

**Catalysts for High Cetane Ethers as Diesel Fuels**

Kamil Klier, Richard G. Herman, James G. C. Shen, and Qisheng Ma  
Zettlemoyer Center for Surface Studies  
and Department of Chemistry  
Sinclair Laboratory, 7 Asa Drive  
Lehigh University  
Bethlehem, PA 18015

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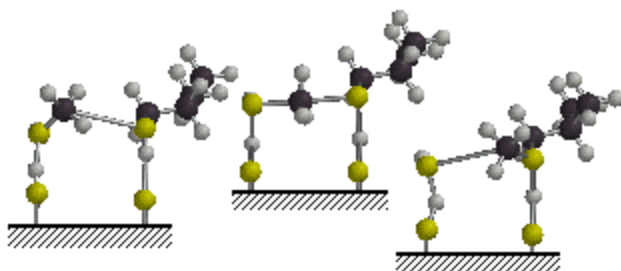
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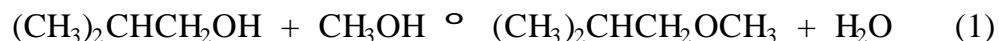
### ABSTRACT

A novel 1,2-ethanediol, bis(hydrogen sulfate), disodium salt precursor-based solid acid catalyst with a zirconia substrate was synthesized and demonstrated to have significantly enhanced activity and high selectivity in producing methyl isobutyl ether (MIBE) or isobutene from methanol–isobutanol mixtures. The precursor salt was synthesized and provided by Dr. T. H. Kalantar of the M.E. Pruitt Research Center, Dow Chemical Co., Midland, MI 48674. Molecular modelling of the catalyst synthesis steps and of the alcohol coupling reaction is being carried out. A representation of the methyl transfer from the surface activated methanol molecule (left) to the activated oxygen of the isobutanol molecule (right) to form an ether linkage to yield MIBE is shown below.

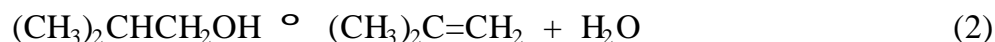


## INTRODUCTION

Methanol and isobutanol are the predominant products formed from CO/H<sub>2</sub> synthesis gas over alkali-promoted Cu/ZnO-based (low temperature) catalysts [1,2], as well as over copper-free alkali-promoted (high temperature) catalysts [3,4]. Since the two alcohols are produced together, their direct coupling to synthesize ethers for a number of applications is of interest. One such ether is the unsymmetrical methyl-isobutyl ether (MIBE) that has desirable characteristics as a fuel (cetane number = 53 [5]), and thus, can be employed as an additive to or as a neat fuel to substitute for current diesel fuels [6,7]. MIBE formed by the direct coupling of methanol- isobutanol (Equation 1) was previously investigated over a number of solid acid catalysts [8].



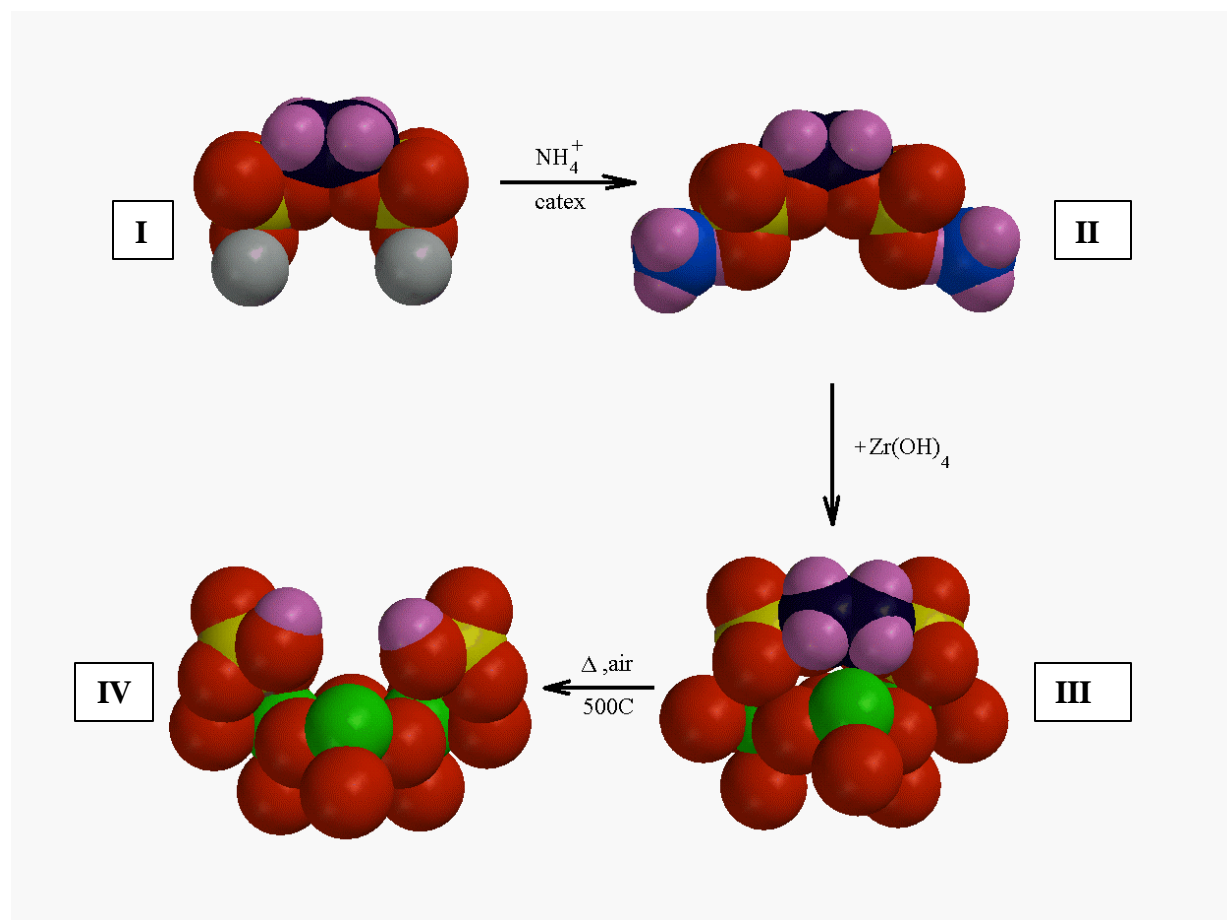
Improvement of product yields, particularly over inorganic oxides, was found to be desirable. Furthermore, if new catalysts were found for selectively converting isobutanol to isobutene, Equation 2, a chemical route to isobutene from natural gas or coal-derived synthesis gas would be provided [5].



Such a process would alleviate isobutene dependence on petroleum feedstock. The kinetic analyses [8b,9], together with theoretical calculations [10] suggest that the mechanism of Reaction 1 is the S<sub>N</sub>2 pathway involving competitive adsorption of reactants on proximal dual Brønsted acid sites on the catalyst surface, while that of Reaction 2 has been proposed to be an E2 reaction [8]. Reactions 1 and 2 are a specific

implementation of a general class of dehydrocondensations and dehydrations occurring in a mixture of a light alcohol and a heavier C<sub>2</sub>-branched primary alcohol.

In the present work, we studied a novel heterogeneous catalyst derived from a (HO)<sub>3</sub>Zr-O<sub>3</sub>SOCH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>-Zr(OH)<sub>3</sub>-type surface precursor that gave rise to proximal strong surface acid functionalities (HOSO<sub>2</sub>O-Zr-O-)<sub>2</sub> as prompted by the requirement to activate the two alcohols [8,10]. Complete characterization of the precursor salt, the synthesized catalyst precursor, and the calcined catalyst before and after use is being carried out. The high resolution X-ray photoelectron (HR-XPS), near infrared (NIR) and <sup>13</sup>C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra confirmed the composition, structure, and physicochemical properties of the catalyst. The results show that the 1,2-ethanediol, bis(hydrogen sulfate) moiety was successfully grafted onto the surface of zirconium hydroxide, as will be reported in detail in the next technical research report when complete characterization of the catalyst has been accomplished. The main features of the preparation sequence are presented in the scheme shown on the next page.



Scheme 1. Color codes for the atoms are as follows: C, black; H, pink; O, red; S, yellow; N, blue, Zr, green; and Na, gray.

## EXPERIMENTAL

The 1,2-ethanediol, bis(hydrogen sulfate), disodium salt precursor **I** ( $\text{NaOSO}_3\text{CH}_2$ )<sub>2</sub> obtained from Dow Chemical Co. was converted to the ammonium form **II** ( $\text{NH}_4\text{OSO}_3\text{CH}_2$ )<sub>2</sub> by exchange over a Rexyn 101 catex column, and an aqueous solution of compound **II** was combined with an aqueous suspension containing zirconium hydroxide to form the derivative **III** ( $-\text{O}_x\text{Zr}-\text{OSO}_3\text{CH}_2$ )<sub>2</sub>. This solid was filtered, dried,

and then calcined in air at 773K to remove the  $-(\text{CH}_2\text{CH}_2)-$  residues, resulting in the surface-derivatized species **IV**  $(-\text{O}_x\text{Zr-OSO}_3\text{H})_2$ , corresponding to proximal acid sites on zirconia. After the calcination treatment, this catalyst exhibited a surface sulfate-to-zirconium surface mole ratio of 0.84, corresponding to 0.72 mmol surface S/g cat., and all of the carbon from the precursor was removed. Thus, the final composition corresponds to the formula  $(\text{HSO}_4)_{0.84}\text{-ZrO}_{2,\text{surf}}$  on the surface of pure zirconia. This material possessed a high thermal stability.

The coupling/dehydration of methanol–isobutanol (2-methyl-1-propanol, 99.9+%, Alfa) was investigated in a downflow stainless steel tubular reactor with control of temperature (398–508K), total pressure ( $101.3\text{--}3.1 \times 10^3$  kPa, 1 atm = 101.325 kPa) and i-BuOH/MeOH molar ratio (0/100–50/50) in a carrier gas of 5%  $\text{N}_2$  diluted in He. The catalyst was centered in the vertical reactor in the heated zone by Pyrex beads above and below the bed. A J-type thermocouple was inserted into the top of the bed using an axial stainless steel thermowell. Product analyses were achieved with an on-line Hewlett-Packard gas chromatograph (Model 5890, Series II) equipped with automated heated sampling valves. A Cpsil-5CB capillary column was used.

## CATALYTIC RESULTS

Maintaining the methanol-isobutanol molar ratio = 1, the reaction temperature was varied. Table 1 shows that as the temperature was increased, the space time yield of MIBE significantly increased. Also observed were small quantities of dimethylether

(DME), methyl tertiarybutyl ether (MTBE), diisobutyl ether (DIBE), and ditertiarybutyl ether (DTBE).

Table 1. Product space time yields (mol/kg cat/hr) in the reaction of MeOH/i-BuOH (1:1 molar ratio) with flow rates of 3.44 mol/kg cat/hr alcohols and 16 mol/kgcat/hr carrier gas at 101.3 kPa total pressure over the (HO)<sub>3</sub>Zr-O<sub>3</sub>SOCH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>-Zr(OH)<sub>3</sub>-derived catalyst.<sup>a</sup>

Temp. (K)	MeOH pressure (kPa)	i-BuOH pressure (kPa)	MIBE	Isobutene	DME	MTBE	DIBE	DTBE	Octenes
398	8.97	8.97	0.002	----	----	----	----	----	----
423	8.97	8.97	0.020	----	----	----	0.008	----	0.004
448	8.97	8.97	0.087	1.430	----	----	0.005	0.003	0.005
448 <sup>b</sup>	8.97	8.97	0.049	1.290 <sup>d</sup>	0.103	0.007	----	----	---
448 <sup>c</sup>	8.97	8.97	0.029	0.378 <sup>d</sup>	0.034	0.014	0.015	0.016	----

<sup>a</sup> Steady state activities were readily achieved within 2 hr of initiating alcohol injection or after altering a reaction variable such as temperature. Extended testing of the (HO)<sub>3</sub>Zr-O<sub>3</sub>SOCH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>-Zr(OH)<sub>3</sub>-derived catalyst under each condition was performed for 8–12 hr. No catalyst deactivation was observed over several hundreds of hours of testing.

<sup>b</sup> SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst [9].

<sup>c</sup> H-montmorillonite catalyst [9; Table III].

<sup>d</sup> Butene included isobutene, n-butene, and cis- and trans-2-butene.

At 448K, the MIBE yield was 0.087 mol/kg cat/hr, which represented an **enhancement of 78%** compared with 0.049 mol/kg cat/hr over previously reported SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> [9], and of 200% compared with 0.029 mol/kg cat/hr on an H-montmorillonite catalyst [9]. The isobutene yield of 1.43 mol/kg cat/hr, also observed at 448K, represented an increase of 11% and ~280%, respectively, from 1.29 mol/kg cat/hr on SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and 0.378 mol/kg cat/hr on H-montmorillonite catalyst [9].



Figure 1 shows the effect of i-BuOH addition on the production of dimethyl ether (DME) and MIBE. MIBE yields (■) increased and DME yields (●) decreased with increasing isobutanol partial pressure. When the ratio of i-BuOH/MeOH reached 12/88, very little DME was observed, resulting in near-100% selectivity in favor of the unsymmetrical MIBE. This suggests that isobutanol suppressed the DME formation more effectively on this catalyst than on any of the previously studied catalysts [8,10].

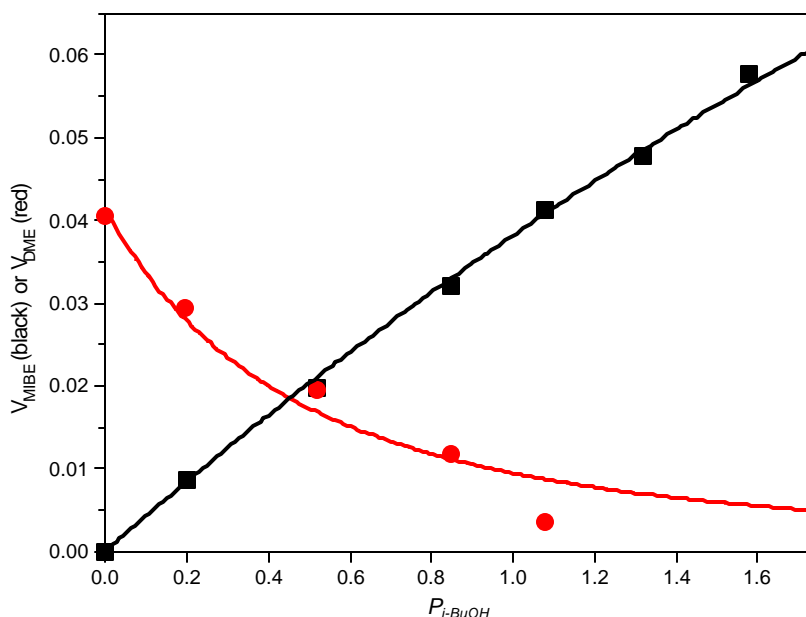


Figure 1. The effect of i-BuOH addition on DME (●) and MIBE (■) production. The abscissa axis is the partial pressure  $P_{i-BuOH}$  in kPa at a constant pressure of methanol  $P_{MeOH} = 8.97$  kPa. The ordinate axis expresses the rates of DME,  $v_{DME}$ , and MIBE,  $v_{MIBE}$ , in mol/kg cat/hr.

The adsorption constants of MeOH ( $K_M$ ) and i-BuOH ( $K_B$ ) were determined by curve fitting of the kinetic laws for the DME and MIBE formation [8].  $K_B$  was derived to be  $0.086 \text{ kPa}^{-1}$  and  $K_M$  was found to be  $0.035 \text{ kPa}^{-1}$ . Here, the ratio  $K_B/K_M = 2.46$  shows that isobutanol adsorbed preferentially on the acid sites, which agrees with its greater basicity over methanol [8b,11]. The distribution of DME and MIBE in Figure 1 can be reasonably explained by kinetics previously observed on other catalysts [8b], with  $K_B > K_M$ . The experimental data also show increasing yields of isobutene with increased molar ratio of i-BuOH/MeOH. In addition, the enhancement of selectivity toward isobutene from 0% at 398K to 94% at 448K (Table 1) results from the increase of  $K_B/K_M$  with increasing temperature. The isobutanol dehydration to isobutene competed with MeOH/i-BuOH coupling to MIBE. At relatively high temperatures, a large ratio of  $K_B/K_M$  resulted in an enhancement of the  $q_{\text{i-BuOH}}/q_{\text{MeOH}}$  ratio ( $q$ , surface coverage), which favored the dehydration of the adsorbed isobutanol to isobutene (Equation 2). The apparent activation energy for the formation of each product was determined from Arrhenius plots, yielding 22 kcal/mol for MIBE and 24 kcal/mol for isobutene. The activation energy of 19 kcal/mol for DME was obtained by theoretical calculations [10].

Table 2 demonstrates that the MIBE yields at 498 K increased, whereas isobutene yields decreased with total alcohol pressure increasing from 7.8 to 240.7 kPa. For example, 0.156 mol/kg cat/hr MIBE at 7.8 kPa kept increasing with pressure to 0.702 mol/kg cat/hr at 240.7 kPa, while isobutene at 7.8 kPa (3.525 mol/kg cat/hr) exhibited a decreasing trend to 0.335 mol/kg cat/hr at 240.7 kPa.

Table 2. Product space time yields (mol/kg cat/hr) and selectivity (%) in the reaction of MeOH/i-BuOH (2:1 molar ratio) at 15.6 mol/kg cat/hr alcohols, 186 mol/kg cat/hr carrier gas and 498K over (HO)<sub>3</sub>Zr-O<sub>3</sub>SOCH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>-Zr(OH)<sub>3</sub>-derived catalyst.<sup>a</sup>

Total pressure (kPa)	MeOH pressure (kPa)	i-BuOH pressure (kPa)	MIBE	Isobutene	DIBE	DTBE	MIBE selectivity (%)	Isobutene selectivity (%)
101.3	5.2	2.6	0.156	3.525	----	----	4.2	95.8
691.0	35.7	17.8	0.393	3.201	----	----	10.9	89.1
1036.5	53.5	26.7	0.521	2.972	----	0.012	14.9	84.8
1727.5	89.1	44.6	0.557	2.197	----	0.006	20.2	79.6
2418.5	124.8	62.4	0.675	1.473	----	0.007	31.3	68.4
3109.5	160.5	80.2	0.702	0.335	0.015	0.007	66.3	31.6

<sup>a</sup> Steady state activities were readily achieved within 2 hr of initiation of alcohol injection or after altering a reaction variable such as pressure. Extended testing of the (HO)<sub>3</sub>Zr-O<sub>3</sub>SOCH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>-Zr(OH)<sub>3</sub>-derived catalyst under each condition was carried out for 8–12 hr. No catalyst deactivation was observed over several hundred hours of testing.

The data in Table 2 are consistent with the Langmuir-Hinshelwood kinetic laws [8b],  $v_{\text{MIBE}} = k_4 K_{\text{M}} p_{\text{M}} K_{\text{B}} p_{\text{B}} / (1 + K_{\text{M}} p_{\text{M}} + K_{\text{B}} p_{\text{B}})^2$  and  $v_{\text{Isobutene}} = k_3 K_{\text{B}} p_{\text{B}} / (1 + K_{\text{B}} p_{\text{B}} + K_{\text{M}} p_{\text{M}})^2$  that were derived on the basis of Reactions 1 and 2 occurring on dual acid sites [8b]. The values of constants fitting the data of Table 2 were  $k_3 = 33.1$  mol/kg cat/hr,  $k_4 = 3.2$  mol/kg cat/hr,  $K_{\text{M}} = 0.035$  kPa<sup>-1</sup> and  $K_{\text{B}} = 0.086$  kPa<sup>-1</sup>.

The kinetic behavior of Equation 1 showed that isobutanol partial pressure ( $p_{\text{B}}$ ) promoted the MeOH/i-BuOH coupling to MIBE, whereas the kinetic behavior of Equation 2 indicated that increasing isobutanol pressure ( $p_{\text{B}}$ ) very strongly suppressed its dehydration, and the kinetic order became negative at high  $p_{\text{B}}$  [9]. At low alcohol partial pressures ( $p_{\text{M}} = 5.2$  kPa and  $p_{\text{B}} = 2.6$  kPa), high selectivity of isobutene (95%) is ascribed to a significant fraction of unoccupied acid sites on the surface of the (HSO<sub>4</sub>)<sub>2</sub>-2ZrO<sub>2</sub> catalyst. These free acid sites are considered to promote the dehydration of adsorbed

isobutanol to isobutene according to the dual site elimination mechanism of Equation 2, whereby one site adsorbs the reacting alcohol and the second site is an acceptor for the product water [8b,9]. At high alcohol partial pressures, the fraction of acid sites occupied by alcohol molecules approaches unity, and the catalyst favors MIBE formation. A maximum selectivity of MIBE reached 68% at 240 kPa total alcohol pressure ( $p_M = 160$  kPa and  $p_B = 80$  kPa) at the reaction temperature of 498K. The ratio of MIBE/isobutene increased with increasing alcohol pressure even at constant  $p_B/p_M$ . Moreover, the effect of pressure was found to be reversible, i. e. when alcohol pressure was decreased to its original value, isobutene production increased and MIBE decreased to their original rates.

The butene formed over the present  $(\text{HSO}_4)_{0.84}\text{-ZrO}_{2,\text{surf}}$  catalyst was pure isobutene, whereas over other catalysts, such as H-montmorillonite and H-ZSM-5, products involved significant amounts of n-butene and cis- and trans-2-butene along with the isobutene. The highly concentrated Brønsted acid sites on this catalyst effectively catalyzed removal of OH from the alcoholic carbon and of H from the neighboring carbon, resulting in isobutene formation. On the other hand, the single Brønsted acid site on the surface of other catalysts was associated with carbenium ion chemistry [12], which leads to butene rearrangement in isobutanol dehydration [12,13].

In conclusion, the novel heterogeneous catalyst derived from the  $(\text{HO})_3\text{Zr-O}_3\text{SOCH}_2\text{CH}_2\text{OSO}_3\text{-Zr(OH)}_3$  precursor effectively catalyzes MIBE formation at high pressures and favored isobutene production at low pressures.

## ACKNOWLEDGEMENT

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