Natural Iraqi Mineral Clays , Doping with Chromium Oxide Gel , Characterization and Application in Solid Phase Extraction

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Abstract

Natural Iraqi mineral clays , treated chemically and physically , have been doped with chromium oxides and investigated using powder X-ray diffraction , X-ray Fluorescence , thermal analysis , infrared spectra ,and technical instrumental analysis . Results indicate the presence of penta chromium oxide associated with chromium trioxide supported on clay minerals . The observed physical properties evaluated the scientific and economic utilization of those samples to be applied in solid phase extraction technique as adsorbents to separate Iraqi heavy crude oils into their simple components . Infrared and nuclear magnetic resonance spectra have been applied to study the chemical composition of the separated fractions .

الملخص:

تم معاملة الأطيان المعدنية العراقية الطبيعية فيزيائيا وكيميائيا ومن ثم تم تطعيمها باكاسيد الكروم الهلامية لتفحص بتقنيات حيود وفلورة الأشعة السينية والتحاليل الحرارية وطيف الأشعة تحت الحمراء والتحليل الكيميائي الآلـي .النتائج أكدت ان هذه الأطيان من الممكن استخدامها كسند لاكاسيد الكروم لكي تصبح كعوامل مساعدة كفوءة تستخدم كمواد مازة في عمليات الفصل الكروموتوغرافي لتجزئة النفط العراقي الثقيل . استخدمت تقنيات طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي لتشخيص الأجزاء المفصولة .

Introduction

Interest in catalytic behaviour of natural rocks and clay minerals is prompted primarily by concern over their possible adsorption activity and selectivity of macrorganic compounds (1) . Such compounds present in petroleum, for example, as a complex matrix of mainly aromatic, naphthenic and aliphatic hydrocarbons. The use of adsorbents in petroleum refining , in general, and especially in separation of the above three hydrocarbons is well known (2). Many investigators (3-5) reported that all the aromatics could be separated from the naphthenes and paraffins when allowed to diffuse upward through a tube packed with silica gel, Fuller’s earth, alumina …..etc.

In our country large massive of silica rich rocks named Ninivite(6) occurred naturally was reported. Such rocks were closely associated with numerous occurrences of clay minerals and employed and investigated in fractionation processes as adsorbent materials by many workers(2,7,8). They have been suggested to be a satisfactory catalysts in activity and selectivity behaviours.

On the other hands, it is clear that Iraq is considered as one of the important country in the world in term of petroleum resources and reserves(9). Some of the reported petroleum occurred as a heavy crude oil and might be useful at the present time and in the future. Therefore, the demand for all kinds of fossil fuel sources such as heavy crude oils, as alternative energy sources to petroleum has been the subject for many workers(10-12). The evaluation of such crude oils to light fuels and petrochemicals have also been studied(13).

As a result of the above description, and in order to continue researching for our country raw materials and investigation the benefit use of natural Ninivite rocks and clay materials in heavy petroleum refining , several works were reported recently(14-16). Moreover, the present study is undertaken to extend the investigation of using clay mineral samples as adsorbent materials and the study is concerned with the grafting, physical properties, structural, and ability of such samples to fractionate Hammam Al-Alil Bitumen (HAB) and to study the chemical composition of the eluted fractions using infrared and nuclear magnetic resonance spectroscopy.

Experimental

Sources and Collections of Samples

Local natural mineral clay was used as a natural clay sample, which was obtained from area around Mosul city/Iraq. This sample was pale red in colour and has no strange impurities seen by necked eye and was treated chemically and physically, as it will be mentioned in the next section, grained in (80-120mesh) to be chromatographic grade and ready as a supported materials for solid phase extraction.

Chemical and Physicochemical Analysis

Chemical composition of the collected and related samples were obtained by x-ray fluorescence and classical chemical analysis. Stock solution for the later analysis was obtained by sodium fusion technique(17) followed by dissolving the content in 6m HCl . Moreover, physiochemical properties also were determined like pH, which was 6.6 (solid: distilled water, 1:1 w/v), density, porosity and specific surface area, which was determined by ethylene glycole method(14).

C. Preparation of Activated Mineral Clays

For adsorption chromatography to be more satisfactory, the adsorbent materials should be of clay minerals kind and calcined in defined temperature . In order to obtain such materials the natural clay sample was treated with 10% acetic acid to get ride of most carbonate compounds . Treating by 10% oxalic acid also done to remove the liberated iron oxides. Finally, the resulted sample was ordered to wet gravimetric technique to obtain light clay minerals as a part separated from heavy nonclay minerals like quartz and gypsum(18). The resultant minerals clay sample was then heated in certain programmed temperature determined by DTA technique, in order to obtain an activated clay sample.

D. Preparation of Chromium Trioxide Sample

Black brownish gelatinous precipitate of chromium trioxide was prepared using method described in the literature; it was oxidation reduction reaction between chromic oxide and ethanol(19) .

E. Grafting of Mineral Clay Sample

Impregnation method(20) was carried out to prepare the wanted sample for investigation. Chromium trioxide gel was mixed with clay in a ratio 1:80 stirred with distilled water and small amount of ethanol for several hours, filtered, dried at 110C° , and calcined at 360C° for three hours.

F. Instrumental Techniques

Thermo Gravimetric (TG) and Differential Thermal Analysis (DTA) were recorded between 25 and 460C° on TG and DTA analyzer constructed and built in our department . The heating rate was of 5C°/min and $\alpha - Al_2O_3$ was used as standard reference .

The absorption spectra for samples under investigation were recorded on a perkin-Elmer 557 spectrophotometer using KBr and NaCl cell(21).

Meanwhile, measurement of nuclear magnetic resonance was carried out at Irbid University/Jordan , using $CDCl_3$ as the main solvent.

Powder x-ray diffraction studies were carried out using Cuk_α radiation, and diffraction pattern were recorded using phillips powder x-ray diffractometer fitted with a vertical goniometer. Meanwhile, x-ray fluorescence data were obtained using phillips pw 1450/10 flourescence analyzer.

G. Application

Solid phase extraction technique of HAB was applied in order to separate such petrolene into its simple components of paraffinic, naphthenic and aromatics. Themple fractionation columns containing clay samples were employed in the extraction processes. A known weight (~2g) of HAB was fractionated into four fractions using four eluants of different polarities in order to evaluate the adsorption capacities of clay samples.

Results and Discussion

A. Chemical Composition

The analysis of natural mineral clay and the grafting samples was determined by means of x-ray fluorescence and instrumental chemical analysis methods as shown in Table(1). It seems that clay samples compose of different oxides most of them related to mineral rocks and clays suggested to be applied in adsorption processes like silica, alumina, jarosite and montmonorolonite(17).On the other hand, chemical composition of the grafted sample under investigation reflects the percentage values of chromium trioxide in the range of 8-10%.

B. Physical Characteristics

It is obvious that minerals clays to be used as a satisfactory adsorption catalysts should have certain characteristics. The major advantages of an adsorption system for petroleum refining are listed in terms of porosity, density, surface area, and water absorption .

Accordingly , such physical properties are studied and presented in Table(2) for both natural and grafted samples. It seems that natural clay sample shows low porosity, high density and low permeability on comparison with that grafted by 8-10% chromium oxide, such results might be attributed to the fact that grafting the natural clay via reported methods could alter its physical properties in the direction of adsorption applications.

C. Structural Investigation

The mineralogy of sedimentary clays and rocks and their related compounds may be determined on the basis of x-ray diffraction, x-ray fluorescence, dehydration characteristics, thermal analysis, infrared absorption….etc(7). Many rock and clay materials are composed of more than one mineral, and the minerals may be mixed in several ways. The most satisfactory single procedure for the identification however is by means of powder x-ray diffraction(22).

Accordingly, such technique has been applied for the original and grafted clays under investigation. Figure(1) shows the pattern of natural clay which obviously reflected the presence of quartz minerals in addition to chlorite, Montmorillonite, palygroskite, alunite, jarosite and traces amount of dolomite and calcite minerals. Meanwhile , Figure (2) shows the grafted sample pattern which contain reflection typical to chromium oxides (Cr_2O_3 and Cr_5O_{12}) in addition to the above mentioned minerals . The two kinds of chromium oxides seemed to be formed during grafting the clay sample. Such mixed unites are presented in Table (3) via their interplanar spacings(22).

Under the proposed experimental observation and referring to the literature(2), clay minerals, in general, like the micas in the atomic structures. They consist of silica tetrahedron and two sheets of closely packed oxygen or hydroxyl in which metal atoms are embeded in octahedral coordination. The water molecules held by the clay minerals might be classified into; the hydration water, which could be removed by heating at low temperature and the geometrical water (lattice hydroxyl) which is diminished above 400C° . The nature of the former water molecules are of great importance, since they determine the chemical adsorption properties of the clay minerals. Therefore, DTA and TG were performed for both clay samples, and are shown in Figures (3) and (4). In general it is noted that three DTA endothermic peaks were found, Figure(3) , corresponding to the three classes of hydrations; hydroscopic, zeolitic or coordination water molecules, and finally the structural hydroxyl groups.

Moreover, to interpret such foundation, TG of both samples were carried out, Figure (4), and it is clear that some variation is noted in comparison between the observed result before and after grafting reflecting the high activation energy of doped clay sample. Such variation might be due to the presence of bonded chromium ions with clay minerals and water molecules in doped sample. Hence, the adsorbed interlayer water molecules need more energy to be liberated.

Finally, it is of interest to investigate the clay mineralogy and the migration and elimination of water molecules by infrared absorption. Therefore, a range of 400-4000cm^{-1} in frequency was applied and the spectra revealed several structural absorption bands including those between 1130 and 650cm^{-1} which are attributed to the Si-O stretching vibrations$^{(21)}$. Also there is absorption bands at 1640cm^{-1}and in the range 3600-3660cm^{-1} which are related to the structural (OH) group. Such absorption shows a significance variation in the position and sharpness of the vibration upon heating the samples in the range of 150-450C° which is related to the dehydration phenomena.

D. Solid Phase Extraction

It is of importance to notice here that the treated clay materials might produce better results in adsorption processes . That is the reason why natural materials should be treated chemically or physically to get rid of unuseful catalyst minerals and to locate and concentrate the others. Accordingly , chemically and thermally activated clay sample was employed on fractionate processes and the results were compared with grafted sample. Solid phase extraction technique$^{(16)}$ was applied to separate Hammam Al-Alil Bitumen (HAB) into four fractions using four elution solvents having gradual increasing polarities. The observed results are shown in Table (4) which reveals the percentage of the fractions eluted. The nature of the eluted fractions was adopted from the data of infrared and nuclear magnetic resonance investigation$^{(21)}$. Such results obviously indicate that straight aliphatic hydrocarbons were eluted in hexane fraction via the absorption bands at 1460 and 2927cm^{-1} in case of infrared, Table (5), which are attributed to the bending and stretching vibrations of methylene groups. The abundance of methylene group in hexan fraction was supported by nuclear magnetic resonance data through the presence of aliphatic proton band of $-CH_2$- in the range (Hmy =0.9-1.8 ppm), Table (6). Interference of branched aliphatic and naphthenic compounds was happened in this fraction and can be see in table (5) and (6) . On studying the toluene fraction it was suggested that such fraction contain mostly of branched aliphatic compounds in addition to naphthenic once and little amounts of aromatics, Tables(5)and (6). This aromatics appeared secondly in chloroform fraction which contain mainly of naphthenic hydrocarbon . Meanwhile, it was noted that ethanol fraction contain aromatic hydrocarbon accompanied with traces of naphthenics.

The observed interference noted an using activated minerals clay sample in fractionation of HAB components, as expected, has been decreased on using grafted clay sample, Table (5). In conclusion, such results suggest that treating the local natural mineral clays physically and chemically followed by grafting them with chromium oxides in certain amount, might yield an activated adsorption catalysts has a promising future.

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Table (1): Chemical Composition of Natural and Grafted Mineral Clay.

Component	***%***	***Component***	***%***
SiO_2	43.80	MgO	4.30
Fe_2O_3	5.18	Na_2O	0.65
Al_2O_3	10.60	K_2O	1.23
CaO	25.50	SO_3	8.74
Cr_2O_3 in grafted sample (8-10%)			

Table (2) : Physical Characteristics of Clay Samples

Sample	**Density g/cm^3**	**Porosity %**	**Water Absorption %**	**Surface Area m^2/g**
Natural Minerals Clay	2.09	75	115	10.86
Grafted minerals Clay	1.92	102	130	12.03

Table (3): Interplanar Spacings for Contributing Phases in Grafted Clay Sample.

Crystaline Phase	***hkl***	$2\theta^0$	***d Values in Å***
Quartz	100	21.0	4.22
	006	28.0	3.32
	110	36.3	2.74
Chlorite	002	9.12	9.68
	202	39.5	2.27
Palygroskite	201	22.2	3.99
Montmorolonite	020	20.1	4.41
Jarosite	112	23.0	3.85
	113	36.2	2.48
Alunite	113	38.6	2.33
Cr_2O_{12}	310	24.45	3.64
	121	25.35	3.51
	411	33.35	2.67
Cr_2O_3	012	24.45	3.64
	113	41.45	2.17
	321	44.75	1.77

Table (4): Solid Phase Extraction Fractions (%) of HAB* Using Clay Samples.

Solvent	*Polarity (deby)*	*Activated Mineral Clay*	*Grafted Mineral Clay*
Hexane	31.0	53.3	42.4
Toluene	33.9	17.6	21.6
Chloroform	39.1	20.5	21.8
Ethanol	51.9	6.1	12.5
Loss	-	2.5	1.7

* Average HAB Composition: 34% straight chain aliphatic, 30% branched aliphatic, 27% naphthenic, and 9% aromatic compounds.

Table (5): Infrared Spectroscopic Data for Eluted Fractions of SPE.

Solvent	***Stretching (ς) and Bending (δ) Bands in cm^{-1}***				
	ς C-H:	δ C-H:	ς C-H:	δ C-H:	ς C-C
	$-CH_2$	$-CH_2$	Naphthenic	Naphthenic	Aromatic
	$-CH_3$	$-CH_3$	Methylene	Methylene	
Hexane	2927(s)	1460(s)	2860(vw)	1450(vw)	-
	2846(bm)	1377(m)			
Toluene	2927(m)	1460(m)	2860(m)	1450(m)	1600(vw)
	2846(s)	1377(s)			
Chloroform	2927(m)	1460(m)	2860(s)	1450(s)	1600(m)
	2846(w)	1377(vw)			
Ethanol	2927(w)	1460(w)	2860(m)	1450(m)	1600(s)
	2846(m)	1377(m)			

(s): Strong , (m): Medium , (w): Weak, (bm): Broad Medium.

(vw): Very Weak.

Table (6): Nuclear Magnetic Resonance Data for the Eluted Fractions of SPE

Chemical Shift $\delta(ppm)$	*Expected Groups*	*Weight of Signal (g) in:*			
		Hexane Fr.	***Toluene Fr.***	***Chloroform Fr.***	***Ethanol Fr.***
0.9-1.8	-C-CH_2-C-	0.0348	0.0216	0.0197	0.0090
0.5-1.4	CH_3-C-	0.0172	0.0437	0.0086	0.0095
1.4-2.2	Naphthenic –CH_2-	0.0035	0.0096	0.0367	0.0113
6.3-8.5	Aromatic Protons	-	0.0041	0.0142	0.0318

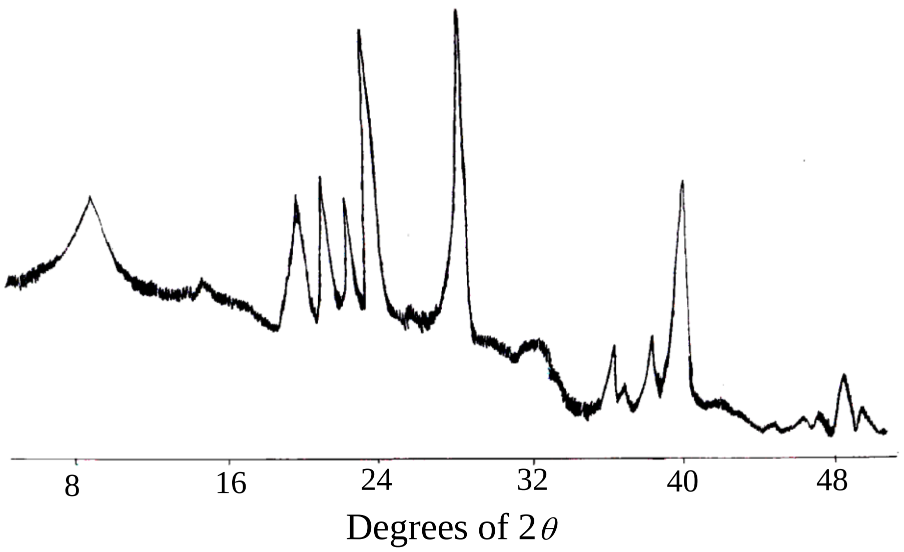

Fig. (1): Powder x-ray Diffraction Pattern of Natural Clay Sample .

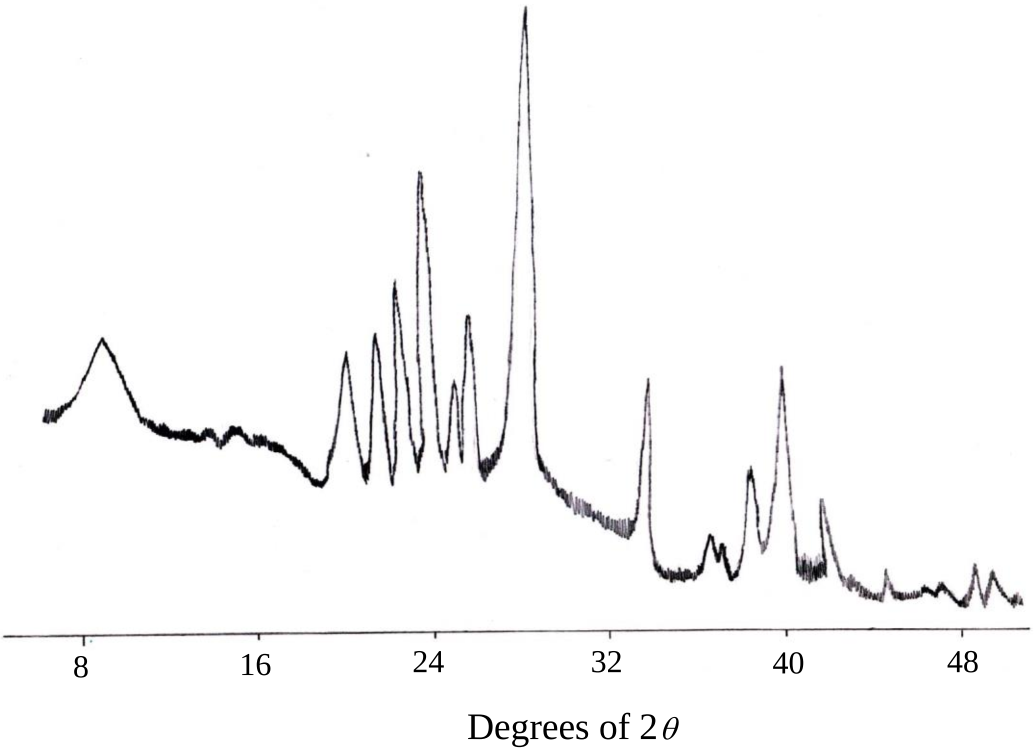

Fig. (2): Powder x-ray Diffraction Pattern of Grafted Clay Sample .

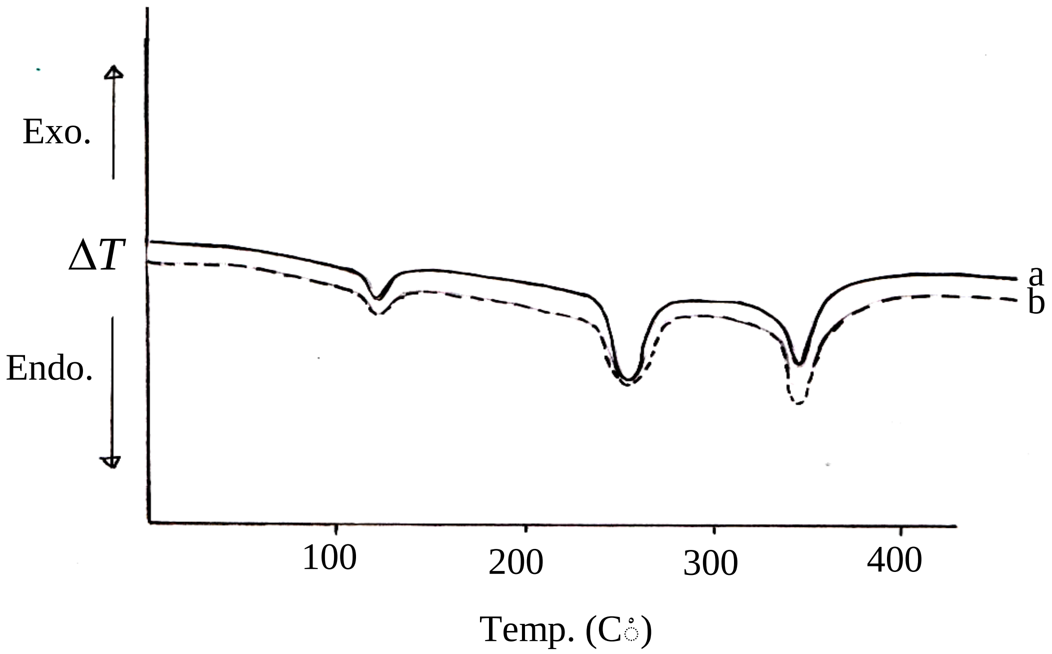

Fig. (3): Differential Thermal Analysis Curves of

a: Natural

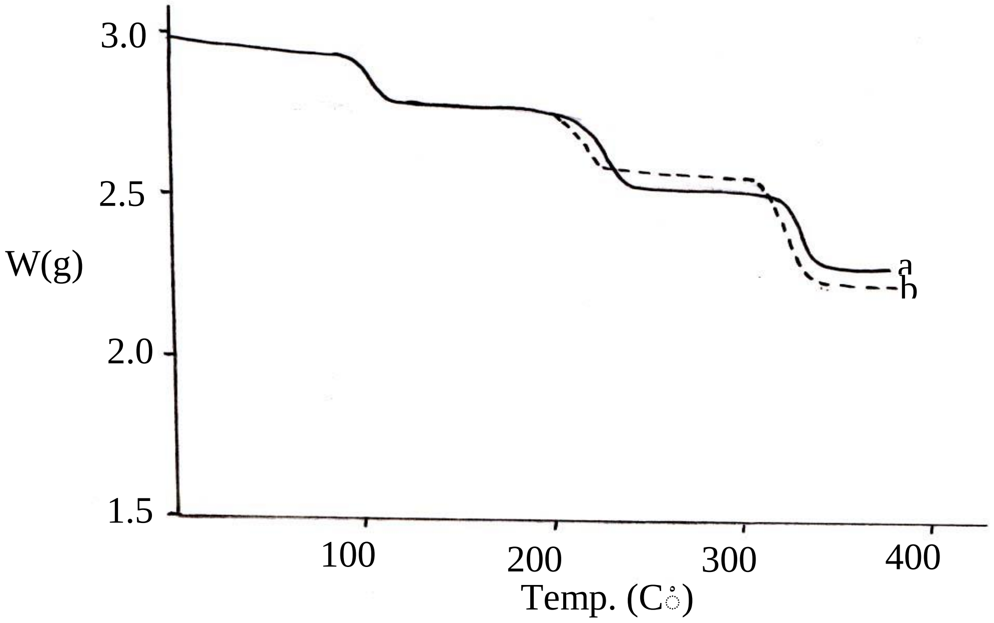

Fig. (4): Thermogravimetric Curves of

a: Natural