

## Isosynthesis Mechanisms Over Zirconium Dioxide

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### Introduction

The isosynthesis process refers to the selective conversion of synthesis gas into branched aliphatic hydrocarbons over metal oxide catalysts. Thoria and zirconia are the most active oxides that catalyze the formation of hydrocarbons containing four to eight carbon atoms, with isobutane as the major product [1]. The reaction requires high pressures, 30-600 atm, and high temperatures, 375 to 475 C.

The reactions occurring during isosynthesis have not been as thoroughly studied as have the reactions occurring during CO hydrogenation to methanol or during Fischer-Tropsch synthesis. The earliest research was conducted in the 1940's [1]. The effects of oxide composition and synthesis conditions are reported and mechanisms, based on these early studies, have been proposed [1,2,3]. These proposed mechanisms relied on the acid/base nature of the catalytically active oxides and involved acid-catalyzed reactions between methanol or dimethyl ether and olefins. More recently, two additional isosynthesis mechanisms have been proposed [4,5]. Both of the recent mechanisms propose CO insertion into an oxygenated hydrocarbon fragment to explain chain growth and involve aldol condensation as one of the termination reactions. The CO insertion and the aldol condensation reactions differ in that different oxygenated fragments and C<sub>1</sub> fragments are proposed to be involved.

The activation of CO on zirconia has been reported in a series of papers [6,7,8,9]. The activation is proposed to involve the initial formation of a surface formate and its subsequent reduction to a methoxide via an oxymethylene. The oxymethylene carbon is bonded to the Zr cations through two oxygen atoms [7]. This proposed structure was based on limited infrared data and other structures, such as those involving carbon bonded directly to a Zr cation, may be present.

### Experimental

The high pressure studies were conducted in a 70 mm section of 6.35 mm OD stainless steel tubing. All of the experiments were conducted at 35 atm and a total flow rate of 100 cc/min. The reactor effluent was analyzed on a gas chromatograph.

A fresh charge (2.0 grams) of zirconia was used for each experiment. The zirconia was pretreated at 425 C in flowing oxygen for 60 min followed by heating at 425 C in flowing hydrogen for 60 min. The treated zirconia was exposed to CO/H<sub>2</sub> at a constant ratio of 1/1 for the data presented in the tables.

Zirconia was prepared by adding concentrated ammonium hydroxide to a 20.3 wt%  $Zr(NO_3)_4$  solution (Nyacol). The resulting hydrous  $ZrO_2$  was washed with distilled water and dried in air at 120 C for 24 hr. The  $ZrO_2$  was subsequently calcined in air for 4 hr at 600 C. The  $ZrO_2$  had a BET area ranging from 30-45  $m^2/g$  and was monoclinic. The activity of the  $ZrO_2$  was a strong function of the degree of drying and the calcination conditions. A thorough drying was necessary to achieve high activity to methanol, dimethyl ether and hydrocarbons. (The causes for this are currently under investigation.)

### Results

A series of experiments was conducted over the zirconia at temperatures ranging from 250 to 425 C and at varying flow rates. Below 350 C methanol and dimethyl ether were the only products formed in significant quantities. Hydrocarbon production was observed above 350 C. The product distribution trends were similar to those reported over thoria [1].

Experiments were performed to test the mechanisms that have been proposed. These involved adding reactants into the  $CO/H_2$  feed gas that should, on the basis of the different mechanisms, adsorb, transform into a reactive intermediate, and become incorporated into the isosynthesis products. The effect of adding propylene, methanol, formaldehyde, acetone, n-propanol, propionaldehyde and 2-methyl-propionaldehyde has been measured. These were added at low concentrations (50-500 ppm) to minimize their effect on existing surface species and reactions.

Propylene was added at the level it was produced at and it passed through the reactor unreacted and had a negligible effect on the  $C_4$  products. This, and other olefin addition experiments, suggests that olefins are not incorporated into the isosynthesis products and it is unlikely that isosynthesis intermediates can be derived from hydrocarbon products. These results also provide evidence that the early acid-based mechanisms [1,2,3] are not correct.

In many cases, the oxygenated additives did not appear to incorporate, in appreciable amounts, into the next higher synthesis products, but rather underwent self-condensation or underwent reduction. The propionaldehyde and acetone additions have provided the most information. Table 1 presents the effect of adding 200 ppm of propionaldehyde to the feed. (Isosynthesis produced at most 4 ppm of propionaldehyde at the conditions reported here.) Table 2 presents the effect of adding 250 ppm of acetone to the feed. The acetone experiments were conducted over a batch of zirconia that had a lower activity; presumably this was caused by a variation in the preparation of the zirconia.

Methane, methanol and dimethyl ether decreased, while ethylene, propylene, propane, isobutene, and the  $C_4$  alcohols increased in concentration in the presence of added propionaldehyde. Propionaldehyde appeared to react with the methane/methanol precursor to form isobutene. Our atmospheric studies [6,7,8] have demonstrated that the

methane/methanol precursor is a methoxide. The amount of propionaldehyde fed can be accounted for in the increase in ethylene, C<sub>3</sub> hydrocarbons and oxygenates, isobutane and the C<sub>4</sub> alcohols.

The majority of the acetone was reduced to propane and propylene. There was a significant increase in the amount of isobutanol formed and an unexpected decrease in isobutene. The linear butenes were moderately affected. Methanol and dimethyl ether decreased substantially in the presence of acetone. Acetone was expected to form an aldehydic-like species by analogy to previous work with formaldehyde [6,7,8].

Isobutanol was seen to increase and isobutene was seen to decrease in the presence of acetone. Both were expected to increase. The significant drop in isobutene, in parallel with the methanol decrease, may be related to acetone interfering with methanol production. Aldol condensation appears to require the methanol precursor (see next section). The majority of the isobutene loss could be associated with the isobutene formed via aldol condensation.

### Discussion

The acetone addition experiments support the CO insertion scheme proposed by Mazanec [4]. This scheme is represented in Figure 1 for a bound aldehyde originating from acetone. This scheme involves CO insertion into a bound aldehyde, I, to form a cyclic acyl, II. The substituents of the cyclic acyl influence subsequent transformations, 1,2-shift of hydrogen (favored over alkyl [4]) through the second valence bond structure, III, or step-wise hydrogenation to the alcohol via the intermediate IV.

The other CO insertion scheme has been proposed by Vedage et al. [5] on the basis of extensive studies of alcohol synthesis over a variety of metal oxide systems. An alkoxide is proposed to undergo CO insertion to form an alkionate which is subsequently reduced to the alcohol. There is an important distinction between the two mechanisms. Secondary alcohols are not observed during isosynthesis; therefore, secondary alkoxides are not formed and the alkoxide-based CO insertion mechanism [5] can only lead to linear products.

Acetone addition led to an increase in isobutanol and a parallel loss of isobutene, which may be related to a suppression of aldol condensation (see below). Isopropanol was not detected, suggesting that acetone did not form the branched alkoxide required, in Vedage et al.'s scheme, to form the increased isobutanol. Additional studies in which n-propanol was added to the feed did not lead to a measurable change in any C<sub>4</sub> product providing additional evidence that alkoxides are unlikely intermediates in CO insertion reactions over zirconia.

Aldol condensation has been proposed as the termination reaction that can account for branching in the synthesis of alcohols [5] and that can account for the non-Flory distribution observed during isosynthesis [4]. The propionaldehyde addition experiments showed a

loss in methanol, methane and dimethyl ether, and an increase in isobutene. These observations suggest that the branching reaction involves the methanol/methane precursor, the methoxide [8,9]. Figure 2 presents the aldol condensation scheme that was suggested by Mazanec [4]. Propionaldehyde is proposed to adsorb as structure V and transform into the enolate anion, VI. The enolate reacts with methoxide to form the next higher aldehyde, that is subsequently reduced to the branched hydrocarbon or alcohol. The alternative scheme involves a reaction between the enolate anion, VI, and a formyl [5]. All the previous work over zirconia [6,7,8,9] is consistent with the conversion of CO via a formate rather than a formyl intermediate. This observation along with the effect propionaldehyde had on the methanol/methane yield supports the aldol condensation scheme represented in Figure 2.

#### Acknowledgements

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Table 1 Isosynthesis Products at 425 C and 35 atm  
over  $ZrO_2$  Made from  $Zr(NO_3)_4$

Feed Gas	$H_2/CO/He$	$H_2/CO/He$ with 200 ppm of $C_2H_5CHO$
$CH_4$	1312 <sup>(a)</sup>	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
$n-C_3H_7OH$	3.1	6.8
$n-C_4H_9OH$	12.3	16.9
$i-C_4H_9OH$	7.9	12.6
$i-C_4H_8/CH_3OH$	1.47	1.94

(a) ppm

Table 2 Isosynthesis Products at 425 C and 35 atm  
over  $ZrO_2$  Made from  $Zr(NO_3)_4$

Feed Gas	$H_2/CO/He$	$H_2/CO/He$ with 250 ppm of acetone
$CH_4$	1307 <sup>(a)</sup>	834
$C_2H_4$	155	128
$C_2H_6$	64.3	34.5
$C_3's$	93.1	338
$i-C_4H_{10}$	1.2	1.8
$i-C_4H_8$	72.3	37.5
$n-C_4H_{10}$	2.9	11.5
$1-C_4H_8$	20.5	23.2
$CH_3OH$	665	356
$(CH_3)_2O$	913	25.2
$(CH_3)_2CO$	0	0
$(CH_3)_2CHCHO$	3.9	6.4
$i-C_4H_9OH$	31.9	69.8
$n-C_4H_9OH$	13.3	5.4

(a) ppm

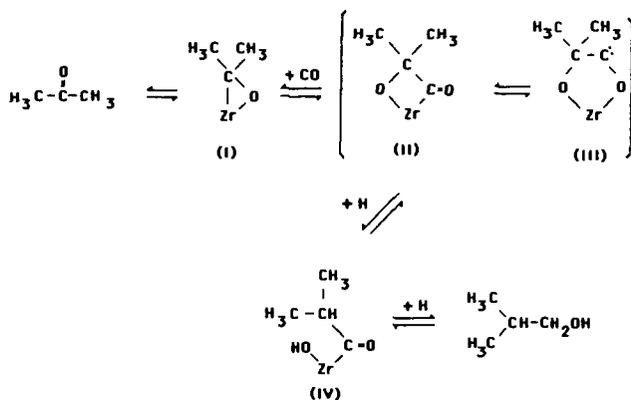


Figure 1. Representative reactions for CO insertion during isosynthesis  
( adapted from Reference 4 )

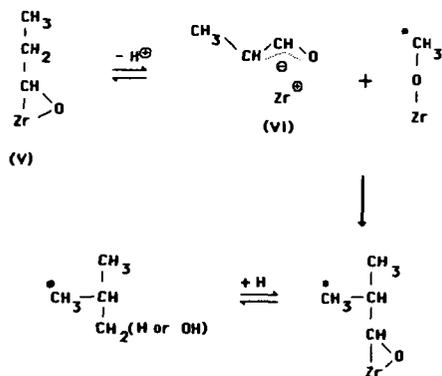


Figure 2. Representative reactions for aldol condensation  
involving alkoxide (adapted from Reference 4 )