

Dehydration of ethanol over zeolites, silica alumina and alumina: Lewis acidity, Brønsted acidity and confinement effects



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ABSTRACT

Ethanol dehydration was investigated over commercial H-FER, H-MFI, H-MOR, H-BEA, H-Y and H-USY zeolite samples, and alumina and silica alumina for comparison. The catalysts were characterized using FT-IR spectroscopy of the surface OH groups and of adsorbed CO and pyridine. UV-vis, Raman and TG-DTA were applied to characterize coke, formed more on H-MOR and H-BEA. H-zeolites are definitely more active than silica alumina and alumina on catalyst weight base. The H-MOR sample is the most active but the H-MFI samples with Si/Al₂ ratios 280 and 50 show higher reaction rates per Al ion, H-FER and faujasites show highest ethylene yield (99.9% at 573 K). At lower temperature and higher space velocities, diethyl ether is formed with high yield (>70% at 453–473 K on H-BEA and H-MFI (50)). Overconversion of ethylene mainly to aromatics is observed on H-MFI (50). The different behaviour of protonic zeolites can predominantly be explained by confinement effects on the different zeolite cavities.

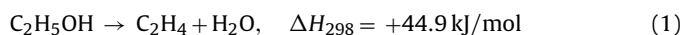
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1. Introduction

Ethylene is the main primary intermediate in petrochemistry: world production capacity exceeds 143,400,000 tpy [1]. Approximately 80% of the ethylene consumed in the USA, Western Europe and Japan is used for production of ethylene oxide, ethylene dichloride, linear low density and high-density polyethylene [2]. Presently, ethylene is produced commercially primarily by two processes: the steam cracking of hydrocarbon fractions performed in petrochemical complexes [3] and, to a lower extent, from the separation of refinery gas mainly obtained as a byproduct of fluid catalytic cracking (FCC) of heavy oils [4]. Both processes are high energy-intensive with large amounts of CO₂ green-house gas emissions.

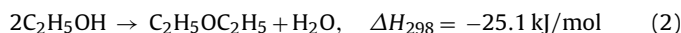
In the frame of a future possible organic chemistry based on renewables, a number of alternatives exist for ethylene manufacture. One of them is the MTO (methanol to olefins) process [5], supposing “biomethanol” (e.g. methanol produced using syn-gases arising from biomass gasification) is available. Alternatively,

bioethanol produced by lignocellulosics could be the primary intermediate to be converted into ethylene by catalytic dehydration:



Reaction (1) is endothermic, but is already largely favoured thermodynamically at moderate temperatures (e.g. 473–573 K). The dehydration of ethanol to ethylene has indeed been applied at the industrial level in the 1960s using aluminas as the catalysts [6,7]. Silica alumina is reported to be more active than alumina as an acid catalyst and also suggested for this reaction [8]. On the other hand, a number of studies reported on the high catalytic activities of different zeolite catalysts such as H-MFI, H-BEA, H-FAU, H-FER and H-MOR for ethanol dehydration [9–17]. The literature in the field has been recently reviewed by Zhang and Yu [18] that concluded that zeolites might be unstable for this reaction. In contrast, Fan et al. [19] judged they are applicable at the industrial level to produce ethylene from bioethanol.

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



which is exothermic thus also favoured at low or moderate temperature. A number of mechanistic studies performed with different techniques [20–25] were published concerning ethanol dehydration on zeolites with some disagreement between the respective conclusions.

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The dehydration of ethanol is also largely used as a test reaction for surface acido-basicity characterization [26–29]. The aim of this work is to investigate the feasibility of ethanol dehydration to ethylene over different Brønsted and Lewis acidic solids, such as zeolites, silica alumina and alumina, and complete [30,31] the picture of ethanol dehydration mechanisms and the nature of the acidity of catalytically active solids.

2. Experimental

2.1. Catalysts

Catalysts properties are summarized in Table 1. Commercial zeolites in the ammonium form were calcined at 773 K for 4 h to thermally decompose NH_4^+ to H^+ and $\text{NH}_3(\text{g})$.

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, to have a ratio between the particle diameter and the internal reactor diameter near 25) and 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 ethanol (96%) maintained at constant temperature (298 K) in order to obtain the desired partial pressures. The temperature in the experiment was varied stepwise from 373 to 623 K.

Ethanol conversion is defined as usual:

$$X_{\text{EtOH}} = (n_{\text{EtOH}(\text{in})} - n_{\text{EtOH}(\text{out})}) / n_{\text{EtOH}(\text{in})}$$

While selectivity to product i is defined as follows:

$$S_i = n_i / (v_i(n_{\text{EtOH}(\text{in})} - n_{\text{EtOH}(\text{out})}))$$

where n_i is the number of moles 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 ($15 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) was used.

2.3. Catalyst characterization

2.3.1. Infrared (IR) spectroscopy experiments

IR spectra were recorded using Nicolet 380 FT-IR spectrometers. Acidity measurements were taken using the pure powders pressed into thin wafers and activated in the IR cell connected with a conventional outgassing/gas-manipulation apparatus with outgassing at 773 K. The activated samples were contacted with pyridine vapour ($p_{\text{Py}} \sim 1 \text{ Torr}$) at room temperature for 15 min, when no further growth of the bands of adsorbed species was observed; after which the IR spectra of the surface species were collected in continuous evacuation at room temperature with increasing temperature. CO adsorption was performed at 130 K (real sample temperature measured by a thermocouple) by the introduction of a known dose of CO gas inside the low-temperature infrared cell containing the previously activated wafers. The sample was saturated with CO using sufficiently high CO pressure (up to 20 Torr), until the intensity of the adsorbed species had reached the maximum. IR spectra of the surface species were collected in continuous evacuation with increasing temperatures between 130 and 273 K.

2.3.2. TG-DTA experiments

TG-DTA (thermogravimetry-differential thermal analysis) experiments were performed using a TG-DSC Netzsch Gerätebau STA 409 (Germany), with a weight sensitivity of 0.1 mg and equipped with a Netzsch410 furnace temperature controller system. For each test, about 50 mg of the sample was placed in an alumina crucible of 6 mm in diameter and then introduced inside the furnace. All the samples were analyzed in the temperature interval 323–1073 K, with a nominal heating rate of 10 K/min in static air.

2.3.3. Raman spectroscopy analysis

Raman spectra were collected over 3–5 mg of catalysts at room temperature on Renishaw microscope, performing at least three analyses at different positions and reducing the exposure to air for avoiding coke oxidation in the case of spent catalysts. A laser of He–Ne was used at 632.8 nm focused on the sample by a microscope.

2.3.4. UV–vis spectroscopy analysis

UV–vis analyses were performed using a Jasco V570 instrument, equipped with a DR integration sphere for the analysis of spent catalysts powder. All the spectra were recorded in air at room temperature.

3. Results

3.1. Characterization of the surface acid sites

To have information on the nature of the active sites involved in ethanol conversion, surface acidity characterization studies were performed using IR spectroscopy. We used this technique to study surface hydroxyl groups and we used molecular probes to test acidity. In our previous work [30], we remarked that the use of very weak bases (such as CO) only, as probes, might not be appropriate in this case because of their much lower reactivity and much higher volatility with respect to the reactant molecule ethanol. The use of the less volatile and stronger base pyridine may give more reliable results. Thus, we used here both probes to characterize the catalyst surfaces.

3.1.1. IR study of the surface hydroxyl groups

The IR spectra of the OH hydroxyl groups (OHs) of zeolites are presented in Fig. 1. All zeolites show a sharp OH stretching band (νOH) at ca. $3740\text{--}3730 \text{ cm}^{-1}$, which is attributed to the weakly acidic terminal silanol groups located on the external surface [32]. One or more bands in the range $3650\text{--}3500 \text{ cm}^{-1}$ are also found, attributed to the bridging Si–OH–Al groups that are exclusively on the inner surface and possess a strong Brønsted acidity [32]. In the spectrum of our H-BEA sample, the intensity of the νOH band of bridging Si–OH–Al groups is very weak at 3605 cm^{-1} , while in the spectra of H-FER, H-MFI and H-MOR it is well evident in the range near $3600 \pm 10 \text{ cm}^{-1}$. The spectra agree with those recorded in previous studies [32–34]. The two faujasite zeolites were the object of previous studies [35,36]. The spectrum of the catalyst H-USY clearly shows two OH stretching bands due to bridging hydroxyl groups at 3627 and 3563 cm^{-1} : the high-frequency (HF) band is due to OH groups located in the supercages (3627 cm^{-1}) and the low-frequency (LF) band to OH groups located in the sodalite cages (3563 cm^{-1}). Their low-frequency shoulders, we observe near 3600 and 3550 cm^{-1} , were assigned to HF and LF species, respectively, interacting with residual extra framework (EF) species [37]. The spectrum of sample H-Y shows an additional split band at 3689 and 3678 cm^{-1} , in the region usually assigned to OH groups located on EF material, together with the band at 3606 cm^{-1} , possibly with several components, in the region of zeolitic hydroxyl groups. This

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