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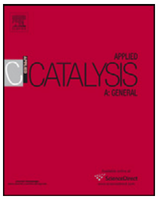

Synthesis of ethyl octyl ether from diethyl carbonate and 1-octanol over solid catalysts. A screening study

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ABSTRACT

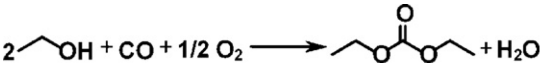
The synthesis of ethyl octyl ether (EOE) from a mixture of diethyl carbonate (DEC) and 1-octanol (1:2 molar ratio) over several solid catalysts was studied in batch mode at 150 °C and 25 bar. Catalyst screening revealed that EOE could be successfully obtained over some acid catalysts. In particular the highest yield was achieved over acid ion-exchange resins (33% after 8 h). A reaction scheme of the process is proposed. Selectivity to EOE was mainly affected by the production of diethyl ether (DEE) and di-n-octyl ether (DNOE). However, EOE was the main ether obtained (60 mol%), followed by DEE (20 mol%) and DNOE (20 mol%). By comparing the behavior of several acid resins, it was seen that the synthesis of EOE was highly related to the structural resin properties. It was found that the accessibility of DEC and 1-octanol to acid centers was improved over highly swollen and low polymer density resins. Thus, gel-type resins with low divinylbenzene content are the most suitable to produce EOE (e.g., Amberlyst 121, Dowex® 50Wx2-100 and CT224).

1. Introduction

In order to reduce the environmental impact of diesel exhaust emissions (particulate matter, unburned hydrocarbons, CO and NO_x), it is mandatory to improve the burning quality of diesel fuels [1,2]. The ideal diesel fuel for accomplishing this aim should be composed by linear paraffins with 10–20 carbon atoms, high cetane number and proper cold flow properties [3]. As a result, oil industry addresses its efforts to increase the yield in diesel cuts of refinery processes and thus commercialize better diesel fuel blends. A complementary strategy could be reformulating diesel fuels by including linear ethers [4–7]. Ethyl octyl ether (EOE) is an interesting candidate to be used in blends with commercial gasoil because of its properties: 10% oxygen content (w/w), 187 °C boiling point, d_4^{20} of 0.771, cetane number of 97 and satisfactory lubricity [8].

Industrially, it has been claimed that linear long chain ethers combined with peroxides as supplements to diesel fuels provide an environmental reduction of air pollutants. An amount of ethers about 1–5% (v/v) increased the cetane number from 2 to 20 points [1]. These ethers can be prepared by the traditional Williamson method from an alkoxide and alkyl halide [9]. However, dialkyl ethers are readily produced by acid catalyzed dehydration of alcohols more efficiently [10–12].

A green alkylation route to produce asymmetrical ethers is achieved with carbonates. Dimethyl carbonate has been proposed as methylating agent of several substances and reacts either as a methoxycarbonylating or as a methylating agent depending on the operation conditions [13]. In particular, the octanol alkylation from dimethyl carbonate clearly showed to be more efficient than using directly methanol [14]. As dimethyl carbonate, diethyl carbonate (DEC) is generally accepted as an environmentally benign ethylating agent [15–19]. An advantage of using DEC is that it can be obtained from ethanol (Eq. (1)). As a consequence, EOE would be a synthetic bio-fuel and could get the proper tax reduction, compensating partially their production costs higher than current commercial diesel.



(1)

A drawback to use alkyl carbonates is that their decomposition generates CO_2 as a by-product. However, the formation of carbonates from CO_2 is an interesting way for recycling it to fuels. Several advances in this direction have been reported and cyclic carbonate synthesis is already been industrialized [20–22]. Focused on linear carbonates, CO_2 reacts with alcohols in the presence of metal complexes (Eq. (2)). Due to the problems with the hydrolysis of the carbonate, 3 Å molecular sieves were used as drying agents to extract out the formed water. By using a dehydrative agent, an

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Nomenclature

DEC	diethyl carbonate
DEE	diethyl ether
DNOE	di-n-octyl ether
DOC	dioctyl carbonate
d_p	particle diameter (mm)
DVB	divinylbenzene
EOC	ethyl octyl carbonate
EOE	ethyl octyl ether
EtOH	ethanol
G	gel-type resin
$[H^+]$	acid capacity (meq/g)
$[H^+]/V_{sp}$	acid centers per volume unit in a swollen polymer state (meq H^+/cm^3)
ISEC	inverse steric exclusion chromatography
M	macroreticular resin
OcOH	1-octanol
$[OH^-]$	basic capacity (meq/g)
$R_{DEC/1\text{-}octanol}$	DEC to 1-octanol initial molar ratio (mol/mol)
S_{BET}	BET surface area in dry state (m^2/g)
S_{DEC}^{EOE}	selectivity to EOE with respect to DEC (%, mol/mol)
T	temperature (°C)
T_{max}	maximum operating temperature (°C)
V_{sp}	volume of the swollen polymer phase (cm^3/g)
W	mass of dry catalyst (g)
X_{DEC}	DEC conversion (%, mol/mol)
Y_{DEC}^{EOE}	yield to EOE with respect to DEC (%, mol/mol)

interesting dimethyl carbonate yield was achieved (55% based on MeOH) and byproducts were not significantly produced [23].

$$2\,R\text{-}OH + CO_2 \rightleftharpoons R\text{-}O\text{-}C(=O)\text{-}O\text{-}R + H_2O \quad (2)$$

Recently, EOE was synthesized successfully from ethanol and 1-octanol over acid gel-type resins at mild conditions ($T = 150\,°C$, $P = 20$ bar) [24]. In addition to EOE, diethyl ether (DEE) and di-n-octyl ether (DNOE) were detected as by-products. The differences between these ethers as diesel components are significant: DNOE has excellent properties to be blended with commercial diesel, whereas the high volatility of DEE is a serious drawback for its addition in large quantities to the diesel pool. Because acid resins easily catalyze the synthesis of short chain ethers, ethanol is preferred to be the limiting reactant in order to reduce DEE formation and to increase EOE production.

The present paper is devoted to study the liquid phase synthesis of EOE from DEC and 1-octanol over solid catalysts. A catalyst screening is carried out in order to select suitable catalysts for obtaining EOE. Moreover, the effect of the catalyst structure is related to DEC conversion and EOE yield.

2. Experimental

2.1. Materials

1-Octanol (≥99.5%, Fluka) and DEC (≥98%, Fluka) were used as reactants. Distilled water, ethanol (≥99.8%, Panreac), DEE (≥99%, Panreac), 1-octene (≥97%, Fluka) and DNOE (≥97%, Fluka) were used for analysis purposes. EOE was obtained and purified by rectification to 99% (w/w) in our lab.

Tested catalyst were supplied by Rohm and Haas (Amberlyst 26 OH, Amberlyst 21, Amberlyst 15, Amberlyst 35, Amberlyst 48, Amberlyst 46, Amberlyst 16, Amberlyst 36, Amberlyst 39, Amberlyst 70 and Amberlyst 121), Purolite (CT124 and CT224), Sigma (Dowex 50Wx8-100, Dowex 50Wx2-100, Nafion® NR 50, acid γ-Al_2O_3, basic γ-Al_2O_3) and Südchemie (H-BEA-25).

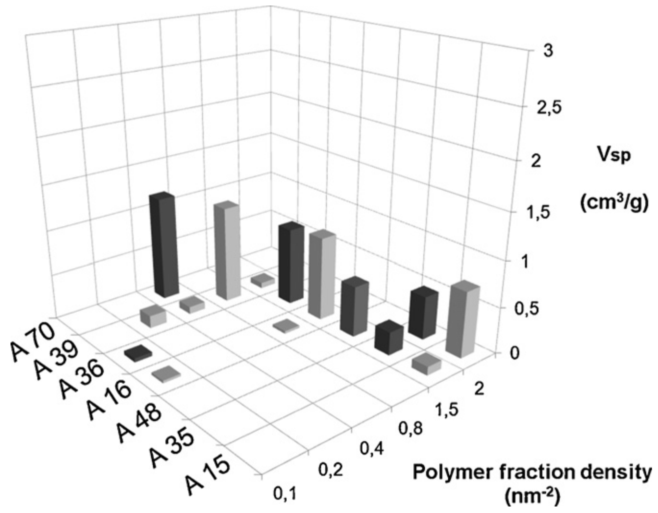

Fig. 1. ISEC pattern for used macroreticular resins.

A wide range of styrene-DVB resins were selected. In particular, a weak and a strong basic resins used in industrial processing were tested to check the behavior of basic catalysts (Table 1) [25]. Besides basic resins, 14 acid resins with different structural properties were tested (Table 2). Resins with low divinylbenzene (DVB) content are less crosslinked, and as a consequence with a more flexible structure. In the present work, the polarity of the reaction medium was high since 1-octanol was the main reactant and ethanol and water were obtained in significant amounts. Since ion-exchange resins swell in polar media, their morphology changes in the course of the reaction and non-permanent pores appear. A useful description of nature and characteristics of these pores in aqueous phase can be obtained from inverse steric exclusion chromatography (ISEC) data [12,26,27]. In macroreticular structures a part of new open spaces in the range of mesopores can be characterized by the cylindrical pore model. However, this model is not applicable to describe spaces between polymer chains formed as a result of polymer swelling. A good view of the three-dimensional network of swollen polymer is given by the geometrical model developed by Ogston [28], in which micropores are described by spaces between randomly oriented rigid rods. The characteristic parameter of this model is the specific volume of the swollen polymer (volume of the free space plus that occupied by the skeleton), V_{sp}. The Ogston model also allows to distinguish zones of swollen gel phase of different density or polymer chain concentration (total rod length per volume unit of swollen polymer, nm^{-2}) [26,29,30].

Distribution of the different polymer density zones of the swollen resins in water is shown in Figs. 1 (macroreticular) and 2 (gel-type). As seen, when the DVB resin content is high the polymer density is accordingly high, and V_{sp} values small. For instance, high crosslinked macroreticular resins such as Amberlyst 15 have a very high polymer density (1.5–$2\,nm^{-2}$) and V_{sp} of about $0.8\,cm^3/g$, being as a result poorly accessible polymer. On the contrary, a very low-crosslinked gel resin such as Amberlyst 121 has much more space between chains (density: 0.2–$0.8\,nm^{-2}$) and V_{sp} is about $3.3\,cm^3/g$. The pore distribution of the swollen gel phase in water is probably quite representative of the morphology of the catalyst in the reaction medium because the resin swelling in alcohols and water is comparable [12,26]. Thus, active centers in swollen state of low crosslinked gel-type resins are by far more accessible, and as a consequence the number of acid centers that could take part in the reaction is far higher.