Application of Iraqi Natural Rich-Bauxite Mineral Clays doped with Chromium Oxides in Upgrading of Iraqi Kerosene

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الملخص

تم تطعيم اتربة معدنية عراقية طبيعية غنية بمعدن البوكسايت بخليط من اكاسيد الكروم. اثبتت نتائج التحاليل الكيميائية والصفات التركيبية لنماذج البوكسايت اهليتها وكفاءتها العلمية والصناعية لاستخدامها كحفازات تسهل عملية الامتزاز الفيزيائي والكيميائي. استخدمت نماذج البوكسايت هذه في المعاملة الحفازية للكيروسين العراقي حيث تم امراره على شكل ابخرة فوق الحفاز الموجود في فرن اسطواني مسخن بدرجات حرارية تتراوح بين 300−475 درجة مئوية, كما تم دراسة التكوين الكيميائي للنماذج المفصولة من الكيروسين المعامل بتقنيات طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي وكروموتوغرافيا الغاز حيث أكدت النتائج حدوث عمليات ازمرة للمركبات البارافينية فضلاً عن تكوين مركبات غير مشبعة.

Abstract

Iraqi Natural rich-bauxite mineral clay samples were doped by mixed chromium oxides. The observed chemical composition and structural properties of the above samples evaluate their scientific and economic utilization as adsorbent material catalysts. They have been applied in catalytic treatment of Iraqi kerosene which was conducted by feeding the kerosene in gaseous phase over the catalyst using tube furnace heated in the range of 300-475ºC. Infrared, nuclear magnetic resonance spectra and gas chromatography techniques have been used to study the chemical composition of the separated fractions. The results revealed that some isomerization and hydrogen removal processes were occurred.

Introduction:

Kerosene is the part which distilled from the crude oil between 160-250ºC and contain in its chemical composition 23% straight paraffins,16% branched paraffins,32% mononuclear naphthenics,11%

poly nuclear naphthenics,15% mononuclear aromatics, and 3% poly nuclear aromatic hydrocarbons[1]. Catalytic activity on such kerosene above 300ºC might catalyzed some isomerization and cracking reactions in addition to the removal of hydrogen and conversion to naphthenic and aromatic hydrocarbons which could be separated and used in the petrochemical industries [2]. On the other hands, it is well known that mineral clay is one of so many catalysts to deal with the above activities[3]. They are very stable during catalytic treatment processes and have a surface endowed with weakly acidic and basic sites.

Bauxite is considered to be one of the important mineral clays naturally occurring in the world, and fortunately it was reported that bauxite-rich rocks occurred naturally in large masses around Al-Anbar city/west of Iraq[4]. In general, bauxite consist from mixed heterogeneous minerals like: Gibbsite ($Al(OH)_3$), Boehmite ($AlO(OH)$), Dispor ($AlOOH$), in addition to small quantities of Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Anatase (TiO_2), Rutile (TiO_2), Halloysite ($Al_2O_3, 2\ SiO_2.\ 2\ H_2O$), Kaolinite ($Al_2Si_2O_5(OH)_4$), and Quartz ($SiO_2$)[5]. Moreover, it was reported that such rocks called Bauxite after Ditter[6] since it is bearing in its chemical composition between 55-65% from aluminum oxides and less than 30% of silica.

Application of Iraqi raw minerals in petroleum industries as adsorbent materials was the interest of many workers. Several works were reported in this field recently[7-9] investigating heavy crude oils since Iraq is considered as one of the important countries in the world in term of petroleum resources[10].

As a continuation of these studies the present study is considered to investigate bauxite sample from Al-Hussaniate area at Al-Anbar governorate/Iraq, which is expected to be rich in aluminum oxides. Purification and grafting of this sample supposed to create, stable, active and selective catalyst employed in catalytic treatment and upgrading of Iraqi kerosene[11].

Experimental

A- Sources and collection of samples:

Natural minerals clay, obtained from area around Al-Hussainiat at Al-Anbar governorate/Iraq, were purified from carbonate and bicarbonate compounds chemically by 25% HCl and used as a natural clay samples. These samples were pale yellow in color have (120-150 mesh ASTM). Individual samples weighed from 1.0 to 3.0 kg; and were thoroughly mixed before their coning and quartering to obtain representative samples. At each sampling site, parent rock, samples were also collected. For x-ray diffraction analysis and bulk mineralogy, the raw sample was powdered by agate mortar and agate tama mill.

Meanwhile, the kerosene sample, which was obtained from local petrol station (Mosul city/Iraq) in order to be dry and clean,was further dried by $CaCl_2$ drying agent.Mixed oxides of (CrO_3 & Cr_2O_3) were obtained via heating CrO_3 at 260ºC for two hours [12].

B- Methods of study:

The identification of clay minerals and their alteration products was carried out by the power diffraction method, which carried out using Phillips x-ray diffraction equipment model pw/1710 with monochromatic, Cu-radiation (λ=1.54178 Aº) at 40 k.v, 35 m.A. and scanning speed 0.02º/sec. were used. The reflection peaks between 2θ=2º and 60º, corresponding spacing (d,Aº) and relative intensities (I/Iº) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. Meanwhile x-ray fluorescence spectrophotometer was employed for natural clays on Phillips/PW 2404 analysis and the absorption spectra were recorded on FTIR 4100 JASCO spectrophotometer using KBr disk[13].

The thermal analysis was by means of Schimadzu DTA-50H, and TGA-50H. Each powdered sample was heated by 10ºC/min. up to 1100ºC with α-Al_2O_3 as a reference material. Temperature, weight change in wt., and the thermal behavior of the sample is recorded on the chart.

On the other hand, the isolated fractions from kerosene also studied and the absorption spectra were recorded on the above IR instrument using NaCl cell. Meanwhile, NMR data were obtained from Shimadzu GcMs-Qp-1000EX Mass Spectrometer at 70 e.v 75.46 MHZ, GC from Perkin Elmer ArNEI Clarus 500 Gas Chromatography, and CHNS from Automatic CHNS analyzer Elemental Vario EL III.

The above technical studies were performed at ministry of petroleum, the Egyptian mineral resources authority, central laboratory sector/ Egypt.

C- Application:

The prepared mixed metal oxides sample ($Cr_x O_y$) was supported over purified bauxite sample by impregnation grafting method[14] and further dried and activated at 550ºC. The prepared catalyst finally employed in catalytic treatment of kerosene under investigation which was conducted by feeding the kerosene in gas phase over the catalyst using tube furnace. The employed temperatures for such processes were (300-475ºC) in addition to five runs at 475ºC. The parent and treated kerosene fractions were further studied by separating the paraffinic content using urea adduction method. IR, NMR, and GC techniques were employed to study the chemical nature of the separated stuff to evaluate the adsorption activity and selectivity of the investigated samples.

Results and Discussion:

Physical characterization, structural, and chemical analysis of natural bauxite, bauxite heated at 700ºC, and the doped samples were studied and reported recently[15]. In general, it seems that all those samples show a significant variations in their chemical compositions, physical properties, and especially in their structural components. It is therefore of interest to get benefit of such foundations which evaluate the studied bauxite samples as a good adsorbents in the catalytic treatment processes[3]. However, in our investigation we thought that it is of interest to concentrate the catalytic activity on the doped sample, so it was employed in upgrading of Iraqi kerosene (165-250ºC) fraction.

On referring to the previous studies[8,9,11], it seems that separation of the paraffinic content from the whole samples under investigation by means of urea adduct method and studying their CHNS elemental analysis yield naphthenic and aromatic hydrocarbons, Table(1). Such result occurred on catalytic treatment in the range 450-500ºC via the hydrogen removal and conversion processes. To prove such proposed results, chemical characteristic nature of the isolated fractions have been investigated via infrared, nuclear magnetic resonance, and gas chromatography techniques. Infrared data which are presented in Table (2) related to the all studied isolated paraffinic fractions. It is obviously clear that the absorption bands at 1377 and 2855 cm^{-1} attributed to the bending and stretching vibrations of methyl groups respectively[13]. Absorption bands at 1463-1459 cm^{-1} and at 2925 cm^{-1} related to the bending and stretching vibrations of methylene C-H respectively, which became less intensive. Finally, it seems that bands at 1608-1607 cm^{-1} and at 1541cm^{-1} respect the aromatic C-C bond, in addition to 722, 740, 767, 806, 1021 cm^{-1} which represent the bending of C-H outside the aromatic ring[16]. These bands seemed to be medium in intensity with more treatment processes.

Such results should be confirmed by nuclear magnetic resonance studies which have been employed for the untreated kerosene, and samples which have been treated at 300, 400, 475ºC only, Figures (1-3). Interpretation of these data has to be depending on the area measured under the curves of the absorption protons[17]. Table(3) show the obtained results which include aromatic hydrogen (Ha), benzylic hydrogen (Hα), naphthenic hydrogen(Hn),methylene hydrogen (Hmy), and paraffinic methyl hydrogen (Hme). On comparing these kinds of hydrogen with each others, the results indicate that doping bauxite materials with chromium oxides clarified them to be a good catalyst for isomerization of paraffinic compounds at low temperature (300-400ºC). Meanwhile, at 475ºC, it seems that removal of hydrogen and conversion to oleffinic compound occurred and definitely such observation can be confirmed by measuring the bromine number factor. It was found that the bromine number for the untreated kerosene was nil, changed to 0.195 for sample treated at 475ºC [2]. On repeating this treatment process five times, it was found that more naphthenic and aromatic hydrocarbons were formed, Table(4) [17].

Finally, it is well known that hydrocarbon compounds are present in petroleum fractions in a very complicated nature, therefore, workers studied the possibility of their separation and identification by gas chromatography technique[18,19]. Accordingly, GC was employed on kerosene samples and the computerized results are presented in Table(5), in addition to one of so many figures selected to be for parent kerosene, Figure(4). The results again reflect the isomerization process in addition to conversion to naphthenic and aromatic compounds, especially at 475°C treatment whereas it was seen that paraffinic compounds percentage changed from 26.6 to 8.62%.

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Table 1:Elemental analysis of untreated kerosene and treated at different temperatures.

Sample	% Calculate Paraffin	%Paraffin from GC	%CHNS			
			C	H	N	S
Untreated Kerosene	25.8	26.6	81.81	18.00	Nil	Nil
300	25.13	25.6				
350	35.98	25.2				
400	33.112	27.4				
450	20.673	25.11				
475	21.066	23.934	83.38	16.50	Nil	Nil

Table 2: Infrared data of untreated kerosene and treated five times.

Part	Absorbance (cm^{-1})														
Untreated kerosene	2957 s	2926 s	2855 s	1608 w	---	---	1464 s	1377 s	1032 w	---	805 w	---	766 w	---	722 w
Treated-1	2957 s	2925 s	2855 s	1608 w	1541 w	1506 w	1463 s	1377 m	1033 w	---	805 w	---	766 w	---	722 w
Treated-2	2957 s	2925 s	2855 s	1607 w	1541 w	1506 w	1463 s	1377 m	1033 w	889 w	805 w	---	767 w	---	722 w
Treated-3	2957 s	2925 s	2855 s	1607 w	---	1506 w	1463 s	1377 s	1021 w	908 w	806 w	---	767 w	740 w	722 w
Treated-4	2957 s	2925 m	2855 s	1607 w	1541 m	1506 m	1459 s	1377 s	1021 w	846 m	806 m	782 m	767 w	740 w	722 w
Treated-5	2957 s	2925 m	2855 S	1607 w	1541 m	1506 w	1463 m	1377 w	1033 w	908 m	806 m	781 m	767 m	740 m	723 w

Table 3: NMR data of untreated kerosene and treated at different temperatures.

Sample	%H a	%H α	%H n	%H my	%H me
Untreated kerosene	13.74	15.12	16.72	42.08	12.34
300° C	9.55	11.63	18.97	39.11	20.30
400° C	9.09	9.12	27.92	29.08	24.72
475° C	13.75	17.44	14.19	44.59	10.04

Table 4: NMR data of untreated kerosene and treated five times.

Sample treated at 475	%H a	%H α	%H n	%H my	%H me
Untreated kerosene	13.75	15.12	16.72	42.08	12.34
Treated-1	20.60	18.01	12.10	28.85	20.42
Treated-2	22.62	20.28	16.99	25.70	14.40
Treated-3	24.69	19.97	12.49	26.61	16.28
Treated-4	27.52	23.37	12.15	21.51	15.44
Treated-5	28.02	18.96	12.51	21.77	18.66

Table 5: Gas chromatography data of untreated kerosene and treated five times.

Part	Retention time R.T	Untreated Kerosene	Treated Kerosene at 475 C°				
			Treated-1	Treated-2	Treated-3	Treated-4	Treated-5
C8	10.2	1.578	1.117	1.190	0.651	1.074	1.033
C9	12.0	3.154	2.441	2.449	2.300	2.323	2.262
C10	17.8	5.730	5.879	5.701	5.090	4.911	5.237
C11	24.9	6.341	6.008	5.906	5.200	4.625	4.830
C12	32.2	5.050	4.709	4.423	3.677	3.334	3.414
C13	39.5	3.587	3.239	3.665	2.410	2.123	2.168
C14	46.5	1.149	1.668	1.645	1.435	1.354	1.502
C15	54.3	0.068	0.322	0.471	0.652	0.762	0.999
Total		26.597	25.183	25.450	21.211	20.506	21.445
Paraffin & Calculated %		21.31	23.93	20.34	15.80	9.82	8.62
Aromatic & naphthenic %		78.9	75.96	79.66	84.20	91.18	91.38
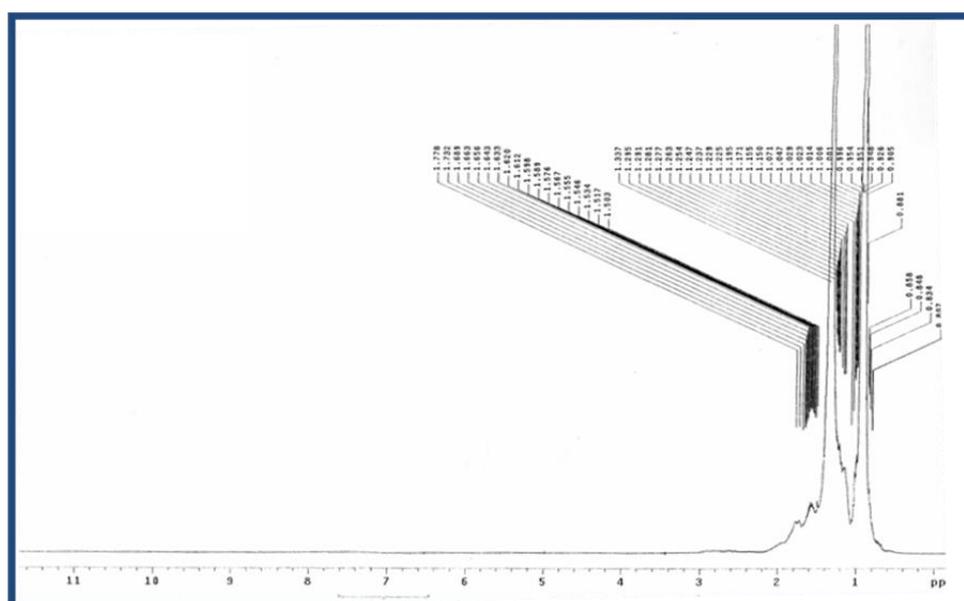
Figure 1: ¹H NMR spectra of the treated kerosene at 300ºC.

Figure 2: ^{1}H NMR spectra of the kerosene treated at 400º C.

Figure 3: ^{1} H NMR spectra of the treated kerosene at 475ºC.

Figure 4: Gas chromatography spectra of untreated kerosene sample.