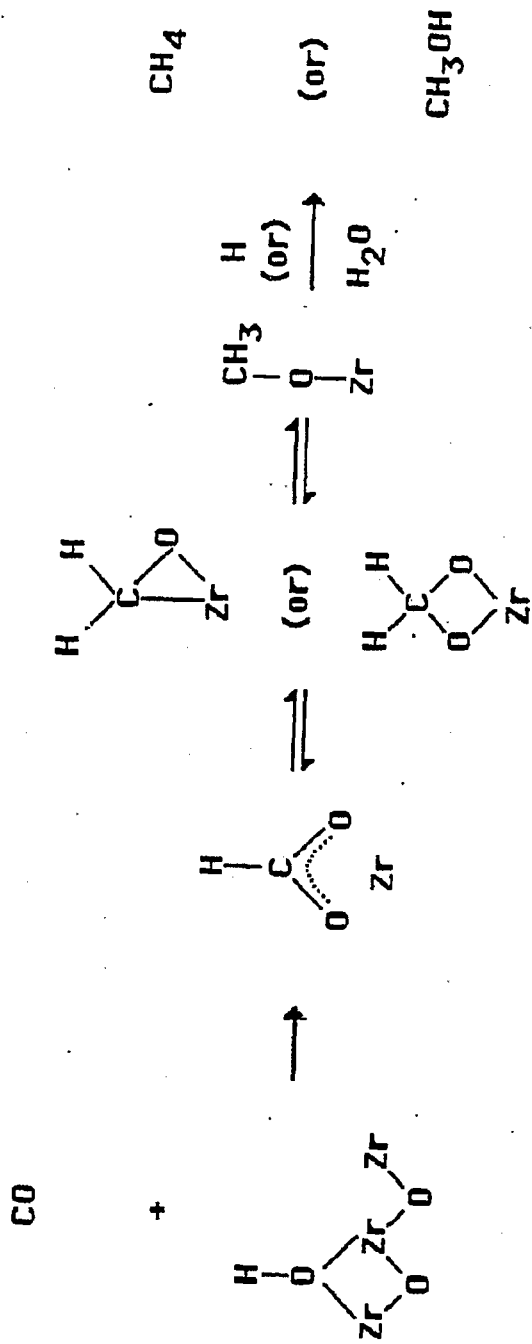


Figure 1. Proposed scheme for CO activation and C₁ synthesis [5,7].

has been shown to proceed by CO insertion into bound aldehyde/ ketone species and by condensation between methoxide and enolate species. The CO insertion reaction appears to dominate, is the only reaction for C₂ formation and may be the only reaction for C₃ formation. Formaldehyde initiates the major chain growth process. The condensation reaction causes an increase in C₄₊ products and accounts for the some of the branching that is observed over ZrO₂.

The conclusions listed above are based on an extensive series of carbon-13 labeling experiments. The experiments involved adding a labeled-oxygenate to the CO/H₂ feed mixture and determining the products into which the oxygenate incorporated. Incorporation or lack of incorporation by various additives was used to discriminate between possible reaction mechanisms. We found that carbon-13 isotopes were needed because the product distribution, as analyzed on the GC, did not always clearly show incorporation into any product had occurred. Carbon-13 isotope distributions provide unambiguous evidence for incorporation. Acetone provides the greatest amount of insight because it reacts to iso-C₄'s by CO insertion and linear C₄'s by condensation and because it can be used to measure the absolute rates of these two propagation reactions. (The reaction paths for acetone incorporation are shown in Figures 2 and 3, respectively.) We found that at 425 °C ZrO₂ catalyzed the insertion reaction four times faster than the condensation reaction.

Identification of the reaction path is a major benchmark in our research program. It is now possible to design experiments that will probe how the metal oxide catalyst influences the relative rates of key reactions in the propagation sequence. Without the mechanisms we would only be able to establish overall changes in selectivity and in kinetic parameters,

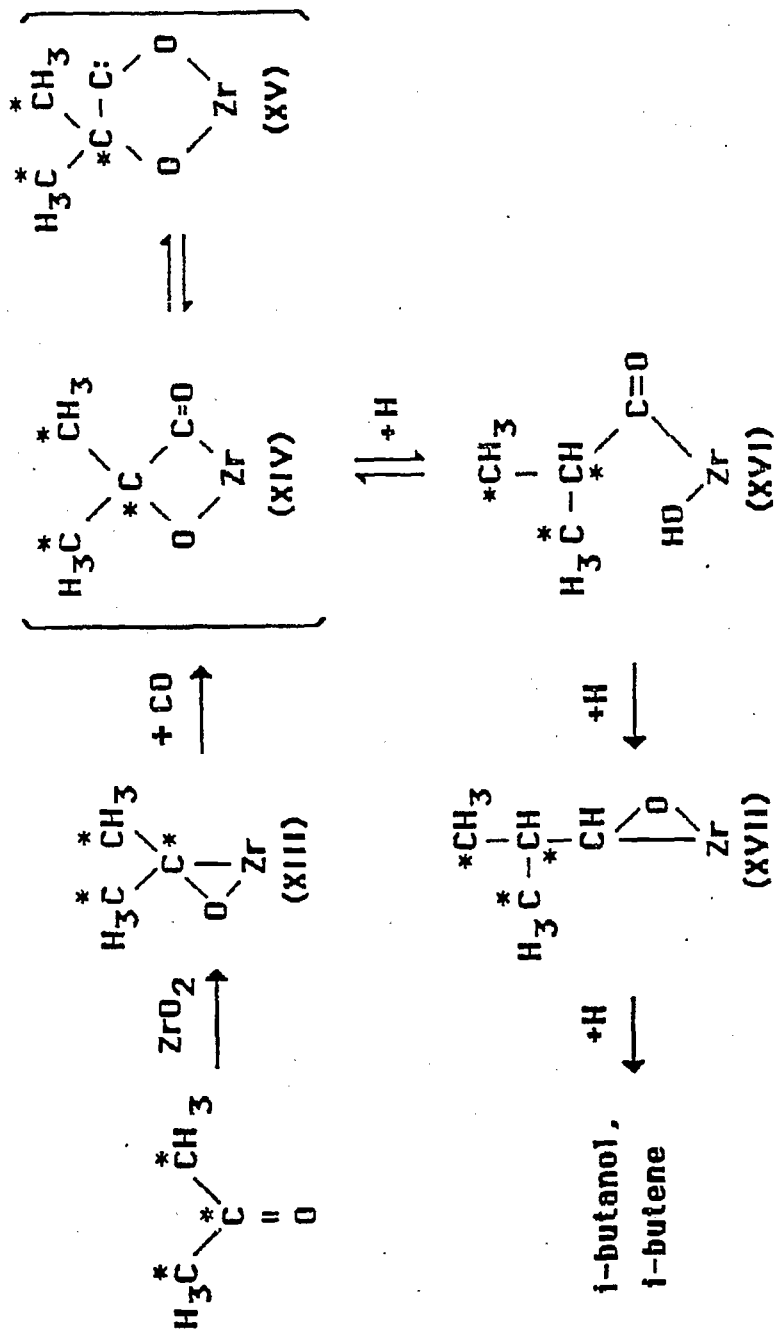


Figure 2. Proposed scheme for CO insertion into bound acetone [7].

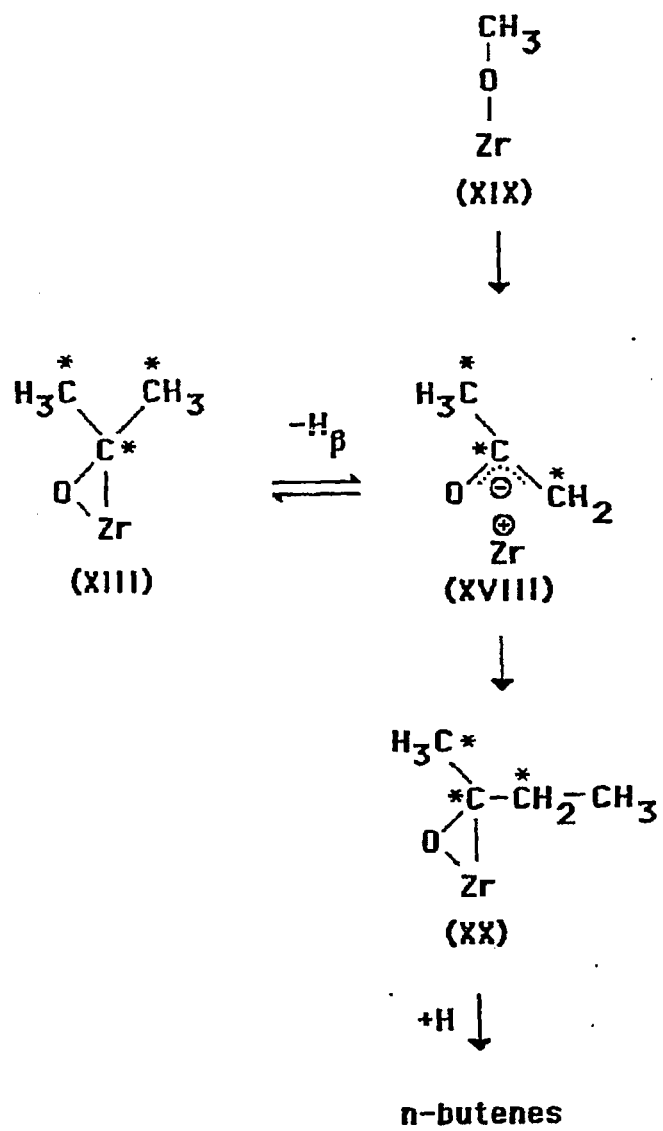


Figure 3. Proposed condensation reaction for bound acetone [7].

activation energies and partial pressure dependence, as the ZrO_2 was modified or as other metal oxides were examined.

We are currently examining the effects of acid and base modifiers on the absolute rates of CO insertion and condensation reactions. Carbon-13 labeled acetone will be added to the reaction mixture and the rate of incorporation into the iso- C_4 's and linear C_4 's will be established. This was done over unmodified ZrO_2 that was 90 percent monoclinic [7] as a means of establishing the technique. We are currently synthesizing a group of modified zirconias and zirconias with different ratios of phases to find systems that have selectivity that differs from the monoclinic ZrO_2 . Our primary thrust involves doping with alkali hydroxides to increase basicity and enhancing the acidic nature of the ZrO_2 with the addition of alumina, yttria or H_2SO_4 . The isosynthesis properties and the product distributions of these catalysts are being examined to identify systems that have significantly different linear to branched or C_4/C_5 ratios. (The labeling studies can only be done on a limited number of systems due the cost of the labeled acetone.)

Zirconia has both basic and acidic sites [9,10]. Pichler and Ziesecke examined the effect of acid and base modifiers on the isosynthesis products and found that ThO_2 modified with alumina and alkali was the most active [11]. The enolate, XVIII (Figure 3), will be stabilized over a more acidic surface and its formation via hydride abstraction should be enhanced by more basic surfaces. These effects should combine to enhance the rate of condensation. The role of acid and base in the propagation reaction is less clear. The valance structure resulting from insertion, XV (Figure 2), may be stabilized by basic sites, and if so, we expect that insertion may be enhanced. The role of acid and base sites in isosynthesis is central to establishing

why certain classes of metal oxides that have acid/base properties are efficient isosynthesis catalysts.

The other aspect of our research is focused on the materials properties of ZrO_2 and how defects are related to synthesis activity. Methanol synthesis is the primary activity probe. A previous study [5] had suggested that oxygen anion vacancies were the sites at which CO was converted into the methoxide. These sites would also be associated [7] with the formation of aldehyde, the chain initiating species. The research involves measuring the anion vacancy concentration over various preparations of zirconia and establishing if the activity for methanol synthesis and anion vacancy concentration are quantitatively related. If relationships are found, we will investigate generation of the vacancies and how the various components present during isosynthesis interact with the vacancies.

Vacancy concentration will be measured with SO_3 . Yamaguchi et al. [12] have established that SO_3 adsorbs at the anion vacancy sites of ZrO_2 and forms an SO_4 anion. The amount of SO_4 is being established with IR and TGA techniques. The anion has characteristic IR stretches that enable us to identify its presence but not the absolute amount present. We have recently rebuilt a TGA for use in our studies and have begun subjecting ZrO_2 to various pretreatment and various calcination conditions in the TGA to determine how these variables affect the amount of SO_3 that adsorbs. The corresponding methanol synthesis activity measurements have already been obtained.

Methanol activity has been determined over monoclinic ZrO_2 (1 to 5 percent tetragonal), monoclinic and tetragonal (5 to 20 percent tetragonal) and over cubic zirconia. The calcination temperature, percentage monoclinic and pretreatment in H_2 or O_2 affect the amount of methanol formed. We should

learn, during the current budget year, if anion vacancies, as measured by SO_3 adsorption, correlate with the methanol activity. We are examining a set of cubic zirconias that have a known amount of bulk anion vacancies as a check on our technique. The surface anion vacancy concentration should be related to the bulk concentration. We have found that on a per unit area basis the one cubic zirconia tested to date has the highest methanol synthesis activity.

FUTURE RESEARCH

The major features of the isosynthesis mechanisms have been identified, namely that propagation involves CO insertion and condensation reactions [7]. The details of these reactions were proposed by Mazanec [13] on the basis of analogies to organometallic chemistry. Information concerning the primary products, the termination reactions to the primary products, and how the synthesis variables of temperature and H_2 and CO pressure influence the reaction remain unknown over a heterogeneous surface. We will examine these issues by the use of steady state rate measurements at varying synthesis pressures, residence times. This rate data will be combined with the mechanistic picture we have proposed [7] to develop a detailed kinetic model. The kinetic model will be useful in probing how the catalyst composition affects the overall isosynthesis process. The model is a necessary component in developing our understanding of CO hydrogenation over metal oxides but cannot be expected to provide information on the elementary processes that are occurring. This information will come from the experiments such as the isotope labeling, which probe identifiable aspects of the reaction.

The use of carbon-13 labeled acetone to probe the relative rates of CO

insertion and condensation will be continued. The labeling work, combined with the kinetic model, should enable us to identify the catalyst features that favor branched product formation and are responsible for the high selectivity displayed by ZrO_2 during CO hydrogenation. This information will be used to begin an examination of other oxide systems that have the same C_1 surface chemistry as ZrO_2 . A previous study [3] had shown that ZnO , TiO_2 and ZrO_2 activated CO and formed a common set of intermediates. We hope to establish if ZrO_2 is unique in its ability to catalyze isosynthesis products or if previous surveys [11] were conducted under the wrong set of conditions. Since a common set of C_1 species are formed over these oxides it should be possible to determine if acetone will undergo CO insertion and condensation with methoxide over all of the oxides. We hope to determine whether the transformations that give rise to isosynthesis selectivity (Figures 2 and 3) are possible over other metal oxides and, if so, what controls the energetics and selectivity of these reactions.

The anion vacancy studies will continue. The alkali promoter studies discussed above are expected to lead to enhancement in the rate of condensation. The alkali will be added as the hydroxide. Alkali under certain conditions can act to alter the solid state properties of ZrO_2 . Proper thermal treatment and dopant levels are used to make a variety of stabilized and partially stabilized cubic zirconias. The alkali hydroxides may incorporate into the outer ZrO_2 surface and lead to higher anion vacancy concentrations, in addition to increasing the basicity. The SO_3 adsorption studies should permit us to assign changes in activity more accurately to specific chain branching reactions or to CO activation.

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