

# Exhausted fluid catalytic cracking catalysts as raw materials for zeolite synthesis

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## Abstract

The utilization of exhausted fluid catalytic cracking (FCC) catalysts as raw materials for the zeolite synthesis was analyzed. Samples of the catalysts directly released from FCC units and the corresponding impact grinding pretreated samples were used. Mechanical treatment was observed to decrease catalyst crystallinity and particle size. The catalyst reactivity was analyzed in terms of conversion in zeolite and product properties. Hydrothermal synthesis experiments in NaOH medium were performed. Catalysts conversion in A and X type zeolites was obtained for treated and not treated samples. In particular, high conversion in NaX type were achieved using the more siliceous catalyst, whereas grinding activation produces a decrease of particle size and Al/Si ratio of the zeolites obtained.

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## 1. Introduction

Gasoline production in refineries is conventionally carried out by catalytic cracking in fluidized beds, where the catalyst used is composed of 20–40% zeolite Y dispersed in a matrix of inorganic oxides [1]. It was reported that the worldwide annual demand for fluid bed catalytic cracking (FCC) catalyst in oil refineries is around 300 thousand tons [2]. Although, spent FCC catalysts are classified as a non-hazardous waste, the quantity is significant, so when its useful life is over, the exhausted catalyst constitutes a difficult-to-handle solid residue. Treatment of such wastes has drawn interest from researchers committed with environmental protection, who attempt to make rational use of these materials.

Up to now, most of the waste catalysts are solidified and disposed as landfills. Several papers reported the feasibility of reusing this spent catalyst as an aggregate in the formulation of building materials, mainly in concrete manufacture [3–7]. Besides, it was demonstrated that zeolites can be incorporated as a minor component in concrete formulation without affecting quality. Interesting results were obtained when cation-exchanged

zeolites were immobilized in cement mortars, aiming at using this methodology for the solution of environmental problems related to the removal of hazardous metals [8].

On the other hand, the most widely used and best-known methods in mechanochemistry include treatment of different types of mill and other similar apparatus. These lead to materials with increased surface free energy, which makes them more reactive. Among the various methods proposed for this purpose, attrition by “high-energy ball milling” (HE-milling) proved to be of the most promising one. This technique is part of the so-called tribochemical treatments, of current interest [9–12]. As observed in previous works, the HE-milling produces a reduction of the particle size accompanied by structural modifications of the treated solids [11,12]. Applied to kaolinitic clays, a gradual collapse of the crystalline structure is obtained. It was demonstrated that the amorphous aluminosilicates produced in this way are a very reactive product for zeolite synthesis, similar to those obtained by calcination [13]. So, we believed that such activation could be used to attain effective modifications in catalysts conversion.

On these bases, by considering the quality and quantitative composition of exhausted FCC catalysts, in this work we study their conversion into zeolites and the effects of impact milling on catalyst structure and so on reactivity. The purpose is to explore an effective way to substantially utilize exhausted FCC

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Table 1  
Chemical analysis of samples SA and SB

Component (wt%)	Sample SA	Sample SB
SiO <sub>2</sub>	60	50
Al <sub>2</sub> O <sub>3</sub>	30	40
Na	0.6	0.3
Fe	0.6	0.6
TiO <sub>2</sub>	1.0	1.5
La <sub>2</sub> O <sub>3</sub>	0.5	1.2
P <sub>2</sub> O <sub>5</sub>	0.5	0.6
Other metal oxides	<0.2	<0.2

catalysts by developing an environmentally friendly, sufficiently performing and cost-effective zeolite-based product.

## 2. Experimental

### 2.1. Materials and methods

#### 2.1.1. Catalyst samples

Two exhausted catalysts were received from two FCC commercial units. These were termed samples A (SA) and B (SB), their chemical analysis being shown in Table 1.

Samples obtained from these two catalysts were grounded during 20 min (SA<sub>ground</sub> and SB<sub>ground</sub>, respectively). High-energy ball milling was conducted in a Herzog HSM 100 vibration grinding mill, following the procedure described earlier [11].

#### 2.1.2. Hydrothermal synthesis

Zeolite synthesis was carried out starting from mixtures of the grounded or original catalyst and a NaOH solution. Alkaline solution was added at the beginning of the reaction to establish the Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio = 2, which is suitable to obtain NaA zeolite as the main product [1]. Reaction mixture compositions are detailed in Table 2.

Once a reaction mixture was prepared, it was transferred to a 250 ml capacity hermetically sealed polypropylene reactor. Reactors were set to the reaction temperature, without stirring, to take samples at reaction times of 2, 4, 6, 10, 16 and 18 h. Experiences were done at three different temperatures: 80, 92 and 100 °C. Solids so obtained were washed and dried at 110 °C.

### 2.2. Physicochemical characterization

Characterization of both the initial solids used for the synthesis and of reaction products was conducted by different

techniques. The types of zeolite obtained were established by X-ray diffraction (XRD), comparing their XRD spectra with those reported in the literature [14]. To obtain the diffractograms, a Philips 1732/10 type equipment fitted with CuK $\alpha$  radiation was used. Conversion to zeolite NaX was estimated according to the standard ASTM D 3906-03, considering a 13 X Grace commercial sample as 100% pure phase.

Particle size and morphology were observed by scanning electron microscopy (SEM), by means of a Philips 505 microscope, using samples coated with a thin layer of Au. The semi quantitative chemical analysis aimed at estimating Si/Al ratio was carried out by X-ray diffraction analysis (EDX), using a DXPRIME 10 coupled to the scanning electron microscope. The EDX analyses were done as described in a previous work [15].

Analysis by FT-IR spectroscopy was conducted in Bruker IFS 66 equipment, using the technique of samples supported in KBr pellets.

## 3. Results and discussion

### 3.1. Samples used as starting materials for zeolite synthesis

X-ray diffraction and FTIR techniques were used to analyze the changes produced by milling. It was expected that if mechanochemical activation occurred, the amorphous halo in the region 15–30° 2 $\theta$  would increase by grinding, and the crystalline peaks of the material would be reduced in intensity. Fig. 1 shows DRX and FT-IR studies conducted on the samples A and B employed for the hydrothermal synthesis, before (SA and SB) and after milling activation (SA<sub>ground</sub> and SB<sub>ground</sub>). For both catalysts, the crystalline material of the sample before grinding is of much greater intensity than that of the grounded sample, while the grounded sample has a greater amorphous phase. Those peaks that were present in XRD diagrams of original catalysts, belonging to the FAU phase (Fig. 1a) disappear as a consequence of exhaustive milling.

Besides, it is interesting to note that when long times of mechanochemical activation were employed, ball mill attrition could be observed. In this case, the treated solid become darker. In the present experiences, the original catalysts samples were grey and changes in color were not observed after milling.

Modifications in FT-IR spectra also indicate structural changes as seen in Fig. 1b. In the latter graph, milling is observed to increase definition of the characteristic bands of Si compounds in tetrahedral coordination (approximately at 1000, 750 and 400 cm<sup>-1</sup>).

Table 2  
Chemical composition of reaction mixtures

Sample	H <sub>2</sub> O (g)	NaOH (g)	Al <sub>2</sub> O <sub>3</sub> (g mol)	SiO <sub>2</sub> (g mol)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O/SiO <sub>2</sub>	H <sub>2</sub> O/Na <sub>2</sub> O
SA (30 g)	182.71	29.69	0.0882	0.3000	3.40	1.20	28.30
SA <sub>ground</sub> (30 g)	182.71	29.69	0.0882	0.3000	3.40	1.20	28.30
SB (20 g)	161.04	26.17	0.1176	0.2500	2.10	1.90	28.30
SB <sub>ground</sub> (20 g)	161.04	26.17	0.1176	0.2500	2.10	1.90	28.30

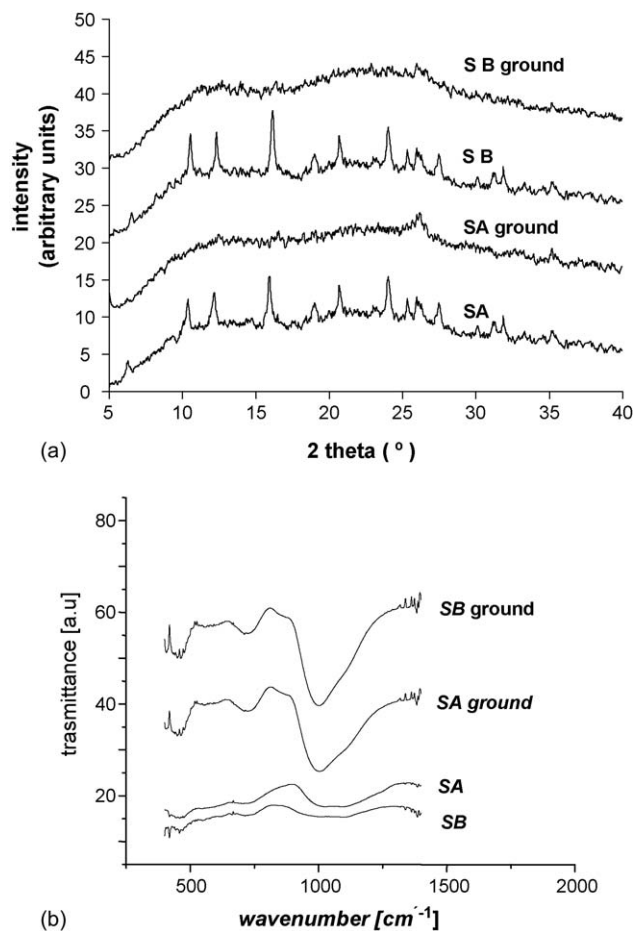


Fig. 1. Diffractograms and FT-IR spectra of samples used for synthesis.

SEM micrographs of these solids can be seen in Figs. 3 and 4. Milling causes particle size reduction and change of shape. Original samples are composed mostly of micro spheres having the usual diameters of cracking catalysts (40–80 μm, Fig. 4a and d). After milling, irregularly shaped particles are observed with sizes below 10 μm (Fig. 4b and e).

### 3.2. Products obtained after the hydrothermal syntheses

The conversion in zeolites was determined by DRX analysis of the solids obtained after the hydrothermal treatments. For short reaction times, XRD-based conversions were rather negligible in all samples. Nevertheless, for longer reaction times, all samples exhibited good conversion to zeolitic products. The yields of particular syntheses varied from 60% to 90%, depending mainly in the reaction temperature. As expected, prolonged hydrothermal treatments lead the solids to form hydroxysodalite (HS), a more stable phase. It was shown that the temperature modified the crystallization period. The better results were obtained working at temperatures above 90 °C.

### 3.3. Analysis of the products obtained at 92 °C

Fig. 2 shows the DRX patterns corresponding to the products obtained at different reaction times using SA (Fig. 2a), SB

(Fig. 2b), SA<sub>ground</sub> (Fig. 2c) and SB<sub>ground</sub> (Fig. 2d) as starting materials. Concerning ungrounded catalysts, the SB sample leads to a mixed structures type FAU + LTA, while SA sample produce exclusively FAU. This result is a consequence of the higher Si/Al ratio presented by the starting catalyst A, which in turn influences the kind of zeolite formed. A catalyst with higher Si/Al ratio, operating in constant alkaline conditions would favor crystallization in the more siliceous phase, which is precisely what is observed. For both ungrounded solids, DRX diffractograms corresponding to samples taken after 16 or 18 h reaction time were identical.

With regard to the use of grounded catalysts for synthesis (samples SA<sub>ground</sub> and SB<sub>ground</sub>, a good conversion in type FAU phases are obtained for 16 h reaction time, being crystalline impurities unnoticed. The incipient HS crystallization was observed at 18 h reaction time, whose main reflections appeared at 2θ = 14.15 and 24.5. The actual Si/Al molar ratio existing in the starting reaction mixture corresponding to the effective concentration of nutrients is higher than the ratios required to crystallize LTA structures. Unit cell parameters measured for FAU indicate synthesis of X type zeolites in all cases. If values measured for SA and SA<sub>ground</sub> are compared, a slight shrinkage is observed in the zeolite obtained from the grounded sample ( $a_0 = 24.91$  and  $24.83$  Å, respectively). Milling can thus be said to produce an increase of the effective Si concentration in both samples. The structural participation of the Al source, which would be reflected by its lower availability, cannot increase in this treatment. Characterization of structural changes is currently under study.

Zeolite products obtained and conversion values for both catalysts after a reaction time = 16 h are summarized in Table 3. It is important to note that high conversion into FAU structures can be attained using the grounded samples. In this case, almost pure LTA zeolite instead of FAU could be synthesized using an additional Al source in the crystallization mixture. Taking into account that A and X zeolites are among the most used cation exchangers, further studies will focus the utilization of the obtained products for heavy metal retention and inertization in cementitious mortars.

SEM analyses of initial solids and their reaction products can be seen in Fig. 3. In the top, a microsphere is shown (Fig. 3a) while a close view of its surface can be observed in Fig. 3b, which is characteristic of particles from sample SA exactly as it is at the exit from the FCC unit, where it is not possible to perceive crystalline forms. After the hydrothermal reaction, the solid obtained is in this case a

Table 3  
Product characteristics after a reaction time of 16 h at 92 °C

Initial sample	Zeolites obtained	Si/Al (molar, EDX)	Conversion (DRX)
SA	NaX	2.81	65
SB	NaX + NaA	2.13	62 <sup>a</sup>
SA <sub>ground</sub>	NaX	2.55	78
SB <sub>ground</sub>	NaX	2.34	76

<sup>a</sup> Value for conversion in A + X zeolites.

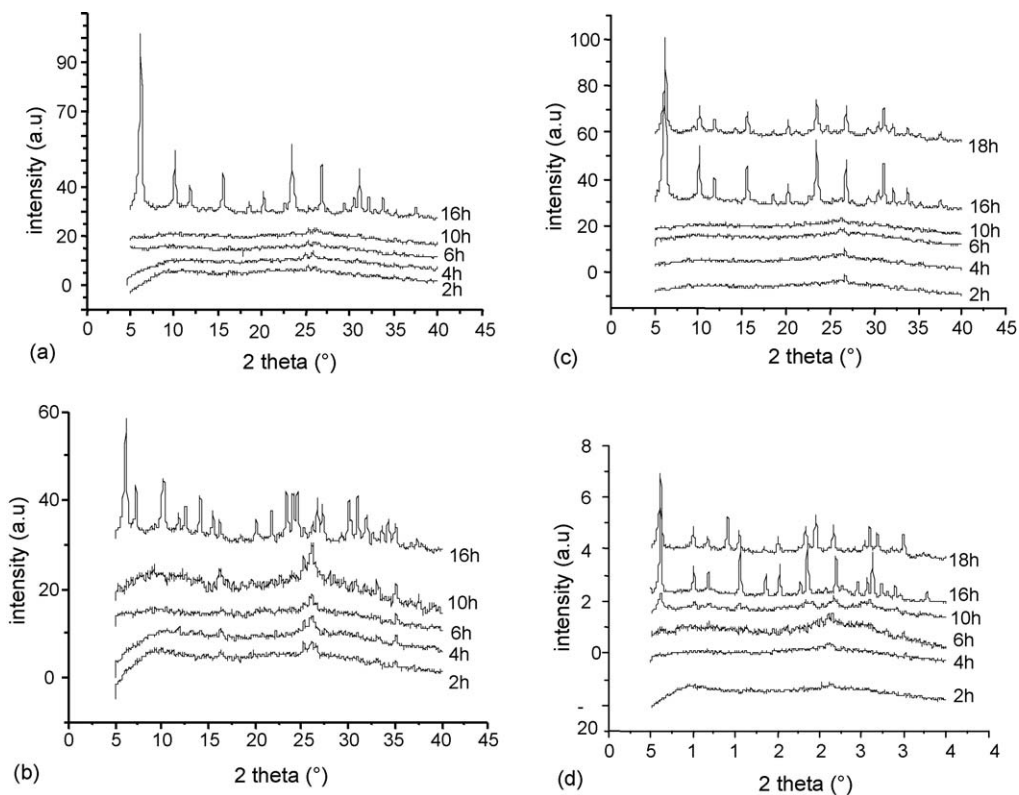


Fig. 2. DRX patterns corresponding to the products obtained at different reaction times for the four different starting materials. (a) Products obtained from SA, (b) from SB, (c) from SA<sub>ground</sub> and (d) from SB<sub>ground</sub>.

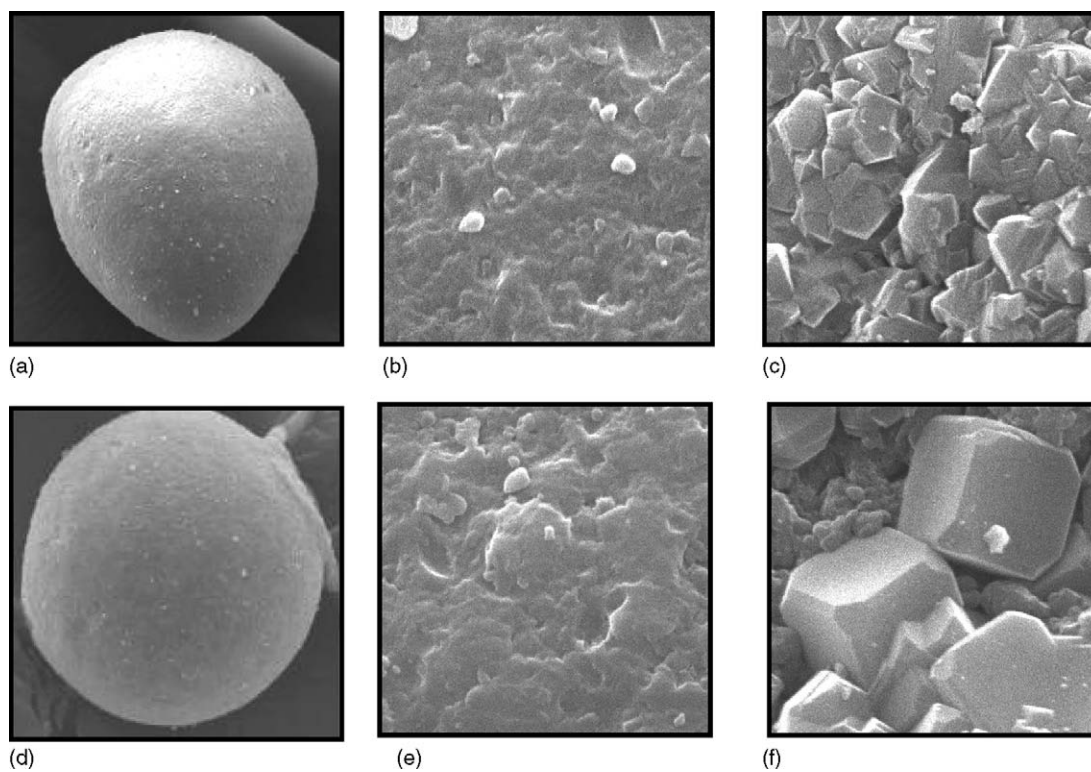


Fig. 3. SEM micrographs of initial solids and reaction products obtained from not activated catalysts. Sample SA: (a) microsphere; (b) microsphere surface; (c) product obtained after 16 h reaction time. Sample SB: (d) microsphere; (e) microsphere surface; (f) product obtained after 16h reaction time. (a and d) Image width: 68  $\mu\text{m}$ ; (b, c, e, f) image width 6.41  $\mu\text{m}$ .

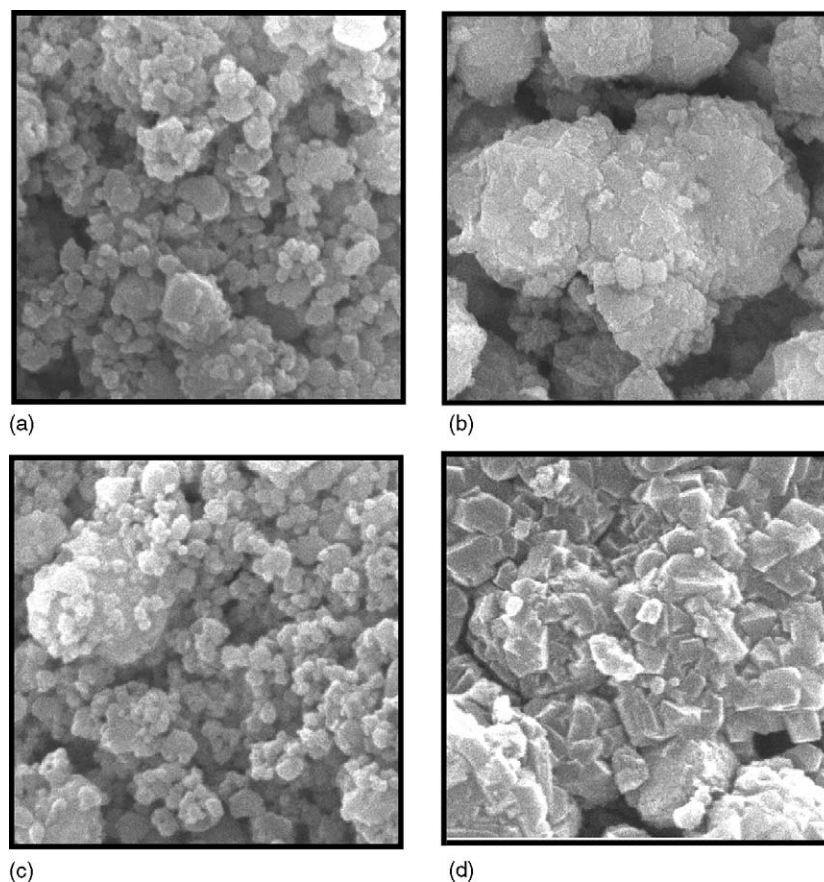


Fig. 4. SEM micrographs of initial solids and reaction products obtained from activated catalysts (a) starting grounded solid SA; (b) product obtained after 16h reaction time; (c) starting grounded solid SB; (d) product obtained after 16 h reaction time. a–d: Image width 6.41  $\mu\text{m}$ .

particle agglomerate which must be grounded in a mortar before characterization. The corresponding tetrahedral crystals of synthesized NaX obtained after this desegregation treatment are shown in Fig. 3c. They present an average size rather below 1  $\mu\text{m}$ , where the presence of macles can be seen.

By analogy with the sample SB, Fig. 3d–f, show a microsphere, its surface and the crystals that were obtained. In this last image, NaA cubes are clearly observed with an average size of 2.3  $\mu\text{m}$  and, again, macled NaX tetrahedra.

Micrograph of the SA<sub>ground</sub> sample (Fig. 4a) indicates the drop in size as caused by milling, while in Fig. 4b the NaX crystals of very small size produced from this solid are shown.

For the SB<sub>ground</sub> sample, the micrographs shown correspond to the solid at the starting (Fig. 4c) and at 16 h reaction time (Fig. 4d). In this case and as in the sample SA<sub>ground</sub>, the sizes of the produced zeolite crystals are considerably inferior to those synthesized from the ungrounded sample.

In the zeolitized samples, the presence of chemical oxides other than SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O, do not exceeded 0.3% (w/w).

#### 4. Conclusions

High conversion of exhausted FCC catalysts to zeolitic products of commercial interest is possible and constitutes a valid alternative to disposal. On the other hand, thorough milling procedure was found to modify reactivity and

characteristics of the crystals produced. Depending on the synthesis conditions and activation treatments, it is possible the conversion of the exhausted catalysts in aluminum rich zeolites type A, X or their mixtures. Therefore, the proposed recycling of FCC catalysts, which normally are accumulated in petroleum refineries before a proper and expensive final disposal, constitutes a technically feasible and environmentally appropriate alternative.

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