

Chromium removal by zeolite-rich materials obtained from an exhausted FCC catalyst: Influence of chromium incorporation on the sorbent structure

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ARTICLE INFO

Article history:

Received 27 March 2013

Accepted 20 June 2013

Available online 16 July 2013

Keywords:

Heavy metal removal

Zeolite synthesis

Catalyst reutilization

Chromium sorption

Cation exchange

ABSTRACT

A spent FCC catalyst was converted into a zeolitic mixture, and the product obtained was afterward used as trapping material for Cr(III) species frequently found in aqueous solutions. Eventual changes in the sorbent structure produced by Cr incorporation were studied by different characterization techniques such as point of zero charge determinations (PZC), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and infrared absorption (FTIR). The XRD and FTIR analyses indicated that chromium incorporation produces an amorphization of the material, and PZC measurements show no surface adsorption of charged chromium species. SEM and EDX analyses clearly show that after chromium sorption, the initial microspheroidal catalyst morphology was maintained, and the presence of chromium species was mainly detected in the outer microsphere surface, where the zeolite crystals were hydrothermally grown.

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1. Introduction

Every year, the petrochemical industry generates over 300,000 tons of spent FCC catalyst [1], which makes solid waste management difficult. In the oil companies, during the catalytic reactors operation, part of the catalyst with low activity was removed from the cracking units and replaced with fresh or regenerated catalyst for maintaining the overall catalytic activity. Most of those exhausted catalysts are disposed of as ground filler; therefore, it is attractive to analyze their use as a low-cost starting material for other applications. Considering the aluminosiliceous nature of this type of catalyst, it is interesting to study its conversion into a zeolitic structure that can act as a heavy cation retainer, which in turn provides an efficient procedure for immobilizing cations. In this paper, a sample of spent catalyst from a catalytic cracking unit (FCC) was converted into a zeolitic product mainly consisting of zeolite Na-A. The procedure for this transformation was outlined in previous publications [2,3]. Afterward, the ability of the synthetic material to remove the Cr(III) cations present in aqueous solutions and the physicochemical characteristics of the chromium-containing product were studied.

2. Experimental

2.1. Hydrothermal synthesis

To obtain the zeolite-containing product, an exhausted FCC catalyst was used as silica and alumina source, following the methodology described in [3]. A complete characterization of the spent catalyst (DRX, FTIR, chemical analysis) was made in previous work [2]. The synthesis was performed by preparing an aqueous solution of sodium hydroxide (Carlo Erba, 98%) and commercial sodium aluminate ASC (36.5% w/w Al₂O₃, 9.2% w/w Na₂O, 64% w/w H₂O). A given quantity of catalyst previously calcined together with Na₂CO₃ (Baker, analytical grade) was added to this solution. The initial mixing composition is detailed in Table 1. This reaction mixture was transferred to a polypropylene reactor hermetically closed and maintained at a temperature of 90 ± 2 °C for 6 h. The solid obtained was washed to pH = 10 and dried at 110 °C. The product of this reaction (sample 4033) was used for cation exchange.

2.2. Cr(III) exchange

Cr(III) exchange runs were carried out by contacting 3 g of sample 4033 with 1 L of chromium solutions (42 or 135 ppm of Cr(III)) at 20 °C and under continuous stirring, as was detailed in [4]. Samples of the suspension were collected at predetermined times, and the liquid was separated from the solid by filtration. The solid

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Table 1
Composition of the initial reaction mixture.

Sample	Spent FCC catalyst (% w/w)	NaOH (% w/w)	Al ₂ O ₃ Na ₂ (% w/w)	H ₂ O (% w/w)
4033	9.4%	3.5%	1.1%	86%

phases were oven-dried at 110 °C. The concentration of chromium in the starting and remaining liquid phases was determined by atomic absorption spectroscopy (AAS).

2.3. Characterization

Sample 4033 and the two samples obtained after the cation exchange reaction (samples 4055 and 4036) were characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR), point of zero charge determination (PZC), and scanning electron microscopy (SEM). To obtain the XRD patterns, a Philips 3020 was used. The Rietveld method [5] and the program "FULLPROF" [6] were used for the quantitative determination of the crystalline components. The infrared spectra were recorded in the range 400–1500 cm⁻¹ using a Bruker IFS 66. For PZC determination, a 90Plus/Bi-MAS Brookhaven Particle Multi Sizing (used in the zeta potential mode) was used, operating at $\lambda = 635$ nm, 15 mV, solid-state laser, scattering angle 90°, and temperature 25 °C. The samples were suspended (0.5 g/L) in 10–3 M KCl (inert electrolyte), and concentrated HCl or KOH were used to adjust the suspension pH. Particle size and morphology were observed by scanning electron microscopy (SEM), by means of a FEI Quanta 400 microscope, using samples coated with a thin layer of Au. The semiquantitative chemical analysis aimed at estimating chromium concentration was carried out by EDX, using an EDAX SDD Apollo 40, coupled to the scanning electron microscope. The EDX analyses were performed as described in previous work [7]. The solid product 4036 was pressed to obtain a cylindrical pellet that was then transversely polished with fine sandpaper in order to expose a flat surface corresponding to a cross-section of the microspheres that can be analyzed by SEM and EDX.

3. Results and discussion

The results of the Rietveld analysis corresponding to sample 4033 are listed in Table 2. It can be seen that the hydrothermal product presents a high degree of conversion into zeolite Na-A.

Table 3 shows the evolution of pH and chromium concentration when the product 4033 is contacted with solution (a) containing 42 ppm of Cr(III) and with solution and (b) containing 135 ppm of Cr(III). The final solid samples obtained were named 4055 and 4036, respectively. According to the data presented, Cr uptake becomes faster and more effective for the smaller chromium concentration. Moreover, the addition of zeolite produces a fast increase in pH up to values close to 7. For times longer than 120 min, chromium was almost completely removed from solution (a), whereas for solution (b), cation concentration was stabilized at about 54 ppm.

The pH increase produced by the sorption of Cr(III) could be attributed to the occupation of the cation exchange sites by the

Table 2
Chemical analysis of sample 4033.

Sample	Linde A	Na-nepheline	Low carnegieite	Mullite	Hydroxy sodalite	Anatase
4033	75%	13%	4%	1%	6%	<1%

Table 3
Evolution of pH and [Cr(III)] in the liquid phase for 3 g of solid in 1000 mL of chromium solution.

Run	4055		4036	
	pH	Cr(III) (ppm)	pH	Cr(III) (ppm)
0	3.58	43.5	3.46	128
1	5.1	15.2	4.18	107
5	5.42	10.9	4.89	98
20	5.78	0.22	5.22	90
60	6.08	0.1	5.85	83
120	6.24	0.07	6.08	65
150	6.35	0.04	6.22	54

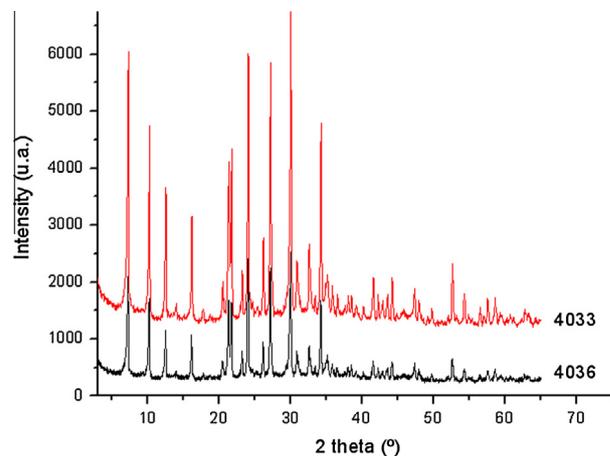


Fig. 1. X-ray diffraction patterns for test products 4033 and 4036.

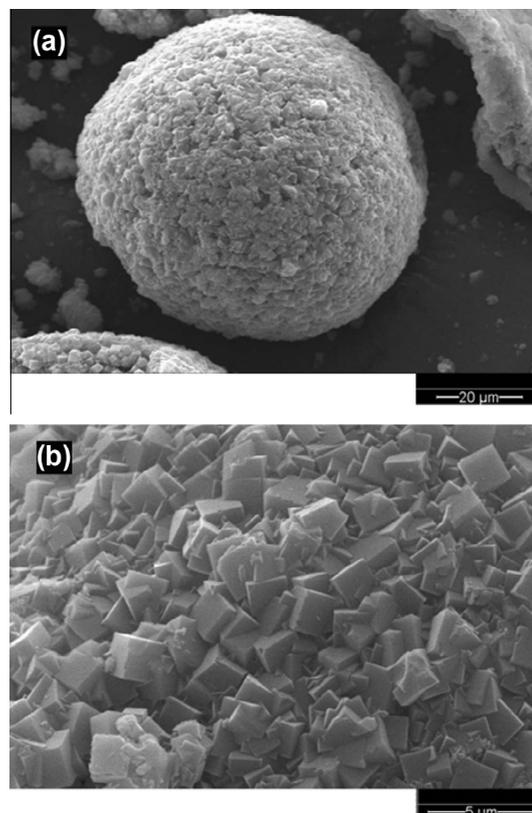


Fig. 2. SEM micrographs for test product 4036. (a) Magnification 1000× and (b) magnification 5000×.

hydrolyzed Cr(III) species and the corresponding desorption of sodium cations. Competition for exchange sites with hydrogen also decreased rapidly as the pH was raised in the range 1.5–5.0 and contributed to the increased sorption.

Fig. 1 shows the XRD spectra of the product obtained before (4033) and after chromium exchange (4036). The presence of the

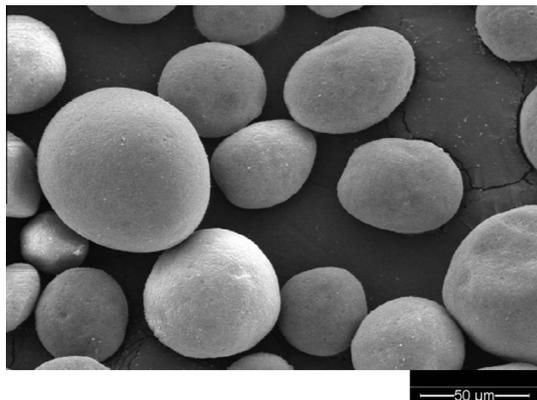


Fig. 3. SEM micrographs for exhausted FCC catalyst. Magnification 500 \times .

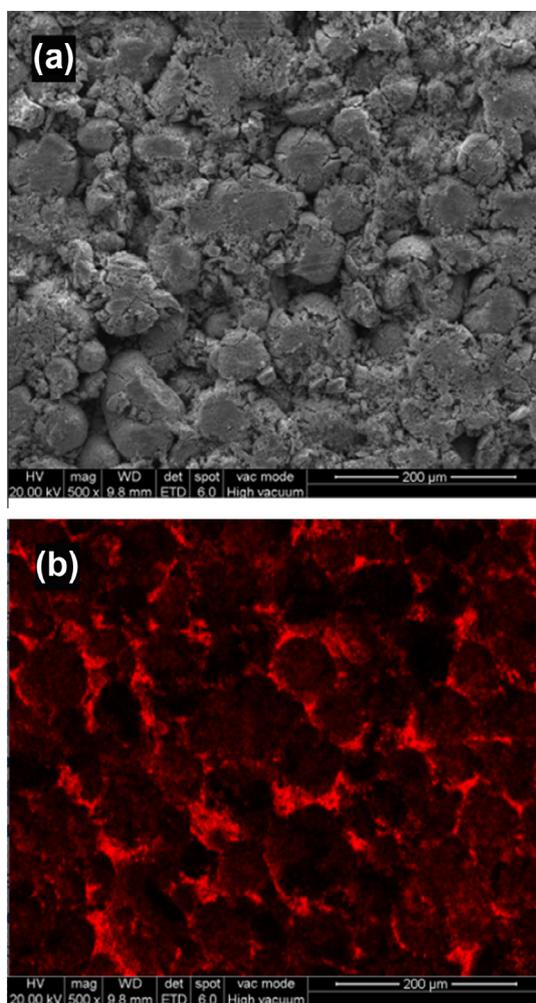


Fig. 4. SEM-EDX analyses for test product 4036. (a) SEM micrograph showing a selected flat area exposed by polishing. (b) Chromium EDX mapping corresponding to the micrograph showed in (a).

amorphous halo in the zone $20^\circ < 2\theta < 25^\circ$, typical of silica glasses, was observed in both samples.

The XRD patterns obtained before and after cation exchange (Fig. 1) show no difference in the positions of the characteristic peaks associated with the presence of zeolitic structures, indicating that the network parameters are preserved, and chromium incorporation has not modified the crystal structures. This spectra similarity is usually observed in cationic reversible replacements, although other authors find that the exchange Na(I)/Cr(III) in A zeolite has a high degree of irreversibility [8]. An appreciable decrease in peak intensities after chromium exchange was also observed.

SEM micrographs clearly show that the hydrothermal product (Fig. 2) maintains the morphology of the starting catalyst (Fig. 3). After Cr(III) sorption, spherical particles 60–100 μm in diameter, similar to those of the original cracking catalyst, are observed (Fig. 2a), the surface of these particles being fully covered by zeolite crystals (Fig. 2b).

When the microspheres were broken, the SEM images showed that cubic crystals of A zeolite were mainly formed on the outer microsphere surface. EDX analysis results of the broken surface are shown in Fig. 4. The chromium atom percentages are significantly higher in the outer surface, where the zeolite crystals are situated (values of about 3%), than the values determined in the interior of the microspheres (0.1%). Then, it is believed that chromium cations replace sodium cations and play the role of counteracting the negative charge of A zeolite framework.

Fig. 5 shows the FTIR spectra of the zeolitic material obtained before and after being in contact with a solution whose initial concentration was 135 ppm Cr(III).

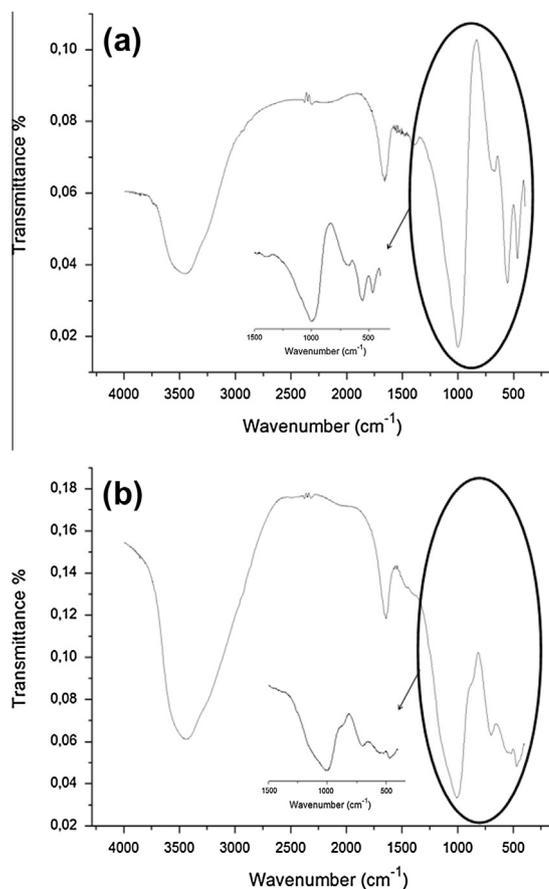


Fig. 5. FTIR spectrum of zeolitic material before and after contact with a solution of 135 ppm Cr(III).

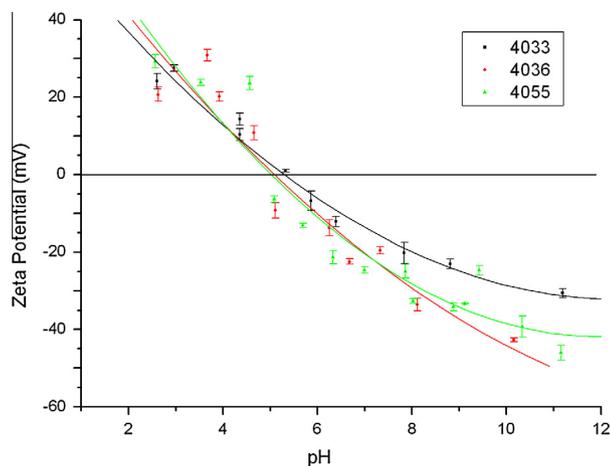


Fig. 6. Zeta potential curves for the indicated samples.

Absorption bands representing the zeolite secondary structure (related to D4R) were observed between 450 and 600 cm^{-1} , with intensities usually related to structural ordering. These band intensities decrease markedly after contact with the Cr(III) solution to give rise to a new band between 800–900 cm^{-1} , which, in turn, may be ascribed to the onset of amorphization in the zeolite structure. These results are very similar to some previously published using pure Na-A [9].

Fig. 6 presents the zeta potential curve versus pH for the zeolitic material before (sample 4033) and after Cr(III) exchange using solutions of 42 and 135 ppm (samples 4055 and 4036, respectively).

The changes in the surface charge parameter PZC of the obtained FCC catalyst (PZC at pH = 5.2, Fig. 6) and the pure zeolite (Na-A, PZC at pH = 8.1) [10] could be assigned partly to the mineral content determined by XRD (Table 1), as was obtained previously for soil samples with different mineral contents [11] or SiO_2 and Al_2O_3 mixtures [12], taking into account that anatase, mullite, Na-nepheline, and hydrosodalite have PZC of 5.9, 7.3, 4.0, and 11.0, respectively [13–15,10]. It is known that in acid solutions, Cr(III) hydrolyzes to species such as $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_2$, $\text{Cr}_2(\text{OH})_4$, $\text{Cr}_6(\text{OH})_{12}$, and $\text{Cr}_6(\text{OH})_{15}$ [16], so if there was a surface adsorption of Cr(III) or one of its hydrated species, this phenomenon would shift the PZC toward pH values higher than those of hydrous Cr(III) oxides, around pH 8.45 [17].

The pH difference of PZC found among sample 4033 and Cr-containing samples 4036 and 4055 of 0.2 (0.5 pH unit) corresponded to half of a standard deviation [14].

The absence of a net charge change observed in the pH range 2–7 for zeolite surfaces with and without sorbed Cr(III) (Fig. 5) and similarities found in their XRD patterns (Fig. 1) could indicate that Cr(III) cation was predominantly present in the zeolite framework

occupying exchange sites as happened in Cr(III) adsorption on bentonite [18] or Pb(II) on zeolites [19].

4. Conclusions

The results indicate that the material obtained by reconversion of an exhausted FCC catalyst has a large percentage of zeolite Na-A. This material effectively retains Cr(III) cations present in aqueous solutions. The XRD and FTIR analyses indicated that chromium incorporation produces an amorphization of the material, and PZC shows no surface adsorption of charged chromium species. SEM analysis shows that after chromium sorption, the initial microspheroidal catalyst morphology was maintained. The chromium atom percentages are significantly higher in the outer microsphere surface, where the zeolite crystals are situated, than the values determined in the interior of the microspheres. Chromium cations replace sodium cations, occupying exchange positions, and play the role of countering the negative charge of A zeolite framework. The incorporation of Cr(III) cations within the crystal structure might be considered beneficial for cation inertization, because electrostatic attraction contributes to avoiding leaching.

Acknowledgment

M.R. Gonzalez thanks CONICET for a doctoral scholarship.

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