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Characterization of Chromium-Substituted Zeolite BEA

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Chromium-incorporated BEA zeolite samples (CAB) are synthesized via a hydrothermal procedure, and their chemical compositions are analyzed by both the ICP-AES and EDX techniques. Synthesized samples are characterized for the local environment of chromium through FTIR, thermal analysis and cyclic voltammetry. An observation of a notable band in FTIR (at 955 $\mathrm{cm^{-1}}$) of calcined/acetic acid-washed samples of CAB revealed that at least a part of chromium is associated with the framework. In a thermal analysis, a high-temperature (643–773 K) desorption peak of $\mathrm{TEA^+}$ was noticed; the peak size increased along with an increase in the chromium content. Cyclic voltammograms of as-synthesized, calcined and acetic acid-treated samples gave ample evidence for the incorporation of chromium into the framework. Acid-washed CAB samples showed framework-stabilized chromium in a zeolite BEA structure, possibly under two different local environments, i.e. tetrahedral and square pyramidal sites.

A combination of isolated transition-metal ions with the shape-selectivity feature of zeolites makes them fascinating as heterogeneous oxidative catalysts.[1] Chromium-substituted Crβ, Cr-MCM-41, CrS-1, CrAPO-5, CrAPO-11 and CrAPSO-37 are found to be active for hydroxylation and oxidation reactions.[2–7] Chromium substitution in microporous materials, such as CrS-1, CrS-2, CrZSM-5, CrMOR, CrAPO-5, CrAPO-11, CrAPSO-11 and CrAPSO-37, and also in mesoporous material, MCM-41, has been reported in the literature.[3–24] Since chromium is weakly bound to an oxygen framework, the characterization of the local environment for chromium in the above-mentioned materials always requires a combination of several spectral techniques and pretreatments.

Cyclic voltammetry using modified electrodes is an additional tool for probing the nature and co-ordination of the electroactive species present in the framework of zeolites. Because the method is very sensitive, it is possible to know the nature of electroactive metals even at very low concentrations. Venkatathri et al[25,26] and de Castro Martins et al[27] have already proved that only lattice vanadium and titanium species in respective materials of VS-1, VS-2, VAlβ, VAPO-5 and TS-1 can undergo redox cycles, but not the extra-lattice species. Chromium containing as-synthesized MCM-41 and Silicalite-1 materials have also been found to have a similar pattern of results with a set of redox peaks at $E_{1/2} \approx +588$ mV approximately corresponding to a two-electron transfer ($\mathrm{Cr^{3+}/Cr^{5+}}$) system.[12,28] This paper discusses a detailed study on chromium substitution in large-pore zeolite BEA using FTIR, TG-DTG and cyclic voltammetry.

Experimental

A brief synthesis procedure towards the preparation of chromium-incorporated samples follows. Part of tetraethyl ammonium hydroxide (TEAOH) was diluted with the required amount of water, to which sodium aluminate and tetraethyl orthosilicate (TEOS) were added at room temperature with stirring. A solution of chromium(III) nitrate and the remaining TEAOH were added for the completion of TEOS hydrolysis. The mixture was stirred for one hour at room temperature (298 K) and five hours at 338 K to distill-off any formed ethanol. Finally, a resultant transparent light green gel was poured into a 100 mL Teflon-lined autoclave and heated at 408 ± 2 K in an oven for 10 days. After cooling the autoclaves, the samples were centrifuged, washed, dried at 383 K and calcined at 723 K for 16 h. The synthesized samples are designated in this manuscript as AB for aluminum beta and CAB for chromium-aluminum beta samples. CAB samples were further arranged from 1 to 5 in order to show any change in the chemical composition with respect to pretreatments, like calcination and an acetic acid treatment. Compositional details of gel (G), calcined (C) and acid washed (W) samples are presented in Table 1. AB-E was a 2 wt% Cr(III) ion-exchanged sample of AB-A, that was calcined before and after ion exchange. The compositions of as-synthesized AB-A and CAB-xA (x = 1–5) samples were essentially the same as those of AB-C and CAB-xC (x = 1–5), except for the amount of template, whose values are given in Table 2.

The chemical analysis of synthesized samples was performed by ICP-AES (inductively coupled plasma atomic emission spectroscopy, ARL 3410 with minitorch) and EDX (energy dispersive X-ray, JSM 5200, SEM combined with EDX) techniques. All FTIR (Fourier transform infra red) spectra were recorded on a Bruker IFS 66V spectrometer using a KBr pellet technique. The TGA (thermo-gravimetric analysis) and DTG (differential thermo-gravimetry) spectra of as-synthesized AB and CAB samples were recorded with a Mettler TA 4000 series instrument. For cyclic voltametric (CV) experiments, modified carbon-paste electrodes were prepared by mixing 100 mg of graphite, 100 mg of zeolite and 10 mg of polystyrene in 2 mL of THF. An electrode was then coated with the above-mentioned paste. Experiments were carried out in a cyclic voltammeter (Model RE 0091 with X-Y recorder) with a three-electrode single-compartment cell. A standard calomel electrode was used as a reference and a platinum foil was used as a counter electrode. The working electrode was a

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Table 1. Chemical Composition of Gel (G), Calcined (C) and Acetic Acid Washed (W) Samples of Aluminum Beta (AB) and Chromo-Aluminum Beta (CAB).

Sample	$Na_2O \times 10^{-2}$	SiO_2	$Al_2O_3 \times 10^{-2}$	$Cr_2O_3 \times 10^{-3}$	Si/Cr [a)]	Si/Cr [b)]	Si/Al	Surface area/$m^2\ g^{-1}$
AB-G	3.5	1	3.7	—	17.2 [c)]	0.435 [d)]	13.5	—
CAB-1G				7.9	63.3			
CAB-2G				3.7	135.1			
CAB-3G				2.9	172.4			
CAB-4G				2.2	227.3			
CAB-5G				1.5	333.3			
AB-C	3.0		3.3	—	—	—	15.2	470
CAB-1C	1.9		2.6	3.21	156.0	139.0	19.2	456
CAB-2C			2.8	2.74	183.0	162.0	17.9	482
CAB-3C			2.8	2.20	227.0	194.0	17.9	486
CAB-4C			3.2	1.83	273.0	220.0	15.6	475
CAB-5C			3.0	1.32	379.0	315.0	16.7	439
CAB-1W	0.36		2.2	1.92	260.0	244.0	22.7	389
CAB-2W	0.32		2.5	1.62	308.0	287.0	20.0	397
CAB-3W	0.32		2.4	1.31	381.0	323.0	20.8	401
CAB-4W	0.38		2.7	1.12	446.0	384.0	18.5	398
CAB-5W	0.27		2.7	0.93	537.0	463.0	18.5	405

a) from ICP-AES ; b) from EDX ; c), d) molar ratios of water and $(TEA)_2O$ respectively.

Table 2. Results of Thermal Analysis

Sample	Chromium content (molar ratio, $\times 10^{-3}$)	T = 453–643 K, TEAOH		T = 643-773 K, TEA^+		Overall loss, ($TEAOH + TEA^+$)	
		Weight loss in		Weight loss in		Weight loss in	
		Millimoles	(%)	Millimoles	(%)	Millimoles	(%)
AB-A	—	1.09	16.00	0.16	2.35	1.25	18.35
CAB-1A	3.21	0.99	14.53	0.34	4.99	1.33	19.52
CAB-2A	2.74	1.02	14.97	0.27	4.01	1.29	18.98
CAB-3A	2.20	0.98	14.38	0.25	3.67	1.23	18.05
CAB-4A	1.83	0.87	12.77	0.23	3.42	1.10	16.19
CAB-5A	1.32	0.89	13.06	0.23	3.33	1.12	16.39

A: As-synthesized sample.

graphite-disc electrode and 0.5 M NaCl was used as the electrolyte. The electrolyte solution was deoxygenated by purging argon, and all of the experiments were carried out at 298 K.

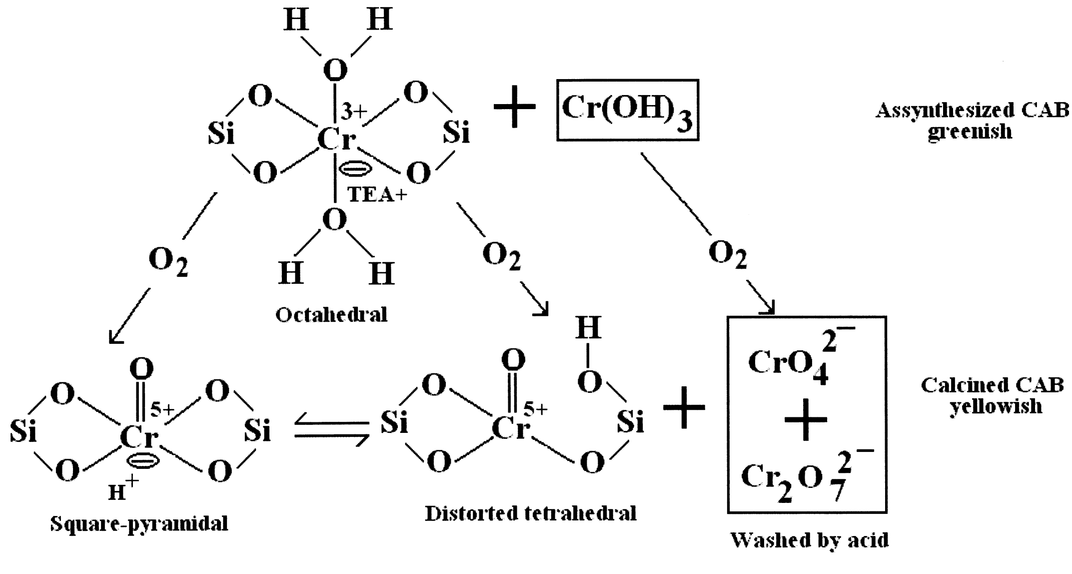
Physico-Chemical Characterization

The crystallinity and phase purity of the synthesized beta samples were good, based on the XRD (X-ray diffractogram), surface area (Table 1) and SEM (scanning electron microscope, 0.5–1.0 (μm size cuboid-like crystals) results. Upon calcination, as-synthesized light-green chromosilicate with octahedral[2] Cr(III) ions became yellow in color. The yellow coloration strongly suggested the formation of an anionic external framework of Cr(VI)-like CrO_4^{2-} or $Cr_2O_7^{2-}$ species.[2,10] This was confirmed by a positive silver nitrate test of the washings.

As shown in Scheme 1 the framework Cr(III) was oxidized to the Cr(V)[1,7,21–24] species, which has been reported to occupy either a square-pyramidal site[22] or a distorted-tetrahedral site.[21–24] It is presumed that the presence of abundant external chromium (~60%, leachable) may link framework-Cr(V) species at different sites, and its deposition at the pore opening may cause pore blockage.

In an attempt to eliminate any extra lattice anionic species, the calcined chromium beta samples were washed with 1 M acetic acid[2,10] and re-calcined (became cream color). The acidic treatment removed all leachable chromium (weakly bound chromium to the framework and external framework species, like CrO_4^{2-} and $Cr_2O_7^{2-}$) from CAB samples. Also, the acid treatment may clear any pore blockage in the channels. Hence, the remaining unleached chromium (Table 1) may exist as an isolated framework-stabilized Cr(V) species in both square-pyramidal and distorted-tetrahedral sites. Also, based on Table 1, dealumination invariably occurred during the acid treatment.

FTIR. As can be seen from Fig. 1, the spectra of as-synthesized Al(AB-A) and Cr-Al beta samples (CAB-1A) differ from the respective spectra of calcined samples (AB-C and CAB-1C) at a stretching region of the Si–O bonds (~1060 cm^{-1}) and at a template region (~1460 cm^{-1}). The latter region disappeared because of the calcination procedure. Additionally, chromium samples showed a remarkable difference at



Scheme 1.

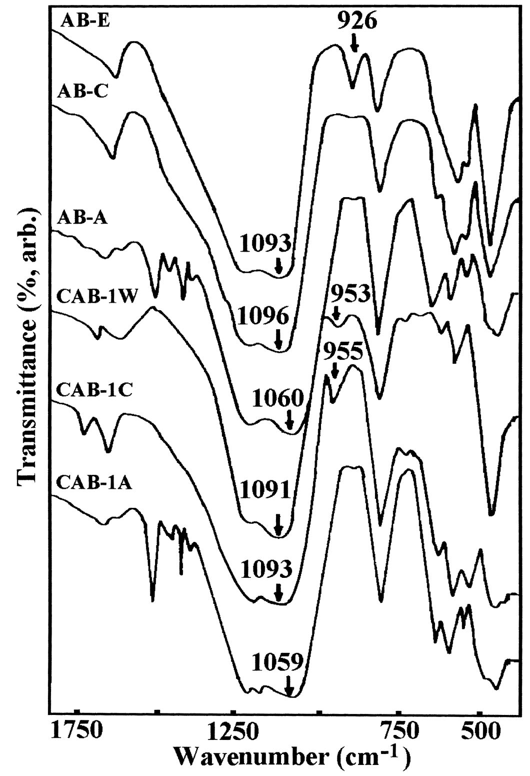


Fig. 1. FTIR spectra: CrAlβ — CAB-1A, CAB-1C and CAB-1W; Alβ — AB-A and AB-C; Alβ ion-exchanged with Cr^{3+} ions - AB-E.

955 cm^{-1} due to Si–O^- defect sites,[10] which might have been created by the framework-attached chromium. This band was retained by the acetic acid treated sample (CAB-1W), indicating a possible inclusion or attachment of chromium in the framework. The 955 cm^{-1} band is generally taken as a proof for the incorporation of metal in the zeolite matrix.[1,2,10] On the contrary, a calcined Cr(III) ion-exchanged AB sample (AB-E) showed a distinct peak at 926 cm^{-1} for extra-lattice Cr(III) ions. Further, the sensitive asymmetric Si–O stretching band at ~1060 cm^{-1} is shifted to a high wavenumber (1094–1096 cm^{-1}) for calcined and acid-treated samples. Upon calcination and the subsequent acid treatment, the framework became enriched with silicon as other framework species were removed. The shift is thus quite conceivably from the vibration of silicon-enriched framework.[29]

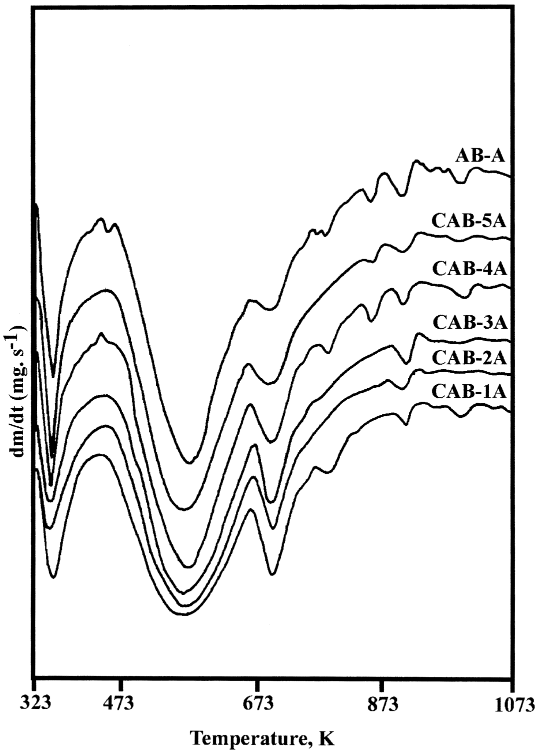


Fig. 2. DTG curves: CAB-1A – CAB-5A and AB-A samples.

Thermal Analysis. Three different temperature ranges can be distinguished from the DTG curves (Fig. 2). The temperature range, 323–473 K, is due to the desorption of water from the channels and the surface. Occluded template molecules present in the channels are desorbed around 453–643 K.[30,31] The framework-interacted tetraethyl ammonium template cations (TEA$^+$, as charge balancing cations) are desorbed at a high temperature range, 643–773 K. Although the first two temperature ranges are not very informative, the 643–773 K range can give information regarding metal substitution, since the charge-balancing cations must be around at anionic sites of the framework i.e., the aluminum centers or the substituted metal (chromium) centers.[30] Quantitative information regarding TEA$^+$ is presented in Table 2. The increasing trend of desorbed TEA$^+$ with chromium content (CAB-5A → CAB-1A) revealed that at least a part of the chromium is incorporated into the framework, or is firmly attached to the framework.

Cyclic Voltammetry. Strictly speaking, a voltammogram is a characteristic of a particular metal with symmetrical shape and equal heights of anodic and cathodic peaks. Figure 3 represents the positively scanned cyclic voltammograms of AB and CAB samples. No peak can be observed with as-synthesized and calcined samples of AB, because they do not contain any electroactive species. However, although CV studies on as-synthesized (CAB-1A) and calcined (CAB-1C) samples of CAB showed a single broad redox couple, the acid-washed sample (CAB-1W) gave two sets of redox couples that may correspond to chromium in two different environments in the framework of BEA zeolite, as depicted in Scheme 1.

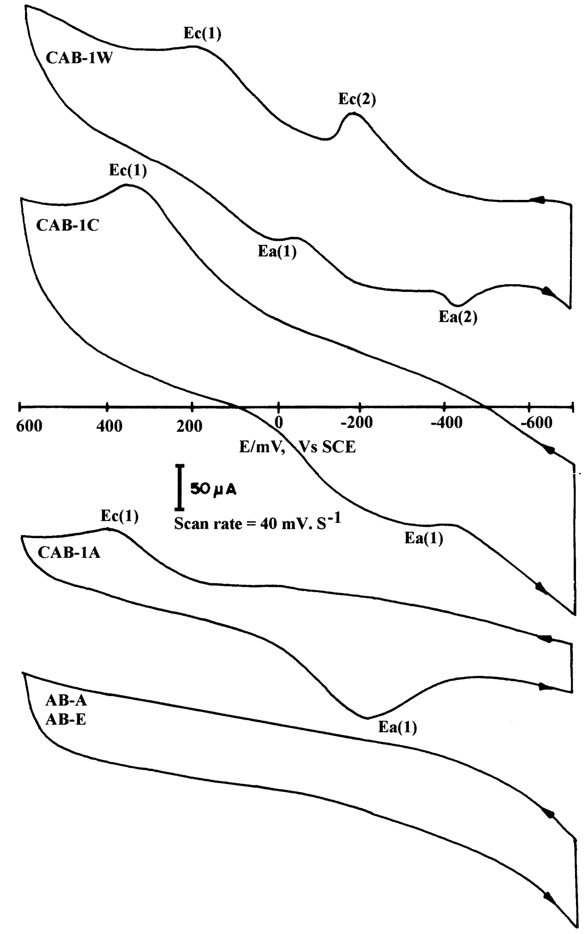


Fig. 3. Cyclic voltammograms: Alβ (AB-A); Alβ ion-exchanged with Cr^{3+} ions (AB-E) and CrAlβ (CAB-1A, CAB-1C and CAB-1W) samples.

The cathodic and anodic peak potentials and peak currents of CAB-1A, CAB-1C and CAB-1W are given in Table 3. As can be seen from Table 3, the anodic peak current (I_a) of as-synthesized CAB-1A is much larger than the cathodic peak current (I_c), indicating a difficulty concerning the reversible reduction process at the cathode. Consequently, the I_a/I_c ratio increased with the scan rate. If the sample is either CAB-1C or CAB-1W, the peak currents are almost equal to each other and I_a/I_c is around unity, indicating easy reversibility of the redox couple.

The above-mentioned cyclic voltammetric results envisage the following: initially, Cr(III) ions in an as-synthesized sample might occupy octahedral sites, and a part (deeply inside the channels) of them would be inaccessible to the electrolyte due to a blockage of the channels by both occluded TEAOH and charge-balancing TEA$^+$ cations. The blockage can be understood from the peak currents, which are relatively smaller for a CAB-1A sample than for CAB-1C. Also, within the framework structure, electrochemically formed Cr(V) ions from CAB-1A may pose a difficulty concerning the reversible reduction process. This difficulty, however, seems to be eliminated in a CAB-1C sample, whose framework might be associated with the oxo-chromium(V) ion[1,7,21–24] in either tetrahedral[21–24] or square-pyramidal[22] geometries. The easy reversibility of the redox system is in agreement with the observed I_a/I_c ratio (~1.00) for a CAB-1C sample. The presence of Cr(V) ions in CAB-1C and CAB-1W samples was confirmed by ESR.[2] A similar oxo-species has also been proposed in the literature for titanium[27] and vanadium[25,28] - containing molecular sieves.

Further, a close analysis of Table 3 reveals that the peak current [$I_a(1)$] of CAB-1C is almost equal to the summation of the currents [$I_a(1) + I_a(2)$] of both peaks of CAB-1W. Because it is known that the peak current is proportional to the number of redox species,[32] it is clear that the number of chromium species involved in the redox cycle is almost equal in both the CAB-1C and CAB-1W samples. This observation further validates the earlier presumption that the Cr(V) species in both environments might have connected through external framework chromium species, and thus resulting in a single redox couple for CAB-1C. The interconnection between Cr(V) ions may be further stressed from an observation that the anodic peak potential of the CAB-1C sample is nearly an average of the anodic potential of the CAB-1W peaks. However, there is a drift from an average value to a high value in the cathodic peak potential. This drift may arise from the heterogeneity of the sample, which causes a slower rate of the reduction process at the cathode compared to the anodic oxidation process, which is often encountered with solid samples.[32]

It is difficult to draw any conclusion about the number of electrons involved in the redox process. Table 3 shows that the ΔE values (~600 mV) are much larger than even that for a single-electron redox system ($\Delta E = 59/n$ mV, where n = number of electrons involved in the reaction). This is also mostly due to the heterogeneity and complex nature of the zeolite system, whereas the available equations are more applicable to a ho-

Table 3. Cyclic Voltammetric Data of CAB Samples

Sample	Scan rate, mV S^{-1}	Cathodic current, I_c/μA.		Anodic current, I_a/μA.		Cathodic potential, E_c/V, vs SCE		Anodic potential, E_a/V, vs SCE		I_a/I_c		ΔE/V		$E_{1/2}$/V	
		$I_c(1)$	$I_c(2)$	$I_a(1)$	$I_a(2)$	$E_c(1)$	$E_c(2)$	$E_a(1)$	$E_a(2)$	$I_a/I_c(1)$	$I_a/I_c(2)$	$\Delta E(1)$	$\Delta E(2)$	$E_{1/2}$ (1)	$E_{1/2}$ (2)
CAB-1A	40	35	—	90	—	0.44	—	−0.20	—	2.57	—	0.64	—	0.12	—
	60	40	—	100	—	0.41	—	−0.20	—	2.50	—	0.61	—	0.11	—
	80	40	—	115	—	0.41	—	−0.19	—	2.88	—	0.60	—	0.11	—
	100	40	—	120	—	0.42	—	−0.18	—	3.00	—	0.60	—	0.12	—
CAB-1C	40	90	—	100	—	0.33	—	−0.29	—	1.11	—	0.62	—	0.02	—
	60	100	—	115	—	0.33	—	−0.29	—	1.15	—	0.62	—	0.03	—
	80	115	—	125	—	0.33	—	−0.28	—	1.09	—	0.61	—	0.02	—
	100	125	—	130	—	0.34	—	−0.26	—	1.04	—	0.60	—	0.04	—
CAB-1W	40	40	40	35	40	0.18	−0.18	0.02	−0.43	0.88	1.00	0.16	0.25	0.10	−0.31
	60	45	50	40	50	0.21	−0.17	−0.02	−0.44	0.89	1.00	0.23	0.27	0.10	−0.31
	80	55	70	50	65	0.23	−0.15	−0.04	−0.45	0.91	0.93	0.27	0.30	0.10	−0.30
	100	60	70	55	65	0.24	−0.15	−0.06	−0.45	0.92	0.93	0.30	0.30	0.09	−0.31

$\Delta E = E_c - E_a$ and $E_{1/2} = E_a + E_c/2$.

mogeneous system.[32] Similar discrepancies were also reported in the literature for vanadium species in zeolites.[25,28] Also, under similar conditions the Cr(Ⅲ) ion-exchanged sample (AB-E in Fig. 3) does not show any redox couple in the working-potential region. The ion-exchanged chromium might have been extracted to the solution phase and performed redox at different potential regions. In conjunction with ESR,[2] the redox couple found in the cyclic voltammograms of CAB-1A, CAB-1C and CAB-1W might be the Cr^{3+}/Cr^{5+} system, which is in good agreement with the redox couple found in the CrS-1 sample.[12]

Moreover, the invariance nature of the CV spectra of CAB-1A, CAB-1C and CAB-1W with continuous cycling confirms the existence of structure-stabilized chromium in zeolite BEA. Cyclic voltammetric studies of acid-washed samples strongly suggest the possible inclusion of a part of chromium ions within the framework structure.

Conclusions

The characterization of a calcined/acetic acid-treated sample by chemical analysis, thermal analysis and FTIR showed that a part of the chromium ions present in the as-synthesized material are firmly attached with the framework oxygen, possibly through the formation of oxo-chromium species. Cyclic voltammograms of the calcined/acid treated samples confirmed the existence of a structure-stabilized chromium in its framework.

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