

SYNGAS TO ISOBUTYLENE

by

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OBJECTIVE

The objective of this program is to develop an improved catalyst and process for the conversion of syngas to isobutylene. The research will identify and optimize the key catalyst and process characteristics that give improved performance for carbon monoxide (CO) conversion by a non-Fischer-Tropsch process.

INTRODUCTION

The need for development of alternate fuels in the United States is a national priority. This need may be characterized in terms of two basic problems: quantity and quality. First, existing energy resources need to be replaced as they are depleted. However, even if supplies of existing fuels were adequate to meet all future demands, the question of environmental acceptability of current automotive fuels would still need to be answered.

Gasoline reformulation has become a priority throughout the refining industry. Certain components of gasoline have been linked to increased exhaust emissions of CO, nitrogen oxide (NO_x), and photoreactive unburned hydrocarbons. Refiners have introduced new gasoline formulations that are designed to minimize the production of these harmful compounds. Eliminating aromatics, olefins, and butanes from gasoline to meet the new environmental regulations would significantly lower the octane of the gasoline pool if other high-octane blending components were not available to replace them. In most proposed new gasoline formulations, the

addition of oxygenates, such as methanol, ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), or gasoline-grade tertiary butyl alcohol (GTBA), is being considered to maintain an acceptable octane.

The production of the ethers (MTBE and ETBE) will ultimately be limited by the availability of isobutylene ($iC_4=$). Traditional commercial routes for producing $iC_4=$ will be unable to meet the large growth in demand anticipated for fuel ethers. The only potential route to $iC_4=$ that has the growth potential to meet the high volume of oxygenate demand that would be created by blending ethers into the gasoline pool at 1-2 wt-% oxygen is the isomerization and dehydrogenation of butanes. These processes are expensive, and they are dependent on the supply of butane feedstocks. More likely, the increased butane demand would be met by large-scale foreign plants that have access to huge reserves of natural gas and field butanes. Therefore, the probability exists that the major source of oxygenates would be from OPEC countries and that this country's balance of trade could deteriorate further.

To take advantage of its vast coal reserves, the United States needs to develop a process in which coal can be converted to oxygenated gasoline-blending components. The technology already exists for making methanol from coal-derived syngas. Numerous commercial processes are also available to make MTBE from methanol and $iC_4=$. A new technology that could be used to make $iC_4=$ from syngas would complement the syngas-to-methanol process and help ease the anticipated shortages of $iC_4=$. A combined methanol, $iC_4=$, and MTBE facility would allow the expensive coal gasification section to be shared between the methanol and $iC_4=$ facilities for reduced overall capital cost. The main goal of this research is to develop a catalyst and technology that is capable of producing $iC_4=$ directly from coal-derived syngas and using a lower (0.5 to 1.0) $H_2:CO$ ratio.

BACKGROUND

Over the last 50 years, a variety of catalysts have been identified for the conversion of syngas to C_4 compounds. These materials can be divided into two classes: isosynthesis catalysts, which yield butanes or butenes or both, and catalysts for higher alcohol synthesis, which give butanols. The former catalysts, modified to selectively give branched olefins, can be considered for the direct conversion of CO and H_2 to isobutylene. For the latter class of catalysts, a subsequent step to

dehydrate the butanol is required. This process is well established in the chemical industry. Therefore, by selectively yielding branched C₄ alcohols, syngas conversion catalysts provide an indirect route to isobutylene.

Direct Production of Isobutylene from Syngas

In the 1930's and 1940's, German workers conducted pioneering work on an alternative process for syngas conversion: the isosynthesis reaction [1,2,3]. In this process, CO and H₂ are selectively converted to branched hydrocarbons.

The German work on the isosynthesis reaction during World War II focused on the use of thoria-based catalysts at high-pressure conditions (30 to 300 atm). A survey of precipitated metal oxides identified thoria as the most active material for the production of liquid hydrocarbons at 450°C and 150 atm [2]. The C₄ and C₃+ yields are 6% and 13%; 88% of the C₄ fraction is branched. The product observed with the thoria-based catalysts is almost completely saturated; only small amounts of olefins, mainly isobutylene, and oxygenated products are reported. Table 1 gives the reported conversions and yields for unmodified ThO₂/Al₂O₃, ThO₂/Al₂O₃ + 0.2 wt-% K₂CO₃, and ThO₂/Al₂O₃ + 0.5 wt-% K₂CO₃. These levels of alkali addition increase the yield of iC₄ and CH₄ without affecting CO conversion. Higher levels of K₂CO₃ (>1%) substantially suppress the activity of the thoria catalyst. A 100-day durability test of the ThO₂/10% Al₂O₃ catalyst is described in the reviews of this German work.

The early German work on the isosynthesis reaction identified ZrO₂ as the second most active material for the formation of C₄+ hydrocarbons from syngas. In the last five years, additional reports have been published on the use of ZrO₂-based catalysts for syngas conversion to hydrocarbons. Shell Canada Ltd. has also been granted French and Canadian patents for alkaline earth, or Group IIb metal-promoted ZrO₂ for this application. These systems are of particular interest because they give high selectivity to isobutylene. In contrast, isobutane predominates with other isosynthesis catalysts.

Table 1
ThO₂ Isosynthesis Catalysts

Catalyst	20% Al ₂ O ₃ , ThO ₂	0.2% K ₂ CO ₃ , 20% Al ₂ O ₃ , ThO ₂	0.6% K ₂ CO ₃ , 20% Al ₂ O ₃ , ThO ₂
Temperature, °C	450	450	450
Pressure, atm	300	300	300
H ₂ :CO, molar	0.84	0.84	0.84
CO GHSV, cc/cc cat/hr	217	217	217
CO conversion %	73.2	72.2	78.4
Yield, % C:			
C ₁	3.8	4.1	5.7
C ₂	2.8	2.5	2.0
C ₃	2.6	—	—
nC ₄	2.6	2.9	2.9
iC ₄	17.5	18.5	23.7
C ₅ +	9.7	10.0	7.1
CH ₃ OH	0.4	0.1	—
CO ₂	33.8	34.0	37.0

Mayura, Onishi, and co-workers have examined the conversion of syngas over ZrO₂ as well as other metal oxides at low pressures (< 20 atm) [4,5]. Preliminary testing (Table 2) was conducted in a gas-circulating reactor using ZrO₂ prepared by precipitation of Zr(O)NO₃ with NH₄OH and calcination at 500°C. Other methods for the preparation of ZrO₂ have been evaluated but give inferior catalytic performance [6]. These results cannot be placed on the same yield basis as the other data in this section because the total amount of CO fed over the catalyst is not given. In addition, the use of a gas-circulating reactor in these experiments gives a much higher overall CO contact time over the ZrO₂ catalyst than that obtained in conventional fixed-bed flow reactors. A temperature of greater than 350°C was required to achieve complete conversion of the MeOH and Me₂O intermediates to hydrocarbons and CO₂. The highest isobutylene yield (130 μmol/g catalyst over 24 hours) was obtained at 400°C; 88% of the C₄ product is the desired isobutylene.

Table 2
ZrO₂ Isosynthesis Catalysts

Catalyst	ZrO ₂	ZrO ₂	ZrO ₂
Temperature, °C	350	400	450
Pressure atm	0.68	0.68	0.68
H ₂ :CO, molar	3	3	3
Yield, μmol C/1.5 g cat/25 hr:			
C ₁	1.6	12.4	54.0
C ₂	0.2	3.5	25.6
C ₃	5.3	8.8	17.5
C ₄	—	2.7	32.2
C ₅	6.0	12.7	8.2
C ₆	1.4	9.6	31.4
C ₇	128.0	211.8	120.3
C ₈ +	2.5	20.4	19.0

Higher temperature (450°C) gives a greater total hydrocarbon yield but less isobutylene because of increased formation of CH₄ and butanes. This group has also described, in a separate report, the evaluation of ZrO₂ in a conventional flow system [7]. Total hydrocarbon yield at these conditions was only 0.4%: of this yield, 77% was isobutylene, and 11% was other C₄ and C₅ compounds. The extremely low level of conversion in this test, compared with the ZrO₂ result of the early German work, suggests the need for high pressure to obtain economical yields of higher hydrocarbons.

The reaction of syngas over ZrO₂ at higher pressure has been examined by Ekerdt's group at the University of Texas [8]. Fixed-bed flow reactor tests at 35 atm are reported to give low CO conversion (<1%) and yields of total hydrocarbons (0.6%) and C₄ hydrocarbons (0.3%) [40]. Branched C₄ compounds, which are greater than 93% isobutylene, account for more than 70% of the C₄ products.

In contrast to the results obtained by the University of Texas group, substantially higher conversions of CO to hydrocarbons at comparable temperature and pressure but lower space velocities have been claimed by workers at Shell Canada [9]. Table 3 gives a summary of the patent

examples. This work reports low isobutylene selectivity in the hydrocarbon product (5 wt-%) over precipitated ZrO_2 , and a $C_4 + C_3$ yield of 3.9%. Yields to $iC_4=$ and total $C_4 + C_3$ are increased by the addition of Ca, Ba or Y to the ZrO_2 catalyst. These modifications also reduce the production of CH_4 ; however, the loss of carbon to nonuseable lights (CH_4, CO_2) is still substantial.

Table 3
Modified ZrO_2 Isosynthesis Catalysts

Catalyst	1% Ca/ ZrO_2	ZrO_2	1% Ba/ ZrO_2	1% Y/ ZrO_2
Temperature, °C	450	450	450	450
Pressure, atm	20	20	20	80
$H_2:CO$, molar	1.0	1.0	1.0	0.3
Yield, % C:*				
C_1	7.1	17.9	8.2	4.1
C_2	0.6	5.0	1.5	0.7
$C_3=$	0.8	0.6	1.4	0.3
$C_3=$	0.4	2.1	0.5	0.9
$C_3=$	0.4	0.5	0.8	0.2
$iC_4=$	1.6	0.8	1.4	0.9
$iC_4=$	2.8	1.7	4.0	3.7
$nC_4 + nC_4=$	0.7	0.7	2.0	0.9
$C_3+ + C_3+=$	2.6	0.7	1.7	4.3
* to hydrocarbons only				

Rare earth oxides (La_2O_3 and Dy_2O_3) have been found to catalyze the isosynthesis reaction at high pressures to give selective formation of isobutane in the hydrocarbon product [10]. The conditions used and yields are summarized in Table 4. The addition of palladium to these catalysts increases the hydrocarbon yield, but selectivity to isobutane is reduced because of increased CH_4 and linear C_4 's formed by secondary reactions.

Table 4
Rare Earth Oxides for Isosynthesis Reaction

Catalyst	La ₂ O ₃	Dy ₂ O ₃
Temperature, °C	475	475
Pressure, atm	400	400
H ₂ :CO, molar	1	1
CO GHSV, cc/cc cat/hr	1,000	1,000
CO conversion, %	23.9	26.4
Yield, % C:		
C ₁	1.6	1.7
C ₂	0.7	0.6
C ₃	1.0	0.8
C ₄	3.5	3.2
C ₅	0.4	0.6
C ₆ +	1.1	2.1
CO ₂	12.7	13.4
MeOH/Me ₂ O	2.9	4.0

Mayura and Onishi have reported the evaluation of several early transition metals (Y, Zr, Hf, Nb) and rare earth oxides (La, Ce, Th) for syngas conversion at low pressure in the gas-circulation reactor as previously described (Table 5) [11]. With the exception of Nb₂O₅, which affords a Schulz-Flory distribution, these oxides all give an excess of C₄'s in the hydrocarbon product. The best results were obtained with a ZrO₂ catalyst (70 mole % C₄'s in the hydrocarbon product). High selectivity to isobutylene (>85%) in the total C₄ product is obtained with CeO₂, ThO₂, ZrO₂, and HfO₂. The high olefin yield with ThO₂ contrasts with the early German work using this catalyst and indicates that variation in paraffin-olefin selectivity is possible with these systems. The most active catalysts for hydrocarbon production at the conditions of these tests also give the highest CO₂.

Table 5
Group IIIA, IVA and Rare Earth Oxides for Isosynthesis

Catalyst	Y ₂ O ₃	La ₂ O ₃	CeO ₂	ThO ₂	ZrO ₂	HfO ₂
Temperature, °C	400	400	400	400	400	400
Pressure, atm	0.66	0.66	0.66	0.66	0.66	0.66
H ₂ :CO, molar	3	3	3	3	3	3
Yield, μmol C/1.5 g cat/24 hr CO ₂	810	247	1050	648	350	247
MeOH + Me ₂ O	0.3	4.2	—	3.9	0.2	—
C ₁	35	2.4	70	56	12	8
C ₂	18	2.0	122	36	12	18
C ₃	30	1.8	63	22	15	20
C ₄	84	15.2	188	219	222	112
C ₅	65	8.5	140	52	17	11
C ₆	24	3.0	42	9	10	3

Workers at Amoco have reported that cadmium on an acid support, such as zeolite, amorphous silica-alumina, or clay, yields isoparaffins, particularly isobutane and isopentane, from syngas [12,13]. The acidic support is used to prevent the volatilization of the cadmium at the reaction conditions but may also have a role in the formation of paraffins by promoting acid-catalyzed reactions of MeOH intermediate. Table 6 summarizes results obtained with 5% CdO on 30% rare-earth-exchanged Y-type zeolite and alumina at 34 and 68 atm and 360°C; lower temperature or pressure reduces the amounts of hydrocarbons and CO₂ formed. The isobutane yields given in the Amoco report represent the highest branched C₄ production obtained in previous work, with the exception of the early German work with K-modified ThO₂ catalysts. However, the hydrogenation activity of this catalyst must be reduced for it to have potential for isobutylene production.

Table 6
Cd Catalysts for Isosynthesis

Catalyst	5% CdO/30% REY/Al ₂ O ₃	5% CdO/30% REY/Al ₂ O ₃
Temperature, °C	360	360
Pressure, atm	34	68
H ₂ :CO, molar	2	2
CO CHSV, cc/g cat/hr	490	470
CO conversion (%)	19.6	37.0
Yield, % C:		
C ₁	0.3	0.5
C ₂	0.1	0.4
C ₂ =	0.3	0.4
C ₃	0.8	2.0
C ₃ =	0.3	0.2
iC ₄	7.5	13.4
nC ₄	0.5	1.3
iC ₅	4.1	7.1
nC ₅	0.3	0.4
iC ₆	2.6	3.1
nC ₆	0.1	—
C ₆ +	0.8	2.0
CO ₂	1.9	6.2

Proposed Reaction Mechanisms

The early German research on the isosynthesis reaction using ThO₂-based catalysts included only limited mechanistic work. Higher branched alcohols and other oxygenates were found to be the major products formed on the conversion of syngas over ThO₂ catalysts at temperatures below those required for isosynthesis [2,3]. This result suggests that alcohols are formed as the primary products and are subsequently dehydrated to olefins and hydrogenated to the observed paraffins. In contrast, ZrO₂ gives the unsaturated product, apparently because of its inability to catalyze olefin hydrogenation.

Further characterization of the reaction pathway of the ZrO_2 system has been done by the University of Texas group [8]. This work implicates at least two chain growth steps involving oxygenated intermediates. Methanol, which has been shown by IR studies to convert to methoxide and formate species on the catalyst surface [14,15], is found to incorporate only into the branched products. This result suggests that linear products arise from the direct insertion of CO rather than the involvement of a reduced C_1 intermediate such as formyl. Acetone was also found to be more efficiently incorporated into the branched C_4 products than isopropanol. Thus, CO insertion into an aldehyde or ketone is much more facile than into a bound alkoxide [8]. The CO insertion step occurs four times faster than condensation over ZrO_2 .

The apparent intermediacy of alcohols in isosynthesis suggests that the mechanisms of this process and the higher alcohol synthesis over modified methanol synthesis catalysts are closely related. In addition, both systems give selective formation of branched C_4 products. In the 1980's two mechanisms have been proposed by Mazanec [16] and Klier, et al. [17,18] for the conversion of syngas to C_2+ products over metal oxide catalysts. Manzanec's proposal is based on analogies from zirconium organometallic chemistry. The primary C-C bond-forming step is proposed to involve the insertion of CO into a metal-bound aldehyde intermediate. Subsequent hydrogenation and hydrogen shifts can give both linear and branched products. Condensation of metal bound η^3 -enolate and methoxide ligands is proposed as a second route to branched products to explain deviations from Schulz-Flory distribution. The results of the mechanistic experiments on the ZrO_2 system described above are consistent with this mechanism. An alternative mechanism presented by the Lehigh group is based on studies of the Cs/Cu/ZnO catalyst for higher alcohol synthesis.

Indirect Production of Isobutylene from Syngas via Higher Alcohol Synthesis

Many of the catalysts described in the literature for this application give high selectivity to branched alcohols, in particular, isobutanol, which can be readily dehydrated to the corresponding olefins. A disadvantage of this route is that most higher alcohol synthesis processes produce more methanol than higher alcohols. Methanol in excess of that needed for ether formation must be recycled for further conversion to higher alcohols.

The isosynthesis reaction over metal oxides and higher alcohol synthesis over alkali-modified Cu-ZnO catalysts give comparable selectivity to branched compounds in the C₄+ products. It has been suggested that the reaction mechanisms over these catalysts are similar and that the selection of the primary product (alcohol, olefin, or paraffin) depends on the ability of the catalyst to promote the final steps of alcohol dehydration and olefin hydrogenation at the reaction conditions. However higher alcohol synthesis over MoS₂-based catalysts, gives a different product distribution consisting primarily of linear compounds. Thus, another mechanism, similar to that of the Fischer-Tropsch reaction, has been proposed for this system.

The synthesis of higher alcohols from syngas using alkali-modified methanol synthesis catalysts has been known since the 1920's [19]. In general, the function of the alkali promoters (K, Rb, Cs) is independent of the type of methanol synthesis catalyst used. Substantial work prior to 1957 was done using alkali-modified ZnO-Cr₂O₃. Isobutanol is the primary C₂+ product obtained with these catalysts, and the highest yields are reported for Rb/ZnO-Cr₂O₃ and Cs/ZnO-Cr₂O₃ [19]. Other methanol synthesis catalysts that appear to be similar to ZnO-Cr₂O₃, by giving high isobutanol in the C₂+ product when modified with alkali include ZnO alone [20], Cr₂O₃-MnO [21], ZnO-MnO-Cr₂O₃ [22], Cu-ZnO-Cr₂O₃ [23], V₂O₅-CuO [24], and CdO-Cr₂O₃ [25]. In contrast with alkali-modified methanol synthesis catalysts, several Co-containing catalysts, such as CuO-MnO-CoS [26] and CoO-ZnO [27], give ethanol as the primary higher alcohol product.

In the early 1960's, high-activity Cu-ZnO-based catalysts were developed. These catalysts allow the use of lower temperatures and pressures in the methanol synthesis reactor. Modification of these materials with alkali also affords higher alcohols. Smith and Anderson found that the addition of K₂CO₃ to a commercial Cu-ZnO-Al₂O₃ catalyst increases higher alcohol selectivity and gives an isobutanol-rich higher alcohol distribution similar to that obtained with other modified methanol catalysts [28]. This work also demonstrated that decreasing the H₂:CO feed ratio from 2.0 to 0.5 and operating at a high H₂ + CO conversion level increases selectivity to butanol. Klier and co-workers at Lehigh University have reported that Cs at 0.5 to 1.0 wt-% is the most effective modifying alkali metal for Cu-ZnO [17,29]. Yields obtained with unmodified Cu-ZnO and 0.6 wt-% Cs/Cu-ZnO are given in Table 7 [18].

Table 7
Cs Modified Cu-ZnO for Higher Alcohol Synthesis

Catalyst	Cu-ZnO	0.34 wt-% Cs/Cu-ZnO
Temperature, °C	310	310
Pressure, atm	75	75
H ₂ :CO, molar	0.45	0.45
CO GHSV, cc/g cat/hr	2250	2250
CO Conversion, %	21.3	26.2
Yield, % C:		
CO ₂	8.3	9.1
C ₁	0.2	0.5
C ₂	0.8	0.3
C ₃	0.1	0.07
MeOH	6.4	4.9
EtOH	1.0	0.7
1-PrOH	0.5	1.9
1-BuOH	0.2	0.4
2-BuOH	0.04	0.1
<i>i</i> -BuOH	1.1	2.6
1-PeOH	0.05	0.3
2-PeOH	0.05	0.2
2-Me-1-BuOH	0.5	0.9
3-Me-2-BuOH	0.1	0.1
C ₆ Alcohols	0.5	1.3
C ₃ -C ₄ Aldehydes	0.04	0.2
C ₄ -C ₆ Ketones	0.2	0.6
Methyl Esters	1.1	2.0
Propyl Esters	0.1	0.07

A new process for the production of mixed alcohols using a catalyst consisting of potassium-promoted molybdenum sulfide and cobalt molybdenum sulfide was announced by Dow in 1984 [30]. This process can be operated to give either a mixture of alcohols containing up to 50% methanol or, by recycling the methanol for homologation, an ethanol-rich blend of C₂-C₆ alcohols. Table 8 gives typical single-pass results [31]. Alkali- or alkaline earth-modified molybdenum sulfide catalysts have also been claimed for the conversion of C_n olefins to C_{n+1} alcohols with syngas [32].

Table 8
MoS₂ Catalysts for Higher Alcohol Synthesis

Catalyst	MoS ₂	Co/Mo Sulfide	Co/Mo Sulfide
Temperature, °C	265	305	295
Pressure, atm	102	102	102
H ₂ :CO, molar	1.04	0.98	0.98
CO GHSV, cc/cc cat/hr	1200	1300	1050
CO Conversion, %	33.2	39.0	29.2
Yield, % C:			
C ₁	4.6	3.3	2.3
C ₂ +	1.0	1.5	0.6
CO ₂	10.4	13.1	9.1
MeOH	7.3	4.2	4.6
EtOH	7.2	10.3	8.2
PrOH	1.9	3.8	2.5
BuOH	0.4	1.1	0.7
PeOH	0.1	0.1	0.3
Others (C _n)	0.4	1.6	0.9

The alcohol products produced using this class of catalysts are predominantly linear, indicating that the chain growth mechanism is similar to the Fischer-Tropsch reaction. Thus, dehydration yields the straight-chain olefins, such as 1-butene and 2-butene. The secondary ethers that are prepared by etherification of these compounds with alcohols are of little use for fuel blending to increase octane. Therefore, any synthetic route for the production of ethers using this type of alcohol synthesis catalyst must include either a skeletal isomerization step or a process for the homologation of a linear C_n alcohol or olefin to C_{n+1} branched product.

Proposed Reaction Mechanisms

The formation of higher alcohols over alkali-modified methanol synthesis catalysts, such as CuO-ZnO, has been shown to occur by the condensation of lower alcohols. Smith and Anderson have proposed a growth scheme for the synthesis of higher alcohols from CO and H₂ involving

distribution parameters for the addition of one and two carbon fragments to the α and β positions of adsorbed, oxygenated intermediates [33].

The Klier group at Lehigh has conducted a more extensive investigation of the mechanistic steps of higher alcohol synthesis over Cs-modified Cu-ZnO catalysts [17,34,18]. They propose the formation of a metal-bound formyl by insertion of CO into a metal hydride bond. Linear products are formed by nucleophilic attack of the metal-bound formyl on the α -carbon of a C_n alcohol or aldehyde to displace the oxygen (after hydrogenation in the case of an aldehyde) [18]. This results in a linear C_{n+1} aldehyde, which is hydrogenated to the alcohol. Branched products are proposed to arise from aldol coupling with oxygen retention reversal involving the condensation of a metal-coordinated C_n -enolate species with methanol or formaldehyde. This coupling gives a β -ketoalkoxide intermediate which rearranges via dehydration and hydrogenation to the C_{n+1} branched alcohol with retention of the oxygen of the C_1 starting fragment.

In contrast to the mechanisms just discussed for isosynthesis and alkali-modified methanol catalysts, the formation of linear alcohols over MoS_2 -based catalysts is believed to occur by a mechanism similar to that of the Fischer-Tropsch reaction. Chain growth is proposed to occur over these catalysts by the insertion of CO into a metal alkyl intermediate to give a metal acyl species followed by hydrogenation [35]. Labelling experiments involving the addition of $^{13}CH_3OH$ to unlabelled syngas feed over alkali-modified MoS_2 have shown that only the terminal carbons of the higher alcohol products are ^{13}C -enriched. Methanol and total alcohol yields are very dependent on the alkali content of the catalyst, which has a maximum at about 20 wt-% Cs [35]. This suggests that this catalyst system is bifunctional and that the alkali component is responsible for the associative activation of CO while MoS_2 dissociatively activates H_2 . The addition of cobalt promotes the formation of ethanol over methanol, most likely by providing a second, more active catalytic site for the CO insertion step.

Dehydration of Butanols to Isobutylene

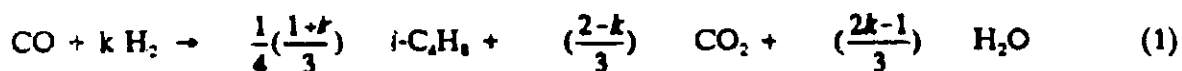
Technology for the dehydration of branched C_4 alcohols is well established in the chemical industry [36]. *t*-Butanol dehydration is typically done at about 200°C and 10 atm using a TiO_2 -supported catalyst [37]. The process operates at 100% conversion and 93 to 95% selectivity to isobutylene.

Equilibrium Limitations on Conversion

The conversion of syngas to C₄ alcohols and hydrocarbons is affected by equilibrium limitations similar to those encountered in methanol synthesis. Because of the exothermicity of the reaction, isobutylene formation is favored by low temperature. The CO conversion falls off rapidly at temperatures above 450°C. Total pressure greater than 20 atmospheres is also required to obtain more than 90% CO conversion. The use of higher pressures (up to 100 atm) does not afford any substantial thermodynamic advantage, although it may have beneficial kinetic effects.

The conversion of syngas to hydrocarbons or C₄ + alcohols requires the coproduction of either CO₂ or H₂O to account for the released oxygen. Water is the most desirable coproduct because it prevents the diversion of carbon from the desired product to CO₂. Because the catalysts used for isosynthesis and higher alcohol synthesis are active for the water gas shift reaction, the H₂O:CO₂ product ratio is determined by this equilibrium.

The stoichiometry for the maximum production of isobutylene from syngas as a function of the H₂:CO feed ratio is given in Equation 1.



Where: k = H₂:CO molar feed ratio

Thus, a H₂:CO feed ratio of at least 2:1 is required to achieve 100% theoretical carbon-based yield to hydrocarbon. At lower H₂:CO feed ratios, CO₂ must be formed, or CO conversion cannot be complete.

TECHNICAL APPROACH

The review of the previous work on catalyst systems for syngas conversion to branched C₄ products indicates that no catalyst exists for the selective production of either isobutylene or branched C₄ alcohols in greater than 5% yield from CO and H₂. Therefore, the primary emphasis of the

research program is the development of new catalysts and processes with improved activity and selectivity to the desired products. To achieve this end, desirable catalyst characteristics will be identified, and methods will be developed for the preparation of materials with the desired properties. In addition, process modifications and multistage process concepts will be explored.

RESEARCH RESULTS

A stainless steel reactor system was constructed (Figure 1). The system consists of:

- A gas feed section for the 1:1 H₂:CO or nitrogen feeds with flow rates set by a metering valve with a controlled pressure drop
- A liquid-feed section with flow rates set by a metering valve and a controlled pressure drop
- The reactor, rated for 2,250 psig at 550°C
- An on-line GC system for analysis of oxygen-containing products and heavier (C₄+) hydrocarbons
- A liquid trap for collection of the heavier product for mass balance and more detailed analysis
- A gas sample tube for collection of the gaseous products for analysis by off-line GC
- A gas-flow measuring system for determination of the effluent gas volume, which, combined with the gas analysis, is used for mass balance.

The first catalyst, IS-1, was prepared by adding ammonium hydroxide to a solution of zirconyl chloride and precipitating ZrO₂. The precipitate was filtered, washed with distilled water to remove residual chloride, and dried at 150°C. The dried catalyst was calcined at 500°C for 2 hours in flowing air. The calcined catalyst had a surface area of 63 m²/g.

The catalyst was placed in the reactor and activated to 450°C in flowing nitrogen. The catalyst was reduced at one atmosphere and 450°C in flowing 1:1 H₂:CO for four hours. A series of tests at various temperatures, pressures, and space velocities was completed. For each data point, conditions were maintained for at least two hours, and a one-hour sample was taken. The results are presented in Tables 9-11.

Table 9 compares results at constant temperature and space velocity as a function of pressure. Conversion of CO and H₂ both increase with pressure. Total C₄ selectivity increases with pressure but shifts toward increasing paraffin content. Table 10 compares results at constant pressure and space velocity as a function of temperature. Conversion of CO and H₂ increases with temperature. Selectivity to hydrocarbons increases, as does the paraffin-to-olefin ratio, with increasing temperature. Table 11 compares results at constant temperature and pressure as a function of space velocity. As expected, CO and H₂ conversion decrease with increasing space velocity. Carbon dioxide selectivity is essentially constant, and the paraffin-to-olefin ratio decreases with increasing space velocity. This data provides a baseline for future catalyst comparisons.

Table 9
Test Results of ZrO₂ Isosynthesis Catalyst

Period	2	3	4
Temperature, °C	450	450	450
Pressure, psig	300	600	1,200
H ₂ :CO, molar	1.0	1.0	1.0
CO GHSV, cc/cc cat/hr	960	970	960
CO conversion	6.3	13.6	20.9
Selectivity, % C:			
CO ₂	67.7	53.6	54.5
C ₁	19.4	17.4	19.1
C ₂ - C ₃	12.9	10.1	10.9
iC ₄	0	5.8	7.3
iC ₄ =	0	5.8	3.6
nC ₄ + nC ₄ =	0	0	0
C ₃ + + C ₃ +	0	7.2	4.5

Table 10
Test Results of ZrO₂ Isosynthesis Catalyst

Period	6	4	5
Temperature, °C	353	450	500
Pressure, psig	1,200	1,200	1,200
H ₂ :CO, molar	1.0	1.0	1.0
CO GHSV, cc/cc cat/hr	960	960	960
CO conversion	1.7	20.9	42.3
Selectivity, % C:			
CO ₂	87.5	54.5	45.3
C ₁	12.5	19.1	21.3
C ₂ - C ₃	0	10.9	17.9
iC ₄	0	7.3	10.5
iC ₄ =	0	3.6	0
nC ₄ + nC ₄ =	0	0	3.0
C ₅ + + C ₅ +	0	4.5	1.9

Table 11
Test Results of ZrO₂ Isosynthesis Catalyst

Period	8	4	7
Temperature, °C	450	450	450
Pressure, psig	1,200	1,200	1,200
H ₂ :CO, molar	1.0	1.0	1.0
CO GHSV, cc/cc cat/hr	540	960	2,100
CO conversion	36.8	20.9	16.7
Selectivity, % C:			
CO ₂	48.8	54.5	49.4
C ₁	17.5	19.1	15.7
C ₂ - C ₃	10.1	10.9	11.1
iC ₄	11.1	7.3	9.0
iC ₄ =	3.7	3.6	9.0
nC ₄ + nC ₄ =	1.8	0	0
C ₅ + + C ₅ +	6.9	4.5	5.6

FUTURE WORK

Catalyst Formulation

This section discusses work in the first part of a three-year contract. The preliminary evaluation of catalysts will consist of two phases. In the first phase of catalyst evaluation, materials that have been previously reported for the selective production of branched C_4 products from syngas will be reproduced and tested. The testing will provide a base of catalyst performance data that can be used for the direct comparison of different catalyst systems.

In the second phase of catalyst testing, new formulations will be evaluated to identify approaches for the development of a catalyst with performance exceeding that of previously described materials. Specific performance factors to be emphasized are catalyst activity and selectivity to C_4 -branched products rather than C_1 - C_3 lights and saturated by-products. The primary goal will be to identify relationships between catalyst properties and performance for syngas conversion. Based on this understanding, further catalyst improvements can be developed.

Many of the previous reports of catalysts for the conversion of syngas to branched C_4 + products indicate that C_2 compounds, methane or methanol, are primary by-products. This result suggests that the initial C-C bond-forming step to form a C_2 intermediate from a C_1 species is a slow step in the overall process. Thus, a multistage process using C_2 or C_3 intermediates formed in a first stage as feed to an isosynthesis second stage may be much more efficient than a single-stage system.

The use of new methods for the preparation of metal oxide catalysts with improved properties, such as regulation of crystallite size, increased uniformity throughout the metal oxide particle, and increased surface area, is another approach that will be investigated. Variation of precipitation methods for the control of the metal oxide structure, the use of sol-gel technology for the preparation of metal oxide materials, and supported metal oxide catalysts will be examined to achieve these goals.

Elucidation of Reaction Mechanism

An understanding of the reaction pathways occurring over the catalyst is important for the development of improved catalysts. Therefore, experiments will be carried out to probe the mechanism of syngas conversion over the best catalysts found in the first phase of catalyst screening. The emphasis of these studies will be to obtain practical mechanistic data sufficient to guide the development of further catalyst improvements. Experiments that can be used for the elucidation of specific aspects of the reaction pathway include testing at high space velocity, spiking experiments, and ^{13}C labeling.

Process Concepts

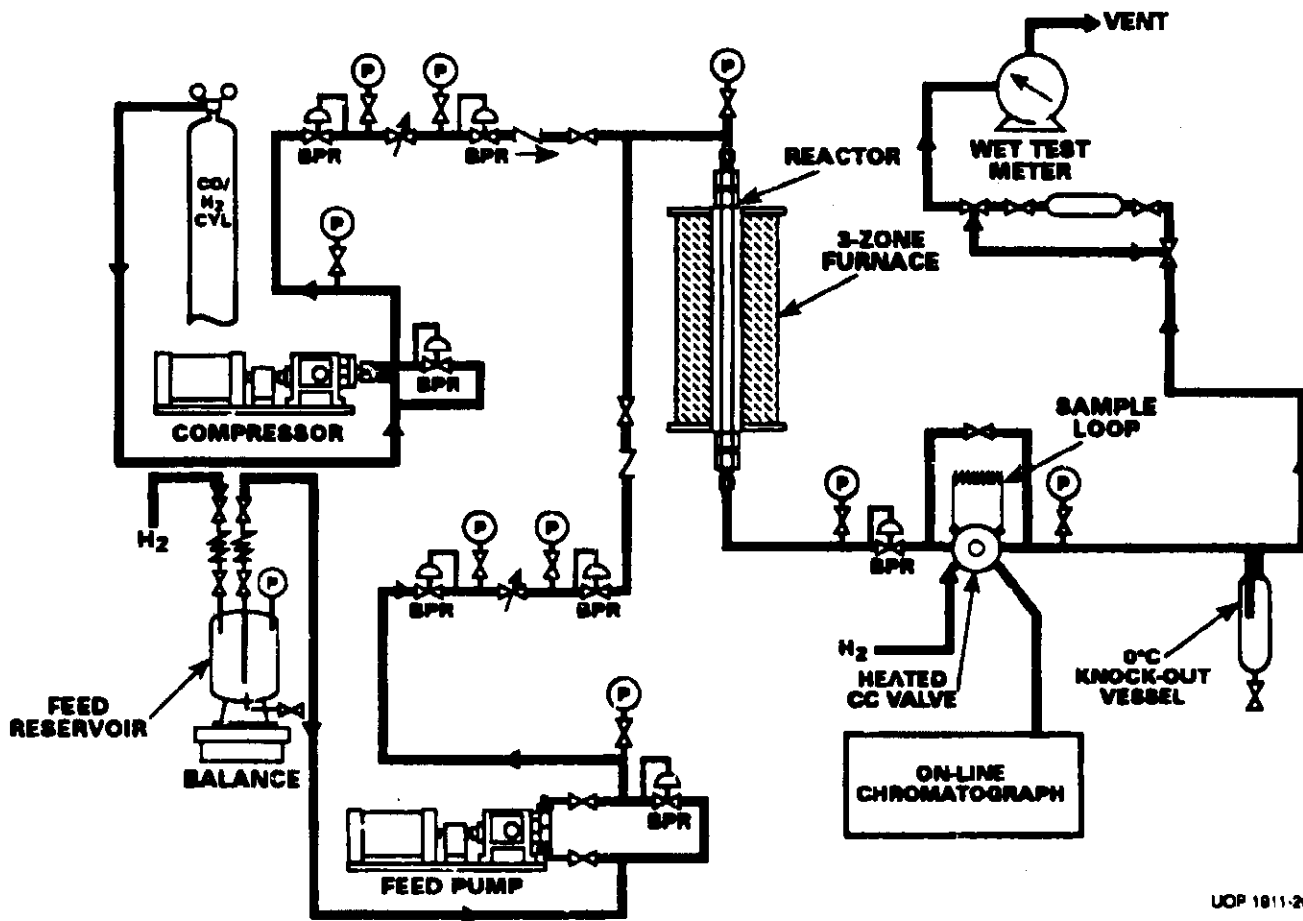
The final goal is to identify potential process configurations that result in either improved activity or selectivity to the desired branched C_4 olefin or alcohol products. Approaches that will be evaluated include recycle of C_1 - C_3 unsaturated intermediates, such as alcohols, aldehydes, and olefins (C_2 - C_3) and multistage processes. Examples of multistage process concepts include the conversion of C_1 - C_3 intermediates formed over the syngas conversion catalyst to C_4 -branched compounds and the initial conversion of syngas to methanol and higher linear alcohols followed by a separate aldol condensation step to give the desired branched products. One such process would use a first-stage catalyst to selectively produce linear higher alcohols from syngas, such as the recently discovered MoS_2 -based catalysts that operate by a Fischer-Tropsch type mechanism. A portion of the methanol and normal propanol that are produced over this first stage catalyst is then passed over an dehydrogenation-aldol coupling catalyst in the second stage to produce branched C_4 products.

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FIGURE 1
CATALYST EVALUATION PLANT DIAGRAM



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