



Short communication

Preparation of Fe-BEA zeolites by isomorphous substitution for oxidehydration of glycerol to acrylic acid



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ABSTRACT

The preparation by post-synthesis isomorphous substitution of Fe_x-BEA-Y in one step was investigated for the oxidehydration of pure glycerol. TPR and DR UV–vis highlighted the presence of Fe^(+III) species in the framework of zeolites. Iron allows the activation of the catalyst by the reduction by glycerol of part of Fe^(+III) into Fe^(+II) species, which stabilizes the glycerol conversion. Total glycerol conversion is obtained with 4 wt% of iron and acrylic acid yield reaches 23% over this catalyst. The Fe^(+III) tetrahedral species are thought to be the main active redox sites for the formation of acrylic acid.

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1. Introduction

The increase of the biodiesel production worldwide involved the abundance of glycerol that is the main by-product of biodiesel synthesis and can be used as a cheap raw material for the synthesis of various products [1,2]. Glycerol may be converted to acrylic acid, which is mainly involved in the synthesis of polymers to produce paint and adhesives [3]. Commonly, the synthesis of acrylic acid is carried out in two consecutive steps over two catalytic beds; firstly, over acid catalysts and after over metal oxide catalysts. Generally, the acid catalyst is a zeolite [4]. Indeed, zeolite is one of the most versatile solid acid catalysts used in heterogeneous catalysis. Acid zeolites allow completing dehydration of glycerol to acrolein and a large variety of mixed oxides could be used to perform acrolein oxidation to acrylic acid, such as Mo–V, Mo–Co and V–Sb [5]. The usual industrial catalyst has a complex structure of V–Mo–W oxides [6]. Over Mo–V–Te–Nb mixed oxides the selectivity to acrylic acid achieved 28% [7]. The best catalysts are a double bed of W/Nb (or zeolite) and W/V/Mo with yields between 50 and 62% [4,8,9].

The aim of this study was to evaluate the catalytic performances in oxidehydration of glycerol to acrylic acid of a single bed Fe-BEA bifunctional catalyst prepared by an easy post-synthesis isomorphous substitution method, which was previously reported in the literature [10]. Recently, a vanadium-impregnated BEA zeolite was used to perform directly this reaction in one-step process to acrylic acid with an 18% yield [11]. The insertion of metal over acid zeolite allows the direct formation of acrylic acid, which is beneficial to the whole process and reduces its cost. Moreover, iron is an abundant and inexpensive metal that can fit

quite easily into the framework of the zeolite. In addition, the BEA zeolite was found to be very suitable to isomorphous substitution and one in which the more iron can be inserted [12]. Iron zeolites are also well known for catalyzing several redox processes like CO oxidation [13], oxidation of phenol [14], NO_x abatement [15] and to our knowledge this study is the first to evaluate the properties of such solids in the oxidehydration of glycerol to acrylic acid.

2. Experimental

The catalysts were prepared by isomorphous substitution according to reliable methods previously reported in the literature [10,16]. The starting material was a commercial ammonium-exchanged BEA zeolite (CP814E, Zeolyst) with Si/Al ratio of 10 (see supplementary material for details). In this study the targeted substitution ratios were 15, 25 and 50%. Fe_{4.0}-BEA-50-Red was obtained by the reduction of Fe_{4.0}-BEA-50 with 10% of H₂ in Ar (30 ml/min) at 450 °C for 1 h.

The prepared samples were characterized with various techniques including X-ray diffraction spectroscopy (XRD) to identify the type of structure and to evaluate the degree of crystallinity of the materials, specific surface area and porous volume measurements, elemental analysis by Inducted Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Temperature programmed reduction (TPR) of the catalysts, UV–vis spectroscopy as well as temperature programmed desorption of ammonia (TPD-NH₃) were also carried out. Full details of all these characterizations are given in the supplementary material file.

The oxidehydration of glycerol was carried out at 275 °C and at atmospheric pressure in a Pyrex reactor (80 cm length, 0.6 cm diameter). The catalyst was loaded at the middle of reactor on a quartz wool bed using 100 mg placed in a furnace. Prior to the reaction, the catalysts

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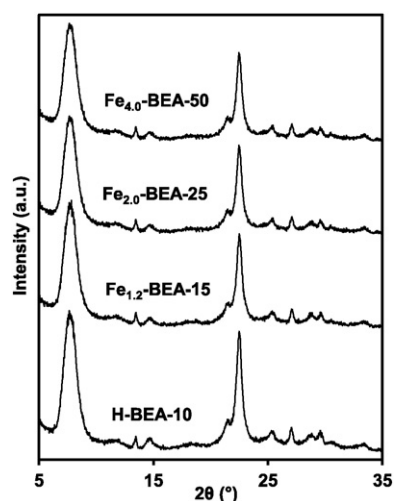


Fig. 1. XRD patterns of H-BEA, Fe_{1.2}-BEA-15, Fe_{2.0}-BEA-25 and Fe_{4.0}-BEA-50 samples.

were pretreated at 400 °C in N₂ (40 ml/min) for 1 h. The feed was a solution of pure glycerol (99%, Sigma-Aldrich). This solution was introduced with a syringe pump at a 0.01 ml/min flow on air (40 ml/min) as a carrier gas to achieve a gas hourly space velocity (GHSV) of 9146 h⁻¹. The products were collected in a condenser connected to the reactor outlet and kept at 4 °C. The samples were analyzed online on a gas chromatograph (Bruker 450GC) equipped with a methanizer to detect CO₂ and offline each hour by another gas chromatograph (Agilent Technologies 7820 A) with a capillary column (CBwax, 30 m, 0.32 mm, 1 μm) and FID detector for the other products. Before each injection, 1-butanol was added as external standard to the sample.

3. Results and discussion

3.1. Catalysts characterization

The method used in this work for the preparation of the solids directly derived from previous works of the literature that proved the actuality of the isomorphous substitution by specific techniques like MAS NMR. However, to ensure that no incident occurred during our experimental procedure and that no objective indication of defective isomorphous substitution exists, several easy to carry out characterizations were performed.

Powder X-ray diffraction experiments were preliminary carried out in order to evaluate the physical properties of the prepared catalysts. The XRD patterns presented in Fig. 1 show that diffraction peaks of all Fe_x-BEA-Y are identical to that of the parent H-BEA, which proves that the zeolite structure is preserved after preparation by isomorphous substitution with FeF₃. Nonetheless, diffraction peaks are slightly reduced after preparation, which implies a little loss of crystallinity. Indeed, crystallinity ratio presented in Table 1 reveal a decrease at high iron content in the zeolite. This crystallinity was calculated from the height of the intense peak at 22° in comparison with that of H-BEA [17], which is considered fully crystalline. However, crystallinity of iron zeolites is always above 67% (Table 1) and thus confirmed that the material is not

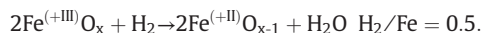
dramatically affected by preparation despite the extensive substitution ratio. On the other hand, since no other crystalline phase was observed, these results suggest a relatively good dispersion of iron over the zeolite [6,9].

Afterward, the textural properties of catalyst were investigated. All isotherms curves (see supplementary Fig. S1) obtained by nitrogen adsorption at 77 K are similar and correspond to a hybrid of types I and IV typical of microporous and mesoporous solids (presence of hysteresis). This is confirmed by BET surface areas, external surface area, micropore volume and mesoporous volume which are always in the same range (around 600 m² g⁻¹, 180 m² g⁻¹, 0.19 cm³ g⁻¹ and 0.5 cm³ g⁻¹ respectively, Table 1). Thus, there are neither significant differences between iron zeolites and the parent one nor collapse or excessive dealumination of the zeolites, which demonstrates that the structure was preserved upon the expected dealumination and introduction of iron. These results confirm that the physical and textural properties of materials were maintained after preparation.

To elucidate the substitution of aluminum by iron, ICP-OES elemental analysis was performed to verify Si/Al ratios as well as iron content before and after preparation at different targeted substitution ratios. Fig. 2 represents the theoretical and experimental Si/Al and Si/(Al + Fe) ratios versus the desired degrees of substitution of aluminum by iron. Firstly, the measured Si/Al ratio increases continuously and perfectly match the desired value up to 50% of substitution degree. These results confirm that dealumination effectively occurred well on the prepared catalysts by fluoride treatment.

Si/(Al + Fe) ratios were also determined and compared to the expected values. In the case of a real and selective substitution these ratios should always equal the Si/Al ratio of the parent solid. Fig. 2 clearly demonstrates that over BEA zeolite the Si/(Al + Fe) ratio is quite stable with targeted substitution ratio. This observation indicates clearly that up to 50% of substitution iron replaces well aluminum previously removed from the framework of BEA zeolite and therefore that isomorphous substitution actually took place over our Fe_x-BEA-Y catalysts. Moreover, iron amounts in zeolites that are summarized in Table 2 follow the desired amounts.

To better identify the iron species and their location, temperature programmed reduction (TPR) and DR-UV-vis analysis were performed. Firstly, the oxidation states of iron in the zeolites were studied by TPR. The reduction peaks of iron zeolites are shown in the supplementary Fig. S2. For Fe_{1.2}-BEA-15, Fe_{2.0}-BEA-25 and Fe_{4.0}-BEA-50 samples a peak is observed around 430 °C and could be attributed to reduction of framework tetrahedral iron species from Fe^(+III) to Fe^(+II) oxidation state [13,16,17]. These results are confirmed by the H₂/Fe ratio calculated from the amount of consumed hydrogen (Table 2) that is close to 0.5 for all samples as expected by following equation:



However, a small contribution at 495 °C appears over Fe_{4.0}-BEA-50, which could be attributed to reduction of extraframework Fe₂O₃ to Fe₃O₄ generally formed and virtually unavoidable at high iron content and during the calcination process [13,18–22].

To confirm the results obtained by TPR, DR-UV-vis experiments were carried out. All samples exhibit a main band at 275 nm (supplementary Fig. S3), which could be assigned to oxygen-to-metal charge

Table 1
Physical and textural properties of H-BEA, Fe_{1.2}-BEA-15, Fe_{2.0}-BEA-25, and Fe_{4.0}-BEA-50 zeolites.

Zeolite	Crystallinity (%)	BET surface area (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesoporous volume (cm ³ g ⁻¹)
H-BEA	100	636	178	0.19	0.49
Fe _{1.2} -BEA-15	82	617	182	0.19	0.52
Fe _{2.0} -BEA-25	73	651	190	0.20	0.61
Fe _{4.0} -BEA-50	68	614	176	0.19	0.53

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