

Comparison of Catalytic Activity of Clays on Locally Available Petroleum Fractions

¹M.A RAUF*, ²M IKRAM, ²M.J.IQBAL AND ²S. MANZOOR

¹Department of Chemistry, UAE University, Al-Ain, UAE

²Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

(Received 15th January, 2002, revised 26th November, 2003)

Summary: The purpose of the present work is to explore the catalytic activity of locally available clays in petroleum fractions. The chemical analysis indicated mainly the presence of aluminosilicate dominance in the clay mineral composition. The major, minor and trace elements in clays were determined by employing X-ray Fluorescence (WD) and the mineral nature of clays were determined by IR spectroscopy. UV/Visible spectrometry was employed to observe the concentration of naphthalene and benzene in gasoline of premium and naphtha brand. Clay sample no 1 and 2 showed the maximum catalytic reforming, whereas, sample no 4, 7 and 10 showed the maximum catalytic cracking. Sample no. 3, 5, 6, 8, and 9 showed no appreciable catalytic activity.

Introduction

The significance of chemical analysis of clays for geological and related studies is now well established [1]. The systematic analytical scheme underwent continuous modification in the light of the increasing knowledge of the principles of analytical chemistry. The classified methods are still widely used, but now various analytical techniques have been proposed as an alternative to previous methods [2].

The use of aluminosilicates in catalysis is almost as old as the catalytic concept itself. Earlier, aluminosilicates have been used as catalyst in various organic transformations because of the ease of handling and work up, low corrosive nature and low cost. [3,4]. They are also suitable for the conversion of large molecules. Gurwitsch in 1912 used polygorskite to polymerize pentanes and hexanes to dimer and trimers, and to layer polymers [5]. The use of polygorskite as a catalyst for oxidation of alcohols to aldehyde and for the cleavage of hydro-benzene to benzene and aniline has also been reported [6]. The use of clays as catalysts for the gasoline production was disclosed in German patents in 1923 and subsequent years [7].

The present study deals with the analysis and identification of mineral nature of the clay samples by both classical and instrumental methods, followed by their use as catalyst in activated and inactive state in locally available petroleum fractions. The concentration of Benzene and Naphthalene was

observed in premium brand gasoline and petroleum Naphtha. The clay samples were selected from the Potohar area, Punjab, Pakistan, for chemical investigations and petroleum fractions were selected from Attock Oil Refinery, Rawalpindi, using the crude oil from the Potohar area oil wells.

Results and Discussions

Gravimetric

In gravimetric analysis, the major elements, Si, Al, Fe, Mg, Ca and P were estimated as their respective oxides. The most abundant oxides were found to be SiO₂ and Al₂O₃. The data reveals the aluminosilicate nature of these rock samples. The moisture contents were also determined by drying the samples at 100°C. At this temperature, hygroscopic water (H₂O) was lost. Loss on ignition was determined by igniting the samples at 1000°C.

X-ray Fluorescence Spectroscopic Method

The qualitative and quantitative analysis of samples was done by XRF, which reveals the presence of, Si, Al, Fe, Na, and K. From the results given in Table-1, it was obtained that silica, alumina and iron were abundant in all the clay samples, which confirm the aluminosilicate nature of these rocks. The concentration of SiO₂ and Al₂O₃ found in clay samples was in well agreement with the literature values for aluminosilicate clays [9].

*To whom all correspondence should be addressed.

Table-1: XRF analysis of various clay samples reported as % of elements

Clay	Si	Al	Fe	Ca	Mg	K	P	Ti	Mn	Cr
1	33.85	8.75	5.55	0.20	--	1.95	-	1.25	0.25	0.05
2	33.75	9.65	6.90	0.25	-	1.85	0.05	1.65	0.40	0.05
3	27.25	15.35	10.70	0.05	-	1.55	0.20	1.40	-	-
4	27.00	18.40	0.85	0.90	0.90	0.30	0.15	0.65	-	-
5	20.45	6.20	4.90	1.25	0.70	2.05	0.20	0.80	0.35	0.05
6	24.25	4.95	2.10	8.90	1.55	3.15	0.10	0.40	0.15	0.05
7	30.55	7.00	7.20	1.70	-	2.25	0.20	1.10	0.95	-
8	28.95	0.85	0.40	0.10	2.40	0.05	-	-	-	0.05
9	41.45	3.15	0.50	0.20	-	2.10	0.05	0.10	-	-
10	30.30	16.45	0.40	0.10	1.30	-	0.15	3.55	0.15	0.05

SD lies within $\pm 5\%$ in each case

Infrared Spectroscopic Method

Infrared spectroscopy is useful in the identification of minerals. It was rather difficult to assign the bands because clays are not simple compounds but complex mixture of minerals. The basic layout of all the spectra is nearly similar, which indicated almost the same chemical composition of clays. The infrared spectroscopy is extremely sensitive to short range ordering. Intermediate values for the principle absorption may be considered diagnostic of solid solutions.

IR spectra were taken for all the clay samples and were compared with the spectra already reported in the literature [10-12]. A representative infrared spectrum of sample number 7 compared with the reported literature spectra is shown in Figure-1.

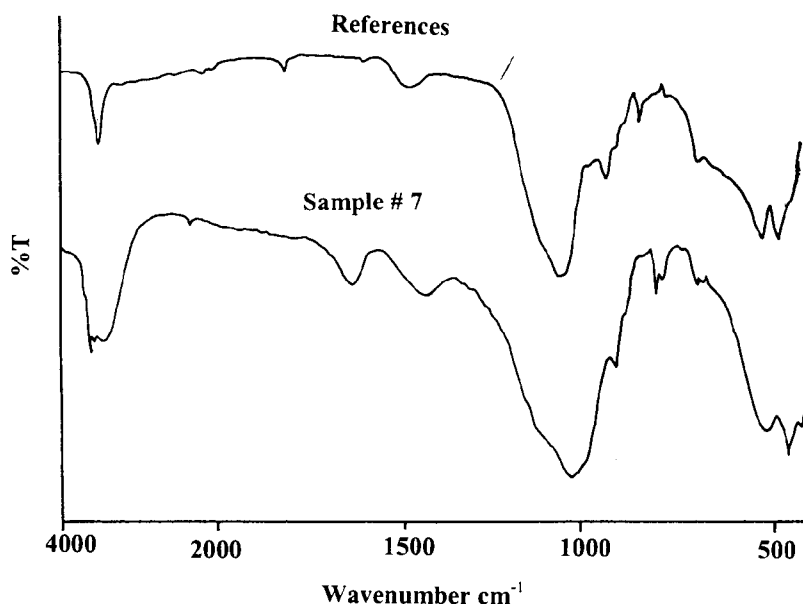


Fig. 1: A representative infrared spectrum of sample #7 compared with the reported literature spectra [10].

Table-2 indicates the mineral nature of all the clay samples identified by gravimetric and instrumental techniques.

Table-2: Minerals identified in various clays from IR spectral analysis

Clay No.	Mineral Nature	Formulae
1	Anaxite (Kandite)	$Al_2Si_2O_7(OH)_4$
2	Dicite (Kandite)	$4[Al_2Si_2O_7(OH)_4]$
3	Kaolinite (Kandite)	$2[Al_2Si_2O_7(OH)_4]$
4	Gibbsite (Bauxite)	-
5	Kaolinite (Kandite)	$2[Al_2Si_2O_7(OH)_4]$
6	Kaolinite (Poorly Crystallized)	$2[Al_2Si_2O_7(OH)_4]$
7	Montmorillonite (Smectite)	$\frac{1}{4}(Ca,Na)_2(A,Al,Mg,Fe)_4(Si,Al)_4O_{20}(OH)_4nH_2O$
8	Phyllosilicate (Talc)	$4[Mg_3(Si_4O_{10})(OH)_2]$
9	Fused Quartz	$3[SiO_2]$
10	Gibbsite	-

UV-Visible Spectrometry

Absorbance value of the two noted fractions namely benzene and naphthalene in each of the two petroleum fractions at their respective wavelengths, were monitored at regular time intervals. Any change in absorbance value is an indicator of the change in

the product concentration. This property was explored in the present studies. Some clay samples showed cracking of the benzene and naphthalene in these petroleum fractions. Table-3 shows the concentration values of benzene in catalytically treated premium brand. Similarly Table-4 shows the change in concentration values of catalytically treated naphtha brand with clay sample no. 7. The results are summed up for blank, activated and inactivated form of various clay samples.

Table-3: Concentration of benzene in catalytically treated motor gasoline (premium brand) in clay sample no. 1 (Anauxite)

Time (min.)	Concentration ($\times 10^{-3}$ Mol L $^{-1}$)		
	Blank	Inactivated	Activated
0	1.203	1.203	1.203
10	1.203	1.303	1.303
20	1.203	1.303	1.453
30	1.203	1.453	1.503
40	1.203	1.403	1.503
50	1.203	1.303	1.453
60	1.203	1.353	1.503

Table-4: Concentration of naphthalene in catalytically treated naphtha on clay sample no. 7 (Montmorillonite)

Time (min.)	Concentration ($\times 10^{-3}$ Mol L $^{-1}$)		
	Blank	Inactivated	Activated
0	4.019	4.019	4.019
10	4.019	3.769	3.516
20	4.019	3.642	3.315
30	4.019	3.66	3.215
40	4.019	3.642	3.240
50	4.019	3.742	3.215
60	4.019	3.692	3.215

A comparison of the present data reveals that the activated form of clays showed promising results as compared to the inactivated form of these clays when used as catalyst. Maximum increase in concentration of benzene in premium brand was shown by clay sample number 1, 2, 3, 4 and 6, where reforming of benzene was achieved up to 25% for clay sample number 1 and 20% for clay sample number 2. Similarly increase in concentration of naphthalene in premium brand was up to 17% for clay sample number 1 and 19% for clay sample number 2. The concentration of naphthalene in naphtha brand increased up to 17% for clay sample number 2 and 14% for clay sample number 1.

Clay sample number 4, 7, and 10 showed maximum decrease in concentration of benzene in premium brand. In such cases, cracking was achieved up to 20% for clay sample number 7. Similarly

cracking of naphthalene in naphtha brand was achieved up to 20% for clay sample number 7 and 17% for clay sample number 4 and 10.

It is clear that aluminum in aluminosilicates give rise to the acidic nature of the clay as shown by figure 2 [13]. The primary accomplishment of the acid activation procedure is the removal of the metallic ions, mostly aluminum and magnesium from the octahedral sheet of the mineral. Al^{3+} proxying for Si^{4+} in tetrahedral coordination in an aluminosilicate give rise to a net negative charge. A charge balancing H_3O^+ associated with such tetrahedral aluminium corresponds to a Bronsted, or protonic acid site. Aluminum in three fold coordination perhaps occurring at an edge, or arising from a Si-O-Al rupturing dehydroxylation of the Bronsted site, would correspond to the Lewis site. Solomon and Roser [14] have proposed that an octahedral Al^{3+} , located at platelet edge, will function as a Lewis site after thorough dehydration. Such aluminum ions would be electron pair acceptor and would function as a protic acid in the Lewis sense. Water which acts as a Lewis base, will cover Lewis site proton from a Bronsted site. It thus acts as a source of catalytic activity.

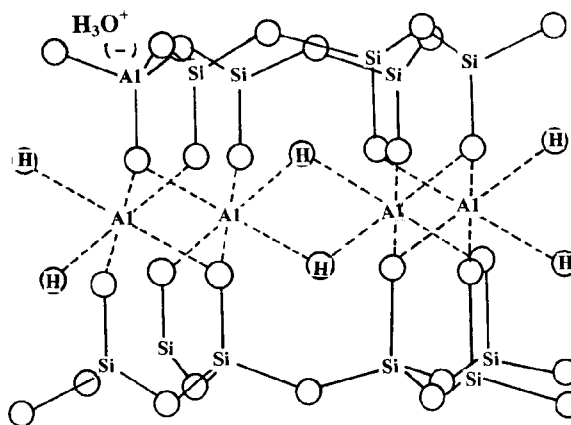


Fig. 2: Sheet layer structure showing acidic nature of

Experimental

All the clay samples were procured from the Pakistan Museum of Natural History, Islamabad. The samples, originally present as chunks were crushed, ground, dried and stored properly in plastic bottles. These were then studied by gravimetric, X-ray fluorescence, and infrared spectroscopic methods.

Gravimetric

The classical analysis for the estimation of Si, Ca, Mg, Fe and Al was performed following the standard reported methods [8]. These elements were estimated as their oxides. The moisture content was also determined by drying the samples at 100°C. At this temperature, hygroscopic water (H₂O) was lost. Loss on ignition was determined by igniting the samples at 1000°C.

X-ray Fluorescence

The major and minor elements were estimated by using the WD-XRF spectrometer PW- 1606, Philips. For determining the major and minor elements, the glass beads making procedure was selected for the solution preparation. In this method the sample was prepared by mixing 4 g of sample with 4 g of flux (lithium tetra borate Li₂B₄O₇). For this, high frequency bead sampler (OYO Danki Co-Japan) was used. For glass making the platinum gold alloy crucible was used.

In order to determine the trace elements, sample was prepared by powder press method, utilizing 12 g of finely powdered of 200 Mesh. The finely powdered sample was pressed by hydraulic press at a pressure of 20 ton/cm² to obtain transparent discs.

Infrared Spectrometry

IR studies were made on Infrared Spectrophotometer, Shimadzu, model IR-460. All the samples were finally ground and pressed by hydraulic press at high pressure for the formation of disc. All the spectra were scanned in full wavelength range of the instrument. Peak position and % transmittance of the peaks were recorded and printed by data processor accessory connected with the instrument.

UV-Visible Spectrometry

Concentration of Benzene and Naphthalene in petroleum samples was observed by Hitachi model UV/Visible spectrophotometer UV 2000 at their respective wavelengths. Percentage concentration of these components in the petroleum samples was observed with the help of the standard plots at different time intervals and with different clay samples.

Preparation of Acid Activated Clay

Powdered clay was dried for 12 hours at 110°C. It was then cooled in a desiccator and designated

as dried clay samples. One part by weight of clay samples was boiled with four parts of commercial HCl for 45 minutes. The leached samples were then washed to get free of chloride ions and dried at 110°C for 12 hours. These were finely grinded to be used in the experiment as catalyst.

Catalytic Treatment of Petroleum Samples with Clay

An amount of 5 gm of a given type of clay either in its activated or inactivated state was added to 100 mL of the petroleum samples as such. The mixture was then refluxed for one hour. A portion of the refluxed sample was then analyzed for benzene and naphthalene production by noting the absorbance of the two products spectrophotometrically. The fractions were collected every ten minutes for such analysis. A change in absorbance values at the respective analyzing wavelengths (248 nm for benzene and 238 nm for naphthalene) indicated the concentration change of these two products.

References

1. M. Ikram, M.A Rauf, and Z. Akhter, *J. Chem. Soc. Pak.* **16**(3), 196(1994)
2. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, ELBS publishers, Singapore, (1997)
3. P. Laszlo, "*Applied & Pure Chemistry*", **62**, 2027 (1990)
4. W. G. Dauben, and V. Congan, *Tetrahedron Lett.*, **31**, 3241 (1990)
5. David I. Eggenberger; "*Encyclopedia of Sci. and Tech*", McGraw Hill Pub., pp.164 (1966)
6. L. Gurwitsch, "*Adsorption Z Chem*", *Ind., Kolloide*, **11**, 17(1992)
7. L. B. Ryland, M. W. Tawade and J. N. Wilson, "*Cracking Catalyst*", 2nd Ed., Willey- Eastern Limited, London. pp 232 (1960)
8. C. Barber, *Chemical Geology*, **14**, 273(1974)
9. H. Kodama, and K. Ginuma, *Proc. 11th Nat Congr.*, 236 (1985)
10. H. Moenke, *Mineral Spectrum*, Academia Verlag, Berlin., **9**, 324(1966)
11. P. G. Nahin, H. Merrill, W. C., *J. Pet. Techn. Am Inst. Min. Met. Eng. Petroleum Trans.*, **192**, 151 (1951)
12. R. E. Newnham, *Minerology. Mag.*, **32**, 683 (1961)
13. A. C. D. Newman, *Chemistry of clay and clay minerals.*, 277 (1987)
14. D. H. Solomon, and M. J. Roser, *J. Appl. Polym. Sci.*, **9**, 1261(1962)