



Ion exchange resins as catalysts for the liquid-phase dehydration of 1-butanol to di-n-butyl ether



M.A. Pérez, R. Bringué, M. Iborra, J. Tejero*, F. Cunill

Department of Chemical Engineering, University of Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Spain

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ABSTRACT

This work reports the production of di-n-butyl ether (DNBE) by means of 1-butanol dehydration in the liquid phase on acidic ion-exchange resins. Dehydration experiments were performed at 150 °C and 40 bar on 13 styrene-codivinylbenzene ion exchangers of different morphology. By comparing 1-butanol conversions to DNBE and initial reaction rates it is concluded that oversulfonated resins are the most active catalysts for 1-butanol dehydration reaction whereas gel-type resins that swell significantly in the reaction medium as well as the macroporous thermostable resin Amberlyst 70 are the most selective to DNBE. The highest DNBE yield was achieved on Amberlyst 36. The influence of typical 1-butanol impurities on the dehydration reaction were also investigated showing that the presence of 2-methyl-1-propanol (isobutanol) enhances the formation of branched ethers such as 1-(1-methylpropoxy) butane and 1-(2-methylpropoxy) butane, whereas the presence of ethanol and acetone yields ethyl butyl ether and, to a much lesser extent, diethyl ether.

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1. Introduction

Dependence on fossil fuels has raised two main concerns: on one hand, the associated environmental effects; on the other, oil reserves limitation and future depletion. Given the severity of these threats the European Union has ruled increasingly stringent specifications for: (1) quality of petrol, diesel and gas-oil (Directive 2009/30/EC); (2) emissions from light passenger and commercial vehicles (Regulation EC 715/2007); and (3) promotion of the use of energy from renewable sources, setting a mandatory 10% minimum target to be achieved by all Member States for the share of biofuels in transport petrol and diesel consumption by 2020 (Directive 2009/28/EC).

Although very efficient, diesel engines have had difficulties achieving desirable emission targets, especially for soot and NO_x formation [1]. Reformulation of diesel fuel to include oxygenates has proven to be an effective way to provide satisfactory engine power and cleaner exhaust without modification of existing diesel engines [2–5].

A number of oxygenates have been considered as components for diesel fuel including various alcohols, ethers and esters. Alcohols have several drawbacks: high water solubility, which can cause phase separation problems; high Reid vapor pressure (RVP), which

may lead to the plugging of the fuel flow by increasing the vapor pressure; high volatility, which increases the volatile organic compounds emissions; high latent heat of vaporization, which raises cold start-up and drivability issues; and low heating value [6]. Vegetable oil methyl esters have a number of properties non suitable for diesel fuels such as higher boiling point, viscosity, and surface tension that may contribute to increase the NO_x emissions [7]. On the other hand, ethers show the best properties for diesel blends such as high cetane number, cold flow properties and mixture stability. In a comprehensive study on the blending properties of different oxygenates in diesel fuel, including monoethers, polyethers and esters, it was observed that linear monoethers with more than 9 carbon atoms showed the best balance among blending cetane number and cold flow properties which are measured by the Cloud Point (CP) and the Cold Filter Plugging Point (CFPP) [8]. Linear ethers have also shown to be effective in reducing diesel exhausts such as CO, particulate matter and unburned hydrocarbons and to substantially improve the trade-off between particulate and NO_x due to the presence of oxygen in the ether molecules [9].

It is quoted in the open literature that linear symmetrical ethers are produced by bimolecular dehydration of primary alcohols over acid catalysts [10,11]. Nowadays the main synthesis route of primary alcohols is based on the oxo process. It consists of selective hydroformylation and hydrogenation of linear olefins from fluid catalytic cracking in the presence of Rh and Co phosphines [12]. In this way 1-butanol is mainly produced by the oxo synthesis process of propylene in which aldehydes from propylene

* Corresponding author. Tel.: +34 93 402 1308; fax: +34 93 402 1291.
E-mail addresses: jtejero@ub.edu, tejero@angel.qui.ub.es (J. Tejero).

Nomenclature

AAS	amorphous aluminosilicate
ABE	acetone-butanol-ethanol
BET	Brunauer–Emmet–Teller
CFPP	cold filter plugging point
CP	cloud point
d_{pore}	mean pore diameter (nm)
EBE	ethyl butyl ether
DEE	di-ethyl ether
ISEC	inverse steric exclusion chromatography
DNBE	di-n-butyl ether
MSO	mesityl oxide
n_{DNBE}	mole number of di-n-butyl ether (mol)
RVP	Reid vapor pressure
r_{DNBE}^0	initial reaction rate (mol/(h kg of dry catalyst))
S_j	selectivity to product j
S_{area}	surface area determined from ISEC data (m ² /g)
S_{BET}	BET surface area (m ² /g)
S/DVB	styrene-divinylbenzene
t	time (h)
V_{pore}	pore volume (cm ³ /g)
V_{sp}	volume of the swollen polymer (cm ³ /g)
W_{cat}	catalyst mass (dried) (g)
WHSV	weight hourly space velocity (h ⁻¹)
X_{BuOH}	conversion of 1-butanol
Y_{DNBE}	yield of di-n-butyl ether

Subscripts

BuOBu'	1-(1-methylpropoxy) butane
BuOH	1-butanol
2-BuOH	2-butanol

Greek letters

θ	porosity (%)
ρ_s	skeletal density (g/cm ³)

hydroformylation are hydrogenated to yield 1-butanol. With this hydrogenation step 1-butanol is obtained jointly with 2-methyl-1-propanol (isobutanol) as byproduct. Afterwards, the bimolecular dehydration reaction of the primary alcohol gives the corresponding ether. Although superior alcohols can also be produced from biomass by condensation of bioethanol and/or biomethanol (Guerbet Catalysis) [13], this is still a developing technology which is not yet commercialized [14]. However, biomass fermentation by microorganisms of the genus Clostridium giving place to 1-butanol along with acetone and ethanol (Acetone Butanol Ethanol or ABE fermentation) is being performed on the industrial scale [15,16]. Thus, di-n-butyl ether can be considered a promising oxygenate to blend with diesel fuel as it keeps a good balance between cetane number and cold flow properties [17] and, in addition, it can be obtained from biomass and therefore, it could compete in the bio-fuel target.

Both an intermolecular dehydration (ether formation) and an intramolecular dehydration (olefin formation) may occur in the alcohol dehydration reaction. The prevailing pathway depends on the reaction conditions as well as the reactant and catalyst used. Solid acids such as zeolites [18], aluminum phosphates [19], amorphous aluminosilicates (AAS) [18], microporous niobium silicates [20], η -alumina [17], and heteropolyacids [21,22] have been tested as catalysts in the dehydration of 1-butanol. In the gas phase selectivity is highly dependent on conversion. Over AlPO_4 the dehydration of 1-butanol gives place mainly to butenes at 1-butanol conversions >75% (fixed-bed reactor, atmospheric

pressure, $T = 300^\circ\text{C}$), which suggests that the intramolecular dehydration of 1-butanol to 1-butene and the subsequent isomerization to trans-2-butene and cis-2-butene take place [19]. Butene was the major product for the dehydration reaction on AAS over the whole temperature tested (flow microreactor, 105–185 °C, 1 atm) [18]. At the same set-up and experimental conditions, selectivity to ether over H-ZSM-5 was higher than on AAS at about 2% alcohol conversion, but it decreased remarkably on increasing 1-butanol conversion [18]. In the dehydration of C_5 – C_{12} linear alcohols over η -alumina (fixed bed reactor, 250–350 °C, 0–4 MPa, $\text{WHSV} = 1$ – 4 h^{-1}) it was observed that temperatures as high as 300 °C were necessary to achieve over 60% conversion of 1-butanol; selectivity to ethers being lower than 30% [17]. Finally, 1-butanol dehydrated selectively to butenes over microporous niobium silicate as well (150–300 °C, 1 atm) [20]. On the contrary, the liquid phase etherification of 1-butanol to di-n-butyl ether has been studied on heteropolyacids with different heteroatoms (200 °C, 30 bars) showing that 1-butanol dehydrates selectively to di-n-butyl ether achieving over 80% ether selectivity with 1-butanol conversions ranging from 30 to 80% [22].

It is a well-known fact that acidic ion-exchange resins are highly selective catalysts to produce linear symmetrical ethers from n-alcohols, avoiding byproducts as olefins [23–26]. However, to the best of our knowledge the synthesis of di-n-butyl ether has not been reported on ion-exchangers. Thus, the aim of the present paper is to study the liquid-phase dehydration of 1-butanol to DNBE over ion-exchange resins of different morphology and discuss the relationship between resins properties and their catalytic behavior. Influence of typical 1-butanol impurities on 1-butanol dehydration reaction is also discussed.

2. Experimental

2.1. Chemicals

1-butanol ($\geq 99.4\%$ pure; $\leq 0.1\%$ butyl ether; $\leq 0.1\%$ water) and 2-methyl-1-propanol ($\geq 99.45\%$ pure; $\leq 0.05\%$ water) supplied by Acros Organics, acetone ($\geq 99.8\%$ pure; $\leq 0.2\%$ water) supplied by Fisher Chemical and ethanol ($\geq 99.8\%$ pure; $\leq 0.02\%$ water; $\leq 0.02\%$ methanol; $\leq 0.02\%$ 2-Butanol) supplied by Panreac were used as reactants.

DNBE ($\geq 99.0\%$ pure; $\leq 0.05\%$ water) supplied by Acros Organics, 1-butene ($\geq 99.0\%$ pure) supplied by Sigma–Aldrich, cis-2-butene ($\geq 98.0\%$ pure) supplied by TCI and bidistilled water were used for analysis purposes.

2.2. Catalysts

Tested catalysts were acidic styrene-codivinylbenzene ion exchange resins: the monosulfonated macroreticular ones Amberlyst 15, Amberlyst 16 and Amberlyst 39 (high, medium and low crosslinking degree, respectively); the oversulfonated macroreticular resins (in which the concentration of $-\text{HSO}_3$ groups has been increased beyond the usual limit of one group per benzene ring [27]) Amberlyst 35 (high crosslinking degree) and Amberlyst 36 (medium crosslinking degree) which are oversulfonated versions of Amberlyst 15 and Amberlyst 16 respectively; the chlorinated macroreticular resins Amberlyst 70 and CT482; the macroreticular resin sulfonated exclusively at the polymer surface Amberlyst 46; and the monosulfonated gel-type resins Dowex 50W \times 8, Dowex 50W \times 4, Amberlyst 31, Dowex 50W \times 2 and Amberlyst 121 containing from 8 to 2 DVB%. Short names and properties are given in Table 1.

It is well known that ion-exchange resins swell in polar media. As a result, morphology changes and non-permanent pores appear.

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