

Full Length Research Paper

The textural property of chromium pillared clay

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Accepted 25 May, 2011

Hydroxy-chromium beidellite is of interest for use in catalysis and as adsorbents. The micro porosity of the materials differing in pillar density has been explored. Nitrogen adsorption data obtained at very low relative pressures were used. This paper determines the influence of the OH-Cr species on the structure and texture of modified dioctahedral smectites (beidellite). Minerals varying in cation exchange capacity pillared with various Cr pillar precursor ions can provide a family of catalysts that differ in surface area, porous structure and concentration of active sites. These data were analyzed by means of the method α_s and the BET, Langmuir and Dubinin–Radushkevich approaches. Different types of isotherm equations are used, one to describe adsorption in micro pores while another one for describing adsorption on external surfaces. All methods applied demonstrated that these solids possess micro pores over a broad pore-size range. Chromium pillared clays contain a significant amount of ultramicropores. Interlayer with larger spacing resulted in different specific surface areas and micro pore volumes. Generally, this behaviour could be related to the different structural characteristics of the smectites.

Key words: Chromium pillared clays, micro porosity analysis, nitrogen adsorption-desorption, textural study.

INTRODUCTION

The synthesis of pillared clays has led to the development of new microporous materials of enhanced potential in catalysis and use as adsorbents (Thomas et al., 1992; Baksh et al., 1992).

The chromium pillared clays are traditionally formed via insertion of a poly-hydroxy-metal species into beidellite clay followed by calcinations of the flocculated product to obtain materials in which pores vary according to the cationic species used in the exchange process.

Pillared clays have potential interest for catalysts and adsorbents. Rengasamy and Oades (1978); Brindley and Yamanaka (1979); Vaughan et al. (1979), Vaughan and Lussier (1980); Carr (1985); Pinnavaia et al. (1985); Vaughan et al (1988); Tzou and Pinnavaia (1988); Drljaca et al. (1992) and Volzone et al. (1993, 1995) wrote papers referred to OH-Cr-clay study. Species present in hydrolyzed chromium solution on preparation of OH-Cr smectite were observed by Drljaca et al. (1992) and Volzone et al. (1993), but there are no references

about amount of Cr added to smectite to obtain this one good textural and structural characteristic.

The oxide form of chromium pillared beidellite which is the subject of the present study exhibits a high activity and selectivity in conversion of cyclohexane to benzene (Volzone et al., 1993) ethanol production (Volzone and Clays, 1995) ester formation (Atkins et al., 1983), hydrate alkene (Ballantine et al., 1984; Adams et al., 1981), hydrocracking of n-decane (Bradley and Kyd, 1993), toluene disproportionation (Adams et al., 1982), and elimination of water from alcohols (Ballantine et al., 1983; Ballantine et al., 1984).

Followed from the previous studies, the synthesis of textural properties and structural change of the dioctahedral beidellite being intercalated differing in pillar densities have been investigated in this work. The aim of this work is to deal with approaches of characterization of chromium pillared clay micro porosity.

THEORETICAL PART OF MICRO-PORE ANALYSIS

Many porous materials, such as chromium pillared clays, are characterized by their surface area, micro-pore

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volume and pore size distribution, which are very important properties for their application as catalysts or adsorbents.

Several methods have been developed to deduce the pore structure of micro porous solids from adsorption isotherms, among which the t , α_s and Dubinin-Radushkevich methods are often used (Gil and Montes, 1994; Dubinin, 1985). The method comparison of adsorption data obtained for non-porous sample insure that only the adsorption on the external surface influence the isotherms (Kaneko, 1994).

When the adsorbed volume at each experimental point is plotted against the statistical thickness, t , a linear relation between the adsorbed volume and the t values can be obtained (Sychev et al., 1992).

The estimation of t based on the reference isotherm, leads to determine the same BET constant (C_{BET}) for the tested material. The standard t function and the part of the V - t curve used for linear fitting influence the external surface values and micro pore volume. A strong influence was proved on the evolution of t as a function of P/P_0 (Remy et al., 1996).

Sing (1967) introduced and developed the α_s method in which the normalized adsorption, $\alpha_s (= n/n_{0.4})$ is derived from the isotherm of a reference material by using the amount adsorbed at a relative pressure of 0.4 ($n_{0.4}$) as the normalization factor.

The adsorption in micro pores based on thermodynamic Dubinin-Radushkevich equation (Dubinin, 1985) allows combining a variety of adsorption systems. This equation proves the hypothesis of exhibition of adsorbed molecules and adsorption potential, A , which governs the fractional pore filling. The DR equation is expressed by:

$$V_a/V_0 = \exp. (-(A/\beta E_0)^2)$$

V_a , V_0 , E_0 and β being the amount of adsorption at equilibrium pressure, the micropore volume, the characteristic adsorption energy, and the affinity coefficient characterizing the adsorbate, respectively.

The intersection of the linear part with the lower slope of the plot $\ln V$ according to $\ln^2 (P_0/P)$ brings the micro pore volume. The distribution of pore sizes can be described by the Sum of the contributions from individual pore groups having a pore volume, V_i , and an adsorption energy E_i . Two term DR equation (Gil and Montes, 1994; Kaneko, 1994), expressed as:

$$V = V_1 \exp (-(R^2 T^2 \ln^2 (P_0/P)/E_1^2)) + V_2 \exp (-(R^2 T^2 \ln^2 (P_0/P)/E_2^2))$$

Describe adsorption on micro porous solids having two kinds of micro pores.

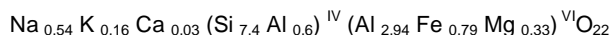
Besides, Horvath and Kawazoe invent a method calculating the effective micro pore volume distribution of slit-shaped pores (Horvath and Kawazoe, 1983). They

described the interaction between adsorbent and adsorptive based on parameter interaction nature. The results obtained using these methods are in good agreement with the data of other approaches (Baksh et al., 1992; Zhu et al., 1994) in the case of materials containing pores with a width less than 1nm. In other hand, for zeolites characterized by their small pores, as well as for alumina-pillared clays with a free space (interlayer free spacing) of 0.7 to 0.8 nm, the H-K approach gives reasonable pore size distributions (Baksh et al., 1992; Zhu et al., 1994). However, for super micropores materials, data obtained by this method were found to be unrealistic (Zhu et al., 1994).

For the determination of PILCS micro pore size distribution, Zhu et al. (1994) proposed a low-pressure part method of the adsorption isotherm. The relative pressure of each type of micro pores depends on the number of nitrogen layers found. So that, the micropore range can be split into five pore groups as a function of the nitrogen monolayer adsorbed. The N_2 adsorption isotherm is replotted as $\log (P/P_0)$ vs. the ratio of the nitrogen volume adsorbed at each relative pressure to the total volume adsorbed. Thermodynamically said, it can be concluded that the curve obtained is related to the pores filling of a certain size. Based on the previous methods, the pillared clays yield different micropore volumes. This work shows the determination of the microporosity of pillared bentonite in various pillar density through nitrogen adsorption. The different methods previously named are used to distinguish the microporosity of this pilcs.

MATERIALS

A Tunisian interstratified illite/smectite beidellite mineral from the Haidoudi deposit (Arfaoui et al., 2005) is used in this study. Beidellite form 2:1 layer phyllosilicates, one sheet of aluminium in octahedral coordination forms between two sheets of silica in tetrahedral coordination (triple-layer sheet) (White, 1999). The beidellite is dioctahedral smectites, where the Si^{4+} in the tetrahedral sheets is substituted by Al^{3+} . The elemental formula of the sample after the Na exchanged purified fraction is:



The preparation method of chromium pillared clays is similar to the proposed by Tzou, Pinnavaia (Tzou and Pinnavaia, 1988; Tzou, 1983). The pillared reagent containing Cr oligomers was formed by heating a 0.1M $Cr(NO_3)_3$ or $Cr(Cl_3)$ and Na_2CO_3 at 350K for 36 h.

Prior to this operation, the base was gradually added to the vigorously stirred $Cr(NO_3)_3$ or $Cr(Cl_3)$ solution at room temperature so that the molar concentration ratio of hydroxide to the Cr ion was equal to 1. The suspension of the clay was added slowly to the vigorously stirred pillaring reagent at 400K and the mixture was stirred for 1.5 h.

After completion of the pillared reaction, the chromium-pillared clays were separated by centrifugation, washed several times with de-ionized water and heat-treated in vacuum at 450K for 2 h.

The amount of Cr incorporated in the beidellite was analyzed by Flame Absorption Spectrometry AAS analytik Jena. The samples synthesized are referred to Cr- NO_3 (20), Cr- NO_3 (40), Cr- NO_3

(60), Cr -Cl (20), Cr-Cl (40), Cr-Cl (60) where the number in parentheses indicates the proportion of chromium cation to clay while the nitrate and chloride are the counter-anions.

The surface areas (BET), pore volumes, average pore diameters and pore size distributions were determined by nitrogen adsorption-desorption method at liquid nitrogen temperature (77K) using Quanta chrome AUTORORB. Prior to adsorption-desorption measurement all samples were degassed at 395K at 10^{-4} torr for 4 h. Since the validity of t-plot based on C values of the BET equation has been criticized, the use of α_s plot, defined as $\alpha_s = (n / n_s)$ (n_s is the amount adsorbed by the reference solid at $P/P_0 = S$) has been proposed (Sing et al., 1985; Gregg, 1982).

According to Sing (1970) it is convenient to place $\alpha_s = 1$ at $P/P_0 = 0.4$; since monolayer coverage and micro pore filling occurs at $P/P_0 < 0.4$. While capillary condensation takes place at $P/P_0 > 0.4$, we have used Na-beidellite as the reference material having lower micro porosity.

RESULTS AND DISCUSSION

N_2 adsorption-desorption isotherms of the Cr-pillared clays at low relative pressures, are identified to Type I of the IUPAC classification (Sing et al., 1985) which are similar to those reported earlier (Sychev et al., 1997). All isotherms show that the pillared clays are essentially microporous (Kostoglod et al., 1998). The N_2 adsorption isotherms obtained are shown in Figure 1. The lower relative pressures, approximately up to $p/p_0 = 0.2$ indicates the presence of ultramicropores (<0.7 nm width), while the higher relative pressures indicate that of supermicropores (0.7 to 2.0 nm width) (Kaneko, 1994), shown by Gil et al. (1995). The natures of the intercalated species yield the idea of the presence of pore groups.

In addition, the pore nature is proportional to pillar concentration. Moreover, based on Table 1 the specific total pore volume (V_t) derived from the adsorption isotherms, except for the Cr- NO_3 (60) sample containing a small fraction of incompletely pillared clay (40), increases with decreasing pillar population. Figure 2 shows the α_s -plots derived from the N_2 adsorption isotherms. Each α_s -plot lays out a plateau with an insignificant slope, and can be extrapolated to the origin. For the Cr-pillared samples, the lowest α_s values part of these plots do not accurately fit the extrapolation due to an upward swing. This kind of deviation in the α_s -plot has been designated as the filling swing, suggesting the presence of ultramicropores (Kaneko, 1994).

The BET and Langmuir approaches were served to analyse N_2 adsorption isotherms. The two former methods were applied for P/P_0 values between 0.05 and 0.35 whose results are shown in Table 1. The adsorption isotherms give a good fit on both the Langmuir and BET equations for the Cr-pillared materials. In comparison between correlation coefficient for Langmuir and BET equation, it can be concluded as an improvement in the correlation coefficient with a decrease in pillar density observed in BET approach. For all materials studied, the $S_{Langmuir}$ is larger than the S_{BET} . Table 1 also contains the surface areas calculated from α_s -plots via the slope of

the extrapolation line passing through the origin (Kaneko, 1994). Furthermore Table 1 shows the increase of external surface areas obtained from the α_s -plots with the pillar density reduction. Therefore, the Dubinin-Radushkevich method (Dubinin, 1985) was also applied to characterize the textural properties of our PILC materials. For all pillared clays the general features of the DR plots are similar. Figure 3 shows the filling of micropores with different sizes (Gil and Montes, 1994; Gil et al., 1995), with a general decrease with reduced pillar density.

In fact, the adsorption on microporous solids has been described by a two-term DR equation. The same conclusion can be derived from the micro-pore size distributions calculated by the method presented in Zhu et al. (1994), shown in Figure 4. The ultramicropores of the Cr-pillared clays contribute significantly to the micro-pore volume. The face-to-face stacking of collapsed or non-intercalated clay layers (Cool and Vansant, 1996) are probably proved by the presence of pores in the range of 0.71 to 1.06 nm.

The chromium-pillared clays' isotherms are more of Type I-like, suggesting a significant contribution of ultramicropores, especially for the sample with maximal pillar density (Cr- NO_3 (60)). For the Cr-pillared materials, at low relative pressures, a reduction of the pillar density causes an adsorption decrease. The contribution of ultramicropores to the total microporosity tends to decrease with the reduced pillar density. The total pore volume increases systematically with decreasing pillar density (Table 1). This can be explained by the increase in lateral pillar distance, leading to the development of a total sorption capacity of the pore system. Also, the α_s -plots (Figure 2) show that the microporosity of the various samples is similar. According to latter studies, the α_s - plots of the Cr-pillared clays show an upward deviation at low values due to the filling of ultramicropores (Kaneko, 1994). This makes it less pronounced when the pillar density decreases, thereby, a lowering of the contribution of those pores is detected. It can be concluded that the porous structure of the Cr-pillared clays are comprised of a huge amount of ultramicropores. Based on works by Remy et al. (1996), the N_2 - adsorption isotherms of PILCs related to the adsorption within the micro-pores is more valuable when the adsorption is made on the external surface (S_{ext}). Table 1 indicates that the S_{ext} tends to increase with decreasing pillar concentration. From this work, it is noticeable that the α_s method provides important information about the porous structure of PILCs. From Table 1 and plots presented in Figure 3, it follows that for the Cr-pillared clays, the adsorption isotherms are fitted by both the Langmuir and BET equations. Nevertheless, the latter method shows lower correlation coefficients (Table 1). The correlation coefficients of the BET equation were improved with increased pillar density (Table 1).

Indeed, for those samples having the largest fraction of

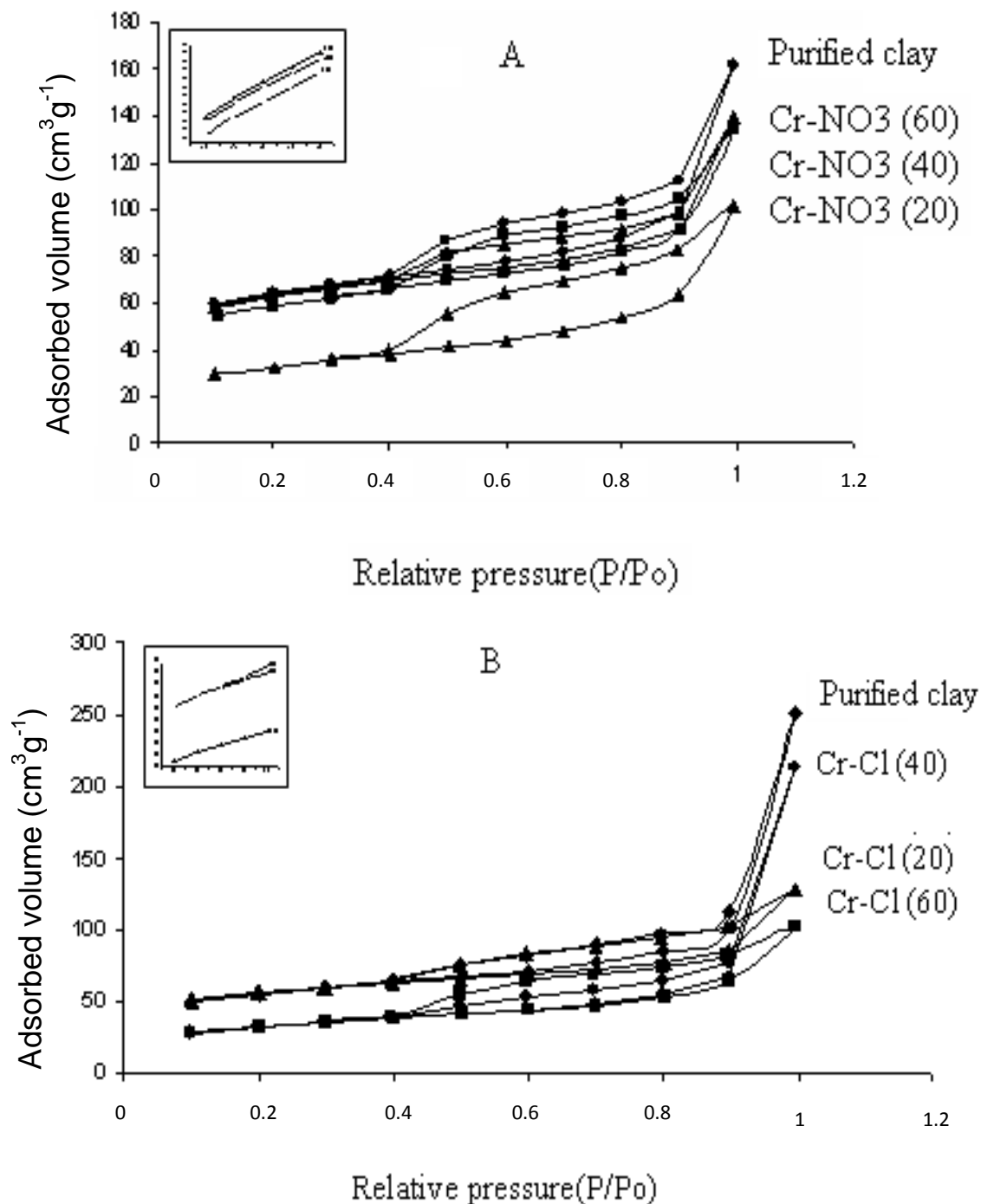


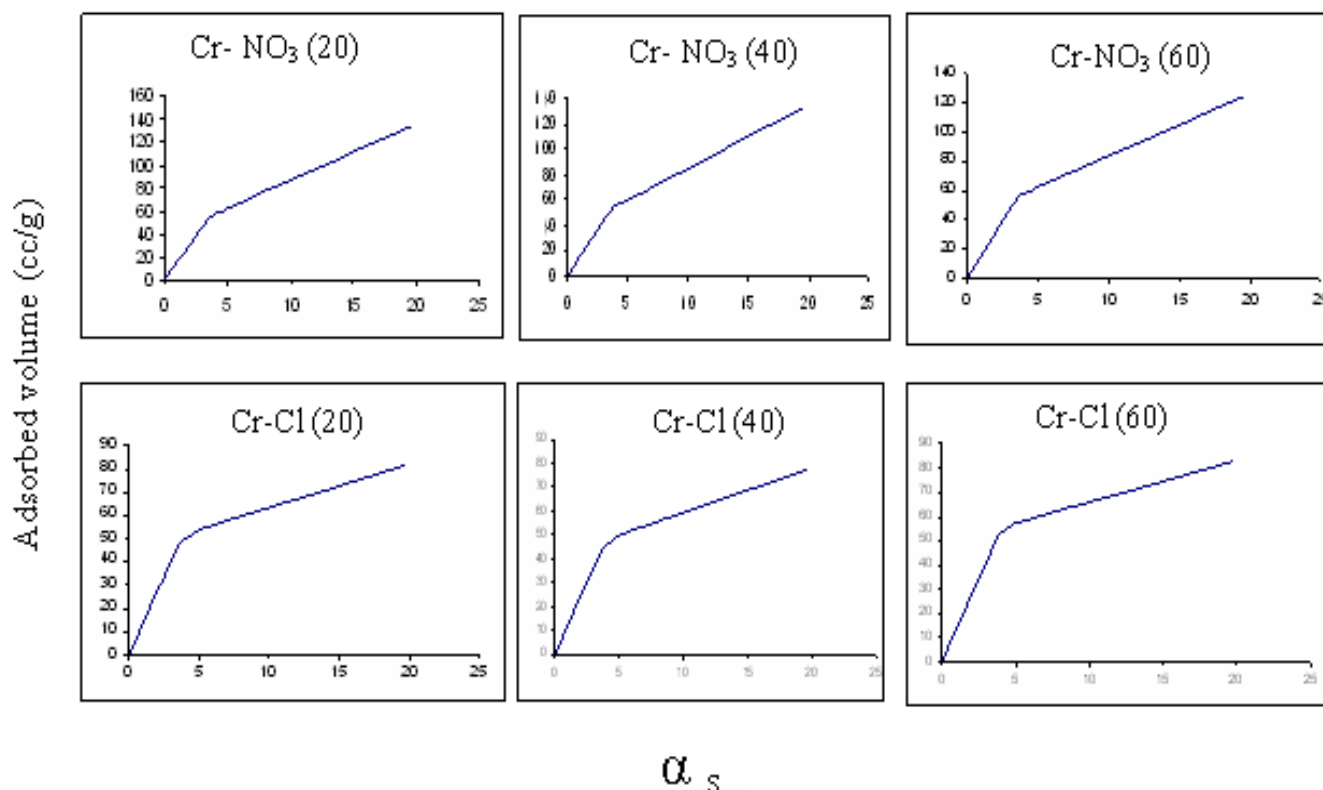
Figure 1. Nitrogen adsorption isotherms: (A) (1) Cr-NO₃ (60), (2) Cr-NO₃ (40), (3) Cr-NO₃ (20), and (B) (1) Cr-Cl (60), (2) Cr-Cl (40), (3) Cr-Cl (20).

such pores (Cr-NO₃ (60)), the difference between S_{α} and S_{BET} is most pronounced. According to $S_{Langmuir}$, the surface area derived from the α_s -plots increases with decreasing pillar density. For the sample Cr-NO₃ (60) has the highest contribution of ultra-micropores, and the surface areas derived from both methods are very close to each other α_s . Based on this work, it is possible to

conclude that the BET method underestimates, whereas the Langmuir approach overestimates are in good agreement with results reported by Remy et al. (1996). On the other hand, S_{α} gives realistic values of total surface area of PILCs. Additionally, the pillar density results are decreased with an increase in the external surface of the samples (Table 1). Therefore, the DR

Table 1. Specific surface areas and specific total pore volume (V_t) for chromia pillared clays.

Parameters Samples	Cr (%)	S_{Lang} (m^2g^{-1})	Correlation coefficient	S_{BET} (m^2g^{-1})	Correlation coefficient	S_{α} (m^2g^{-1})	S_{ext}^{α} (m^2g^{-1})	V_t (mlg^{-1})
Cr- NO_3 (60)	8.43	793.7	0.9961	183	0.9999	139	66.31	0.1928
Cr- NO_3 (40)	6.81	791.5	0.9944	180	0.9998	126.8	76.22	0.2052
Cr- NO_3 (20)	5.63	699.8	0.9932	175	0.9994	115.5	76.9	0.2063
Cr-Cl (60)	7.26	408.3	0.9965	167.4	0.9993	116.6	28.46	0.1193
Cr-Cl (40)	6.69	402.7	0.9960	157.6	0.9992	103.8	30.7	0.1259
Cr-Cl (20)	5.27	385.6	0.9951	146.2	0.9991	98.06	30.8	0.128

**Figure 2.** α_s -plots of chromia pillared clays

equation is applicable for microporous solids (Baksh et al., 1992). This provides important information about textural differences.

Figure 4 presents the micro-pore size distribution calculated by the method of Zhu et al. (1994). Moreover, for all kinds of pillared clays, the content of such micro-pores decreases when the pillar density decreases.

Conclusion

The micro pore structure of pillared clays is determined at low relative pressures. The porous structures of those materials are figured with N_2 adsorption isotherms and α_s -

plots. This analysis approach confirms the existence of micro-pores in the Cr-pillared clays. The surface area calculated by the α_s method can be considered as S_{ext} . The BET method underestimates the total surface area of these pillared clays, whereas the Langmuir approach overestimates it. The Dubinin–Radushkevich method can be applied only for determination of the specific total micro-pore volume for pillared clays. In such a case, the DR method gives a realistic picture of the structural features of the pillared clays.

The method of Zhu et al (1994) is in good agreement with those obtained by the α_s method yielding specific total volume.

All the methods applied show that the chromia-pillared

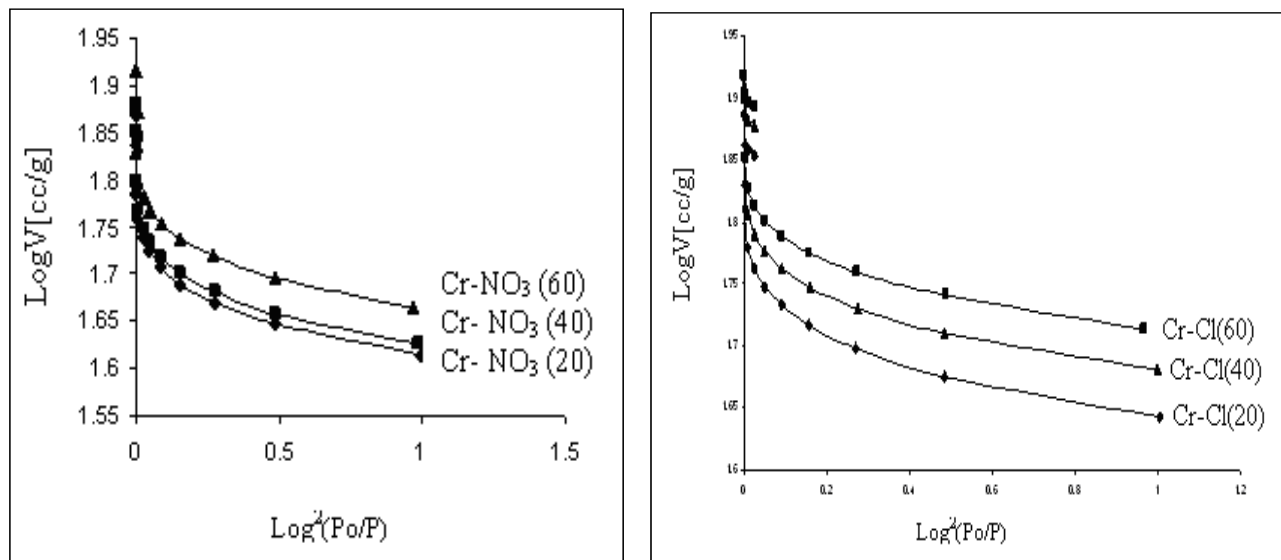


Figure 3. Dubinin–Radushkevich (DR) plots obtained at low relative pressures: Cr-NO₃ (60), Cr-NO₃ (40), Cr-NO₃ (20), Cr-Cl (60), Cr-Cl(40), Cr-Cl(20).

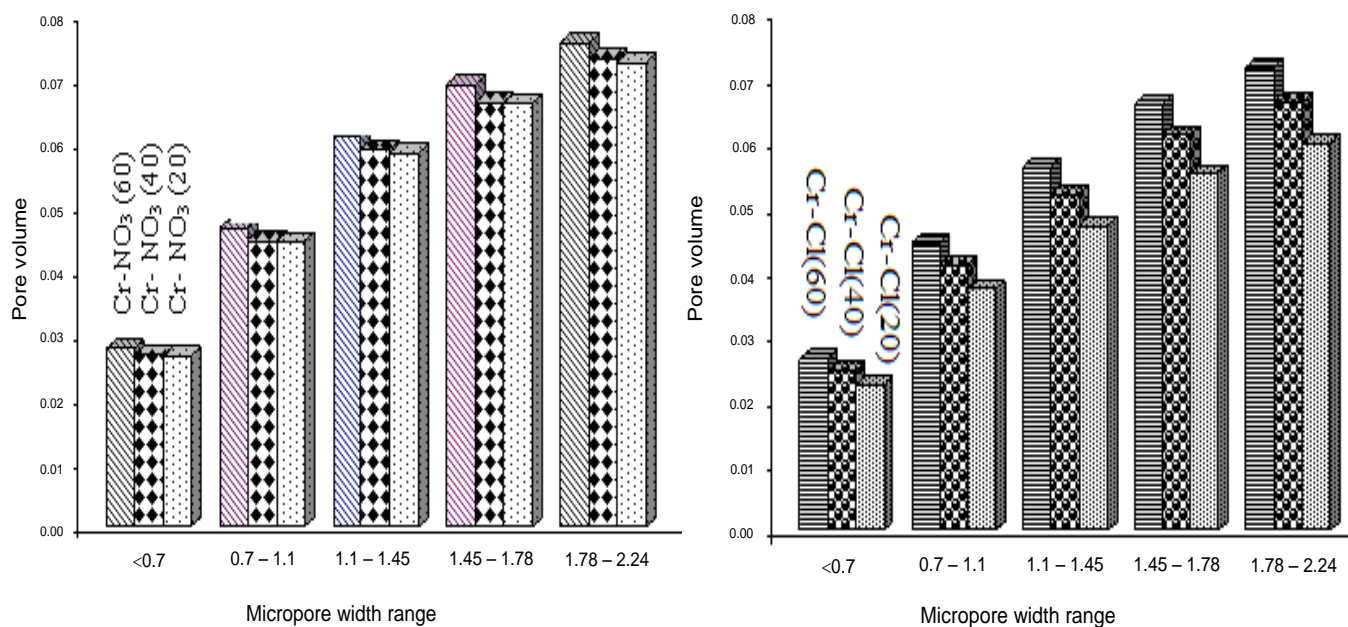


Figure 4. Micropore width distribution of Cr-NO₃ and Cr-Cl.

montmorillonites contain a significant amount of ultramicropores. Changes in the surface area, micro-pore volume and pore-size distribution of these materials are caused by the variation of the pillar density.

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