

SYNTHESIS OF OXYGENATES FROM H₂/CO SYNTHESIS GAS AND USE AS FUEL ADDITIVES

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ABSTRACT

Alternative processes for synthesizing fuel-grade oxygenates are centered on conversion of synthesis gas into C₁-C₃ alcohols and ethers. Over Cs/Cu/ZnO-based catalysts, mixtures of methanol/ isobutanol are predominantly formed. It has been found that these alcohols can be directly coupled over certain strong acid organic-based catalysts to form unsymmetric C₄ ethers, mainly the kinetically favored methyl isobutyl ether (MIBE) with some of the thermodynamically favored methyl tertiarybutyl ether (MTBE), the symmetric ethers of dimethylether (DME) and diisobutylether (DIBE), or selectively dehydrated to form isobutene over sulfated zirconia. Based on these reactions, a 2-stage, dual catalyst configuration can be utilized to give MTBE as the dominant ether product. The octane numbers and cetane ratings of the oxygenates have been determined and are compared, e.g. adding 10 vol% MIBE and MTBE to 82.3 MON gasoline altered the MON of the gasoline by -1.5 and +1.4 units, respectively, and MIBE has a high cetane number of 53, compared to 42 for typical U.S. diesel fuel.

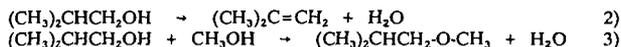
INTRODUCTION

Beginning in the 1970s, environmental concerns led to a phasing out of lead in gasoline, and recent legislative requirements are inducing the lowering of aromatics and light (high vapor pressure) hydrocarbons in reformulated gasoline. To maintain the required octane level of gasoline and to provide environmental benefits, oxygenate additions, either as alcohols or ethers, to gasoline have been steadily increasing. At the present time, the preferred oxygenate is methyl tertiarybutyl ether (MTBE) because it compensates for the loss in octane number caused by a reduction in aromatics, reduces the vapor pressure of the gasoline fuel, and provides some reduction in vehicle tailpipe hydrocarbon and carbon monoxide emissions [1]. Currently, MTBE is manufactured from methanol and isobutene *via* a liquid phase synthesis over acid resin catalysts, as represented by Equation 1, where isobutene is usually obtained as a side product from petroleum refinery FCC units [2-4]. Although older FCC units can produce 8 wt% C₄ products in their output [5], the typical FCC refinery product slate now contains 1.4 wt% C₄ compounds [6], and improved processes utilizing catalytic additives such as improved ZSM-5 tend to decrease the yield of C₃ and C₄ olefins in the light ends further still [7]. Thermal cracking of the isobutane in the light ends can also be carried out to obtain isobutene [6]. Although cracking processes are being modified to yield more C₄ as a by-product, the availability of refinery supplied isobutene is limited.



Alternative feedstocks and processes not directly dependent on isobutene for the synthesis of oxygenates are highly desirable, and new catalysts and catalytic processes are being investigated and developed. One of the alternative processes that have been developed for the synthesis of pure isobutene is the endothermic dehydration of tertiary butanol [8]. Another possible source of isobutene for ether synthesis is dehydration of isobutanol, represented by Equation 2, that is produced from synthesis gas. An overall scheme of using coal as the initial resource involves gasification of the coal to synthesis gas, purification (and water gas shifting if necessary) of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers from the alcohols. Both the

alcohols and ethers can be used as fuels and fuel additives as desired. Methanol and isobutanol are the predominant products formed from H_2/CO synthesis gas over alkali-promoted Cu/ZnO -based catalysts [9-14], as well as over non-copper-containing high temperature alkali-promoted alcohol synthesis catalysts [15,16]. Since the two alcohols are produced together, direct coupling of these two alcohols to produce fuel-grade ethers is also of interest. It has been shown [17,18] that over acid resin catalysts, the dominant reaction is direct coupling that results in the formation of methyl isobutyl ether (MIBE), Equation 3. However, if a selective catalyst were found for converting isobutanol to isobutene (even as a transient intermediate) with subsequent reaction with methanol (Reaction 2 followed by Reaction 1), a desirable route to high octane MTBE from natural gas or coal-derived synthesis gas would be provided [19]. Such a process would alleviate isobutene dependence on petroleum feedstocks.



EXPERIMENTAL

A variety of organic resin catalysts and inorganic oxide and zeolite catalysts have been probed for alcohol conversion reactions [20,21], and the catalysts investigated in the current study consisted of Amberlyst-15 (used as received) and sulfated zirconia. The sulfate-modified zirconia (SO_4^{2-}/ZrO_2) was prepared as described by Hino and Arata [22]. Zirconium chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was added to aqueous ammonia to precipitate high surface area $Zr(OH)_4$, that was washed and then dried at $100^\circ C$ overnight. The dried $Zr(OH)_4$, e.g. weighing ≈ 10 g, was placed on a folded filter paper, and 150 ml of 1 N H_2SO_4 was poured through it. The wet powder was dried at $110^\circ C$ overnight and then calcined in air at $620^\circ C$ for 3 hr. The BET surface area of this catalyst was found to be 60 m^2/g and the sulfur content was 0.84% by weight.

The catalysts were tested for ether synthesis from binary methanol/isobutanol (2-methyl-1-propanol) reactant mixtures in the vapor phase in a downflow stainless steel bench-scale reactor system that is automated so that testing can be carried out under continuous operation at designed experimental conditions. A schematic of the reaction system was shown previously [19]. Typically, N_2/He gas was utilized as the carrier/inlet gas, and the alcohol mixture was added at the top of the reactor via a high pressure Gilson pump or an ISCO piston pump provided by Air Products and Chemicals, Inc. The conversion and product composition was monitored by *continual sampling*, e.g. 0.5 hr, of the exit stream by GC analysis using in-line, heated, automated Valco sampling valves and by collection of the liquid product for analyses by GC, NMR, and GC/MS.

The dedicated Hewlett-Packard Model 5890 Series II gas chromatograph (GC) with a capillary column (25 m x 0.32 mm ID wall coated open tube (WCOT) with a chemically bound 5.0 μm thick methyl silicon coating) is interfaced and controlled by a PC data station using chromatographic software (Chrom Perfect) from Justice Innovations, Inc. At the same time, the GC is interfaced with a Hewlett-Packard Model 3396 Series II recorder/integrator, which can also produce a hardcopy of each chromatogram and listing of the associated integrated peak areas.

All of the catalytic tests reported here were carried out at 1 atm. According to our standard procedure, the catalysts were diluted with 0.5 or 3 mm Pyrex beads to a total volume of 20 ml. The catalyst bed was centered in the stainless steel reactor between two glasswool plugs. The remainder of the reactor volume was filled with 3 mm Pyrex beads that served to preheat and mix the entering gas, as well as minimizing dead volume in the reactor. The charged reactor was brought to the reaction temperature in a flow of approximately 80% He and 20% N_2 . When the temperature was stabilized, the equimolar alcohol mixture was pumped into the reactor at the preset flow. The reaction was carried out at each temperature for at least 3-6 hr. Steady state conversions of methanol and isobutanol were usually obtained within the first 1-2 hr time-on-stream.

RESULTS AND DISCUSSION

Direct Coupling or Dehydration of Alcohols Over Amberlyst-15 and $\text{SO}_4^{2-}/\text{ZrO}_2$

Thermodynamic calculations of the direct coupling of methanol and isobutanol indicate that low temperatures, i.e. 50-90°C, are necessary to achieve favorable selectivity to desired products, especially MTBE and MIBE [18,19]. The upper temperature of 90°C was chosen for this study in order to maximize conversion. Low pressure, i.e. 1 atm, is utilized in these reactions in light of the findings of Nunan et al. [17,18] that indicated lower pressures favored greater isobutene formation, the precursor of MTBE. The alcohol partial pressure was chosen such that no condensation would occur within the reaction system, and this was determined empirically under reaction conditions. A summary of the experimental conditions used with the Amberlyst-15 catalyst is given below:

Catalyst weight	5.00 g (dry)	MeOH flow rate	1.72 mol/kg cat/hr
Reaction temperature	90°C	i-BuOH flow rate	1.72 mol/kg cat/hr
Total Pressure	1 atm	He + N ₂ flow rate	16 mol/kg cat/hr.

The space time yields (STY) of the products are given in Table 1. It is seen that the molar yields of DME, butenes, and MIBE were comparable, while only 0.5% of each reactant was converted to MTBE. The entry "Butenes" includes iso-, *trans*-2-, and *cis*-2-butene with isobutene predominating (greater than 85% of the butene content).

The *sulfate-modified zirconia* catalyst (5 g) was tested under the same conditions employed with Amberlyst-15, but higher temperatures were also utilized. At 90°C, only MIBE was detected, but the yield was very low. However, at higher temperature isobutanol was selectively dehydrated to butenes in the presence of methanol. Indeed, at 175°C, the $\text{SO}_4^{2-}/\text{ZrO}_2$ showed 95% conversion with over 80% selectivity to butenes, principally *isobutene* (Table 1). At the latter temperature, small amounts of C-8 and C-12 products (0.5 mol%) were observed. Non-sulfated zirconia was found to be totally inactive for the dehydration of either methanol or isobutanol over the temperature interval tested (90-175°C).

Dehydration of Isobutanol Only Over the $\text{SO}_4^{2-}/\text{ZrO}_2$ Catalyst. The activity and selectivity of dehydrating isobutanol over $\text{SO}_4^{2-}/\text{ZrO}_2$ in the absence of methanol was investigated. The $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst (5 g) calcined to 620°C was centered in the reactor as described previously. The reaction conditions utilized included the temperatures of 125, 135, 150, 175, 200, and 225°C and isobutanol feed rates of 1.69-20.28 mol/kg catalyst/hr while maintaining the He + N₂ flow = 18.78 mol/kg catalyst/hr. The isobutanol space velocity of 1.69 mol/kg cat/hr was used in an initial temperature dependence study from 125 to 175°C. At 175°C, 85% of the isobutanol was converted to butenes. Comparison to the first entry row in Table 1 indicates that absence of the methanol reactant produced only a small increase in isobutanol conversion.

At the temperature of 200°C, the isobutanol flow rate was raised sequentially to 6.76, 13.52, and 20.28 mol/kg cat/hr. A final test was performed at 225°C using 20.28 mol isobutanol/kg cat/hr. Testing was carried out for several hours at each point of temperature and space velocity. The only major products observed with the on-line GC analysis were isobutene, *trans*-2-butene, and *cis*-2-butene. Trace amounts of octenes and C₈ ethers were seen. At higher reaction temperatures, small amounts of methanol and other products believed to be cracking products of isobutanol were seen as was seen for isobutanol only dehydration over H-mordenite. The yields of the major products under these conditions are presented in Table 1. It can be seen that the predominant product was isobutene in each case. The highest productivity of isobutene of 11.35 mol/(kg cat. × hr) was obtained at 225°C and a flow rate of 20.28 mol isobutanol/kg cat/hr. The selectivity of isobutene among the butenes at this high productivity was 79% (12.2 mol% *trans*-2-butane and 8.7 mol% *cis*-2-butene). This production of isobutene corresponds to 1.1 kg isobutene/kg cat/hr, and therefore the dehydration of isobutanol over $\text{SO}_4^{2-}/\text{ZrO}_2$ is a fast reaction at this temperature.

Dual Reactor Synthesis of MTBE. The concept of this experiment was to selectively dehydrate isobutanol in the reactant alcohol mixture to isobutene over one catalyst and then to couple the isobutene with methanol to form MTBE over a second catalyst. In this dual bed experiment at ambient pressure, the first catalyst bed contained 5 g of $\text{SO}_4^{2-}/\text{ZrO}_2$, calcined to 620°C, while the second bed contained 0.5 g of Amberlyst-15. The reactant gas flow of the methanol/isobutanol = 1/1 mixture was 1.72 mol/kg cat/hr of each alcohol with a carrier gas flow of 17.2 mol/kg cat/hr of N_2 and He. The first bed was maintained at 175°C to effect the selective dehydration of isobutanol to isobutene, while the second bed consisting of the resin catalyst was kept at 90°C for the MTBE synthesis reaction. A short line of copper tubing connected the two beds and served as a heat exchanger. The space time yields of the products are given in Table 1.

In this experiment, the conversions of isobutanol and methanol corresponded to ≈ 77 mol% and ≈ 20 mol%, respectively. This productivity of MTBE is more than an order of magnitude higher than that obtained by the direct coupling of methanol and isobutanol over the Amberlyst-15 resin at 90°C. The butenes consisted of 0.90, 0.09, and 0.08 mol/kg cat/hr of isobutene, *trans*- and *cis*-2-butene, respectively. In addition, 0.03 mol *tert*-butanol/kg cat/hr was also observed. It was observed that lowering the second bed temperature to ca. 40°C (non-steady state conditions) increased the yield of MTBE to ≈ 0.35 mol/kg cat/hr, which principally reflected the enhanced reaction of methanol with the isobutene that is favored by lower reaction temperatures. Indeed, the decrease in the yields of "butenes" was due solely to a lower amount of isobutene (≈ 0.70 mol/kg cat/hr) in the product mixture, while the *trans*- and *cis*-2-butene yields remained constant.

This experiment under unoptimized conditions shows that it is feasible to considerably increase the yield of MTBE formed from alcohols via a 2-step process, although the yield obtained under these conditions was limited by the low pressure and high temperature employed, as well as the small amount of Amberlyst-15 used as the second catalyst bed. In these experiments, water was not separated from the product stream between the beds.

Fuel Characteristics of Oxygenates. Determination of the octane numbers of MIBE and MTBE was performed by AMOCO Oil Company. The standard ASTM methods D-2699 and D-2700 were used for Research Octane Number and Motor Octane Number, respectively. Cetane determinations were carried out at the Southwest Research Institute. Octane number were determined for MIBE, MTBE, and a 50/50 by volume mixture of MIBE and MTBE. MTBE was obtained from Aldrich, while the MIBE was synthesized in-house by the Williamson ether synthesis as described previously [19]. For the purpose of octane number determination, this product was distilled under nitrogen to yield a >96% purity of MIBE, as determined by gas chromatography. The major impurity was isobutanol. The peroxide level of the ether samples was <20 ppm and was considered to be acceptable for all three samples.

The results obtained by AMOCO Oil Co. are summarized in Table 2. It can be seen that MTBE increased the research octane number by 2.8 units and the motor octane number by 1.4 units, which is in good agreement with values obtained by Spindelbaker and Schmidt [23]. MIBE, on the other hand, decreased both the research octane number and motor octane number by 3.2 and 1.5 units. The gasoline/ether mixture containing both MIBE and MTBE (5 vol% of each) had the same values as the base unleaded regular gasoline. In this case, an appreciable amount of oxygen was added to the ULR gasoline without altering its octane rating.

The blending octane numbers were calculated according to the following equation: Blending Research Number = RON (component A) \times (percent component A) + RON (component B) \times (percent component B). Table 3 lists the blending numbers for MIBE and MTBE. MTBE and MIBE are structurally not very different, but it is clear from the results presented above that MTBE is superior to MIBE for octane enhancing purposes. Comparisons of the blending octane and cetane numbers of oxygenates are given in Table 4. In this table, ETBE = ethyltertiary-

butylether, IPTBE = isopropyltertiarybutylether, DIPE = diisopropylether, and TAME = tertiary-amylnmethyl ether. Changes (Δ) in RON and MON were determined at 10 vol% levels of the oxygenates in gasoline. It is clear that MIBE has a poor octane number but a high cetane number.

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TABLE 1. Product yields (mol/kg cat/hr) over the single bed and dual bed catalysts from methanol = isobutanol = 1.72 mol/kg cat/hr reactants and from isobutanol only at different flow rates at 1 atm at the temperatures utilized in this study.

	T _{Reaction}	DME	Butenes	MIBE	MTBE	C8 Ether
SO ₄ ²⁻ /ZrO ₂	175°C	0.10	1.29	0.05	0.01	trace
Amberlyst-15	90°C	0.04	0.04	0.05	0.01	0.01
Dual Reactor ^a	1. 175°C	0.06	1.07	0.06	0.16	trace ^b
	2. 90°C					
	2. 40°C	0.06	0.87	0.06	0.35	trace ^b
(SO ₄ ²⁻ /ZrO ₂) ^c	175°C	-----	1.44	-----	-----	trace ^b
(SO ₄ ²⁻ /ZrO ₂) ^d	200°C	-----	4.45	-----	-----	trace ^b
(SO ₄ ²⁻ /ZrO ₂) ^e	200°C	-----	6.80	-----	-----	trace ^b
(SO ₄ ²⁻ /ZrO ₂) ^f	200°C	-----	7.75	-----	-----	trace ^b
(SO ₄ ²⁻ /ZrO ₂) ^f	225°C	-----	14.37	-----	-----	trace ^b

^aThe catalyst in Reactor 1 was ZrO₂/SO₄²⁻ and in Reactor 2 was Amberlyst-15.

^bPlus trace of octenes.

^cThe reactant consisted of isobutanol only with a flow rate of 1.69 mol/kg cat/hr.

^dThe reactant consisted of isobutanol only with a flow rate of 6.86 mol/kg cat/hr.

^eThe reactant consisted of isobutanol only with a flow rate of 13.5 mol/kg cat/hr.

^fThe reactant consisted of isobutanol only with a flow rate of 20.3 mol/kg cat/hr.

TABLE 2. Octane numbers of the ether/gasoline fuel mixtures.

Sample	Research Octane Number	Motor Octane Number	Peroxide (ppm)
Unleaded Regular Gasoline (ULR)	92.1	82.3	-
10% MTBE in ULR	94.9	83.7	14
10% (MTBE/MIBE) in ULR	92.0	82.4	6
10% MIBE in ULR	88.8	80.8	17

TABLE 3. Blending research octane number (BRON) and blending motor octane number (BMON) of MTBE and MIBE in unleaded regular gasoline.

Sample	BRON	BMON
MTBE in ULR	120.1	96.3
MIBE in ULR	60.8	67.0

TABLE 4. Selected properties of hydrocarbon fuels and oxygenated additives.

Oxygenate (or Fuel)	Blending Octane Number (R+M)/2	Cetane No.	Δ RON ^a	Δ MON ^a
MIBE	64	53 ^b	-3.3 ^c -1.9 ^d	-1.5 ^c -3.0 ^d
MTBE	108 109 ^e , 110 ^e , 108 ^e	<10	+2.8 ^c +3.4 ^d	+1.4 ^c +2.8 ^d
ETBE	110 ^e , 112 ^f		+2.1 ^d	+2.2 ^d
IPTBE	100.5 ^e , 113 ^f			
DIPE	104.5 ^e , 105 ^f			
TAME	104.5 ^e , 105 ^f			
Methanol	116 ^e , 108 ^f	3		
Ethanol	113 ^e , 115 ^f	8		
i-Propanol	108.5 ^e , 106 ^f			
1-Butanol	87 ^e	25	+1.0 ^d	+0.6 ^d
i-Butanol	102 ^f	13	+3.1 ^d	+2.1 ^d
t-Butanol	101 ^e , 100 ^f		+1.9 ^d	+2.0 ^d
Butane	94 ^e			
Gasoline	-----		-----	-----
Diesel Fuel	-----	> 42	-----	-----

^aDetermined at the level of 10 vol% of additive in gasoline.

^bDetermined by the Southwest Research Institute with a sample submitted by us; J. Erwin, private communication.

^cDetermined by AMOCO Oil Co. with samples submitted by us using an unleaded gasoline having RON = 92.1 and MON = 82.3; W. J. Reagan, private communication.

^dFrom Reference 23 using an unleaded gasoline having RON = 82.4 and MON = 76.6.

^eFrom G. H. Unzelman, *Oil & Gas J.*, 33 (April 10, 1989).

^fFrom W. J. Piel, "Proc. First Biomass Conf. of the Americas," Burlington, VT (1993).

^gFrom W. J. Piel, *Energy Prog.*, 8(4), 201 (1988).