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Role of acidity on the hydrolysis of dimethyl ether (DME) to methanol

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Abstract

The activity of dimethyl ether (DME) hydrolysis was investigated over a series of solid acid and non-acid catalysts, zeolite Y [Si/Al = 2.5 and 15: denoted Y(Si/Al)], zeolite ZSM-5 [Si/Al = 15, 25, 40, and 140: denoted Z(Si/Al)], silica, zirconia, γ-alumina, and BASF K3-110 (commercial $Cu/ZnO/Al_2O_3$ catalyst). Dimethyl ether hydrolysis was carried out in an isothermal packed-bed reactor at ambient pressure.

Acid catalyzed dimethyl ether hydrolysis is equilibrium limited. All solid acid catalysts, with the exception of ZrO_2, attained equilibrium-limited conversions in the temperature range of interest (125–400 °C). Z(15), Z(25), and Z(40) reached equilibrium conversions at 200 °C, while Z(140), Y(15), and Y(2.5) reached equilibrium at 275 °C. γ-Alumina, the most active non-zeolite solid acid, attained equilibrium at 350 °C. Silica and BASF K3-110 were both ineffective in converting dimethyl ether to methanol. The observed activity trend for DME hydrolysis to methanol as a function of Si–Al ratio and catalyst type was:

$$\left\{\begin{matrix}\mathrm{Z(15)}\\ \mathrm{Z(25)}\\ \mathrm{Z(40)}\end{matrix}\right\} > \left\{\begin{matrix}\mathrm{Z(140)}\\ \mathrm{Y(15)}\end{matrix}\right\} > \mathrm{Y(2.5)} \gg \gamma\text{-}Al_2O_3 > ZrO_2.$$

Keywords: Dimethyl ether; Hydrolysis; Zeolites; Methanol; Alumina; Zirconia; Bronsted acidity; Acid site strength; Hydrophobicity; ZSM-5; Y

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells utilizing hydrogen offer the opportunity for compact, lightweight, high-energy delivery devices with energy densities surpassing those of batteries. Hydrogen can be produced from the reforming of various fuels (viz., methanol, ethanol, gasoline, diesel, and methane). Methanol is the only low temperature reforming fuel (250–300 °C). Ethanol, gasoline, diesel, and methane are all high temperature reforming fuels (600–800 °C). The reforming of ethanol, gasoline, and diesel all have the tendency to form carbon. Sulfur impurities are also a concern in the reforming of gasoline and diesel because of catalyst poisoning

Dimethyl ether (DME) is an alternative fuel that has not attracted much attention as a hydrogen carrier for fuel cells. Dimethyl ether can be produced over solid acid catalysts with syngas as the raw material [1–11]. Unlike many fuels considered for production of hydrogen-rich fuel-cell feeds, dimethyl ether is non-toxic, non-carcinogenic, non-teratogenic, and non-mutagenic [12]. Dimethyl ether has already penetrated the commercial sector as aerosol propellants (e.g., Dymel A^{TM}), refrigerants and as diesel substitutes and additives [13–23]. The use of DME as a

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clean fuel, including use for household heating and cooking fuel (thereby eliminating the need for liquefied petroleum gases), is being considered [24,25].

The storage and handling of dimethyl ether is similar to those of liquefied petroleum gases (LPG), e.g., butane and propane; therefore, the infrastructure of LPG fuels can be readily used for the distribution of dimethyl ether [17,26]. In addition, the existing natural gas infrastructure can be used to distribute DME.

Modeling of an automotive fuel-processor reforming dimethyl ether indicates it has intrinsically faster start-up times and higher efficiencies than an automotive fuel-processor using ethanol, gasoline, or methane [27]. It has also been shown that dimethyl ether processed autothermally can produce hydrogen yields comparable to methanol [28]. The thermodynamics detailing the effects of steam-to-carbon ratios, temperatures, pressures, and product compositions on the generation of hydrogen from dimethyl ether steam reforming have also been published [29,30].

The steam reforming of dimethyl ether occurs via a two-step reaction sequence [31–37]. The first step is converting dimethyl ether to methanol via DME hydrolysis, followed by methanol steam reforming over Cu or Cu/ZnO.

DME hydrolysis:

$$(CH_3)_2O + H_2O \underset{\text{Catalyst}}{\overset{\text{Acid}}{\rightleftharpoons}} 2CH_3OH, \quad \Delta H_r^\circ = +37\,\text{kJ/mol}$$

MeOH steam reforming:

$$CH_3OH + H_2O \overset{Cu/Zn}{\rightleftharpoons} 3H_2 + CO_2, \quad \Delta H_r^\circ = +49\,\text{kJ/mol}$$

DME steam reforming:

$$(CH_3)_2O + 3H_2O \overset{Cu/Zn}{\rightleftharpoons} 6H_2 + 2CO_2, \quad \Delta H_r^\circ = +135\,\text{kJ/mol}$$

Most studies [31,32,35,36] have used alumina as an acid catalyst for DME hydrolysis, and did not focus on the role of acidity on the hydrolysis of dimethyl ether. This paper is the first of four articles that will report the role of acidity on dimethyl ether steam reforming.

1.1. Scope

We have investigated the activity of various acid and non-acid catalysts for dimethyl ether hydrolysis. The catalysts used in this study were zeolites having a variety of Si/Al ratios (Y and ZSM-5, Si/Al = 2.5–140), a commercial

Table 1
Catalysts, catalyst vendors, catalysts composition and form, physical properties, and nomenclature used in text

Catalyst/support (vendor notation)	Catalyst family	Vendor	Composition/type/form	Si/Al[b]	Pore volume[b]	Surface area[b]	Nomenclature[c] used in text
CBV3024E	Zeolite	Zeolyst	H-ZSM-5, 1/8″ extrudate form with 20% Al_2O_3 binder and 0.05 wt% Na_2O	15	–	382	Z(15)
CBV5524G	Zeolite	Zeolyst	NH_4-ZSM-5[a], 1/8″ extrudate form with 20% Al_2O_3 binder and 0.05 wt% Na_2O	25	–	391	Z(25)
CBV8014 CY	Zeolite	Zeolyst	H-ZSM-5, 1/8″ extrudate form with 20% Al_2O_3 binder and 0.05 wt% Na_2O	40	–	401	Z(40)
CBV28014 CY	Zeolite	Zeolyst	H-ZSM-5, 1/8″ extrudate form with 20% Al_2O_3 binder and 0.05 wt% Na_2O	140	–	395	Z(140)
CBV300 CY	Zeolite	Zeolyst	NH_4-Y[a], 1/8″ extrudate form with 20% Al_2O_3 binder and 1.50 wt% Na_2O	2.5	–	702	Y(2.5)
CBV720 CY	Zeolite	Zeolyst	H-Y, 1/8″ extrudate form with 20% Al_2O_3 binder and 0.03 wt% Na_2O	15	–	706	Y(15)
γ-Al_2O_3	Non-zeolite	Alfa-Aesar	3.2 mm spherical pellets (>96% metal basis)	N/A	–	280	γ-Al_2O_3
ZrO_2	Non-zeolite	Alfa-Aesar	1/8″ pellets, 99.8% (metal basis), average pore diameter = 80/400 angstroms	N/A	0.31	90	ZeO_2
SiO_2	Non-zeolite	Alfa-Aesar	1/8″ pellets, 99.8% (metal basis), 0.2% Na_2O	N/A	0.78	144	SiO_3
BASF K3-110	Non-zeolite	BASF	1/8″ pellets, 40% CuO, 40% ZnO, 20% Al_2O_3	N/A	–	113	K3

[a] Converted to H-form at 450 °C for 3 h.
[b] Manufacturer's data: surface area (m^2/g catalyst), pore volume (ml/g catalyst).
[c] Zeolite nomenclature formula: zeolite (Si/Al); Z for ZSM-5 and Y for zeolite Y.