

## Catalytic conversion of ethyl acetate over faujasite zeolites



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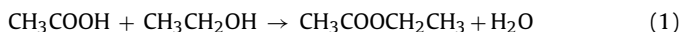
## ABSTRACT

The catalytic conversion of ethyl acetate (EA) has been investigated over faujasite zeolites NaX, USY and HY. Characterization using pyridine adsorption shows that Lewis acid sites only exist on NaX while both Brønsted and Lewis acid sites are evident on both HY and USY. Catalytic experiments were performed in gas phase from 473 K to 973 K at atmospheric pressure with  $2.16 \text{ h}^{-1}$  WHSV in nitrogen. Cracking of EA to ethene and acetic acid is the predominant primary reaction in all cases. As a successive step, ketonization and decomposition of acetic acid occur. Over protonic zeolites Brønsted acidity catalyzes further oligomerization of ethene and cyclization of the further products, that finally produce coke precursors. The low-alumina protonic zeolite USY shows the highest conversion at low temperature, reaching total conversion at 673 K. Protonic zeolites cover by coke and slowly deactivate progressively. Fresh NaX is the least active but its catalytic activity is more stable, significant deactivation starting only after 5 h on stream.

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## 1. Introduction

Ethyl acetate is largely used as a solvent for cleaning, paint removal and coatings. It is manufactured industrially with different processes: the esterification of acetic acid with ethanol is mainly performed in the liquid phase in catalytic distillation processes using  $\text{H}_2\text{SO}_4$  as catalyst [1]:



The reaction of acetic acid with ethene is performed in the presence of Silica-supported  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  heteropolyacid catalyst at 130–230 °C, 0.5–1.5 MPa, and  $\text{C}_2\text{H}_4/\text{CH}_3\text{COOH}$  molar ratio 5–15 [2]:



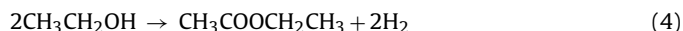
It can also be produced via Tishchenko reaction of acetaldehyde using aluminum triethoxide as catalyst [3]



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A fourth process has been developed recently, based on the dehydrogenation of ethanol [4] likely realized on copper chromite catalysts at 20–30 bar [5].



A number of other routes, such as the oxidative dehydrogenation of ethanol over vanadium catalysts [6], the homologation of methyl acetate with CO over Ru-based homogeneous catalysts [7], the biotechnological conversion of ethanol [8], the indirect fermentation of glucose [9] and the heterogeneously catalyzed two phase esterification (reaction (1)) over zeolite catalysts [10] have also been investigated.

To such a complex synthetic chemistry, a complex conversion chemistry corresponds, in part based on the reverses of the previous reactions. Indeed, few data are reported in the literature concerning the conversion of esters on solid acid catalysts.

Our main interest in the chemistry of esters is related to our attempts to develop selective catalysts for converting vegetable oils to liquid fuels and for refining of biooils. In both cases esters should be decomposed allowing the deoxygenation of the liquid by the removal of  $\text{CO}_2$ . In particular, the conversion of triglycerides [11] has been investigated over many different catalysts. Acid zeolites such as H-faujasites were found to catalyze at quite high temperatures (>500 °C) the deep cracking of vegetable oils mainly producing hydrocarbon rich gaseous mixtures [12].

Additional interest for investigating the conversion of ethyl acetate on zeolite catalysts is related to the possibility to use esters

**Table 1**  
The properties of investigated catalysts.

Zeolite sample	Commercial name	Source	Si/Al ratio	Na <sub>2</sub> O (wt%)	Nominal cation form	Surface area (m <sup>2</sup> /g)
NaX	Sylobead MS C 544	Grace	~1	–	Sodium	~500
HY	CBV 400	Zeolyst	2.55	2.8	Hydrogen	~700
USY	CBV 720	Zeolyst	15	0.03	Hydrogen	~750

as acylating agents in contact with acid catalysts [13] as well as to the reported application zeolite faujasite catalysts [14] for the abatement of ethyl acetate as a typical noxious polluting VOC [15].

In the previous research [16], we studied the conversion of ethyl acetate over Lewis acid alumina. To understand the effect of both Lewis and Brønsted acids, we investigated the conversion of ethyl acetate over three types of faujasite zeolites. We used NaX zeolite supposing to be a neutral, weak Lewis acid and weakly basic material, Al-poor USY supposed to be essentially Brønsted acidic only, and Al-rich HY supposed to be both Lewis and Brønsted acidic. We also performed an accurate surface characterization study to confirm such supposed properties. We will attempt to relate the catalytic behavior to the actual surface chemistry and acid/base properties of the catalysts.

## 2. Experimental

### 2.1. Catalytic materials

Three types of faujasite zeolites were investigated, whose properties are summarized in Tables 1 and 2. According to the information we have, Solybead MS C544 is a typical NaX adsorbent, Zeolyst CBV 400 is a typical HY zeolite while Zeolyst CBV 720, with small amount of Al, is essentially a Ultra Stable Y (USY) zeolite.

### 2.2. Gas phase catalytic ethyl-acetate conversion

The catalytic experiments were carried out at atmospheric pressure in a fixed-bed tubular quartz flow reactor, operating isothermally, loaded with 0.5 g of the catalyst (60–70 mesh sieved), and feeding 12.5% (v/v) ethyl acetate (EA) in nitrogen with 2.16 h<sup>-1</sup> WHSV. The carrier gas (nitrogen) was passed through a bubbler containing high purity EA (99.5%). The temperature in the experiment was varied stepwise from 473 K to 973 K. Products were analyzed at each temperature after one hour running as from changing to desired temperature from previous temperature.

In order to study the deactivation phenomena on the catalyst, other experiments were performed as a function of time on stream using same conditions as above, at 623 K for HY and USY, 673 K for zeolite NaX. The reaction temperatures for this study have been chosen in order to have significant but uncomplete conversion of the reactant at the beginning.

EA conversion was defined as usual:

$$X_{EA} = \frac{n_{EA(in)} - n_{EA(out)}}{n_{EA(in)}}$$

**Table 2**  
Acidity of faujasite zeolites determined by IR-pyridine.

Samples	Brønsted acid sites (μmol/g)		Lewis acid sites (μmol/g)		Total acid sites (μmol/g)		Total acid sites		
	423 K	623 K	423 K	623 K	423 K	623 K	423 K	623 K	
NaX	0.0	0.0	758.8	107.6	758.8	107.6	0.11	0.015	mol <sub>py</sub> /mol <sub>Na</sub>
HY	301.2	111.0	229.3	64.7	530.5	175.8	0.12	0.04	mol <sub>py</sub> /mol <sub>Al</sub>
USY	164.8	103.0	99.9	62.8	264.7	165.8	0.25	0.16	mol <sub>py</sub> /mol <sub>Al</sub>

while carbon selectivity to product *i*, *S<sub>i</sub>* is defined as follows:

$$S_i = \frac{n_i}{n_i(n_{EA(in)} - n_{EA(out)})}$$

where *n<sub>i</sub>* is the moles number of compound *i*, and *v<sub>i</sub>* is the ratio of stoichiometric reaction coefficients, corresponding also to the ratio between the number of carbon atoms in EA (i.e. 4) divided by the number of carbon atoms in the compound *i*.

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

### 2.3. Infrared spectroscopy (IR) experiments

IR studies were done using Nicolet 380 FT-IR spectrometer. For IR skeletal studies the samples, including fresh and spent catalysts, were pressed into thin wafers with KBr and spectra were recorded in air. The acidity measurements were done by pyridine adsorption in an in situ IR-cell. The zeolite pure powders were pressed into thin wafers and activated in the IR cell connected with a conventional gas-manipulation apparatus at 773 K (for fresh catalysts) and 473 K (for spent catalysts) for 1 h. Gaseous pyridine (Py) was adsorbed at room temperature (*p<sub>Py</sub>* ~1 Torr). After 15 min adsorption, pyridine was evacuated using high vacuum pump system (10<sup>-5</sup> Torr), the IR spectra of the surface species were collected at adsorption time at room temperature and upon increasing temperature.

For EA infrared adsorption and reaction studies, 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 (*p<sub>EA</sub>* ~4 Torr).

The evaluation of the density of Lewis and Brønsted acid sites has been performed using the IR spectra of adsorbed pyridine according to Emeis [17].

### 2.4. Raman spectroscopy analysis

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

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