Diethyl ether cracking and ethanol dehydration: Acid catalysis and reaction paths

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HIGHLIGHTS

- H-zeolites are more active than alumina and silica–alumina in ethanol dehydration.
- Reaction of ethoxy-groups with undissociated ethanol produces diethylether (DEE).
- H-zeolites, alumina and silica–alumina are active in DEE cracking and hydrolysis.
- Ethylene is produced by cracking of both DEE (low T) and ethoxy-groups (high T).

ABSTRACT

The catalytic conversion of ethanol and diethyl ether (DEE) was studied over alumina, zeolites MFI, FER and USY, silica–alumina and calcined hydrotalcite. Zeolites, alumina and silica–alumina are active in the temperature range 453–573 K for both ethanol dehydration to DEE and to ethylene and for DEE cracking and hydrolysis, producing back ethanol and ethylene. Protonic zeolites are more active than alumina which is slightly more active than silica–alumina for these reactions. Ethanol dehydration to DEE occurs selectively at lower temperature with a "bimolecular" mechanism involving reaction of ethoxy groups with undissociated ethanol. Ethanol dehydration to ethylene occurs selectively at relatively high temperature with an elimination mechanism via decomposition of ethoxy groups over these catalysts, but also occurs, at lower temperature, with a consecutive path via DEE formation and cracking.

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1. Introduction

In the frame of a future possible organic chemistry based on renewables, bioethanol coming from lignocellulosics could play an important role as a primary intermediate [1]. The production of ethylene from bioethanol as a secondary intermediate can allow the further synthesis of polyethylene and of a large number of tertiary intermediates, produced with the current petrochemical technologies, but arising from renewable feedstock. Ethanol can be converted into ethylene by catalytic dehydration:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad \Delta H_{298} = +44.9 \text{ kJ/mol} \quad (1)$$
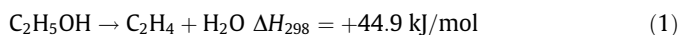
The reaction (1) is endothermic, but is largely favored thermodynamically already at moderate temperatures (e.g. 473–573 K). This reaction has indeed been applied at the industrial level in the sixties using aluminas as the catalysts [2,3]. On the other hand, a number of studies reported on the high catalytic activities

of different zeolite catalysts [4–7]. The literature in the field has been recently reviewed by Zhang and Yu [8], that concluded that zeolites might be unstable for this reaction. In contrast, Fan et al. judged they are applicable at the industrial level to produce ethylene from bioethanol [9].

Reaction (1) suffers somehow of the competition with the production of diethyl ether (DEE):

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \quad \Delta H_{298} = -25.1 \text{ kJ/mol} \quad (2)$$

which is exothermic, also favored at low or moderate temperature. Over most catalysts, reaction (2) occurs very selectively at low temperature and conversion while reaction (1) occurs at higher temperature and very high conversion. Different opinions are reported concerning the path involved in these reactions. The reaction (1) performed in the liquid phase with concentrated sulfuric acid as a catalyst at ca. 450 K is supposed to occur with a "monomolecular" mechanism, either with an E_2 (bimolecular elimination) concerted elimination mechanism, while reaction (2) occurring at lower temperature (410 K) is reported to occur with a S_N^2 (bimolecular nucleophilic substitution) bimolecular mechanism from a protonated

form of ethanol and an non-protonated one [10,11]. According to DFA (density functional analysis) computational studies, the E_2 mechanism should be the most favored also on alumina for reaction (1) [12]. Roca et al. working on silica alumina concluded that DEE and ethylene are produced by parallel reactions [13]. Also DeWilde et al. concluded that the bimolecular mechanism producing DEE and the unimolecular mechanism producing ethylene are parallel on alumina, both being inhibited by water [14]. According to these authors, two ethanol undissociatively adsorbed "dimer" species react together forming DEE, while ethylene is formed by decomposition of ethoxy- groups. Other authors believe that DEE can be formed by reaction of an adsorbed ethanol molecule with an ethoxide group [15] or of two ethoxide groups [16]. Several authors [12,17–22] also suggest that diethyl ether might be an intermediate in the dehydration of ethanol to ethylene.

The selective production of DEE can be of interest because it is in fact a considerable product of the chemical industry, mostly used as a solvent in a number of fine chemistry, fragrance and pharmaceutical chemical processes, and in some processes involved in explosives synthesis [23]. It finds also a number of applications in fuel chemistry [24] as an ignition improving additive in both diesel and gasoline engines according to its many useful properties: high volatility, cetane number higher than 125 [25] and octane number higher than 110 [26], reasonable energy density for on-board storage, high oxygen content, low auto-ignition temperature, broad flammability limits, and high miscibility in diesel fuel and bioethanol. Partial conversion of ethanol to DEE has been studied in order to increase volatility of ethanol to be applicable as a gasoline fuel also in cold start conditions [27]. Disadvantages include the same high volatility, propensity for peroxidation in storage, low lubricity and anesthetic effects [28].

Diethyl ether is currently either produced as a byproduct of ethanol synthesis by ethylene hydration processes [29] or by dehydration of (bio)ethanol either with sulfuric acid or in gas phase over alumina catalysts [30], thus forming a renewable chemical. The reverse reactions, i.e. the cracking of diethyl ether to ethylene and/or to ethanol can be of interest from several points of view: (i) to check the conclusion of some authors [17–20] that DEE acts as an intermediate in the ethylene synthesis from (bio)ethanol; (ii) to recover ethanol or/and ethylene from excess of DEE in the synthesis processes; (iii) to convert spent DEE into more useful products and to abate DEE vapors, which have some toxicity associated to its well-known anesthetic behavior; (iv) to model the conversion of natural and renewable substances containing ether bonds, such as e.g. lignin.

In the present paper, we will summarize the results of a screening study on the catalytic cracking of DEE, a correlation of the acido-basic properties of the catalysts with the catalytic behavior and some consideration on the reaction path concerning ethanol dehydration on acid catalysts.

2. Experimental

2.1. Catalysts

The properties of the catalysts, all commercial, are summarized in Table 1. SA is a commercial cracking catalyst of the silica–alumina type, MFI is a Si-rich form of H-ZSM-5 zeolite and USY (Ultra-Stable Y zeolite) is a dealuminated protonic faujasite. The composition of FER zeolite has a typical ferrierite composition.

2.2. Catalytic experiments

Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor (i.d. 6 mm) using 0.5 g catalyst (60–70 mesh sieved, thus with a ratio between the particle diameter and the internal reactor diameter near 25) and feeding 71.6% v/v diethyl ether (DEE) in nitrogen with 10.42 h^{-1} weight hourly space velocity (WHSV) (total flow rate of 40 cc/min), in the case of ethanol feeding 7.9% v/v ethanol in nitrogen with 1.43 h^{-1} WHSV (total flow rate of 80 cc/min). The carrier gas (nitrogen) was passed through a bubbler containing DEE (Carlo Erba, 99.9%) or ethanol (Sigma–Aldrich, 96%) maintained at constant temperature (298 K) in order to obtain the desired partial pressures. The temperature in the experiment was varied stepwise from 423 K to 723 K for DEE and from 373 K to 623 K for ethanol.

In order to have more information about mechanism, the experiments were performed at atmospheric pressure in a tubular flow reactor (i.d. 6 mm) using 0.5 g catalyst (60–70 mesh sieved) and feeding the mixture of ethanol + water + diethyl ether. An ethanol–water-diethyl ether single phase liquid solution was pumped through a HPLC pump (Shimadzu Corp. LC-D10 AD) in an appropriately heated (573 K) section of the feed line to produce a gas whose composition corresponds to molecular ratio of DEE:water:EtOH = 5:5:3 at atmospheric pressure and 298 K. The helium carrier gas of 67 cc/min will bring the gas mixture of DEE (5 cc/min) + H_2O (5 cc/min) + EtOH (3 cc/min) to the reactor and the reaction temperature was varied stepwise from 423 K to 673 K.

Reactant (R) conversion is defined as usual:

$$X_R = (n_{R(in)} - n_{R(out)})/n_{R(in)}$$

While selectivity to product i is defined as follows:

$$S_i = n_i/(v_i(n_{R(in)} - n_{R(out)}))$$

where n_i is the moles number of compound i, and v_i is the ratio of stoichiometric reaction coefficients.

The outlet gases were analyzed by a gas chromatograph (GC) Agilent 4890 equipped with a Varian capillary column "Molsieve 5A/Porabond A Tandem" and TCD and FID detectors in series. In order to identify the compounds of the outlet gases, a gas chromatography coupled with mass spectroscopy (GC–MS) Thermo Scientific with TG-SQC column (15 m × 0.25 mm × 0.25 μm) was used.

2.3. Infrared spectroscopy (IR) experiments

IR spectra were recorded using Nicolet 380 FT-IR spectrometer. Acidity measurements were done using the pure powders pressed into thin wafers and activated in the IR cell connected with a conventional outgassing/gas-manipulation apparatus at 773 K. The activated samples were contacted with pyridine vapor (p_{Py} ~1 torr) at room temperature for 15 min; after which the IR spectra of the surface species were collected in continuous evacuation at room temperature with increasing temperature.

In order to study the mechanism of reaction, pressed disks of the pure catalyst powders were activated *in situ* in the IR cell connected with a conventional gas-manipulation apparatus before any adsorption experiment. IR spectra of the surface species as well as of the gas phase were collected upon increasing temperature in static conditions (starting p_{EtOH} ~4 torr).

3. Results

3.1. Thermodynamic considerations

The composition of the system starting from pure ethanol at atmospheric pressure, as expected in conditions of thermodynamic control was calculated using the Soave–Redlich–Kwong (SRK) equation [31] and using HSC Chemistry 5.11 program (Fig. 1). Above ca. 400 K ethylene and water are the only products