Synthesis of unsymmetrical ethers and branched olefins from alcohols over a novel $(HO)_3ZrO_3SO–CH_2CH_2–OSO_3Zr(OH)_3$-derived catalyst

J. G. C. Shen,[a] T. H. Kalantar,[b] Q. Ma,[a] R. G. Herman[a] and K. Klier*[a]

[a] *Department of Chemistry and Zettlemoyer Center for Surface Studies, 6 East Packer Avenue, Lehigh University, Bethlehem, PA 18015, USA. E-mail: kk04@lehigh.edu*
[b] *M. E. Pruitt Research Center, Dow Chemical Co., Midland, MI 48674, USA*

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A novel disodium 1,2-ethanediol bis(hydrogen sulfate) salt precursor-based solid acid catalyst is demonstrated to have significantly enhanced activity and high selectivity in producing methyl isobutyl ether (MIBE) or isobutene from a methanol–isobutanol mixture.

Methanol and isobutanol are the predominant products formed from CO/H_2 synthesis gas over alkali-promoted Cu/ZnO-based (low temperature) catalysts[1,2] and copper-free (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) which has desirable characteristics as a fuel additive (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 from direct coupling of methanol–isobutanol [eqn. (1)] was investigated over a number of solid acid catalysts.[8]

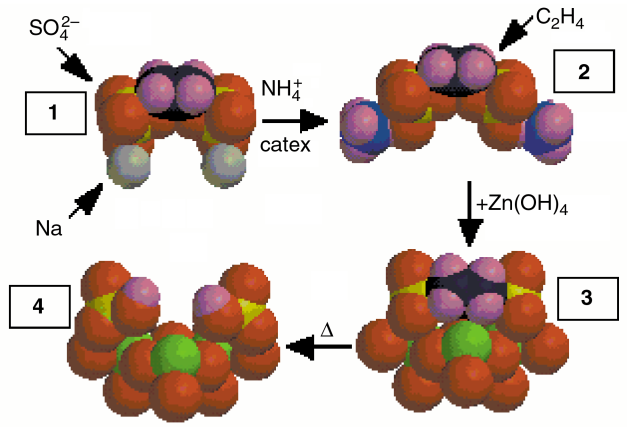
$$(CH_3)_2CHCH_2OH + CH_3OH \rightarrow (CH_3)_2CHCH_2OCH_3 + H_2O \quad (1)$$

Improvement of yields, particularly over inorganic oxides, was found to be desirable. Furthermore, if new catalysts were found for selectively converting isobutanol to isobutene, eqn. (2),

$$(CH_3)_2CHCH_2OH \rightarrow (CH_3)_2C{=}CH_2 + H_2O \quad (2)$$

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. Kinetic analyses,[8b,9] together with theoretical calculations,[10] suggest that the mechanism of reaction 1 is the S_N2 pathway involving competitive adsorption of reactants on proximal dual Brønsted acid sites on the catalyst surface, while that of process 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_2-branched primary alcohol.

In the present work, we studied a novel heterogeneous catalyst derived from a $(HO)_3Zr–O_3SOCH_2CH_2OSO_3–Zr(OH)_3$ precursor which gave rise to proximal strong surface acid functionalities $(HOSO_2O–Zr–O–)_2$, as prompted by the requirement to activate the two alcohols.[8,10] High resolution X-ray photoelectron, near-infrared, and ^{13}C magic angle spinning nuclear magnetic resonance 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 elsewhere in detail.[11] The main features of the preparation sequence are presented in Scheme 1.



Scheme 1 Atom colour codes are as follows: C, black; H, pink; O, red; S, yellow; N, blue, Zr, green; Na, gray.

Here, the disodium 1,2-ethanediol bis(hydrogen sulfate) salt precursor $(NaOSO_3CH_2)_2$ **1** was converted to the ammonium form $(NH_4OSO_3CH_2)_2$ **2** by exchange over a catex column, an aqueous solution of compound **2** was combined with a zirconium hydroxide suspension to form the derivative $(–O_xZr–OSO_3CH_2)_2$ **3**, which was calcined in air at 773 K to remove the $–(CH_2CH_2)–$ residues, resulting in the surface-derivatized species $(–O_xZr–OSO_3H)_2$ **4** with proximal acid sites. Upon calcination, this catalyst exhibited a surface sulfate-to-zirconium surface mol ratio of 0.84, corresponding to 0.72 mmol surface S/g catalyst, and all its carbon was removed. Thus the final composition corresponds to the formula $(HSO_4)_{0.84}$-$ZrO_{2,surf}$ on the surface of pure zirconia. This material simultaneously possessed a high thermal stability.

The dehydration of methanol–isobutanol (2-methyl-1-propanol, 99.9+%, Alfa) was investigated in a downflow stainless steel tubular reactor with controls of temperature (398–508 K), total pressure (101.3–3.1 × 10^3 kPa, 1 atm = 101.325 kPa) and $Bu^iOH/MeOH$ molar ratio (0/100–50/50) in a carrier gas of 5% N_2 diluted in He. Steady state activities were achieved within 2 h of initiation of alcohol injection or after altering a reaction variable such as temperature or pressure. Testing of the $(HO)_3Zr–O_3SOCH_2CH_2OSO_3–Zr(OH)_3$-derived catalyst under each condition was carried out for 8–12 h. No catalyst deactivation was observed over several hundred hours of testing.

At 448 K, the MIBE yield was 0.087 mol/kg cat/h (Table 1), which represented an enhancement of 78% compared with 0.049 mol/kg cat/h over previously reported SO_4^{2-}/ZrO_2,[9] and

Table 1 Product space time yields (mol/kg cat/h) in the reaction of MeOH/Bu^iOH (8.97 : 8.97 kPa) at 3.44 mol/kg cat/h alcohols, 16 mol/kg cat/h carrier gas and 101.3 kPa total pressure over $(HO)_3Zr–O_3SOCH_2$-$CH_2OSO_3–Zr(OH)_3$-derived catalyst

T/K	MIBE	Isobutene	DME	DIBE	MTBE	DTBE
398	0.002	—	—	—	—	—
423	0.020	—	—	0.008	—	—
448	0.087	1.430	—	0.005	—	0.003
448[a]	0.049	1.290[c]	0.103	—	0.007	—
448[b]	0.029	0.378[c]	0.034	0.015	0.014	0.016

[a] SO_4^{2-}/ZrO_2 catalyst. [b] H-montmorillonite catalyst. [c] Butene included isobutene, *n*-butene, *cis*- and *trans*-2-butene.

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Table 2 Product space time yields (mol/kg cat/h) and selectivity (%) in the reaction of MeOH/Bu^{i}OH (2 : 1 molar ratio) at 15.6 mol/kg cat/h alcohols, 186 mol/kg cat/h carrier gas and 498 K over the $(HO)_3Zr–O_3SOCH_2CH_2OSO_3–Zr(OH)_3$-derived catalyst

Total pressure/kPa	MeOH pressure/kPa	Bu^{i}OH 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

of 200% compared with H-montmorillonite catalyst.[9] The isobutene yield of 1.43 mol/kg cat/h, also at 448 K, represented an increase of 11 and ~280% over the SO_4^{2-}/ZrO_2 and H-montmorillonite catalysts, respectively.[9] Other products involved dimethyl ether (DME) and traces of di-isobutyl ether (DIBE), di-*tert*-butyl ether (DTBE), methyl *tert*-butyl ether (MTBE) and octenes.

Table 2 demonstrates that MIBE yields increased, whereas isobutene yields decreased, with total alcohol pressure increasing from 7.8 to 240.7 kPa. For example, 0.156 mol/kg cat/h MIBE at 7.8 kPa kept increasing with pressure to 0.702 mol/kg at 240.7 kPa, while isobutene at 7.8 kPa (3.525 mol/kg cat/h) exhibited a decreasing trend to 0.335 mol/kg cat/h at 240.7 kPa. The data in Table 2 are consistent with the Langmuir–Hinshelwood kinetic laws,[8b] $v_{MIBE} = k_4K_Mp_MK_Bp_B/(1 + K_Mp_M + K_Bp_B)^2$ and $v_{Isobutene} = k_3K_Bp_B/(1 + K_Bp_B + K_Mp_M)^2$, which were derived on the basis of the reactions (1) and (2) occurring on the dual acid sites.[8b] The values of constants fitting the data of Table 2 were $k_3 = 33.1$ mol/kg cat/h, $k_4 = 3.2$ mol/kg cat/h, $K_M = 0.035$ kPa^{-1} and $K_B = 0.086$ kPa^{-1}.

Here, the ratio $K_B/K_M = 2.46$ shows that isobutanol adsorbed preferentially on the acid sites, agreeing with its greater basicity over methanol.[8b,12] When the partial pressure of isobutanol was increased in the range of 0–1.6 kPa while maintaining the partial pressure of methanol constant at 8.97 mPa, the MIBE space time yield increased from zero to 0.057 mol/kg cat/h, while the DME decreased from 0.040 mol/kg cat/h to zero. This distribution of DME and MIBE 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 Bu^{i}OH/MeOH. In addition, the enhancement of selectivity toward isobutene from 0% at 398 K to 94% at 448 K (Table 1) results from the increase of K_B/K_M with increasing temperature. The isobutanol dehydration to isobutene competed with MeOH/Bu^{i}OH coupling to MIBE. At relatively high temperatures, a large ratio of K_B/K_M resulted in an enhancement of the $\theta_{Bu^iOH}/\theta_{MeOH}$ ratio (θ, surface coverage), and favored the dehydration of the adsorbed isobutanol to isobutene [eqn. (2)]. The apparent activation energy for the formation of each product was determined from Arrhenius plots, yielding 22 kcal mol^{-1} for MIBE and 24 kcal mol^{-1} for isobutene. The activation energy of 19 kcal mol^{-1} for DME was obtained by theoretical calculations.[10]

The kinetic behavior of eqn. (1) showed that isobutanol partial pressure (p_B) promoted the MeOH/Bu^{i}OH coupling to MIBE, whereas the kinetic behavior of eqn. (2) indicated that increasing isobutanol pressure (p_B) very strongly suppressed its dehydration, and the kinetic order became negative at high p_B.[9] At low alcohol partial pressures, high selectivity of isobutene is ascribed to a significant fraction of unoccupied acid sites on the surface of the $(HSO_4)_2–2ZrO_2$ catalyst. These free acid sites are considered to promote the dehydration of adsorbed isobutanol to isobutene according to the dual site elimination mechanism of eqn. (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. 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 $(HSO_4)_{0.84}–ZrO_{2,surf}$ catalyst was pure isobutene, whereas over other catalysts such as H-montmorillonite and H-ZSM-5, products involved isobutene, significant amounts of *n*-butene, and *cis*- and *trans*-2-butene. 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, and resulted in isobutene formation. On the other hand, the single Brønsted acid site on the surface of other catalysts was associated with carbenium ion chemistry,[13] which leads to butene rearrangement in isobutanol dehydration.[13,14]

In conclusion, the novel heterogeneous catalyst derived from the $(HO)_3Zr–O_3SOCH_2CH_2OSO_3–Zr(OH)_3$ precursor effectively catalyzes MIBE formation at high pressures and favored isobutene production at low pressures.

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