

Synthesis and Characterization of Zeolites from Spent FCC Catalysts

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Fluid catalytic cracking is one of the major secondary conversion process in petroleum refinery. Nowadays, the spent fluid catalytic cracking catalysts (FCCs) are disposed of in landfill or stocked for a long period. Environmental risks and lack of space suggest that the management of FCCs needs to be reviewed. The FCC catalysts contain about 3-3.5 %wt. of rare earth (RE) oxides; rare earth elements (REEs) are important for stabilization of the matrix of FCC catalysts. The main challenge is to develop an efficient process based on recovery of REEs and reuse of the solid leaching residue for some applications. In this paper a new process is proposed to recover cerium and lanthanum from FCCs combined with reuse of the leaching solid residue for the production of synthetic zeolites. Three different zeolites were synthesized by using the solid residues from hydrochloric, nitric and sulfuric acid leaching. The chemical and physical properties of zeolites were characterized by different spectroscopic techniques including Scanning Electron Microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) for evaluating the surface morphology. The X-Ray Diffraction (XRD), the Brunauer–Emmett–Teller (BET) and Infrared Spectroscopy (FT-IR) analyses were used to characterize the structure of such zeolites. In addition, the X-ray Fluorescence (XRF) was used to identify the chemical composition. Zeolite is a solid porous material widely used as adsorbent in different processes, particularly applied to wastewater treatments. In this paper, adsorption of heavy metals onto zeolites were investigated by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). The best results in terms of metal removal were achieved by the zeolite synthesized from the sulfuric acid leaching residue.

Keywords: FCC catalyst, rare earths, zeolite, characterization

1. Introduction

Fluid catalytic cracking catalysts (FCCs) play a fundamental role in conversion processes in petroleum industry, that consumes annually 840,000 t (Vogt and Weckhuysen, 2015). Large volumes of spent FCCs are produced by refineries as a solid waste. The open landfill and the temporary storage sites have been applied to manage such waste for many years, but new environmental regulations suggest that the management of FCCs needs to be reviewed. The first step in minimizing the effects of industrial wastes is to reduce the volume through their recovery and reuse. The FCC catalysts contain about 3-3.5 %wt. of rare earth (RE) oxides; rare earth elements such as lanthanum and cerium improve the catalyst activity and act as a “bridge” to stabilize aluminum atoms in the zeolite structure. The recycling of rare earths is becoming important in the transition to a green economy. In recent years, there have been a few studies that used the spent FCCs as secondary raw material to recover REEs. Wang et al. (2017) proposed a stepwise leaching to recover aluminum and REEs by FCC waste slag. Another process to recover rare earths from exhaust FCC catalysts by solvent extraction was investigated by Ye et al. (2017). The aim of this paper is to develop a hydrometallurgical process to recover cerium and lanthanum from spent FCCs and simultaneously reuse the leaching solid residue to synthesize the synthetic zeolites. The exhaust FCCs can be used as raw material for zeolite synthesis (Basaldella et al., 2006). Zeolites are crystalline microporous aluminosilicates that have many applications, including wastewater treatment as adsorbent material. Heavy metal adsorption can be

carried out by means of different techniques such as ion exchange, membrane nanofiltration (Mikulášek and Cuhorka, 2016), chelation, precipitation, adsorption by activated carbon. Heavy metals such as cadmium, lead, copper, cobalt and copper are toxic contaminants and must be removed from industrial effluents before they are discharged into the environment. In this paper, the chemical and physical properties of zeolites were determined by different spectroscopic techniques and their capacity to adsorb heavy metals was investigated. The kinetics of adsorption for the treatment of heavy metals contained in wastewater has been discussed in the literature (Terdkiatburana et al., 2009); for example, the capability of sericin/alginate particles of adsorbing cadmium ions was studied using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models (Lima et al., 2017). In this paper, the experimental activity was conducted through batch tests investigating the adsorption kinetics; the kinetic pseudo-first and pseudo-second order models were used to fit the experimental data.

2. Materials and methods

2.1 Materials

The spent fluid catalytic cracking catalysts were obtained from ORIM Spa (Macerata, Italy) and were used without any pretreatment. Hydrochloric acid (37 %wt.), nitric acid (65 %wt.) and sulfuric acid (96 %wt.) were purchased from Carlo Erba and used to prepare the leaching solutions. Oxalic acid (Carlo Erba, ≥97 %wt.) was used as precipitating agent for lanthanum and cerium and sodium hydroxide (Carlo Erba, 35 %wt.) for adjusting the pH during the selective precipitation and in zeolite synthesis. Zeolites were characterized by various techniques. The heavy metal synthetic solutions, containing Ni, Cu and Zn for adsorption tests, were prepared by diluting the stock solution to the desired concentrations (500 mg/l each) using distilled water; concentrated sulfuric acid was used to adjust the pH.

2.2 Methods

The REE leaching experiments were performed with three different acids: hydrochloric acid, sulfuric acid and nitric acid. For the acid leaching tests, the acid solution with the desired concentration was prepared in a beaker of 100 ml and mixed with 20 g of spent FCCC powder. The mixture was stirred at 353 K for 2 h. All the leaching experiments were conducted in triplicate; the results were the average of the three obtained values. The leaching solutions were filtered and used for the selective precipitation of REEs. Recovery of rare earth elements was performed by precipitation with oxalic acid. After leaching and filtration, the obtained solutions were neutralized by NaOH (HCl and HNO₃ solution) and NH₃ (Carlo Erba, 30 %wt.) for H₂SO₄ solution to pH 4.0 and 3.3, respectively. The solid leaching residues were mixed with NaOH in a mass ratio equal to 1:1.2. The mixture was heated in a muffle oven at 973 K for 1.5 h and, after cooling, mixed with distilled water. The solution was then stirred at room temperature for 8 h and thus heated at 363 K for 24 h. The solid was washed with distilled water up to neutral pH, thus dried at 373 K for 24 h. The properties of zeolites were investigated by different spectroscopic techniques including the Scanning Electron Microscope (SEM), the X-Ray Diffraction (XRD), the Brunauer–Emmett–Teller (BET) and Infrared Spectroscopy (FT-IR). In addition, the X-ray Fluorescence (XRF) was used to identify the chemical composition and the Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) to determine the concentration of REEs and Cu, Ni and Zn in the synthetic solutions used to assess the adsorption capacity of the zeolites.

2.3 Recovery of rare earths

The leach solution samples were analysed by ICP-OES (SPECTRO FM S16) to determine the concentration of lanthanum and cerium and to compare the leaching efficiencies. The initial concentration of lanthanum and cerium in the spent FCCC was equal to 2.3 %wt. and 0.16 %wt., respectively.

Table 1: Leaching efficiencies and precipitation yield (Y %), where $Y \% = \frac{m_0 - m_e}{m_0} \cdot 100$

Agent	Leaching yield		Precipitation yield		
	La	Ce	La	Ce	Si
HCl	87.27	92.22	89.92	94.22	93.51
HNO ₃	62.11	69.87	69.01	75.06	34.51
H ₂ SO ₄	56.34	72.36	50.46	68.80	13.97

The leaching liquors obtained were used to precipitate and recover lanthanum and cerium. The results (Table 1) show that the highest extraction yields were achieved by leaching with hydrochloric acid solution, although

the greatest purity was obtained by sulfuric acid solution with a precipitation yield of silicon equal to 13.97%. The highest precipitation yields were also obtained with HCl solution, and considering that HCl is an economical reagent, it was concluded that such acid is the best leaching agent for the recovery of REEs from FCCCs.

2.4 Characterization of zeolites

Three different zeolites were synthesized using the solid residues from hydrochloric, nitric and sulfuric acid leaching. The products obtained were labelled as ZHCl, ZHNO₃ and ZH₂SO₄, respectively.

2.4.1 Specific surface area

The specific surface area (S_{BET}) and average pore diameter (D) of zeolite samples were determined by the BET analysis. This analysis was performed by NOVA 1200e (Quantachrome instruments) porosimeter. Table 2 shows the analysis results.

Table 2: Characteristic of the synthesized zeolites

Sample	S_{BET} (m ² /g)	D (4V/ S_{BET} , Å)
ZHCl	25.74	49.73
ZHNO ₃	11.84	101.39
ZH ₂ SO ₄	83.13	29.83

The zeolite from leaching with sulfuric acid showed the highest specific surface area and lowest pore diameter. The higher the superficial area, the greater the amount of metals adsorbed; the average pore diameter gives information about the size of a molecule that can pass into the solid: the greater is the pore dimension, the less selective is the sample. The pore size distribution is also important in the ion-exchange process (macro-, meso- and micro-pores).

2.4.2 Mineralogical composition

The mineralogical composition of the synthesized zeolites was investigated by XRD (PANalytical X'Pert PRO) apparatus using Cu-K α radiation ($\lambda=0.154$ nm) with Ni filter. As already mentioned, zeolites are crystalline microporous aluminosilicates with a chemical composition that can be represented by the general formula:

$$A_{y/m}^{m+} \left[(SiO_2)_x \cdot (AlO_2^-)_y \right] \cdot zH_2O, \quad (1)$$

where A is one cation with charge m and x/y is the Si:Al ratio.

Figure 1 shows the X-ray patterns of synthesized zeolites. The samples are characterized by the presence of the phase A, where the silicon atoms of the silicate framework have been substituted by aluminium atoms ($Na_{12}Si_{12}Al_{12}O_{48} \cdot 27H_2O$). The zeolite Na-A present a cubic crystalline system with the lattice parameters $a=b=c=24.61$ Å and $\alpha=\beta=\gamma=90^\circ$. The presence of high crystallinity was demonstrated by the high intensity of the peaks. The ZHCl and ZH₂SO₄ also shows peaks of the phase Na-X, represented by the formula $Al_{92}Na_{92}O_{384}Si_{100}$.

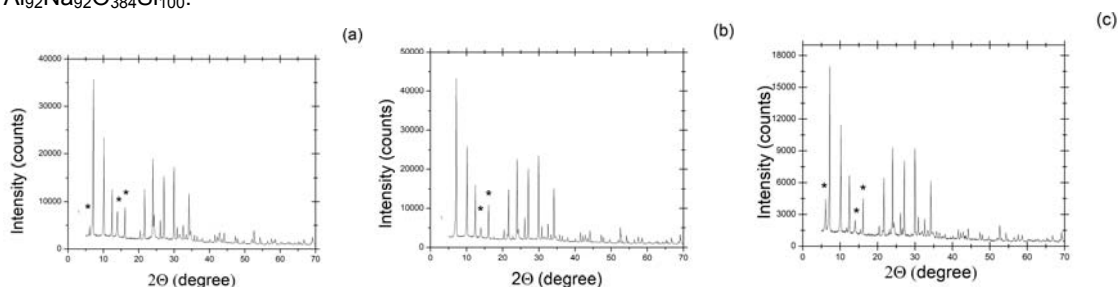


Figure 1: XRD patterns of ZHCl (a), ZHNO₃ (b) and ZH₂SO₄(c)

The phase X is characterized by presence of peaks in correspondence to 6.13, 11.69 and 15.41 degrees, marked by an asterisk in the XRD patterns.

2.4.3 Composition and morphological analysis

The microstructure and surface morphology of the substrates were characterized using SEM (SEM Philips XL30/CP). An accelerating voltage of 20 kV was employed, and secondary electron images were recorded. Energy dispersive X-ray spectroscopy (EDXS) was used to acquire the elemental spectra. The SEM-EDS

provides detailed imaging information about the morphology and texture surface of samples as well as the elemental composition.

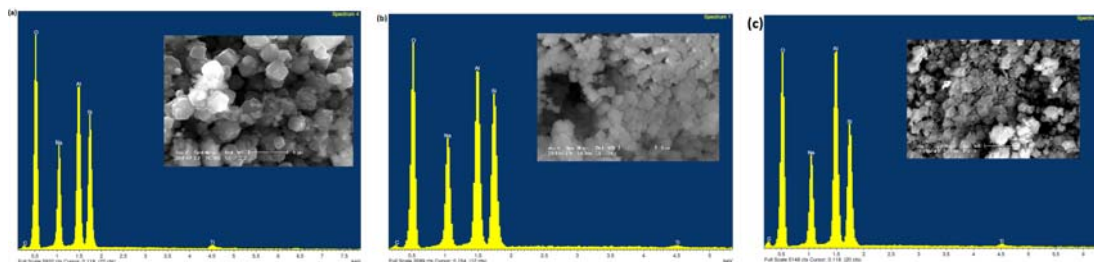


Figure 2: SEM microanalysis of ZHCl (a), ZHNO₃ (b) and ZH₂SO₄(c)

The SEM micrographs confirmed the results of XRD analysis. ZHCl (a) presents an octahedral structure typical of zeolite X and ZHNO₃ (b) shows a cubic structure characterizing zeolite A. The ZH₂SO₄(c) contains zeolite A as the major constituent phase and spheroidal aggregates. Analysis by EDS showed that the spectra are typical of the zeolite phase. The elemental composition is similar for each of the three zeolites: Na, Al, Si and Ti were detected in all the samples. The semi-quantitative analysis of the synthesized zeolites was performed by XRF (SPECTRO, XEPOS III) (Table3).

Table 3: XRF analysis

Sample	Na (%wt)	Si(%wt)	Al(%wt)	Si/Al
FCCC	< 0.010	12.30	15.60	1.27
ZHCl	8.23	12.27	11.93	1.03
ZHNO ₃	7.33	9.03	9.02	1.00
ZH ₂ SO ₄	7.98	11.74	11.59	1.01

The XRF analysis confirmed the presence of a phase of zeolite Y for spent FCCC sample (Si:Al=1.5÷3), zeolite A for ZHNO₃ (Si:Al=1.0) and zeolite X for ZHCl. (Si:Al=1.0÷1.5). The ratio for ZH₂SO₄ is slightly greater than 1.0.

2.4.4 FT-IR analysis

Complementary information about the structure of different zeolites produced was obtained by FT-IR analysis. Fourier Transform InfraRed analysis (FT-IR) was carried out by Thermo Nicolet Nexus FT-IR Spectrometer, using the technique of samples supported in KBr pellets. Figure 3 shows the trend of transmittance (%) as a function of wavenumber (cm⁻¹). The FT-IR spectra showed that no big differences have been found among zeolites samples. According to the literature (Azizi et al. 2012), the characteristic bands can be divided into groups associated with:

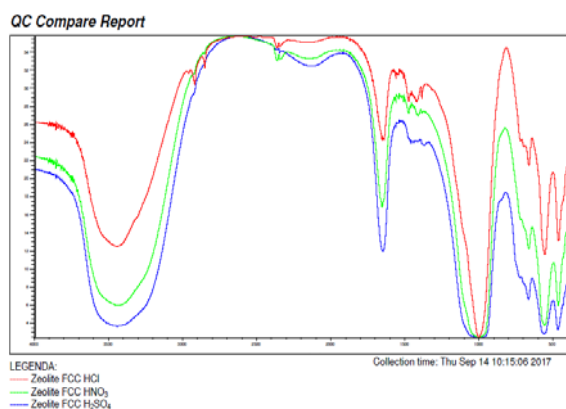


Figure 3: The IR spectra of zeolites samples

- pseudolattice vibrations due to tetrahedral structural units in 800-500 cm⁻¹ range;
- internal vibrations of the Si-O(Si) and Si-O(Al) bonds, present in tetrahedral, in the range 1200-400 cm⁻¹ corresponding to the aluminosilicate structure;
- vibrations of CO₃ groups in the range 1500-1400 cm⁻¹;
- vibrations related to the presence of OH groups and structural water in the range 3700-3200 (stretching vibrations) and around 1660 cm⁻¹ (deformation vibrations), confirming the presence of hydrated aluminosilicates in the synthesized zeolites.

The position of the higher band in the range 650-1000 cm^{-1} is due to the Si(Al)-O stretching vibrations and may be associated with the Si:Al ratio in the zeolites. The peak shifts to the lower wave numbers, increasing the aluminium amount; ZHCl peak is shifted about 20 wavenumbers with respect to the peaks of ZHNO_3 and ZH_2SO_4 . Furthermore, the ZHCl spectrum shows the characteristic peaks at 2918 and 2852 cm^{-1} corresponding to asymmetric C-H and symmetric C-H stretching, respectively.

2.5 Adsorption study

The adsorption tests were carried out with a solution containing heavy metals with initial concentration of 500 mg/l each. The three adsorption kinetic tests were performed at pH 3 and room temperature in flasks shaken at 180 rpm with 1.5 g of zeolite in 100 ml of the initial solution. The kinetic tests were conducted in the range of 0–1440 min to check the selectivity of the adsorbent to the three metals, i.e. copper, nickel and zinc. Experimental data were fitted to pseudo-first and pseudo-second order adsorption kinetic models in order to identify the adsorption mechanism for the given system. The pseudo-first model is that expressed by the Lagergren's equation:

$$q_t = q_e(1 - e^{-k_1 t}), \quad (2)$$

and the pseudo-second model described by the Ho-McKay equation:

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t}, \quad (3)$$

where, q_t (mg/g) and q_e (mg/g) are the amount of heavy metal adsorbed at time t (min) and at the equilibrium, respectively, whereas k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first and pseudo-second order rate constants. Lagergren and Ho-McKay model's curves are shown in Figure 4. The corresponding kinetic parameters and the metal adsorption percentage are summarized in Table 4.

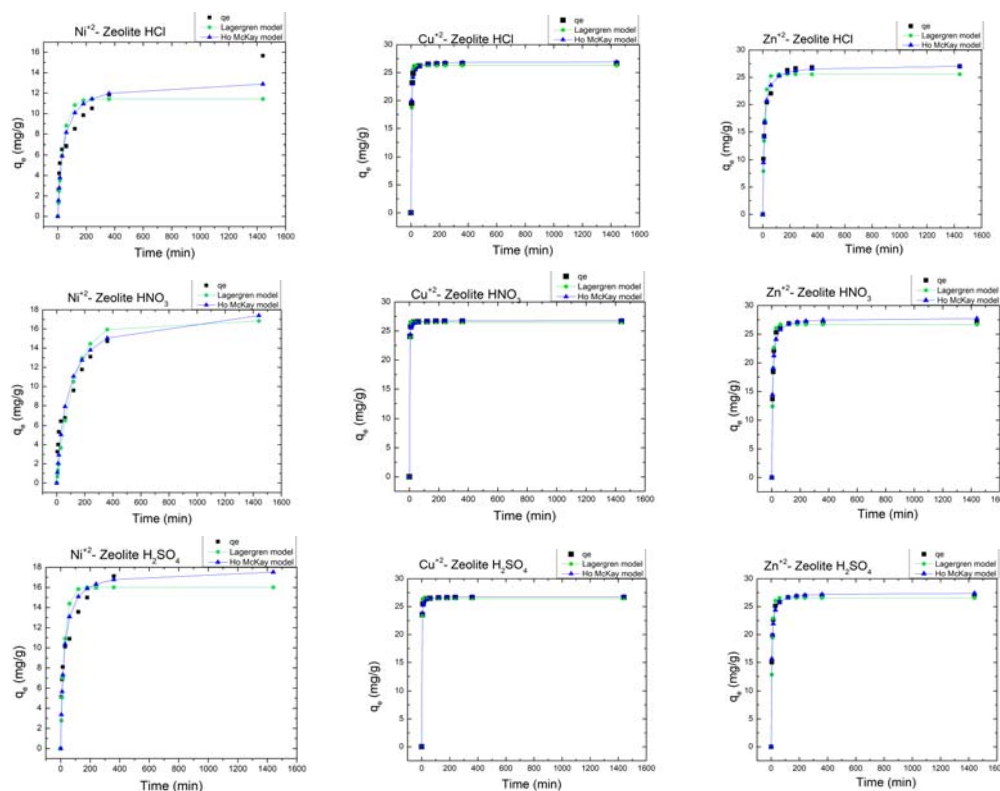


Figure 4: Comparison of experimental and fitted data by Lagergren and Ho McKay models

As it can be inferred from Table 4, the adsorption data for Ni^{+2} , Zn^{+2} and Cu^{+2} onto different zeolites show a better fitting to the pseudo-second order model; the application of the Ho Mc-Kay-model showed a higher correlation coefficient (R^2) for each system metal-zeolite. The maximum adsorption capacity was determined for the zeolite synthesized by the sulfuric acid leaching residue, confirming BET analysis. These results show that the synthesised zeolites can be used effectively for the removal of heavy metals from wastewater.

Table 4: Parameters in the kinetic models and metal adsorption percentage

Sample	k_1	k_2	R^2_1	R^2_2	Ad %
Ni ⁺² -ZHCl	0.025	0.002	0.708	0.851	56.38
Zn ⁺² -ZHCl	0.074	0.003	0.961	0.995	99.43
Cu ⁺² -ZHCl	0.250	0.022	0.974	0.988	99.68
Ni ⁺² -ZHNO ₃	0.008	0.001	0.862	0.924	72.56
Zn ⁺² -ZHNO ₃	0.125	0.008	0.995	0.995	99.67
Cu ⁺² -ZHNO ₃	0.466	0.074	0.999	0.999	99.66
Ni ⁺² -ZH ₂ SO ₄	0.038	0.003	0.862	0.934	77.80
Zn ⁺² -ZH ₂ SO ₄	0.132	0.010	0.999	0.960	99.54
Cu ⁺² -ZH ₂ SO ₄	0.430	0.060	0.999	0.999	99.70

3. Conclusions

REEs play a fundamental role in the production of green and technologically innovative products. The increasing demand for REEs implies the development of new processes for recycling of some critical rare earths. FCC catalysts, widely used in the petroleum industry, represent a fundamental secondary source of REEs, in particular La and Ce. In this paper a new hydrometallurgical process is proposed for recovery of cerium and lanthanum from spent FCCs, combined with reuse of the leaching solid residue for the synthesis of zeolites. The results showed that the highest precipitation yields of cerium and lanthanum were achieved by leaching with hydrochloric acid solution, equal to 89.92 % and 94.22 %, respectively; thus, HCl is the best leaching agent for the recovery of REEs from FCCs, although the highest purity was obtained by sulfuric acid solution. Three different zeolites were synthesized using the solid leaching residues. The zeolites were characterized in terms of specific surface area (BET), mineralogical composition (XRD) and morphological analysis (SEM). Complementary information about the structure was obtained by FT-IR analysis and the XRF semi-quantitative analysis. The zeolites showed a porous microstructure and can be used as adsorbents for removing various chemicals in different processes. In this work, their capacity of adsorbing heavy metals dissolved in wastewater was studied. Experimental data were fitted with Lagergren and Ho-McKay's models. Kinetic tests showed a highest ability to adsorb metals onto the zeolite synthesized by the sulfuric acid residue, even though the ZHCl exhibited similar properties. The hydrometallurgical process investigated in this paper requires further research and optimization, but it is very promising for a whole recycling of FCC catalysts and for the implementation at large scale.

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