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SYNTHESIS AND CHARACTERIZATION OF HYDROXY-CHROMIUM PILLARED BENTONITE

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Introduction

Pillared interlayred clays are a very important family of porous solids that has been developed in the last years. Furthermore smectite clay can be pillared with oligomeric metal hydroxide ions for that, many researches have been reported the synthesis and characterization of Al(III)[1]; Zr(IV)[2]; Ti(III)[3]; Fe(III)[4]; Cr(III)[5] and Rh(III)[6] pillared clays. These hydrolytic polynuclear metal cations can form thermally stable materials and micro porous structures where the clay layers are held apart by catalytically active metal oxide pillars. The porous materials are of interest mostly thanks to their potential usefulness in catalysis. In particular, chromium pillared clays have attracted the researchers attention after being tested as catalytic in a wide range of reactions such as catalytic conversion of hydrocarbons [7], ester formations [8] and elimination of water from alcohols[9]. This is due essentially to their high surface area, sizeable gallery height, porous structure and acidity [10], [11], [12], [13] .

In this work the synthesis procedure includes three principal steps: first the preparation of polyoxocations by hydrolysis of certain multivalent cations which under appropriate conditions give rise to cationic polymeric species; second, the formation of the intercalated clays by ion exchange of the original charge compensating cations of swellable smectite clays by the polyoxocations synthesized in first step and finally the formation of the pillared clays by calcination of the intercalated clays to high temperatures at which the metastable polyxocations are transformed into stable oxi-hydroxidic phases, which act as pillars that support the clay layers and maintain them separated. The synthesized pillared clays were characterized focusing mainly on the properties of these new materials (basal spacing, thermal stability surface area and pore structure).

Experimental

Hydroxy-Cr oligomeric solution

A number of methods have been developed to produce the chromium oligomers spaces that are incorporated into the interlamellar space of clays. In our case the Cr(III) oligomers have been prepared as follows: a certain amount of aqueous Na_2CO_3 was gradually added to aqueous chromium nitrate solution or chromium chlorite solution with constant stirring until a final CO_3^{2+}/Cr^{3+} ratio of 1 . The mixture is maintained at a temperature of 80°C for 36h [14], [15],[16].

Pillaring process

Na^+-clay was obtained from the Haidoudi deposit, a Tunisian interstratified illite-smectite bentonite mineral [17]. In this study the illitic fraction represents about 15% of the interstratified material; the smectitic fraction is in sodium form which pronounced a beidellitic character. The average elemental formula determined from the Na exchange purified fraction is

$$Na_{0.54}\,K_{0.16}\,Ca_{0.03}\,(Si_{7.4}\,Al_{0.6})^{IV}\,(Al_{2.94}\,Fe_{0.79}\,Mg_{0.33})^{VI}\,O_{22}$$

The cationic capacity exchange of material is about 80 meq/100g of calcined clay and its nitrogen BET surface area is 100 m^2/g.

The intercalation was achieved by adding slowly a suspension of Na^+- clay to the solution containing Cr (III) oligomers at room temperature. The mixture was stirred continuously for 2h to ensure that the intercalation has been completed and then the suspension was centrifuged, the supernatant removed and the green clay material repeatedly washed with distilled water and centrifuged.

After intercalation the pillared clays are obtained by heating in vacuum at 350°C are denoted as Hp n meq(Cl) or Hp n meq(NO_3), where n indicates the molar ratio of CO_3^{2+} to Cr^{3+} cations.

Analysis of products

The basal spacing d_{001} were measured with X-Ray diffractometer using Ni-filtered CuK α radiation by scanning 1° (2θ) min^{-1} between 2° and 20°. The determination of chemical composition sample was accomplished by atomic absorption spectroscopy (AAS VARIO) after dissolving the clay samples in a mixture

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of three acid extracts (HCl; H_2SO_4; HNO_3) in a known proportion. The proportion of silica was determined by gravimetric method. Thermal studies were performed on Perkin-Elmer analysers, TGA and DTA for thermogravimetric and differential thermal analysis, respectively. All measurements were carried out at a heating rate of 10 °C/min under a flow of nitrogen. The BET surface area and pore size structure data were derived from N_2 adsorption–desorption isotherm at 77K using an Autosorb-1(quanta chrome) device. All pillared clays were degassed at 373K for 2h.

Results and discussion

Characterization

Elemental composition

The chemical compositions of all the solids are given in Table 1. It can be observed a decrease in the amount of Na^+, Mg^{2+} and Al^{3+} cations in modified samples compared to natural clay. In addition, modified clays showed the presence of Cr species. We can estimate from these observations the incorporation of chromium species which have been intercalated in the place of Al^{3+} and Na^+ cations. On the other hand, the amount of fixed chromium species varied almost linearly with the initial concentration of Cr^{3+} cations reaching high fixation amounts, mainly in the case of 60 meq (NO_3). From chemical analysis we cannot confirm the formation of polynuclear chromium. Evidence for the intercalation of hydroxy-chromium species in bentonite is provided by XRD diffractograms.

Table 1. Elemental composition of chromium pillared clays

Sample	Al_2O_3	SiO_2	Fe_2O_3	Mg O	Na_2O	K_2O	Ca O	Cr_2O_3	PF
purified Clay (Hp)	18.1	54.28	7.45	3.5	2.12	1.7	0.089	0	13.73
$(Hp)_{20}$ (NO_3)	17.52	53.8	7.05	2.3	0.63	0.68	0.063	2.45	16.44
$(Hp)_{40}$ (NO_3)	14	51.69	8.23	2.51	0.73	0.99	0.07	3.2	18.87
$(Hp)_{60}$ (NO_3)	12.5	48.35	8.83	3.06	0.79	1.57	0.081	5.84	21.39
$(Hp)_{20}$ (Cl)	17.18	53.32	7.86	2.1	0.5	0.57	0.056	1.95	16.46
$(Hp)_{40}$ (Cl)	14.23	52.3	8.2	2.4	0.68	0.912	0.071	2.6	18.11
$(Hp)_{60}$ (Cl)	12.08	50.81	8.55	2.8	0.77	1.44	0.087	5.6	19.57

XRD Analysis

The XRD patterns along with basal spacing (d_{001}) data of n meq (Cl) and n meq(NO_3) compounds are presented in figure. 1. It reveals that d_{001} is about 13.8 Å for natural clay and it ranged from 18.43 to 21.13 for chromium modified clays. Taking into account the thickness of the silicate layer (about 9.6 Å) an increase of d_{001} has been observed and which varied from 8.83 to 11.53 Å. These values are in agreement with that found in the literature for chromium pillared clays.

In fact, Roulia has reported the synthesis of chromium pillared clays with basal spacing of 24.5 Å, the intercalating solution has been prepared by quick addition of base and acid to Cr (III) monomeric solutions followed by reflux [18]. On the other side C.Volzone has reported the preparation at 60°C of OH-Cr smectites with different proportions of Cr^{3+} to clay. The authors showed a chromium pillared clays gallery heights of 10.9-11.1Å [19]. Other experiments were performed with intercalation of Cr(III) polynuclear species generated by aging hot solutions of Cr^{3+} in base such that OH/Cr=0.5-2.5 [20,21] this method has yielded Cr(III) pillared clays with d_{001} spacing of 21Å. Whereas another method that based on intercalation of individual Cr (III) hydrolytic oligomers gave materials with d_{001} spacing of 15.7Å [22] which were consistent with the geometries of the intercalated oligomers. These methods also allowed the study of the ion-exchange properties of these materials and it was found that when the Cr(III) intercalated clays and the oligomers became covalently bound to the silicate clay sheets and that the intercalated oligomers did not polymerize whilst within the clay layers.

In this work, the larger d_{001} spacing was observed with solutions of higher Cr (III) oligomers content presumably because these solutions contain larger and more highly charged polynuclear cations which are preferentially incorporated into the clay. On the other hand a higher d_{001} was obtained by using nitrate as anion in the intercalating solution. This increase may be attributed to the formation of higher Cr (III) oligomers. From figure 1, we can notice the d_{001} peak are sharper extended in chromium pillared clays compared to unmodified clay especially Hp_{40} (NO_3), $Hp_{40}(Cl)$ and $Hp_{60}(Cl)$ samples. This observation can be attributed to the heterogeneity of intercalated chromium hydroxyl species which has been caused by the incomplete pillaring of the clay, to the insufficient swelling of the host material and to the presence of large Cr (III) oligomers that are adsorbed in the surface, blocking pores, thus hindering intercalation [16].

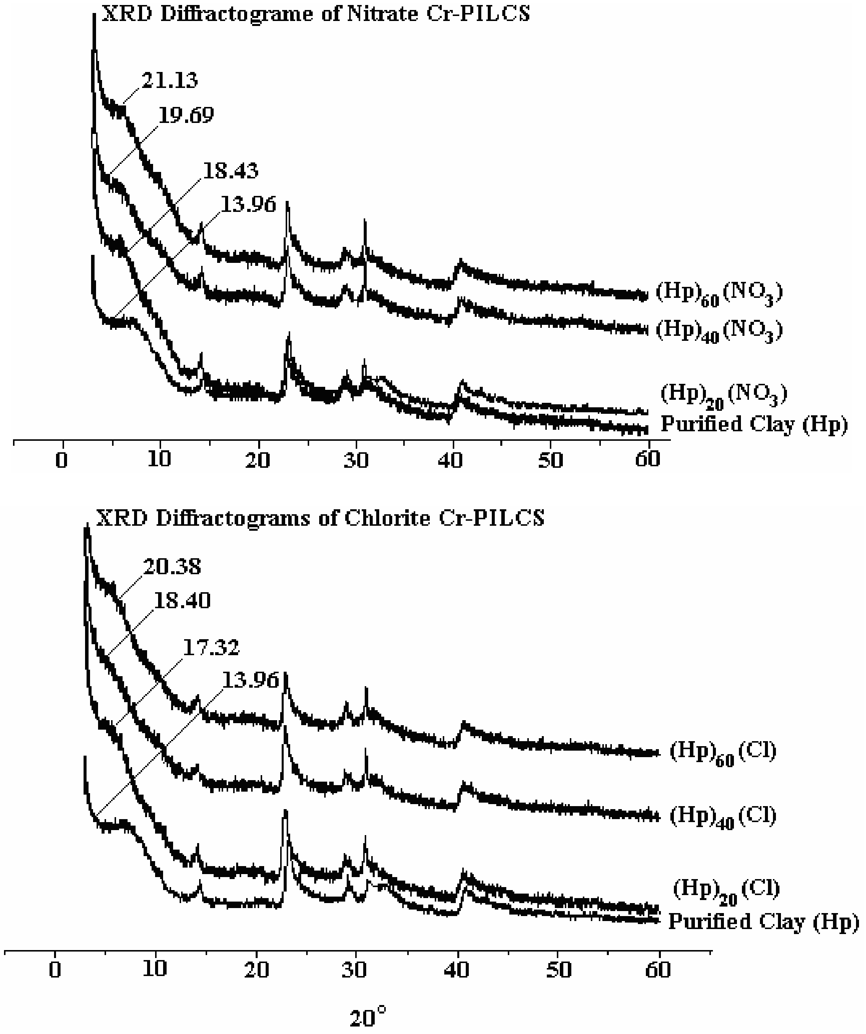


Fig.1. XRD diagrams of crude, purified and chromium pillared clays

Textural Properties

Nitrogen Adsorption

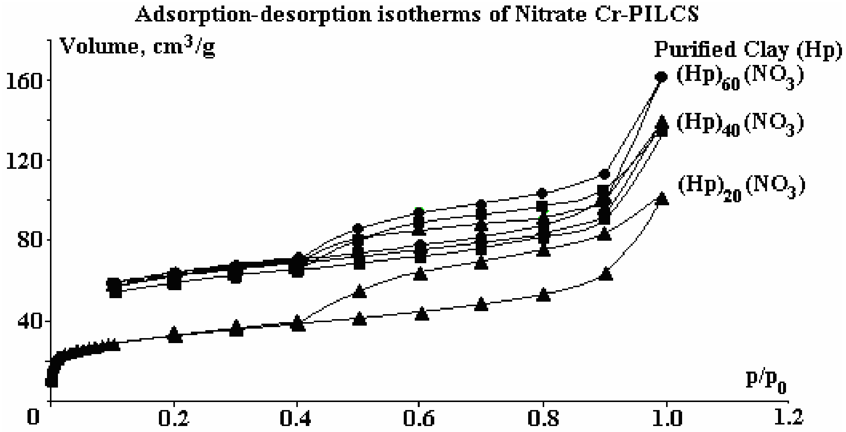
The great importance of textural properties of chromium pillared clays are proved by the amount of published literature related to BET surface area and pore size structure characterizations data .

The BET surface areas, the micro pore and the total pore volumes for all pillared clays are presented in table 2. It can be seen that with increasing of Cr^{3+} cation content the surface area, pore and micro pore volumes increased. The highest surface areas and the most micro pores values have been obtained with pillared clays synthesized using nitrate as anion in the intercalating solution. C .Volzone and co-workers have reported a specific area increase of smectite of about 175 m^2/g after treatment with OH-Cr solution.

The N_2 adsorption–desorption isotherms of different samples are represented in figure 2. It can be noticed that Cr-pillared smectites showed the same shape as the starting material which correspond to H3 type in the IUPAC classification [23]. This hysteresis type corresponds to a system formed by slit-shaped pores having a vertical adsorption branch at a relative pressure close to unity and a desorption branch close to medium pressure. Furthermore the Fig 2 shows that the nitrogen isotherms of Cr(III) intercalated species clay is of type I in the BDDT classification [24] being characteristic of micro porous solids. In the same way, Mikhail Sychev [25] showed a N_2 adsorption isotherm for the chromia-pillared clay of type I.

Table 2. Textural characteristics of chromium pillared clay

Chromium pillared clay	**SBET (m^2g^{-1})**	**Vμp (cm^3/g)**	**Vp (cm^3/g)**
Clay purified	**100**	**0.0125**	**0.18**
Chlorite (Cl) anion			
20	**103.85**	**0.0165**	**0.32**
40	**174.6**	**0.0226**	**0.388**
60	**176.9**	**0.0531**	**0.298**
Nitrate (NO_3) anion			
20	**183**	**0.0562**	**0.25**
40	**194.3**	**0.057**	**0.28**
60	**198.1**	**0.0617**	**0.21**



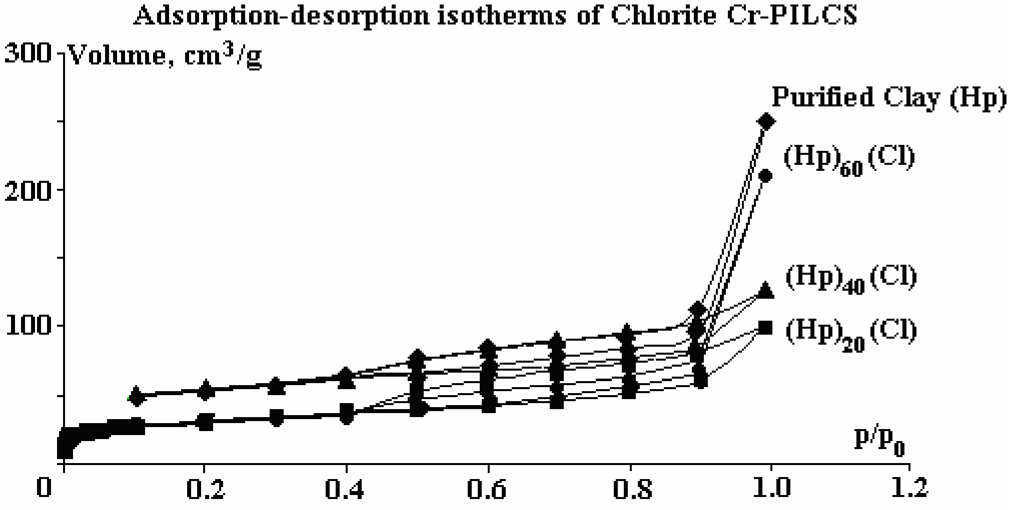


Fig. 2. Isotherms obtained for chromium pillared clays

Thermal stabilities

Differential thermal analysis was used to investigate the thermal stability of pillared clays. As shown in the figure 3 and table 3, for pillared clays, the first endothermic peak in all cases are localised at 42°C-250°C exhibiting a continuous weight loss of about 7-10 wt % which can be attributed to the loss of water. At the same temperature range a shallow endothermic event takes place, which may be possibly related to a rearrangement of the silicate network caused by the water release. Moreover, several other thermal events occur at the pillared clays. For the peak at about 250°C it can be stated that, perhaps, they indicate the presence of different kinds of structural water such as water combined to chromium pillars, axial and equatorial. Other researchers treated this technique on decked chromium pillared clay prepared by various methods for examples chromia–pillared clay has been synthesized from naturally occurring montmorillonite through exchange of interlamellar ions with hydroxychromium polycations exhibits a continuous weight loss of about 24 wt % between 323 and 698K can be attributed to the removal of interlayer water and water coordinated to the hydroxychromium oligomers [25]. A second endothermic peak is observed for temperatures ranged from 250 to 350 °C corresponding to a weight loss of about 5 wt % and can be attributed to the partial oxidation of chromium species and partial collapse of pillars in the clay. Interestingly this peak is observed in natural clay at about 500°C. These results indicated that the pillar structure ameliorates the thermal stability of the clay. In the same way, Sychev proved that the material exhibits a less pronounced and broad weight loss about 3 wt % between 698 and 923 K which most probably reflects the dehydroxylation of pillars [25]. Roula concluded too, after preparation from the samples by different methods that clay pillared with Cr (III) oligomers using the BAR and BA methods as well as clays pillared with Cr (III) monomeric solution were heated at various temperatures under nitrogen, It seems that the first thermal event to occur, in all cases, is the loss of bulk (interlayer) water, which is the most loosely bound, as indicated by the intense non reversible endothermic peak at 373K [18]. On heating under nitrogen the above peak is shifted to about 423K and this has also been observed by Tzou and Pinnavaia [14].

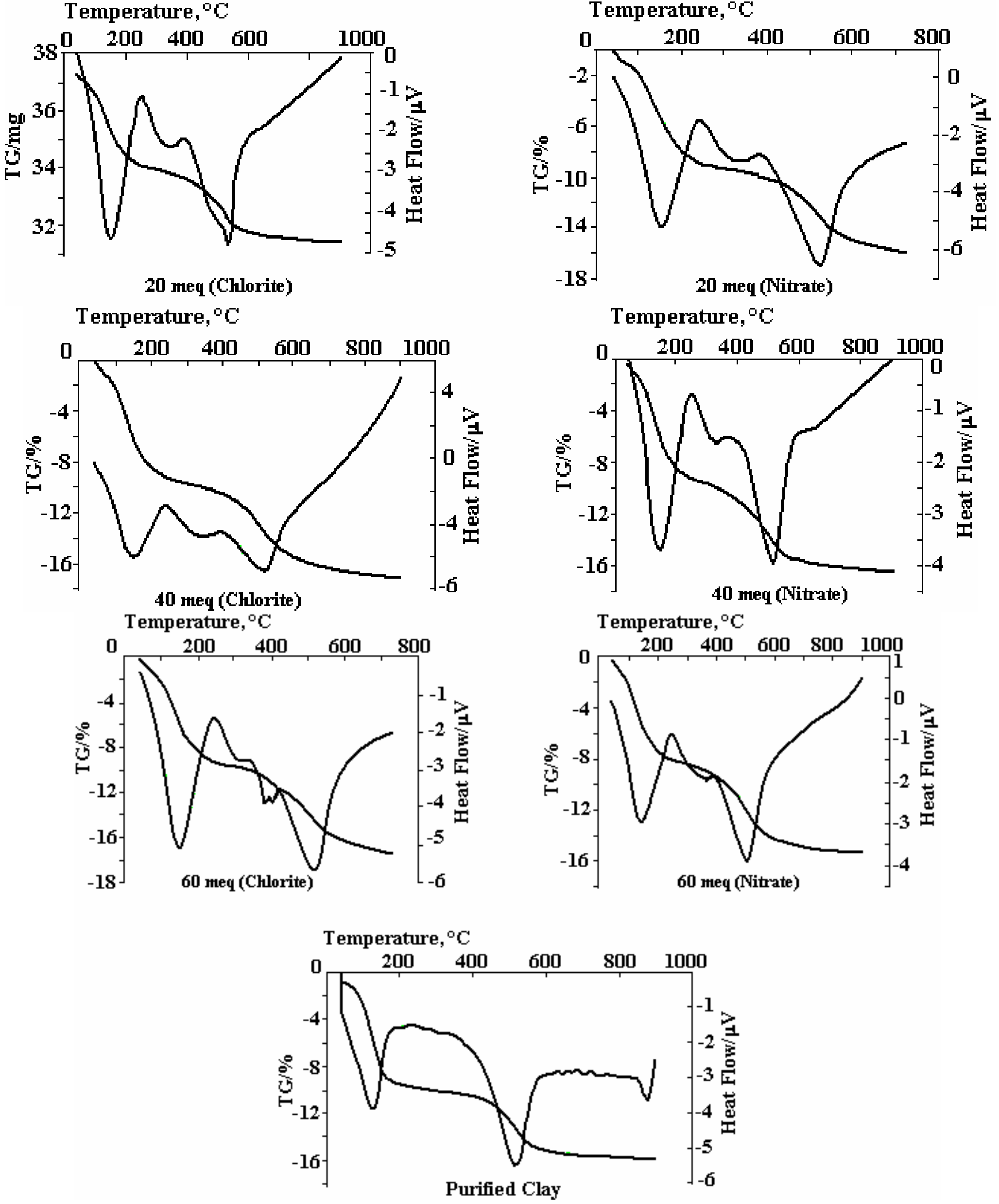
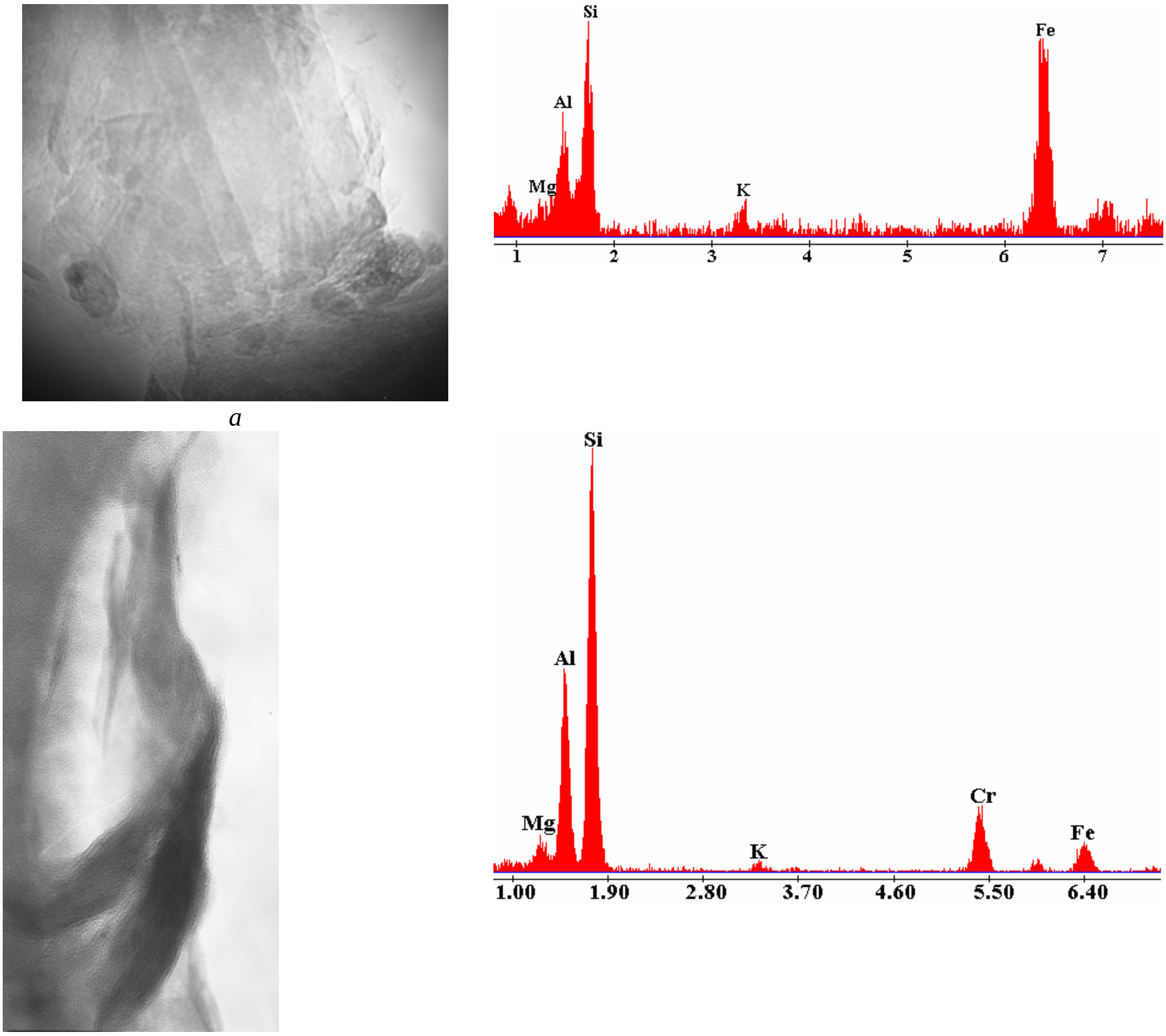


Fig. 3.D.t.a. profiles of chromium pillared clays

Table 3. Thermal weight loss (%) at various stages of thermal analysis of chromium pillared clay

Temperature		Θ = 42-250°C	Θ = 250-350°C	Θ = 350-550°C
Purified clay (Hp)	Weight loss (%)	8.08	4.12	
Nitrate anion				
Hp $_{20}$ (Ni)	Weight loss (%)	8.93	0.83	4.967
Hp $_{40}$ (Ni)	Weight loss (%)	7.562	0.914	5.545
Hp $_{60}$ (Ni)	Weight loss (%)	9.009	1.465	6.03
Chlorite anion				
Hp $_{20}$ (Cl)	Weight loss (%)	7.98	0.636	5.09
Hp $_{40}$ (Cl)	Weight loss (%)	9.23	1.27	5.21
Hp $_{60}$ (Cl)	Weight loss (%)	9.33	1.65	5.367



a

b

Fig. 4.The TEM micrograph of unpillared clays and chromium pillared clays

Scanning electron microscopy

The untreated clay exhibits a distinctively lamellar structure, as the silicate leaves pack after drying (Fig.4,*a*). The clay also exhibits lamellar structure into the particles.

In the other hand pillaring of the smectite causes significant disordering of the stacking structure making the interparticle voids smaller (Fig. 4b).

Due to the insertion of the Cr (III) oligomers, in pillared clays produced, the face-to-face stacking structure of the clay (Fig. 4*b*) is destroyed and a more sponge-like texture appears showing that edge-to-face and edge-to-edge interactions have been developed causing that disordering. These findings are consistent with the broadening of the peaks in the XRD patterns and the decrease of the intensity because of the weakness of scattering along the *z*-axis, observed during pillaring.

The prepared intercalated clays still retain a lamellar structure as indicated in (Fig.4*b*).

Conclusion

Chromium pillared clays are prepared by incorporating Cr (III) oligomeric into the interlamellar space of smectite. Pillaring solution was prepared by addition of Na_2CO_3 to a chromium chlorite solution or chromium nitrate with different concentration.

XRD diffractograms and chemical analysis proved that clays intercalated with Cr (III) oligomers prepared from nitrate intercalating solution presented with a concentration of 60meq /g present the most important gallery height (21.13 Å).

BET surface and micropore analysis demonstrated that the texture of the smectite clay is mostly changed during pillaring. In fact, these pillared clays presented increased BET surface and higher micropore volume. The microporosity is attributed to the Cr oligomers in the interlamellar space and increases with the gallery height.

All Cr-pillared materials are more stable than natural clay (up to 550°C).

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Summary

Chromium pillared clays, in particular, have attracted the researchers attention after being tested as catalyst in a wide range of reactions, like catalytic conversion of hydrocarbons, ester formation and elimination of water from alcohols. The chromium oligomers used for intercalation were prepared by addition of Na_2CO_3 to a chromium nitrate solution or chromium chlorite solution and the mixture is heated at 80°C for 36h.The pillaring clay is obtained by heating intercalated bentonite at 360°C under vacuum. Several Techniques, X-ray diffraction, N_2 adsorption-desorption isotherms and chemical analysis have been used to characterize and to compare the properties of the materials synthesized. Our study consists in determination of the influence of the intercalated OH-Cr group on the structure of Tunisian bentonite. The results showed that the interlamellar distances of pillared bentonite ranged from 17 to 21Å. In addition, the synthesized clays exhibit increased BET surface areas and higher micro pore volumes compared with unmodified clay. On the other hand, the micro pore surface area, the micro pore volume and the d (001) spacing after pillaring increased with the amount of chromium retentions.