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Title: DIETHYL ETHER CRACKING AND ETHANOL DEHYDRATION: ACID CATALYSIS AND REACTION PATHS

Article Type: Research Paper

Keywords: Ethanol dehydration; reaction path; diethylether; ethylene; zeolites; alumina.

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Abstract: The catalytic conversion of ethanol and diethyl ether 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 a "monomolecular" mechanism via decomposition of ethoxy groups over these catalysts, but also occurs, at lower temperature, with a consecutive path via DEE formation and cracking.

Response to Reviewers: Ms. Ref. No.: CEJ-D-14-06431
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Chemical Engineering Journal
Reviewers' comments:

Reviewer #2: This is an interesting work which provides new insights in the ethanol transformations over acidic solids. The work is clear and well structured; I recommend its publication in the Chemical Engineering Journal after properly minor revision. Specific comments follow below:

Results section, first page
-lines 25-29; please rewrite these sentences. Acids sites are not observed, the bands are observed and attributed to the presence of acid sites.
Rewritten

-lines 51-53; the values given are not the catalytic activity, they are values of ethanol conversion
Text modified

IR experiments:

- Bands appearing at high wavenumbers (3300-2800) are shown in the figures, but they are not commented in the text; the characteristic bands of ethylene gas are not given.
The bands in the CH region have been now cited. Their detailed discussion may be heavy and not strictly necessary in our opinion, although they confirm the assignment of the other bands.

3.5 section "Catalytic conversion of diethyl ether"
-lines 7-9; please avoid "the catalytic activity of DEE" and "the catalytic activity trend" if the values given are those of DEE conversion.
Text modified

3.6 section "Conversion of ethanol+DEE+water mixtures"
-lines 35-37; please, rewrite last sentence.
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Figures
- Figure captions must be improved for facilitating the comprehension of the reader. Specifically, please pay special attention to those of Figures 6 and 7. : Done
- Figures must be improved, specifically:
- formulae in figure 1,: Done
- text in Figure 2, : Done
- in the FTIR spectra (Figures 4 and 5), the wavenumber which are indicated should be marked using lines for a better visualization of the bands Done
- in figure 6 clarify what is plotted on the Y axis: Done
- in Figure 7 revise the Y axis notation: Done

Other points:
- In the chemical equations put the "g" of gas phase into parentheses (g). :Done
- Table 2: avoid TC (total conversion), put instead ethanol conversion.: Done

Reviewer #3: This manuscript discusses ethanol dehydration and diethyl ether cracking using various catalysts. Although the discussion is interesting, I strongly suggest the authors address the following issues in order for the manuscript to be published:

1 - The English needs revision and I would suggest a native speaker of English do it;
The text has been reconsidered and, hopefully, English improved.

2 - There are many acronyms that were not described from start to finish;
The acronyms are all described, now

3 - I think readers would like to see schemes, charts or any other form of visual representation, especially to better explain reaction mechanisms, kinetics and the experimental setup. Also, I think the cromatograms would provide support to table 2;
To make visual representation better we put figures instead of Table 2, which has been displaced in the supplementary material. We also added a scheme representing reaction mechanism

4 - Very little attention was paid to thermodynamics. I think the read would be more interesting if the author had provided more details on this subject;
Thermodynamic data were discussed in some pertinent points.

5 - A much better review of literature is needed.
The literature on the subject is large. We cited recent reviews where further literature can be found. We also added some more references.

Dear Editor,

please find attached the revised manuscript entitled:

DIETHYL ETHER CRACKING AND ETHANOL DEHYDRATION: ACID CATALYSIS AND REACTION PATHS

by Thanh Khoa Phung and Guido Busca

modified according to the revieewrs suggestions. We hope it can now be accepted for publication in the Chemical Engineering Journal.

Many thanks in advance for the collaboration.

Sincerely yours,
Guido Busca

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***Highlights (for review)**

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)

DIETHYL ETHER CRACKING AND ETHANOL DEHYDRATION: ACID CATALYSIS AND REACTION PATHS

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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 a “monomolecular” mechanism via decomposition of ethoxy groups over these catalysts, but also occurs, at lower temperature, with a consecutive path via DEE formation and cracking.

1. Introduction

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

$C_2H_5OH \rightarrow C_2H_4 + H_2O$ $\qquad \Delta H_{298} = + 44.9$ kJ/mol $\qquad$ (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 [4,5,6,7]. 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)

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

which is exothermic, also favoured 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 sulphuric 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 favoured also on alumina for reaction (1) [12]. Roca et al. working on ~~Silica~~ 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 [12,17,18,19,20,21,22] also suggest that diethyl ether might be an intermediate in the dehydration of ethanol to ethylene.

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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 sulphuric 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 [17,18,19,20] 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 vapours, ~~that~~ 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 ~~on~~ 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~~ 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 (573K) 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:

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

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 x 0.25 mm x 0.25 μm) was used.

2.3 Infrared spectroscopy (IR) experiments

IR spectra were recorded using Nicolet 380 FT-IR spectrometer~~s~~. 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}~~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 expected, while below 330K diethyl ether and water are the most abundant products. DEE is more abundant than ethanol also in the range 330-400 K. Thus reaction (1) is the most favoured above 400 K while reaction (2) is the most favoured below 400 K.

3.2 Catalyst surface acidity characterization by IR spectroscopy of adsorption of pyridine.

The surface acidity of the catalysts was characterized by IR spectroscopy of pyridine adsorption (Fig. 2). Over all catalysts bands at ca. 1602-1625, 1575, 1489 and 1440-1460 cm^{-1} are observed, due to the 8a, 8b, 19a and 19b modes of molecular pyridine [32], respectively. As it is well-known, the position of the 8a and 19b modes is indicative of the strength of the Lewis acid sites to which pyridine is coordinated. ~~Strong~~ Bands due to pyridine bonded to strong Lewis acid sites (ν8a ca. 1622 cm^{-1}, ν19b > 1455 cm^{-1}) of the Al^{3+} type are well evident over A, SA and USY. Bands due to pyridine bonded to v~~V~~ery weak Lewis sites (ν8a ca. 1602 cm^{-1}) are observed on MgA while bands due to pyridine bonded to Lewis sites are not detected on MFI zeolite. Additional bands attributed to pyridinium ions (ν8a ca. 1635 cm^{-1}, ν19a at 1550-1535 cm^{-1}) are observed in the spectra of ~~on~~ the zeolites as well as of~~n~~ SA, showing that these catalysts also ~~show~~ have Brønsted acid sites [~~33~~7]. The experiment concerning the FER zeolite is not reported because it is not really significant. In fact pyridine cannot enter in these conditions into the small cavities of ferrierite. Thus adsorbed pyridine only reveals external acidity in this case. Previous studies using smaller probe molecules such as acetonitrile showed the presence of strong Brønsted sites with some Lewis site also on the cavities of FER zeolite [34].

3.3 Catalytic conversion of ethanol

The results of catalytic conversion experiments of ethanol over the catalysts under study ~~is~~ are summarized in Fig. 3. The ~~catalytic activity in converting~~ conversion of ethanol shows the following trend, e.g. at 473 K: FER (70.0%) > USY (62.9 %) > MFI (44.4 %) > A (20.8 %) > SA (15.7 %) > MgA (0.1 %). This trend shows that zeolites are the most active in converting ethanol, ~~which is attributed~~due to their strong Brønsted acidity. A and SA catalysts have similar activity, attributed to Lewis acidity [35]. The very weakly acidic material MgA is very poorly active. In all cases, at low conversion, DEE is the largely predominant product, while at higher temperature and conversion, ethylene becomes the predominant product. However, on MgA a relevant amount of products different from ethylene and DEE is formed. They are mainly acetaldehyde and other carbonyl products providing evidence of the basic character of this catalyst.

To have more information, we performed ethanol conversion experiments by varying the contact time. The data on MFI are discussed here, because this catalyst was found to be a purely Brønsted acidic one. The ethanol conversion rate on MFI definitely depends on contact time, as shown in ~~Table 2~~Fig. 4, i.e. the lower the space velocity (SV), the greater the conversion, as expected indeed. The data are reported as Table 2 in the supplementary material. On the other hand, the DEE selectivity clearly has a reverse trend. At lower space velocities the DEE selectivity drops in favour of ethylene selectivity. To look deeper at this we considered the selectivities at the same conversion, at different SV and temperature. As for example, at conversions in the range 81-83 %, the selectivity to DEE drops from 43.6 % to 8.1 % when temperature is increased from 523 to 573 K in spite of the simultaneous strong increase in space velocity from 0.72 to 7.0 h^{-1}. This shows that reaction temperature has definitely a stronger effect, at high conversion levels, to favour ethylene selectivity, than conversion itself, i.e. ethanol partial pressure. Thus the effect of the different activation energy of reaction (1) and (2) may be a discriminant factor.

At low space velocity and high temperature and conversion, ethylene selectivity is lowered by the production of higher hydrocarbons (~~Tab. 2~~Fig. 4). However, selectivities to higher hydrocarbons tend to vanish by increasing space velocity in favour of ethylene and even DEE selectivity, showing that these higher hydrocarbons are formed by over-conversion of ethylene.

Similar experiments were performed by varying space velocity on alumina, a purely Lewis acidic catalyst, with parallel results. In particular, also on alumina at lower space velocities the DEE selectivity drops in favour of ethylene selectivity.

3.4 Catalytic conversion of ethanol on alumina: IR experiments.

IR experiments of ethanol adsorption and conversion were performed in order to have further information. The experiments performed on alumina (Fig. 5~~4~~) show that ethanol adsorbs mainly in the form of ethoxy- groups, characterized mainly by the strong νC-O/νC-C bands at 1116 and 1073 cm^{-1}, together with the CH deformation modes at 1450 and 1390 cm^{-1} and CH stretchings in the region 3000-2800 cm^{-1}. Small amounts of adsorbed undissociated ethanol (δCOH band at 1278 cm^{-1}, νC-O/νC-C band at 1054 cm^{-1}) are also found. The spectra reported in Fig. 5~~4~~ are those of the gas phase and of the adsorbed species detected after "saturating" the alumina surface with ethanol at ~~r.t.~~room temperature and short evacuation of the line. After, temperature was progressively increased in static conditions. By heating up to at 423 K some ethanol is released in the gas phase (bands at 1240 and 1066 cm^{-1}), while correspondingly the bands of undissociated adsorbed ethanol disappear. The bands of ethoxide species are essentially unchanged, thus showing that dissociative adsorption of ethanol is essentially irreversible in these conditions. Gas phase diethyl ether (νC-O/νC-C band at 1142 cm^{-1}) is formed essentially in the step between 473 and 523 K, during which only traces of ethylene also form (CH$_2$ wagging mode at 949 cm^{-1}). It seems interesting to remark that upon this step the bands of ethoxy groups decrease significantly in intensity, and gas phase ethanol decreases significantly but not entirely. This clearly shows that ethoxy groups are indeed involved in the formation of DEE, and probably gas phase ethanol too. It seems also of interest to remark that adsorbed DEE is not found. Indeed parallel experiments, according to previous data [36], show that DEE adsorption is very weak, complete desorption being obtained by outgassing even at room temperature.

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In the following step between 523 and 573 K, ~~instead,~~ DEE gas disappears completely, and surface ethoxides too, almost completely. Also gas phase ethanol is no more observed, only ethylene being produced in big amounts (νCH$_2$s at 3106 and 2988 cm^{-1}, wCH$_2$ at 949 cm^{-1}). The IR experiments, formally consisting of steps at very long contact time, provide evidence of the strong effect of temperature on the reaction steps. It can be concluded that, in the step up to 473 K, the only phenomenon is the essentially irreversible adsorption and saturation of the surface with ethanol. In the range 473 ~~K~~ - 523 K the only fast reaction is the synthesis of DEE implying reaction of ethoxide species together with gas~~-~~ phase or weakly adsorbed ethanol. In spite of the very prolonged contact time, ethylene is essentially not formed. In the range 523 – 573 K both DEE cracking and ethoxy-group cracking become apparently fast, producing gas phase ethylene.

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Similar experiments were performed with zeolite catalysts. The data obtained with FER are reported in Fig. ~~5~~6. The IR spectra of the adsorbed species closely correspond to those reported for H-mordenite by Kondo et al. [37] and attributed to a bridging ethoxy- group. The features of this alkoxy- species disappear in the 473-523 K range, when ethylene is produced as the only product. At lower temperature, alkoxy- groups coexist with gas phase ethanol and very small amounts of physisorbed ethanol. In this range, some DEE is formed in the gas phase ~~and no~~while ethylene is not observed. These results support the idea that both on alumina and on FER, ethoxy- groups have two reactions paths: in the presence of gaseous or adsorbed ethanol, ethoxy- groups participate to the reaction producing DEE~~,~~; when gas phase ethanol is no more available and at higher temperature, ethoxy- groups crack to ethylene.

3.5 Catalytic conversion of diethyl ether.

In Fig. 7~~6~~, the data concerning the ~~catalytic activity of~~ DEE conversion over the investigated catalysts, are summarized. The ~~catalytic activity~~conversion trend is, e.g. at 573 K, ~~is~~ MFI (98.3 %) > USY (83.8 %) > A (55.9 %) > SA (52.1 %) > MgA (0.1 %). Also in this case zeolites are evidently very active, while alumina and silica alumina have the diethyl ether conversion again similar but lower activity, and MgA has very low activity, confirming a scale based on acid strength governing the catalytic activity. Taking into account the apparent activity inversion between MFI and USY, it must be remarked that the activity of MFI is higher than that of USY also in ethanol dehydration at temperature lower than 473 K.

Looking at the product yield of DEE decomposition, the main compounds are ethylene and ethanol, in a ratio not far from 1:1 within experimental error, in the low temperature range. This suggests that the reaction observed is

$$C_2H_5OC_2H_5 \rightarrow C_2H_4 + C_2H_5OH \qquad (3)$$

A slight excess of ethanol with respect to ethylene could also be explained by the DEE hydrolysis reaction:

$$C_2H_5OC_2H_5 + H_2O \rightarrow 2C_2H_5OH \qquad (4)$$

i.e. the inverse of reaction (2), taking into account that the DEE feed contains also small amounts of water. In fact alumina has been patented years ago as an excellent catalyst for reaction (4) [38].

At higher temperature, ethanol disappears among the products, showing that reaction (3) (DEE cracking) is followed by ethanol dehydration (reaction (1)). Thus DEE cracking can be performed producing ethylene with high yields. At high conversion, ethylene yields are lowered by the coproduction of ethane and higher hydrocarbons. As observed also upon ethanol dehydration, MFI zeolite can produce relevant amounts of aromatics thus significantly decreasing ethylene yields (from < 90 % to < 75%). Also on alumina significant amounts of byproducts are obtained thus limiting ethylene yield to 91-93 %. Higher yields to ethylene are obtained on USY (96.8 % at 623 K) and on silica-alumina (> 97 % at > 673 K).

It is actually relevant to remark that the temperature range for the start of DEE cracking reaction (3) ~~is that when~~corresponds to the temperature range where ethanol conversion to DEE (reaction (2)) is already significant and is starting to decline in favour of reaction (1) ~~when~~ with ethanol ~~is~~ feed. This suggests that reaction (3) can indeed be in sequence with reaction (2), producing reaction (1) with a consecutive path. However, it can be remarked that the feed was used in these DEE conversion experiments was definitely more concentrated than the feed was used in ethanol conversion experiments.

3.6 Conversion of ethanol+DEE+water mixtures.

Another set of experiments was performed feeding a mixture of ethanol, DEE and water with a similar molar concentration used in ethanol conversion experiments (Fig. 8). Over alumina at 473 K, DEE and water are consumed and ethanol is formed, while ethylene is not observed. This indicates that, at this low temperature, alumina catalyses DEE hydrolysis (4), i.e. the inverse of reaction (2). As said, alumina has been patented years ago as an excellent catalyst for reaction (4) [38]. At 523 K, instead, the conversions of both DEE and water vanish and also ethanol conversion is near zero. This suggests that in these conditions reactions (2) and (4) very likely ~~equilibrate~~balance. At 573 K ethylene and water and some ethanol are produced, at the expense of DEE conversion. This shows that reactions (3) and (4) start. At 673 K, conversion of both DEE and ethanol is complete with ethylene and water being the only products.

On MFI, ethanol conversion is higher than DEE conversion at 473 K, but is lower at 523 K, both producing ethylene only. Both are almost fully converted starting from 573 K. These data strongly support the idea that DEE can be intermediate in the ethanol dehydration reaction into ethylene: in fact, ~~formation,~~ ~~being indeed~~ DEE ~~cracked~~ cracks together with ethanol to form ethylene.

4 Discussion

The data described above show that over acidic catalysts both ethanol dehydration and DEE cracking are catalysed efficiently. Zeolites are more active than alumina and silica-alumina in both cases, and silica-alumina is slightly less active than alumina in both reactions. Characterization data indicate, as it is well-~~-~~known indeed, that zeolites are strong Brønsted acid catalysts while alumina mostly acts as a Lewis acid catalyst. The behaviour of silica-alumina supports the idea that this material, although characterized also by Brønsted acidity sufficiently strong to protonate pyridine, likely works as a Lewis acid in these reactions. The comparison of the behaviour of silica-alumina with that of the MFI sample~~s~~, characterized by a very low amount of Al and, thus, of Brønsted sites, further confirms that the active sites on silica-alumina are different than those of zeolites: in fact, the different behaviour of MFI and silica-alumina cannot be attributed to the lower concentration of the same sites on SA.

The weakly acidic, or predominantly basic catalyst MgA (calcined hydrotalcite) is weakly active in both reactions, confirming the role of acid sites for them.

Upon ethanol conversion on all acidic catalysts, dehydration to DEE occurs with high selectivity at low temperature and conversion, while the reaction to ethylene occurs at higher temperature and conversion. Thermodynamic calculations indicate that, even in the conditions where DEE is formed with high selectivities, ethylene formation is thermodynamically far more favoured. Thus thermodynamics is not controlling the product selectivity. In those conditions, the evaluation of the apparent activation energies in our experiments at low conversion (> 80 kJ/mol) reveals that the kinetic control is certainly chemical.

This result (DEE formation at low temperature and conversion; and ethylene formation at higher temperature and conversion) was observed also on less active and selective catalysts, but shifted to higher temperatures due to the lower activity of the catalysts. In these cases other compounds such as acetaldehyde, ethane and higher hydrocarbons may also be formed with significant selectivities [39].

Thus, the catalytic experiments show that at low temperature and conversion the reaction occurring in all cases with almost total selectivity is the dehydration of ethanol to DEE, reaction (2). This shows that, in these low temperature conditions, reaction (2) is much faster than reaction (1). At high temperature and conversion, instead, the reaction observed, also with high and almost total selectivity, is the dehydration of ethanol to ethylene (reaction (1)).

IR spectroscopy data confirm the central role of ethoxy groups both on alumina and on zeolites, both for producing DEE at low temperature and for producing ethylene at high temperature, in contrast with the conclusions of other authors [14,40].

As discussed previously [35~~35~~~~33~~], on alumina the formation of ethoxy groups occurs with two parallel mechanisms:

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a) Dissociative adsorption on Lewis acid-base couples

$C_2H_5OH_{(g)} + Al^{3+} + O^{2-} \rightarrow C_2H_5O^- Al^{3+} + OH\cancel{O}^-$ (5)

b) Exchange reaction on surface hydroxy groups

$C_2H_5OH_{(g)} + Al^{3+} OH^- \leftrightarrows C_2H_5O^- Al^{3+} + H_2O_{(g)}$ (6)

Both adsorption mechanisms undergo competition by the presence of water vapour. In fact, the latter is an invertible equilibrium being the acido-basic and volatility properties of water comparable to those of ethanol. The former competes with the dissociative adsorption of water on the same acid-base couples:

$H_2O_{(g)} + Al^{3+} + O^{2-} \rightarrow HO^- Al^{3+} + OH\cancel{O}^-$ (7)

The inhibition of ethanol conversion by water does not need the existence of “dimeric” forms, supposed by other authors [14]. Ethoxy groups are stable on alumina below ca. 450-473 K. Starting from this temperature DEE is produced with very high selectivity and ethoxy groups are concomitantly consumed. This step is likely the following:

$C_2H_5O^- Al^{3+} + C_2H_5OH \leftrightarrows (C_2H_5)_2O_{(g)} + Al^{3+} OH^-$ (8)

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with only very small traces of ethylene coproduced. As confirmed by IR adsorption experiments, the adsorption of DEE is very weak and it easily desorbs. When ethanol gas is not more available and the temperature is higher, ethoxy groups decompose to gas phase ethylene and an hydroxyl group

$C_2H_5O^- Al^{3+} \rightarrow Al^{3+} OH^- + H_2C{=}CH_{2(g)}$ (9)

Ethylene adsorption ~~too~~ is very weak on alumina, thus desorbing easily in the gas phase.

The DEE cracking reaction may likely occur either starting from the reverse of reaction (8) or by decomposition over acid-base couples:

$(C_2H_5)_2O_{(g)} + Al^{3+} + O^{2-} \rightarrow (C_2H_5O^-)_2Al^{3+}$ (10)

followed by reaction (9) and by the reverse of reaction (5).

On zeolites the mechanisms are similar although the ethoxide group has a different geometry and is formed only by the exchange reaction

$C_2H_5OH_{(g)} + Si(OH^-)Al \leftrightarrows Si(C_2H_5O^-)Al + H_2O_{(g)}$ (11)

Some authors suppose that reactions (1) and (2) are parallel [13,14,40] but few studies suggest that ethylene can be produced by a consecutive mechanism with reaction (2) followed by DEE cracking (reaction (3)) [12,17,18]. Our data suggest that indeed both conclusions can be right. In fact, DEE cracking reaction (3) is fast over zeolite, alumina and silica-alumina catalysts in the conditions where DEE is formed by reaction (2). On the other hand, in agreement with several studies, the direct way to ethylene via an elimination reaction of ethoxide species is well substantiated to occur at high temperature over both alumina and zeolites by spectroscopic experiments, and by literature data.

We may mention that reaction (1) is expected to have a low reaction order with respect to ethanol~~,~~ (from one to negative depending on the ratio between adsorption strength and rate of surface reaction), while reaction (2) may have a larger reaction order (up to two) due to the need of two ethanol molecules to react together. This may justify an effect of ethanol concentration, and consequently of ethanol conversion, on the two reactions, favoring reaction (2) at high concentration and/or low conversion and reaction (1) at lower concentration and higher conversion. In agreement with this, Chiang and Bahn [40] found a positive reaction order of DEE formation with respect to ethanol on different zeolites, and a negative reaction order for ethylene formation from ethanol on H-MOR.

On the other hand, reaction (1), supposed to occur as a decomposition of ethoxy species, could have higher activation energy than reaction (2), thus also justifying it to become faster only at higher temperatures. In fact our data support the idea that dehydration to ethylene occurs with two paths, the direct one (through ethoxy groups cracking) and the consecutive one composed of formation of DEE by reaction of an ethoxy group with undissociated ethanol and successive cracking of DEE on the acid sites.

In summary, a likely reaction path on alumina catalyst is summarized in Scheme 1. Taking into account that water is a product of reactions 1 and 2 and that reaction temperature is low, it can be supposed that the surface is largely hydroxylated. Thus the active site can be supposed to be constituted by active hydroxyl groups as discussed previously [35]. Thus the first step, denoted as step A in scheme 1, corresponds to reaction (6), producing ethoxy groups with desorption of water. Later, step B in the scheme gives rise to ethylene through a substantially irreversible elimination mechanism (reaction (9)). As a parallel way, in step C reaction with gas phase ethanol gives rise to diethyl ether in a reversible way. In fact, diethyl ether adsorption can crack with the sequence step –C, step –B producing ethylene too. As said, step B is faster than step C at high temperature and conversion while the reverse is true at lower temperature and conversion. In the case of zeolite catalyst, the scheme of ethanol decomposition is essentially the same.

4. Conclusions

The main conclusions from these data are the following:

1. Acidic catalysts like 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.
2. Protonic zeolites are more active than alumina which is slightly more active than silica-alumina for these reactions. It is confirmed that the active sites of silica-alumina are different and less active than those of protonic zeolites.
3. Ethanol dehydration to DEE occurs selectively at lower temperature with a “bimolecular” mechanism involving reaction of ethoxy groups with unidssociated ethanol.
4. Ethanol dehydration to ethylene occurs selectively at relatively high temperature with an elimination ~~“monomolecular”~~ mechanism via decomposition of ethoxy groups over these catalysts.
5. Ethanol dehydration to ethylene occurs also at lower temperature with a consecutive path via DEE formation and cracking.

Acknowledgements

TKP acknowledges funding by EMMA (Erasmus Mundus Mobility with Asia) in the framework of the EU Erasmus Mundus Action 2. The collaboration of Dr. G. Garbarino for catalytic experiments is acknowledged.

Table 1. The properties of investigated catalysts

Notation	Phase	Composition	Commercial name	Manufacturer	Preparation	S_{BET}[a]
MgA	Calcined hydrotalcite	MgO/Al_2O_3 wt%70:30	Pural MG70	Sasol	calcined at 773 K for 4h	195±10[b]
A	alumina	Al_2O_3	Puralox SBa 200	Sasol	as received	190±10
SA	Silica-alumina	SiO_2- $Al_2O_3$13% wt Al_2O_3	Cracking catalyst	Strem Chemical	as received	330±10
FER	H-ferrierite	SiO_2/Al_2O_3 mol 20	CP 914C	Zeolyst	calcined at 773 K, 4h	400
MFI	H-ZSM-5	SiO_2/Al_2O_3 mol 280	CBV 28014	Zeolyst	calcined at 773 K, 4h	400
USY	H-faujasite	SiO_2/Al_2O_3 mol 30	CBV 720	Zeolyst	as received	780

[a] from manufacturer, [b]BET measurement

~~**Table 2.** Conversion (on C-basis) and selectivity (S) to C-containing products of ethanol over MFI at different space velocities (SV)~~

~~SV~~	~~Temp. (K)~~	~~TC~~[a]Ethanol conversion	~~$S(C_2H_5)_2O$~~	~~SC_2H_4~~	~~$SC_3^=$~~	~~ΣC_4~~	~~ΣC_5~~	~~Others~~[b~~a~~]
~~0.72 h^{-1} WHSV~~	~~373~~	~~0.3~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~393~~	~~1.0~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~413~~	~~3.8~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~433~~	~~12.9~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~453~~	~~31.0~~	~~99.5~~	~~0.5~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~473~~	~~53.1~~	~~98.7~~	~~1.3~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~523~~	~~81.1~~	~~43.6~~	~~56.0~~	~~0.0~~	~~0.4~~	~~0.0~~	~~0.0~~
	~~573~~	~~100.0~~	~~0.0~~	~~96.4~~	~~1.2~~	~~1.3~~	~~0.6~~	~~0.4~~
	~~623~~	~~100.0~~	~~0.0~~	~~97.3~~	~~1.3~~	~~0.8~~	~~0.5~~	~~0.1~~
~~1.43 h^{-1} WHSV~~	~~373~~	~~0.2~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~393~~	~~0.5~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~413~~	~~4.6~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~433~~	~~10.3~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~453~~	~~21.6~~	~~99.8~~	~~0.2~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~473~~	~~44.4~~	~~99.3~~	~~0.7~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~523~~	~~76.9~~	~~73.3~~	~~26.7~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~573~~	~~100.0~~	~~0.0~~	~~98.9~~	~~0.5~~	~~0.0~~	~~0.3~~	~~0.3~~
	~~623~~	~~100.0~~	~~0.0~~	~~99.0~~	~~0.6~~	~~0.0~~	~~0.3~~	~~0.1~~
~~7 h^{-1} WHSV~~	~~373~~	~~0.0~~	~~-~~	~~-~~	~~-~~	~~-~~	~~-~~	~~-~~
	~~393~~	~~0.2~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~413~~	~~0.3~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~433~~	~~1.3~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~453~~	~~4.2~~	~~100.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~473~~	~~11.8~~	~~99.5~~	~~0.5~~	~~0.0~~	~~0.0~~	~~0.0~~	~~0.0~~
	~~523~~	~~47.8~~	~~93.0~~	~~6.8~~	~~0.0~~	~~0.1~~	~~0.0~~	~~0.0~~
	~~573~~	~~83.4~~	~~8.1~~	~~91.3~~	~~0.0~~	~~0.6~~	~~0.0~~	~~0.0~~
	~~623~~	~~100.0~~	~~0.0~~	~~99.3~~	~~0.1~~	~~0.6~~	~~0.0~~	~~0.0~~

~~[a] Total conversion~~ [b~~a~~] ~~mainly mononuclear aromatics~~

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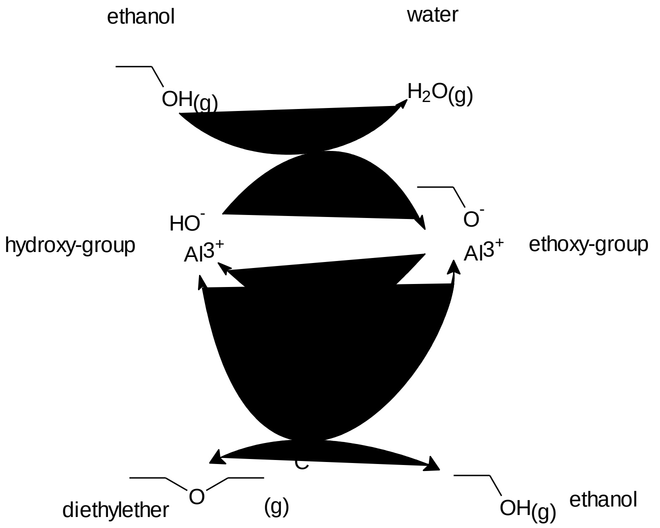

Scheme 1. Schematics of the catalytic cycles.

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Figure captions

Fig 1. Equilibrium compositions curve of ethanol, diethyl ether, ethylene and water in gas phase as a function of temperature.

Fig 2. FT-IR subtraction spectra of surface species arising from pyridine adsorbed on investigated catalysts after evacuated at 373 K.

Fig 3. Conversion and selectivities to C-containing products of ethanol over investigated catalysts at atmospheric pressure in a fixed-bed tubular quartz reactor using 0.5 g of catalysts with 1.43 h^{-1} WHSV in nitrogen, as a function of reaction temperature.

Fig. 4. Conversion and selectivities to C-containing products of ethanol over MFI at different space velocities; Conversion, diethyl ether selectivity and ethylene selectivity on MFI at 523 K as a function of space velocity.

Fig ~~4~~5. FT-IR spectra of subtraction gas phase (top) and surface species (bottom) arising from ethanol adsorbed on alumina (A).

Fig ~~5~~6. FT-IR spectra of subtraction gas phase (top) and surface species (bottom) arising from ethanol adsorbed on FER.

Fig ~~6~~7. Product yields ~~and (1-X) to C-containing products of diethyl ether~~ over ~~investigated~~ MgA, A, SA, MFI and USY catalysts at atmospheric pressure in a fixed-bed tubular quartz reactor using 0.5 g of catalysts with 10.42 h^{-1} WHSV in nitrogen, as a function of reaction temperature~~.~~ ~~X=Conversion~~($Y_{(C_2H_5)_2O}$ = 100-$X_{(C_2H_5)_2O}$). Right top: comparison of DEE conversions $X_{(C_2H_5)_2O}$.

Fig ~~7~~8. ~~The change of~~ Outlet molar flow of reactants and products ~~in~~ (mol/min) (left); and conversions of diethyl ether and ethanol, and selectivity to ethylene (right) over 0.5 g of A and MFI catalysts at atmospheric pressure in a fixed-bed tubular quartz reactor feeding mixture of diethyl ether:water:ethanol = 5:5:3 (mol ratio in gas phase) in helium, as a function of reaction temperature.

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DIETHYL ETHER CRACKING AND ETHANOL DEHYDRATION: ACID CATALYSIS AND REACTION PATHS

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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 a “monomolecular” mechanism via decomposition of ethoxy groups over these catalysts, but also occurs, at lower temperature, with a consecutive path via DEE formation and cracking.

1. Introduction

In the frame of a future possible organic chemistry based on renewables, bioethanol coming from ligneocellulosics 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

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad \Delta H_{298} = +\,44.9\ \text{kJ/mol} \qquad (1)$$

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 [4,5,6,7]. 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)

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

which is exothermic, also favoured 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 sulphuric 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 favoured 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 [12,17,18,19,20,21,22] 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 sulphuric 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 [17,18,19,20] 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 vapours, 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 (573K) 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:

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

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 x 0.25 mm x 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 expected, while below 330K diethyl ether and water are the most abundant products. DEE is more abundant than ethanol also in the range 330-400 K. Thus reaction (1) is the most favoured above 400 K while reaction (2) is the most favoured below 400 K.

3.2 Catalyst surface acidity characterization by IR spectroscopy of adsorption of pyridine.

The surface acidity of the catalysts was characterized by IR spectroscopy of pyridine adsorption (Fig. 2). Over all catalysts bands at ca. 1602-1625, 1575, 1489 and 1440-1460 cm^{-1} are observed, due to the 8a, 8b, 19a and 19b modes of molecular pyridine [32], respectively. As it is well-known, the position of the 8a and 19b modes is indicative of the strength of the Lewis acid sites to which pyridine is coordinated. Bands due to pyridine bonded to strong Lewis acid sites (ν8a ca. 1622 cm^{-1}, ν19b > 1455 cm^{-1}) of the Al^{3+} type are well evident over A, SA and USY. Bands due to pyridine bonded to very weak Lewis sites (ν8a ca. 1602 cm^{-1}) are observed on MgA while bands due to pyridine bonded to Lewis sites are not detected on MFI zeolite. Additional bands attributed to pyridinium ions (ν8a ca. 1635 cm^{-1}, ν19a at 1550-1535 cm^{-1}) are observed in the spectra of the zeolites as well as of SA, showing that these catalysts also have Brønsted acid sites [7]. The experiment concerning the FER zeolite is not reported because it is not really significant. In fact pyridine cannot enter in these conditions into the small cavities of ferrierite. Thus adsorbed pyridine only reveals external acidity in this case. Previous studies using smaller probe molecules such as acetonitrile showed the presence of strong Brønsted sites with some Lewis site also on the cavities of FER zeolite [33].

3.3 Catalytic conversion of ethanol

The results of catalytic conversion experiments of ethanol over the catalysts under study are summarized in Fig. 3. The conversion of ethanol shows the following trend, e.g. at 473

K: FER (70.0%) > USY (62.9 %) > MFI (44.4 %) > A (20.8 %) > SA (15.7 %) > MgA (0.1 %). This trend shows that zeolites are the most active in converting ethanol, due to their strong Brønsted acidity. A and SA catalysts have similar activity, attributed to Lewis acidity [34]. The very weakly acidic material MgA is very poorly active. In all cases, at low conversion, DEE is the largely predominant product, while at higher temperature and conversion, ethylene becomes the predominant product. However, on MgA a relevant amount of products different from ethylene and DEE is formed. They are mainly acetaldehyde and other carbonyl products providing evidence of the basic character of this catalyst.

To have more information, we performed ethanol conversion experiments by varying the contact time. The data on MFI are discussed here, because this catalyst was found to be a purely Brønsted acidic one. The ethanol conversion rate on MFI definitely depends on contact time, as shown in Fig. 4, i.e. the lower the space velocity (SV), the greater the conversion, as expected indeed. The data are reported as Table 2 in the supplementary material. On the other hand, the DEE selectivity clearly has a reverse trend. At lower space velocities the DEE selectivity drops in favour of ethylene selectivity. To look deeper at this we considered the selectivities at the same conversion, at different SV and temperature. As for example, at conversions in the range 81-83 %, the selectivity to DEE drops from 43.6 % to 8.1 % when temperature is increased from 523 to 573 K in spite of the simultaneous strong increase in space velocity from 0.72 to 7.0 h^{-1}. This shows that reaction temperature has definitely a stronger effect, at high conversion levels, to favour ethylene selectivity, than conversion itself, i.e. ethanol partial pressure. Thus the effect of the different activation energy of reaction (1) and (2) may be a discriminant factor.

At low space velocity and high temperature and conversion, ethylene selectivity is lowered by the production of higher hydrocarbons (Fig. 4). However, selectivities to higher hydrocarbons tend to vanish by increasing space velocity in favour of ethylene and even DEE selectivity, showing that these higher hydrocarbons are formed by over-conversion of ethylene.

Similar experiments were performed by varying space velocity on alumina, a purely Lewis acidic catalyst, with parallel results. In particular, also on alumina at lower space velocities the DEE selectivity drops in favour of ethylene selectivity.

3.4 Catalytic conversion of ethanol on alumina: IR experiments.

IR experiments of ethanol adsorption and conversion were performed in order to have further information. The experiments performed on alumina (Fig. 5) show that ethanol adsorbs mainly in the form of ethoxy- groups, characterized mainly by the strong νC-O/νC-C bands at 1116 and 1073 cm^{-1}, together with the CH deformation modes at 1450 and 1390 cm^{-1} and CH stretchings in the region 3000-2800 cm^{-1}. Small amounts of adsorbed undissociated ethanol (δCOH band at 1278 cm^{-1}, νC-O/νC-C band at 1054 cm^{-1}) are also found. The spectra reported in Fig. 5 are those of the gas phase and of the adsorbed species detected after "saturating" the alumina surface with ethanol at room temperature and short evacuation of the line. After, temperature was progressively increased in static conditions. By heating up to at 423 K some ethanol is released in the gas phase (bands at 1240 and 1066 cm^{-1}), while correspondingly the bands of undissociated adsorbed ethanol disappear. The bands of ethoxide species are essentially unchanged, thus showing that dissociative adsorption of ethanol is essentially irreversible in these conditions. Gas phase diethyl ether (νC-O/νC-C band at 1142 cm^{-1}) is formed essentially in the step between 473 and 523 K, during which only traces of ethylene also form (CH_2 wagging mode at 949 cm^{-1}). It seems interesting to remark that upon this step the bands of ethoxy groups decrease significantly in intensity, and gas phase ethanol decreases significantly but not entirely. This clearly shows that ethoxy groups are indeed involved in the formation of DEE, and probably gas phase ethanol too. It seems also of interest to remark that adsorbed DEE is not found. Indeed parallel experiments, according to previous data [35], show that DEE adsorption is very weak, complete desorption being obtained by outgassing even at room temperature.

In the following step between 523 and 573 K, DEE gas disappears completely, and surface ethoxides too, almost completely. Also gas phase ethanol is no more observed, only ethylene being produced in big amounts (νCH_2s at 3106 and 2988 cm^{-1}, wCH_2 at 949 cm^{-1}). The IR experiments, formally consisting of steps at very long contact time, provide evidence of the strong effect of temperature on the reaction steps. It can be concluded that, in the step up to 473 K, the only phenomenon is the essentially irreversible adsorption and saturation of the surface with ethanol. In the range 473- 523 K the only fast reaction is the synthesis of DEE implying reaction of ethoxide species together with gas phase or weakly adsorbed ethanol. In spite of the very prolonged contact time, ethylene is essentially not formed. In the range 523 – 573 K both DEE cracking and ethoxy-group cracking become apparently fast, producing gas phase ethylene.

Similar experiments were performed with zeolite catalysts. The data obtained with FER are reported in Fig. 6. The IR spectra of the adsorbed species closely correspond to those reported for H-mordenite by Kondo et al. [36] and attributed to a bridging ethoxy- group. The features of this alkoxy- species disappear in the 473-523 K range, when ethylene is produced as the only product. At lower temperature, alkoxy- groups coexist with gas phase ethanol and very small amounts of physisorbed ethanol. In this range, some DEE is formed in the gas phase while ethylene is not observed. These results support the idea that both on alumina and on FER, ethoxy- groups have two reactions paths: in the presence of gaseous or adsorbed ethanol, ethoxy- groups participate to the reaction producing DEE; when gas phase ethanol is no more available and at higher temperature, ethoxy- groups crack to ethylene.

3.5 Catalytic conversion of diethyl ether.

In Fig. 7, the data concerning the DEE conversion over the investigated catalysts, are summarized. The conversion trend is, e.g. at 573 K, MFI (98.3 %) > USY (83.8 %) > A (55.9 %) > SA (52.1 %) > MgA (0.1 %). Also in this case zeolites are evidently very active, while alumina and silica alumina have the diethyl ether conversion again similar but lower activity, and MgA has very low activity, confirming a scale based on acid strength governing the catalytic activity. Taking into account the apparent activity inversion between MFI and USY, it must be remarked that the activity of MFI is higher than that of USY also in ethanol dehydration at temperature lower than 473 K.

Looking at the product yield of DEE decomposition, the main compounds are ethylene and ethanol, in a ratio not far from 1:1 within experimental error, in the low temperature range. This suggests that the reaction observed is

$$C_2H_5OC_2H_5 \rightarrow C_2H_4 + C_2H_5OH \qquad (3)$$

A slight excess of ethanol with respect to ethylene could also be explained by the DEE hydrolysis reaction:

$$C_2H_5OC_2H_5 + H_2O \rightarrow 2C_2H_5OH \qquad (4)$$

i.e. the inverse of reaction (2), taking into account that the DEE feed contains also small amounts of water. In fact alumina has been patented years ago as an excellent catalyst for reaction (4) [37].

At higher temperature, ethanol disappears among the products, showing that reaction (3) (DEE cracking) is followed by ethanol dehydration (reaction (1)). Thus DEE cracking can be performed producing ethylene with high yields. At high conversion, ethylene yields are lowered by the coproduction of ethane and higher hydrocarbons. As observed also upon ethanol dehydration, MFI zeolite can produce relevant amounts of aromatics thus significantly decreasing ethylene yields (from < 90 % to < 75%). Also on alumina significant amounts of byproducts are obtained thus limiting ethylene yield to 91-93 %. Higher yields to ethylene are obtained on USY (96.8 % at 623 K) and on silica-alumina (> 97 % at > 673 K).

It is actually relevant to remark that the temperature range for the start of DEE cracking reaction (3) corresponds to the temperature range where ethanol conversion to DEE (reaction (2)) is already significant and is starting to decline in favour of reaction (1) with ethanol feed. This suggests that reaction (3) can indeed be in sequence with reaction (2), producing reaction (1) with a consecutive path. However, it can be remarked that the feed was used in these DEE conversion experiments was definitely more concentrated than the feed was used in ethanol conversion experiments.

3.6 Conversion of ethanol+DEE+water mixtures.

Another set of experiments was performed feeding a mixture of ethanol, DEE and water with a similar molar concentration used in ethanol conversion experiments (Fig. 8). Over alumina at 473 K, DEE and water are consumed and ethanol is formed, while ethylene is not observed. This indicates that, at this low temperature, alumina catalyses DEE hydrolysis (4), i.e. the inverse of reaction (2). As said, alumina has been patented years ago as an excellent catalyst for reaction (4) [37]. At 523 K, instead, the conversions of both DEE and water vanish and also ethanol conversion is near zero. This suggests that in these conditions reactions (2) and (4) very likely balance. At 573 K ethylene and water and some ethanol are produced, at the expense of DEE conversion. This shows that reactions (3) and (4) start. At 673 K, conversion of both DEE and ethanol is complete with ethylene and water being the only products.

On MFI, ethanol conversion is higher than DEE conversion at 473 K, but is lower at 523 K, both producing ethylene only. Both are almost fully converted starting from 573 K. These data strongly support the idea that DEE can be intermediate in the ethanol dehydration reaction into ethylene: in fact, DEE cracks together with ethanol to form ethylene.

4 Discussion

The data described above show that over acidic catalysts both ethanol dehydration and DEE cracking are catalysed efficiently. Zeolites are more active than alumina and silica-alumina in both cases, and silica-alumina is slightly less active than alumina in both reactions. Characterization data indicate, as it is well-known indeed, that zeolites are strong Brønsted acid catalysts while alumina mostly acts as a Lewis acid catalyst. The behaviour of silica-alumina supports the idea that this material, although characterized also by Brønsted acidity sufficiently strong to protonate pyridine, likely works as a Lewis acid in these reactions. The comparison of the behaviour of silica-alumina with that of the MFI sample, characterized by a very low amount of Al and, thus, of Brønsted sites, further confirms that the active sites on silica-alumina are different than those of zeolites: in fact, the different behaviour of MFI and silica-alumina cannot be attributed to the lower concentration of the same sites on SA.

The weakly acidic, or predominantly basic catalyst MgA (calcined hydrotalcite) is weakly active in both reactions, confirming the role of acid sites for them.

Upon ethanol conversion on all acidic catalysts, dehydration to DEE occurs with high selectivity at low temperature and conversion, while the reaction to ethylene occurs at higher temperature and conversion. Thermodynamic calculations indicate that, even in the conditions where DEE is formed with high selectivities, ethylene formation is thermodynamically far more favoured. Thus thermodynamics is not controlling the product selectivity. In those conditions, the evaluation of the apparent activation energies in our experiments at low conversion (> 80 kJ/mol) reveals that the kinetic control is certainly chemical.

This result (DEE formation at low temperature and conversion; and ethylene formation at higher temperature and conversion) was observed also on less active and selective catalysts, but shifted to higher temperatures due to the lower activity of the catalysts. In these cases other compounds such as acetaldehyde, ethane and higher hydrocarbons may also be formed with significant selectivities [38].

Thus, the catalytic experiments show that at low temperature and conversion the reaction occurring in all cases with almost total selectivity is the dehydration of ethanol to DEE, reaction (2). This shows that, in these low temperature conditions, reaction (2) is much faster than reaction (1). At high temperature and conversion, instead, the reaction observed, also with high and almost total selectivity, is the dehydration of ethanol to ethylene (reaction (1)).

IR spectroscopy data confirm the central role of ethoxy groups both on alumina and on zeolites, both for producing DEE at low temperature and for producing ethylene at high temperature, in contrast with the conclusions of other authors [14,39].

As discussed previously [34], on alumina the formation of ethoxy groups occurs with two parallel mechanisms:

a) Dissociative adsorption on Lewis acid-base couples

$C_2H_5OH_{(g)} + Al^{3+} + O^{2-} \rightarrow C_2H_5O^{-} Al^{3+} + OH^{-}$ (5)

b) Exchange reaction on surface hydroxy groups

$C_2H_5OH_{(g)} + Al^{3+} OH^{-} \leftrightarrows C_2H_5O^{-} Al^{3+} + H_2O_{(g)}$ (6)

Both adsorption mechanisms undergo competition by the presence of water vapour. In fact, the latter is an invertible equilibrium being the acido-basic and volatility properties of water comparable to those of ethanol. The former competes with the dissociative adsorption of water on the same acid-base couples:

$H_2O_{(g)} + Al^{3+} + O^{2-} \rightarrow HO^{-} Al^{3+} + OH^{-}$ (7)

The inhibition of ethanol conversion by water does not need the existence of “dimeric” forms, supposed by other authors [14]. Ethoxy groups are stable on alumina below ca. 450-473 K. Starting from this temperature DEE is produced with very high selectivity and ethoxy groups are concomitantly consumed. This step is likely the following:

$C_2H_5O^{-} Al^{3+} + C_2H_5OH \leftrightarrows (C_2H_5)_2O_{(g)} + Al^{3+} OH^{-}$ (8)

with only very small traces of ethylene coproduced. As confirmed by IR adsorption experiments, the adsorption of DEE is very weak and it easily desorbs. When ethanol gas is not more available and the temperature is higher, ethoxy groups decompose to gas phase ethylene and an hydroxyl group

$C_2H_5O^{-} Al^{3+} \rightarrow Al^{3+} OH^{-} + H_2C{=}CH_{2(g)}$ (9)

Ethylene adsorption is very weak on alumina, thus desorbing easily in the gas phase.

The DEE cracking reaction may likely occur either starting from the reverse of reaction (8) or by decomposition over acid-base couples:

$(C_2H_5)_2O_{(g)} + Al^{3+} + O^{2-} \rightarrow (C_2H_5O^{-})_2Al^{3+}$ (10)

followed by reaction (9) and by the reverse of reaction (5).

On zeolites the mechanisms are similar although the ethoxide group has a different geometry and is formed only by the exchange reaction

$C_2H_5OH_{(g)} + Si(OH^{-})Al \leftrightarrows Si(C_2H_5O^{-})Al + H_2O_{(g)}$ (11)

Some authors suppose that reactions (1) and (2) are parallel [13,14,39] but few studies suggest that ethylene can be produced by a consecutive mechanism with reaction (2) followed by DEE cracking (reaction (3)) [12,17,18]. Our data suggest that indeed both conclusions can be right. In fact, DEE cracking reaction (3) is fast over zeolite, alumina and silica-alumina catalysts in the conditions where DEE is formed by reaction (2). On the other hand, in agreement with several studies, the direct way to ethylene via an elimination reaction of ethoxide species is well substantiated to occur at high temperature over both alumina and zeolites by spectroscopic experiments, and by literature data.

We may mention that reaction (1) is expected to have a low reaction order with respect to ethanol (from one to negative depending on the ratio between adsorption strength and rate of surface reaction), while reaction (2) may have a larger reaction order (up to two) due to the need of two ethanol molecules to react together. This may justify an effect of ethanol concentration, and consequently of ethanol conversion, on the two reactions, favoring reaction (2) at high concentration and/or low conversion and reaction (1) at lower concentration and higher conversion. In agreement with this, Chiang and Bahn [39] found a positive reaction order of DEE formation with respect to ethanol on different zeolites, and a negative reaction order for ethylene formation from ethanol on H-MOR.

On the other hand, reaction (1), supposed to occur as a decomposition of ethoxy species, could have higher activation energy than reaction (2), thus also justifying it to become faster only at higher temperatures. In fact our data support the idea that dehydration to ethylene occurs with two paths, the direct one (through ethoxy groups cracking) and the consecutive one composed of formation of DEE by reaction of an ethoxy group with undissociated ethanol and successive cracking of DEE on the acid sites.

In summary, a likely reaction path on alumina catalyst is summarized in Scheme 1. Taking into account that water is a product of reactions 1 and 2 and that reaction temperature is low, it can be supposed that the surface is largely hydroxylated. Thus the active site can be supposed to be constituted by active hydroxyl groups as discussed previously [34]. Thus the first step, denoted as step A in scheme 1, corresponds to reaction (6), producing ethoxy groups with desorption of water. Later, step B in the scheme gives rise to ethylene through a substantially irreversible elimination mechanism (reaction (9)). As a parallel way, in step C reaction with gas phase ethanol gives rise to diethyl ether in a reversible way. In fact, diethyl ether adsorption can crack with the sequence step –C, step –B producing ethylene too. As said, step B is faster than step C at high temperature and conversion while the reverse is true at lower temperature and conversion. In the case of zeolite catalyst, the scheme of ethanol decomposition is essentially the same.

4. Conclusions

The main conclusions from these data are the following:

1. Acidic catalysts like 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.
2. Protonic zeolites are more active than alumina which is slightly more active than silica-alumina for these reactions. It is confirmed that the active sites of silica-alumina are different and less active than those of protonic zeolites.
3. Ethanol dehydration to DEE occurs selectively at lower temperature with a “bimolecular” mechanism involving reaction of ethoxy groups with unidssociated ethanol.
4. Ethanol dehydration to ethylene occurs selectively at relatively high temperature with an elimination mechanism via decomposition of ethoxy groups over these catalysts.
5. Ethanol dehydration to ethylene occurs also at lower temperature with a consecutive path via DEE formation and cracking.

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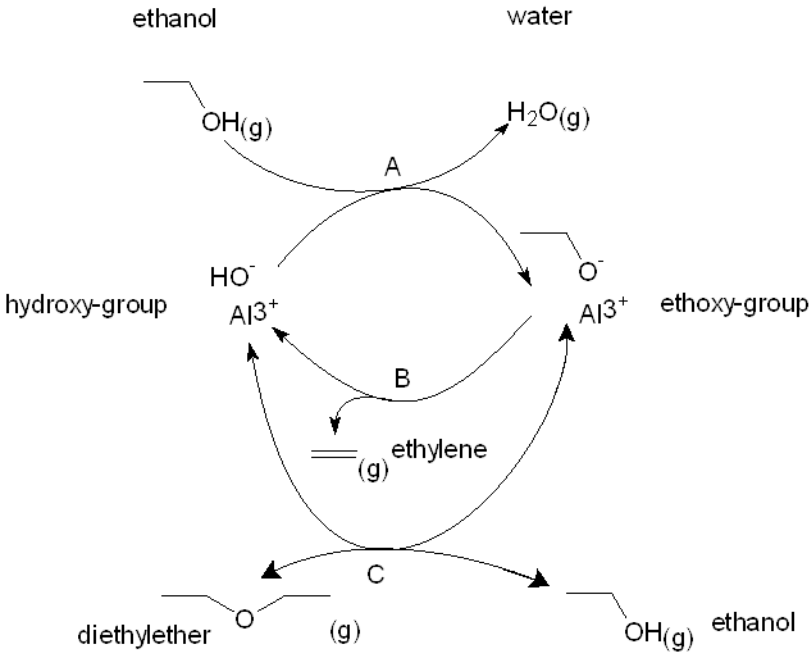
Table 1. The properties of investigated catalysts

Notation	Phase	Composition	Commercial name	Manufacturer	Preparation	S_{BET}[a]
MgA	Calcined hydrotalcite	MgO/Al_2O_3 wt%70:30	Pural MG70	Sasol	calcined at 773 K for 4h	195±10[b]
A	alumina	Al_2O_3	Puralox SBa 200	Sasol	as received	190±10
SA	Silica-alumina	SiO_2- $Al_2O_3$13% wt Al_2O_3	Cracking catalyst	Strem Chemical	as received	330±10
FER	H-ferrierite	SiO_2/Al_2O_3 mol 20	CP 914C	Zeolyst	calcined at 773 K, 4h	400
MFI	H-ZSM-5	SiO_2/Al_2O_3 mol 280	CBV 28014	Zeolyst	calcined at 773 K, 4h	400
USY	H-faujasite	SiO_2/Al_2O_3 mol 30	CBV 720	Zeolyst	as received	780

[a] from manufacturer, [b]BET measurement



Scheme 1. Schematics of the catalytic cycles.

Figure captions

Fig 1. Equilibrium compositions curve of ethanol, diethyl ether, ethylene and water in gas phase as a function of temperature.

Fig 2. FT-IR subtraction spectra of surface species arising from pyridine adsorbed on investigated catalysts after evacuated at 373 K.

Fig 3. Conversion and selectivities to C-containing products of ethanol over investigated catalysts at atmospheric pressure in a fixed-bed tubular quartz reactor using 0.5 g of catalysts with 1.43 h^{-1} WHSV in nitrogen, as a function of reaction temperature.

Fig. 4. Conversion and selectivities to C-containing products of ethanol over MFI at different space velocities; Conversion, diethyl ether selectivity and ethylene selectivity on MFI at 523 K as a function of space velocity.

Fig 5. FT-IR spectra of subtraction gas phase (top) and surface species (bottom) arising from ethanol adsorbed on alumina (A).

Fig 6. FT-IR spectra of subtraction gas phase (top) and surface species (bottom) arising from ethanol adsorbed on FER.

Fig 7. Product yields over MgA, A, SA, MFI and USY catalysts at atmospheric pressure in a fixed-bed tubular quartz reactor using 0.5 g of catalysts with 10.42 h^{-1} WHSV in nitrogen, as a function of reaction temperature ($Y_{(C_2H_5)_2O} = 100 - X_{(C_2H_5)_2O}$). Right top: comparison of DEE conversions $X_{(C_2H_5)_2O}$.

Fig 8. Outlet molar flow of reactants and products (mol/min) (left); and conversions of diethyl ether and ethanol, and selectivity to ethylene (right) over 0.5 g of A and MFI catalysts at atmospheric pressure in a fixed-bed tubular quartz reactor feeding mixture of diethyl ether:water:ethanol = 5:5:3 (mol ratio in gas phase) in helium, as a function of reaction temperature.

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Figure

Figure 1

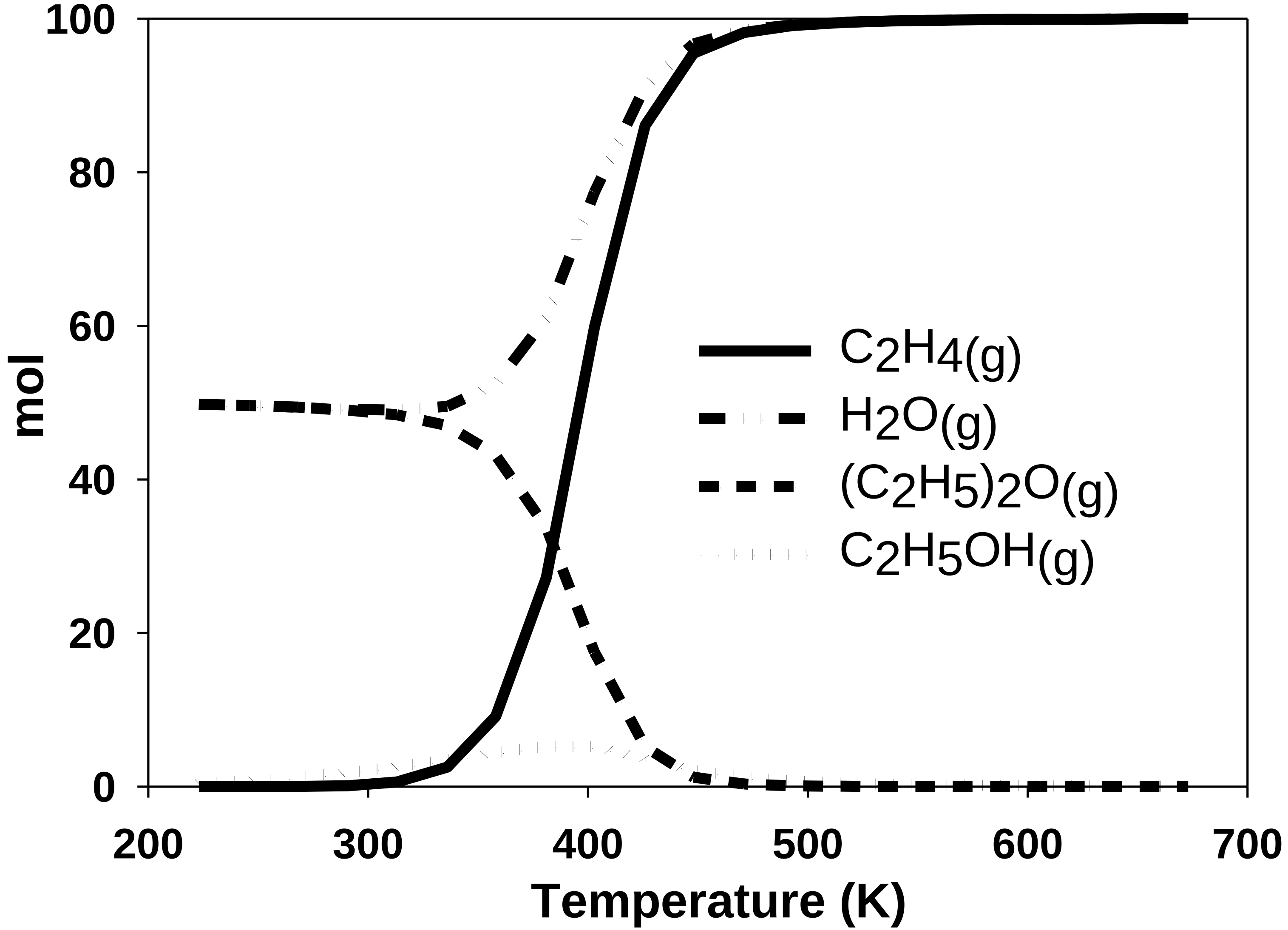


Figure 2.

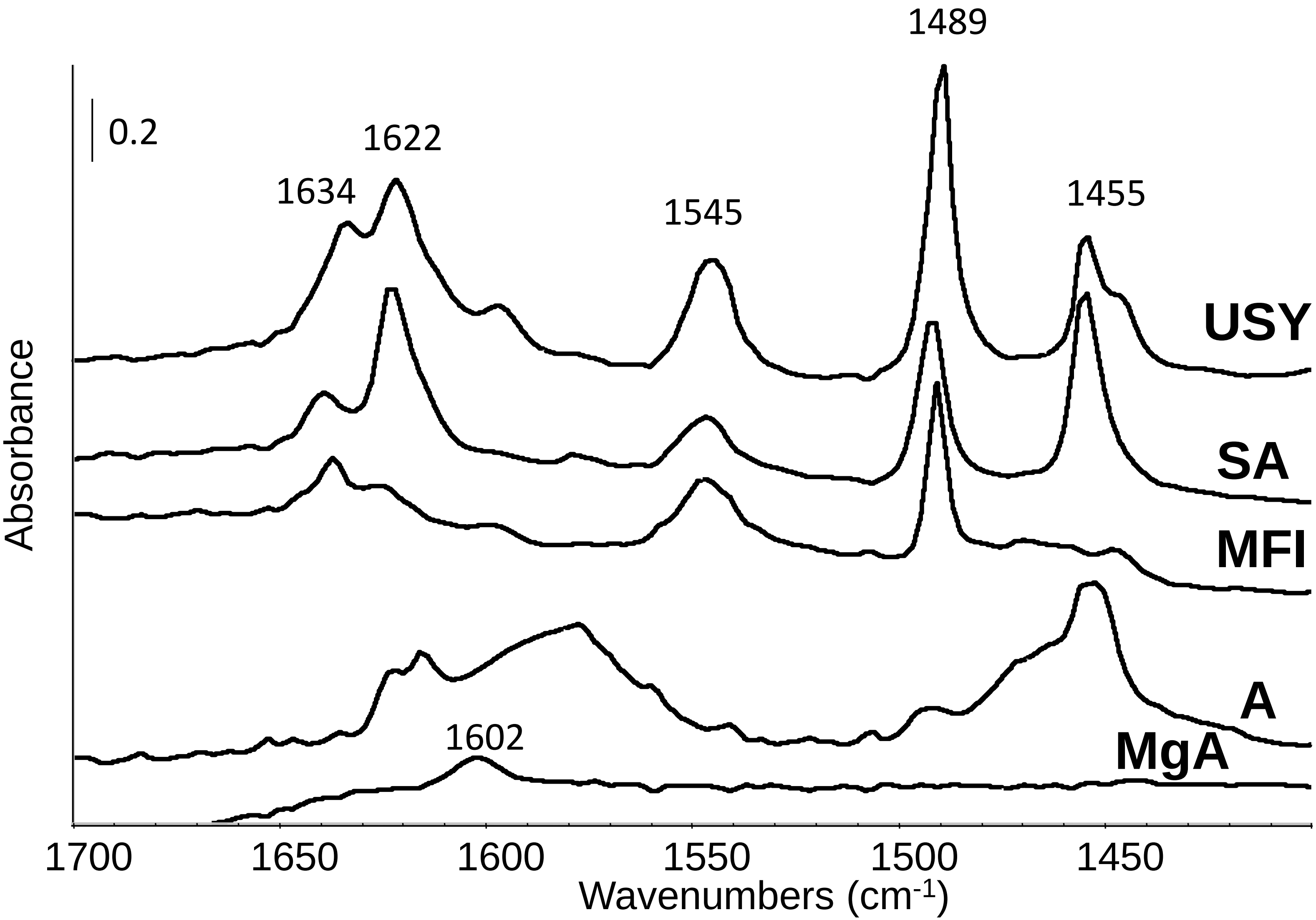

1489
0.2
1622
1634
1545
1455
USY
SA
MFI
A
MgA
1602
Absorbance
1700
1650
1600
1550
1500
1450
Wavenumbers (cm-1)

Figure 3

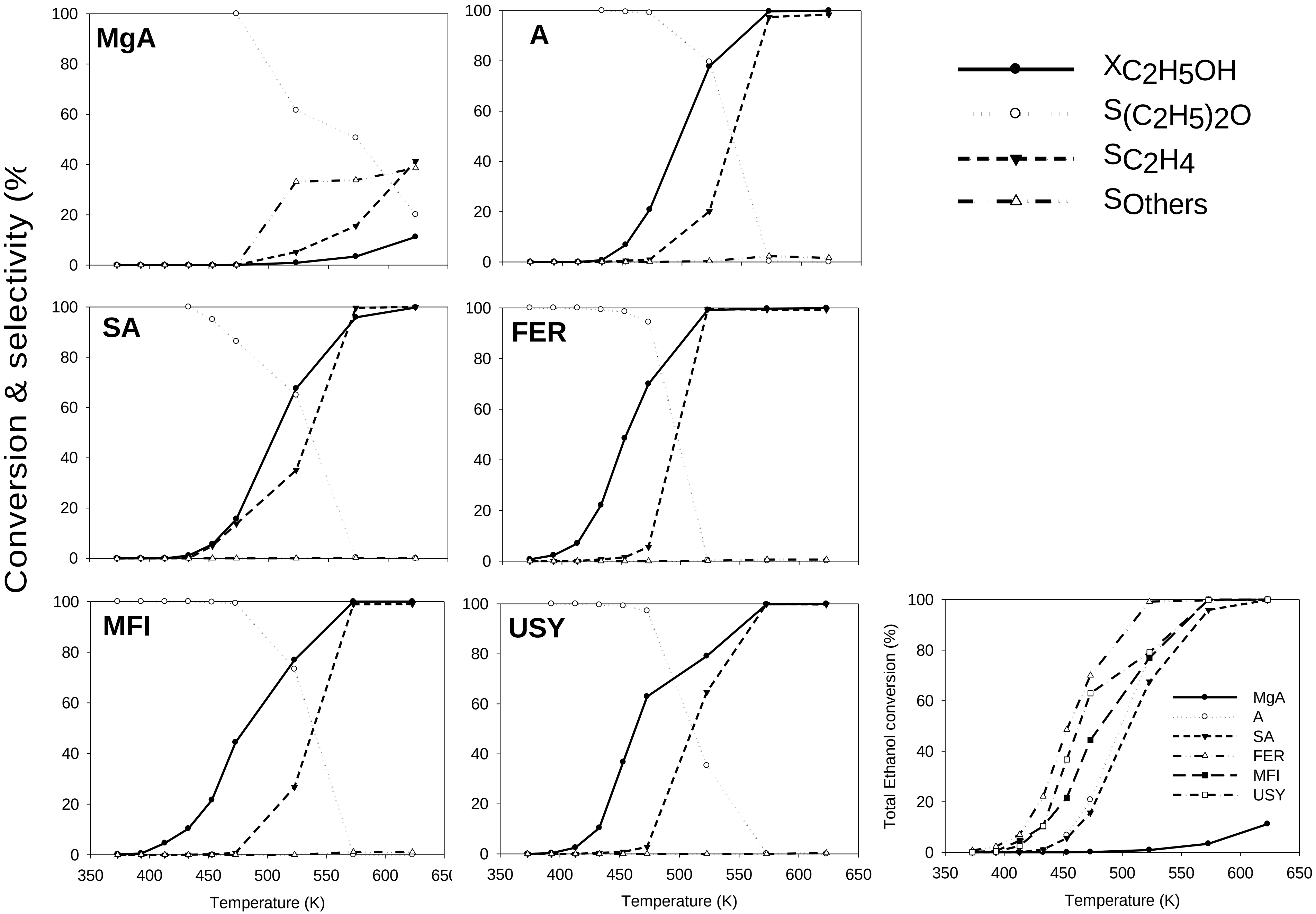
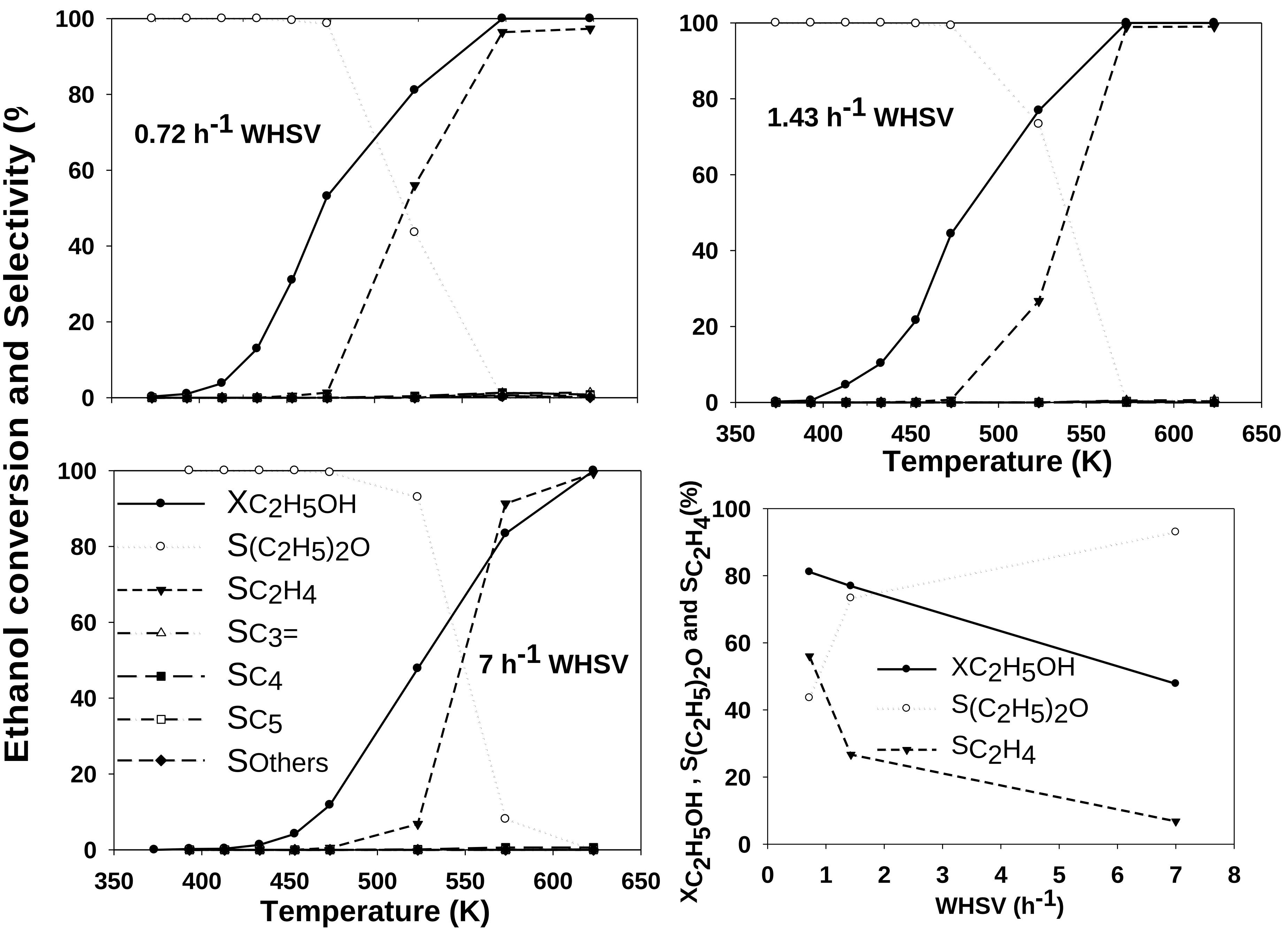

Conversion & selectivity (%
MgA
A
SA
FER
MFI
USY
$X_{C_2H_5OH}$
$S_{(C_2H_5)_2O}$
$S_{C_2H_4}$
S_{Others}
0
20
40
60
80
100
350
400
450
500
550
600
65
650
Temperature (K)
Total Ethanol conversion (%)
MgA
A
SA
FER
MFI
USY

Figure 4



Ethanol conversion and Selectivity (%
0.72 h^{-1} WHSV
1.43 h^{-1} WHSV
7 h^{-1} WHSV
100
80
60
40
20
0
350
400
450
500
550
600
650
Temperature (K)
$X_{C_2H_5OH}$
$S_{(C_2H_5)_2O}$
$S_{C_2H_4}$
$S_{C_3=}$
S_{C_4}
S_{C_5}
S_{Others}
$X_{C_2H_5OH}$, $S_{(C_2H_5)_2O}$ and $S_{C_2H_4}$(%)
0
1
2
3
4
5
6
7
8
WHSV (h^{-1})

Figure 5

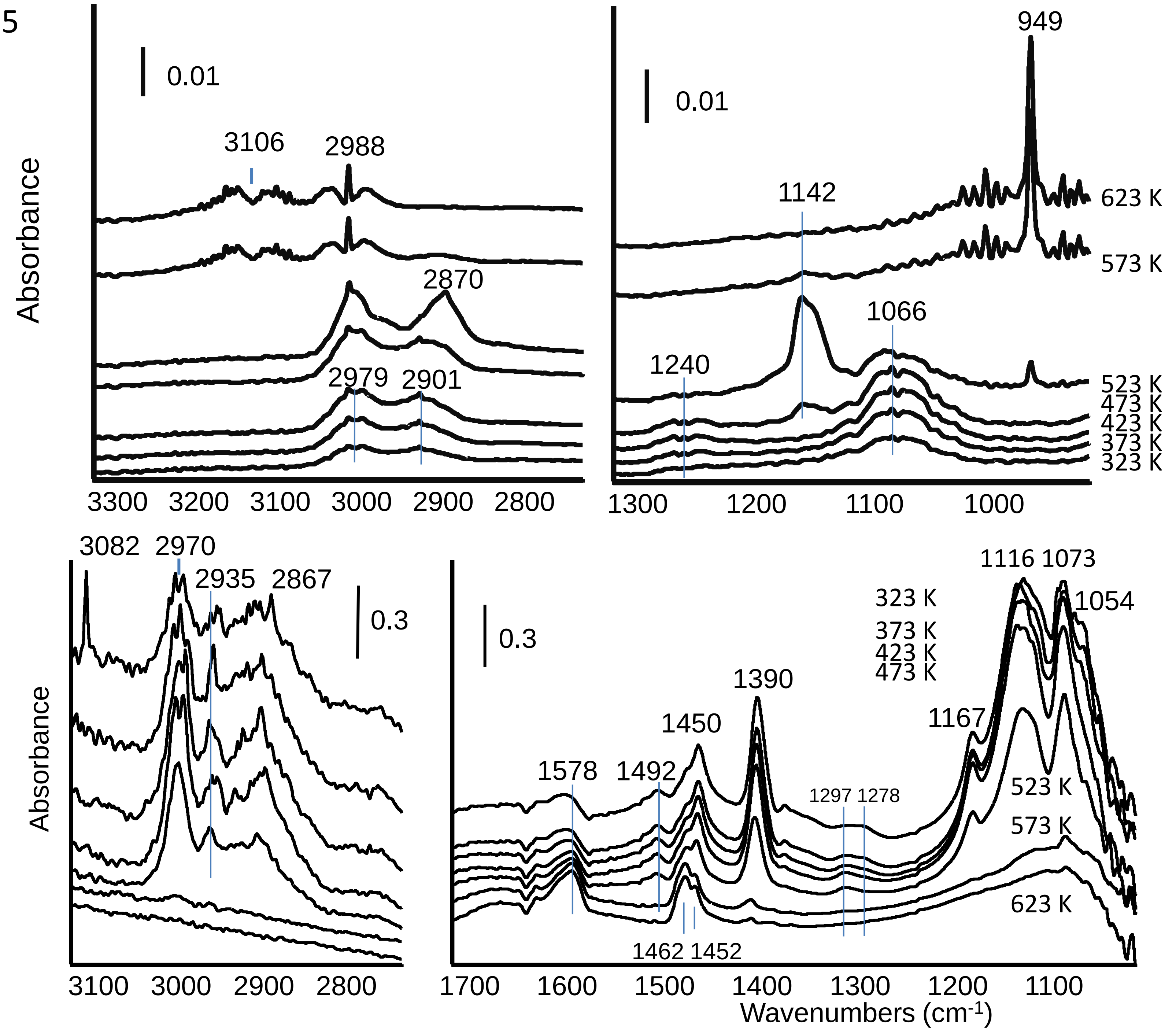

0.01
3106
2988
2870
2979
2901
Absorbance
3300
3200
3100
3000
2900
2800
0.01
949
1142
1066
1240
623 K
573 K
523 K
473 K
423 K
373 K
323 K
1300
1200
1100
1000
3082
2970
2935
2867
0.3
Absorbance
3100
3000
2900
2800
0.3
1116
1073
1054
323 K
373 K
423 K
473 K
1390
1450
1167
1578
1492
1297
1278
523 K
573 K
623 K
1462
1452
1700
1600
1500
1400
1300
1200
1100
Wavenumbers (cm-1)

Figure 6

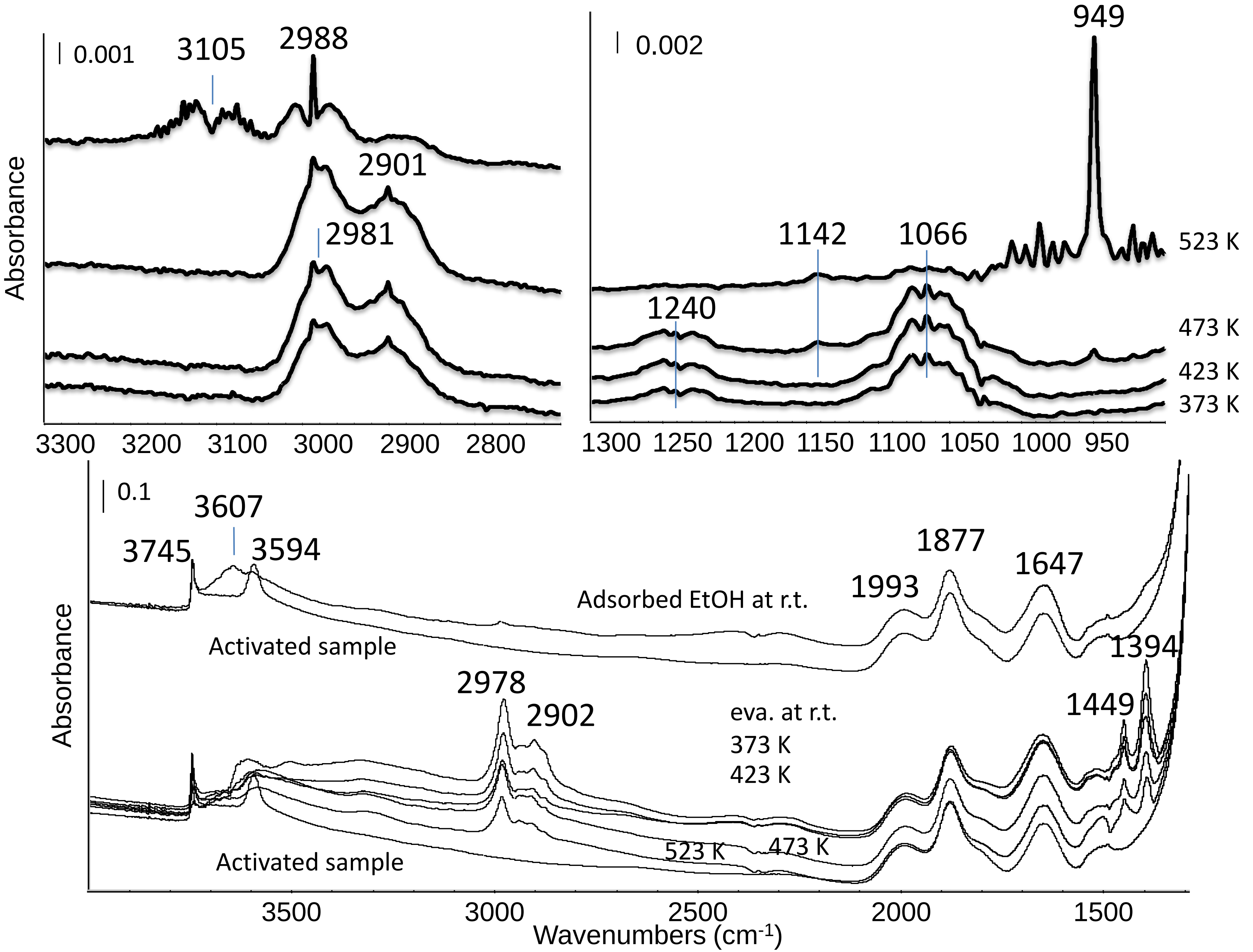
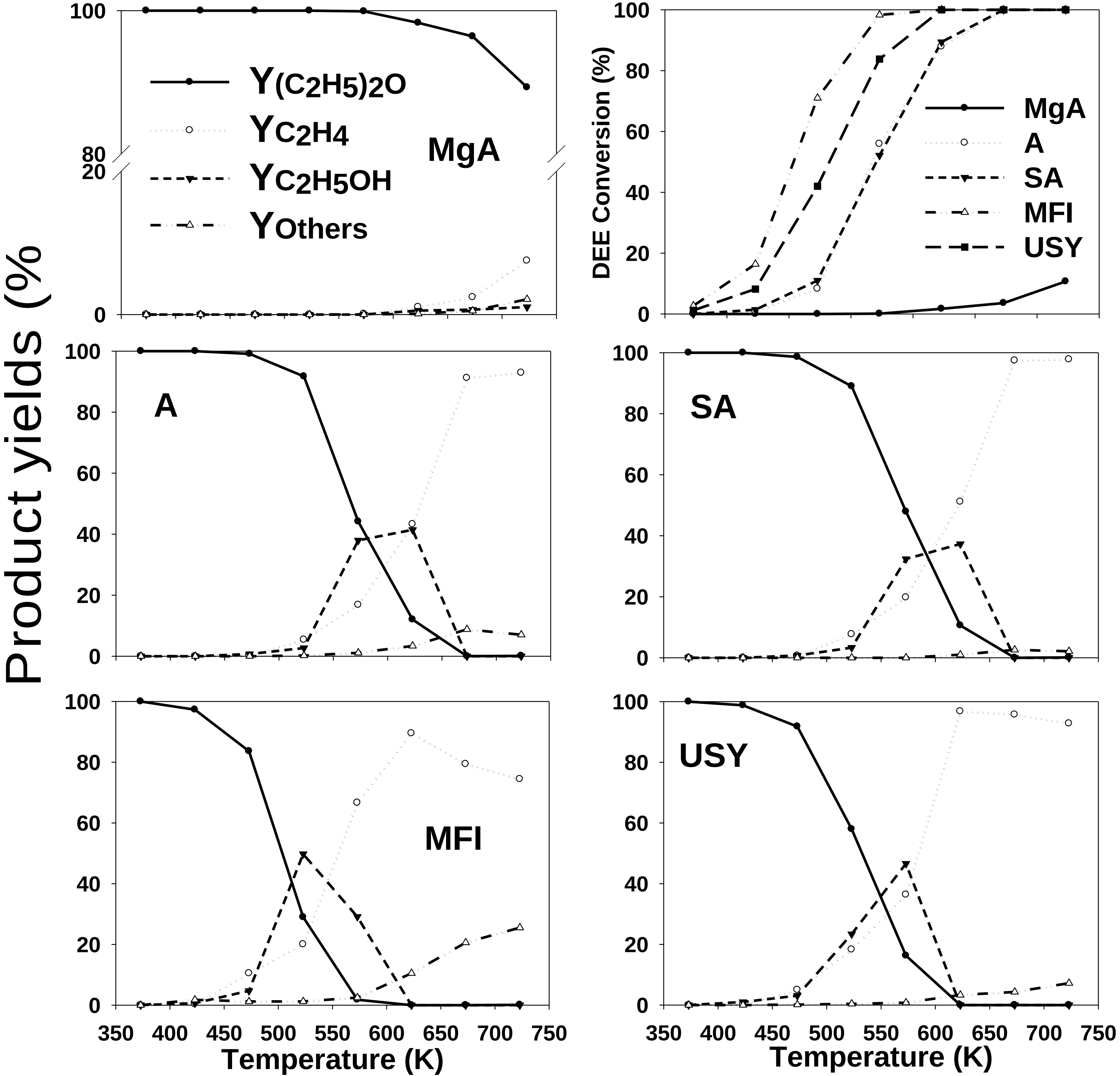
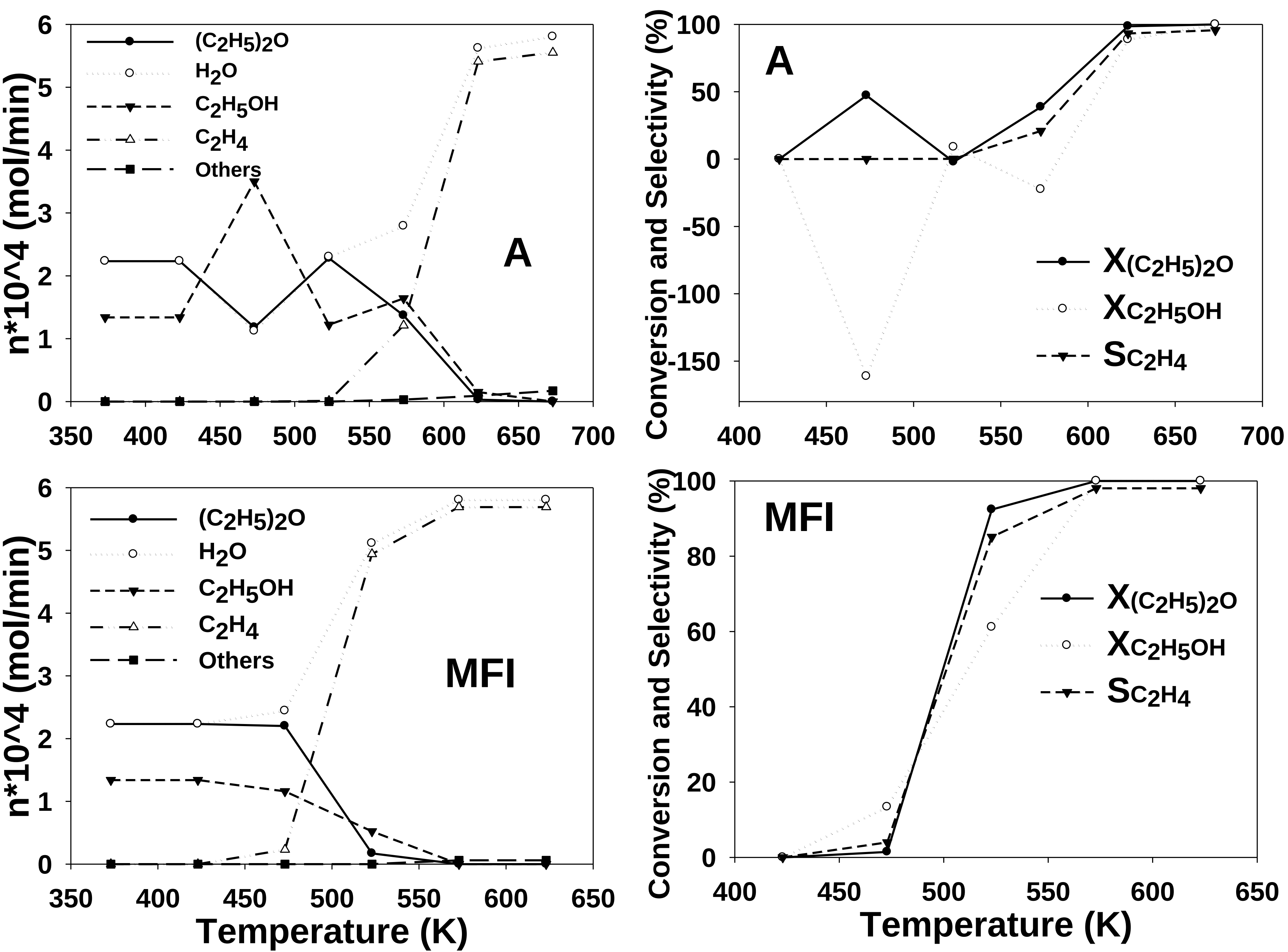

0.001
3105
2988
2901
2981
Absorbance
3300
3200
3100
3000
2900
2800
0.002
949
1142
1066
1240
523 K
473 K
423 K
373 K
1300
1250
1200
1150
1100
1050
1000
950
0.1
3607
3745
3594
Adsorbed EtOH at r.t.
Activated sample
1877
1993
1647
1394
1449
2978
2902
eva. at r.t.
373 K
423 K
523 K
473 K
Activated sample
Absorbance
3500
3000
2500
2000
1500
Wavenumbers (cm-1)

Figure 7



Product yields (%
MgA
$Y_{(C_2H_5)_2O}$
$Y_{C_2H_4}$
$Y_{C_2H_5OH}$
Y_{Others}
100
80
20
0
DEE Conversion (%)
MgA
A
SA
MFI
USY
0
20
40
60
80
100
A
SA
MFI
USY
350
400
450
500
550
600
650
700
750
Temperature (K)

Figure 8


A
n*10^4 (mol/min)
$(C_2H_5)_2O$
H_2O
C_2H_5OH
C_2H_4
Others
0
1
2
3
4
5
6
350
400
450
500
550
600
650
700
A
Conversion and Selectivity (%)
100
50
0
-50
-100
-150
400
450
500
550
600
650
700
$X_{(C_2H_5)_2O}$
$X_{C_2H_5OH}$
$S_{C_2H_4}$
MFI
n*10^4 (mol/min)
$(C_2H_5)_2O$
H_2O
C_2H_5OH
C_2H_4
Others
0
1
2
3
4
5
6
350
400
450
500
550
600
650
Temperature (K)
MFI
Conversion and Selectivity (%)
0
20
40
60
80
100
400
450
500
550
600
650
$X_{(C_2H_5)_2O}$
$X_{C_2H_5OH}$
$S_{C_2H_4}$
Temperature (K)