

Study of the Physical and Structural Properties of some Local Ninivites and Effect of Doping with some Chromium Complexes

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ABSTRACT

Chemical composition, physical properties and structural characterization of natural Ninivite silica rocks have been studied. The study approach is based on using X-ray diffraction and fluorescence, differential and gravimetric thermal analysis, infrared spectroscopy, instrumental and classical chemical analysis techniques.

The results were compared with those obtained from a locally prepared and purified amorphous silica gel. Both samples were doped by selenato and oxalato chromium complexes in order to be a more active and selective adsorbent materials. Chromatographic columns were set for all the above types of adsorbents using four eluants gradually increased in polarity. The fractionation results showed significant variations in the fractions isolated according to their polarities as indicated by percentage results.

INTRODUCTION

Ninivite silica rocks located in massive deposits around the city of Mosul in northern Iraq; discovered after Jassim and AL-Naqib, 1989; are considered to be one of the unique sources of amorphous silica (or silica gel). Such silica has been used as a catalyst for a long period in industry in general and especially in petroleum and petrochemicals. This consideration arises from the fact that such materials accompanied in their locations with heavy crude oil reserves. In other words, Hammam Al-Alil bitument and Qaiyarah heavy crude oil might be useful at the present time and have a promising future as well (Ramadhan and Ghazal, 2004).

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 (Ali *et al.*, 1990; Ramadhan, 1992; Buker and Taher, 2006). Such materials contain a mixture of complex hydrocarbon compounds that can easily be separated by fractionation processes to light fuels and petrochemicals (Buker and AL-Mallah, 2005).

Meanwhile, Ninivite silica rocks and their manufactured compounds (Buker and Taher, 2000, 2006; Kob *et al.*, 1997; Kang and Choi, 2000) are proposed to be good adsorbents and catalysts in the above refining processes. Recently, adsorption of a considerable number of Iraqi heavy crude oils on silica materials have been reported (Buker and Taher, 2000).

As a continuation of these studies Buker and Taher, 2006, in their investigation applied Ninivite silica gel doped with chromium oxides in solid phase extraction. Iraqi virgin olive oil was separated into its simple and useful components. The present study covers an investigation into the application of natural Ninivite and amorphous silica after doping them with some chromium complexes in petroleum refining. They have to be employed as a catalysts in adsorption chromatography to fractionate Qaiyarah petrolene (QP) (Ramadhan, 1992).

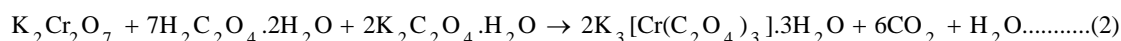
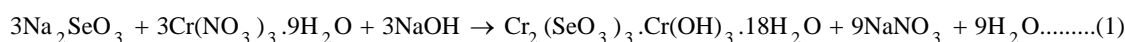
EXPERIMENTAL

A. Sources and Collection of Samples:

Silica gel bearing Ninivite silica rocks were used as a natural silica gel, which were obtained from area around Mosul city/Iraq. These samples were treated basically according to the literature (Buker and Taher, 2000) to obtain the prepared purified silica gel sample. All samples were chemically formulated following several chemical analysis methods (Skoog and West, 1976).

B. Preparation of Complexes:

Selenato chromium complex was prepared according to the reported procedure (Salib and Buker, 1983) and following equation (1). Similarly, oxalato chromium complex was prepared applying equation (2) which was reported (Booth, 1939).



C. Doping of Silica Samples:

Both samples, natural and the purified silica were doped with selenato and oxalato complexes applying the impregnation methods (Buker and Taher, 2006) to prepare four doped samples. Chromium complexes were mixed with silica samples in a ratio 1:8 mole respectively, stirred with distilled water and small amount of ethanol for several hours, filtered, dried at 110 C° , and heated at 320 C° for 2 hours.

D. X-ray Powder Diffraction and Fluorescence:

X-ray powder diffraction studies were carried out using $\text{Cu K}\alpha$ radiation, and diffraction patterns were recorded using Phillips powder X-ray diffractometer fitted with a vertical goniometry. The phase contributing to the X-ray diffraction patterns were identified by reference to the joint Committee on Powder Diffraction Standards Powder Diffraction File. Meanwhile, X-ray fluorescence data were obtained using Phillips Pw 1450/10 Fluorescence Analyzer.

E. Thermal analysis:

Thermo-Gravimetric (TG) and Differential-Thermal Analysis (DTA) were recorded between 25 and 650 C° on (TG) and (DTA) analyses constructed and built in our department. The heating rate was of $5\text{ C}^\circ\text{ min}^{-1}$ and $\alpha\text{-Al}_2\text{O}_3$ was used as standard reference.

F. Infrared Spectra:

The absorption spectra of samples under investigation were recorded on FT-IR Tensor-27-Bruker 2004 Spectrophotometer using KBr pellets and NaCl cell (William and Fleming, 1981).

G. Application:

Six chromatographic fractionating columns were prepared which were packed applying both natural and purified silica and their doped samples as adsorbent materials. All samples were of chromatographic grade (0.212-0.6 mm) and activated to be employed in the processes.

A known weight (2g) of QP was fractionated into four isolated samples according to their adsorption polarities using four eluants of different polarities. IR and NMR will be presented in future article very soon in order to study the chemical nature of the eluted stuff and to evaluate the adsorption activity and selectivity of the investigated samples.

RESULTS AND DISCUSSION

A. Physical and Chemical Characterization:

Physical properties (e.g density, porosity, water absorption, pore size and surface area) have been measured following the methods described in the literature (Iler, 1979). Table (1) shows such data related to the six silica samples under investigation. The capillary action was also measured and the rising of water level was observed as monitored with time is taken as the measurement of this action, Figure (1). It is clear that physical properties of these samples show notable differences. It seems that the purified silica sample has low

density and high porosity and permeability. Meanwhile, the low capillary action of this sample on comparison with natural silica may explain the fact that natural silica samples contain large number of small pores which are well connected by an extremely narrow channels. Moreover, it seems that doping of these samples with chromium complexes affects creating new catalysts with different physical properties. Selenato complexes appeared to be generally the best, regarding adsorption activity (Vartak, 2001).

X-ray fluorescence and instrumental chemical analysis such as atomic absorption and flame photometry, have been used to study the chemical composition of natural semi-pure Ninivite silica rock, and the data of these analyses are shown in Table (2). On the other hand, it is shown that such sample yield 36.7% amorphous silica on treating with basic medium (Buker and Taher, 2006). On doping of those samples, the results of analysis reflect the fact that the percentage values of chromium and selenium ions are in the range agrees with the mentioned doping factor molar ratio of 1:8.

B. Structural Studies:

Since Ninivite silica rocks occurred naturally it is difficult to find a sample containing 100% silica compounds. Therefore, the natural silica sample indeed bears small quantities of other compounds. Careful X-ray powder diffraction studies reveal the presence of such mixed layer structures and frequently indicate their nature and relative abundance (Buker, 1993).

Accordingly, X-ray powder diffraction for Ninivite silica was carried out. Figure (2) shows the sample pattern which contains reflections typical to quartz in addition to montmorillonite, illite, alunite and gypsum phases (Cornelis, 1985).

The amorphous silica may also be defined, on the basis of X-ray pattern, as a broad hump between 2θ (16 and 28) (Brindly and Brown, 1980). However, on doping silica samples with chromium complexes and calcinations to about 700 C°; in order to obtain good crystalline phases; it seems that the prepared samples were destructed and new phases of chromium and selenium oxides appeared. X-ray diffraction charts of these samples (Buker and Taher, 2006) are modified to the data presented in Tables (3 and 4). This type of presentation clearly indicates the interplanar spacings of the contributing phases present in the above samples. Therefore, all samples under investigation were avoided from heating above 450 C° to be active adsorbents whenever they were employed.

The aim of the present study is to prepare a modified silica samples which conation the doped complexes. Such goal to be achieved, differential thermal analysis technique might be employed, followed by thermogravimetric degradation in order to obtain an activated catalyst. Figure (3) shows DTA curve of natural silica sample which contains three endothermic peaks representing the three types of hydration water molecules as reported previously (Buker and AL-Mallah, 2005). Meanwhile, DTA curves of the rest of samples were noted to be similar to the above one except in small variation in the position of the hydration peaks. To interpret such foundation, TG of the investigated samples were performed and Figure (4) represents one of such analyses. It is clear that losses of 14.07, 5.18 and 7.4% from the original weight were observed which correspond to the dehydration phenomena (Stazczuk, 1998).

Finally, it is of interest to study the migration and elimination of the above water molecules from silica samples on increasing the temperature, in addition to the silica

mineralogy by infrared absorption spectroscopy. Therefore, a range of 400-4000 cm^{-1} in frequency was applied and the spectra show several absorption bands including those between (1097-1101 cm^{-1}) which may be attributed to the Si-O stretching vibration (Cornelis, 2003). Also, there are absorption bands at 798-802 cm^{-1} which are related to the Si-O-M groups and those in the range (3625-3742 cm^{-1}) which represent the structural OH groups. Such absorptions show a significant variation in the position and sharpness of the vibrations upon heating the samples in the range of 150-500 C° . This may be related to the dehydration phenomenon.

C. Chromatographic Fractionation:

The above results obtained for the six silica samples in the present research show a significant variation in their chemical compositions, physical properties, and especially in their structural components. It is therefore of interest to get benefit of such findings in evaluating the studied silica samples in order to be applied as good adsorbents in fractionation processes. The silica samples are suitable for the separation of majority of substances or for the separation of complex mixtures into groups of compounds.

Accordingly, six fractionating columns were packed with the chromatographic grade (0.212-0.6 mm) activated silica samples. They were employed in the fractionation of QP using four eluants increased gradually in their polarities and the results are shown in Table (5). The observed results revealing the percentages of the fractions are, indeed eluted according to their adsorption polarities. In general, it is clear that adsorption and desorption of petrolane materials on silica samples has strongly occurred and as a result separated into four components. However, on referring to the previous studies in this field (Buker and Al-Mallah, 2005; Buker and Mubarak, 2001), it seems that the best separation and fractionation occurred in case of amorphous silica sample followed by those samples of doped selenato complex of natural silica and amorphous silica, respectively. To prove such proposed result, chemical characteristic nature of the eluted fractions should be studied via IR and NMR techniques and it will be hopefully presented in a future article.

Table 1: Physical Properties of Samples

Sample	Density g/cm^3	Porosity %	Por Size cm^3/g	Water Absorption %	Surface Water Absorption %	Surface Area g/cm^2	pH
Natural Silica	0.78	98.8	1.52	76	1.08	193.5	7.89
Selenato doped Silica	2.18	222	3.21	160	16.9	65.8	7.12
Oxalato doped Silica	2.22	124	2.16	108	25.31	189.7	8.37
Amorphous Silica	0.63	176	3.96	198	2.11	126.5	12
Selenato doped Amorphous silica	1.8	252.7	4.3	215	17.77	131.6	8.23
Oxalato doped Amorphous silica	2.03	181.5	1.78	121	34.11	63.2	8.88

Table 2: Chemical Composition of Natural Silica

Oxides	ICA* Wt.%	XRF (%)
SiO ₂	90.00	86.14
K ₂ O	1.11	1.90
Na ₂ O	0.47	1.00
CaO	3.26	3.07
TiO ₂	-	2.74
Al ₂ O ₃	0.88	1.94
Fe ₂ O ₃	0.48	0.94
MgO	0.20	0.47
BaO	-	0.57
Nb ₂ O ₅	-	1.16
SO ₃	3.10	-
L.O.I	0.5	0.07

*Instrumental chemical analysis (atomic absorption and flame photometry)

Table 3: Interplanar Spacings of Contributing Phases in Selenato- Doped Silica

Crystalline Phase	$2\theta^{\circ}$	d-spacing in \AA°	hkl
Montmorillonite	17.9	4.946	003
Quartz	26.8	3.318	101
	36.5	2.453	110
	39.6	2.272	102
	45.7	1.979	201
Alanite	31.1	2.870	006
	55.0	1.666	131
KCr ₃ O ₈	20.8	4.253	200
	22.0	4.031	111
	32.7	2.731	020
	40.4	2.229	221
	46.9	1.933	222
	48.5	1.871	313
	55.0	1.666	420
	57.0	1.612	132
SeO ₃	18.3	4.832	-
	26.8	3.318	-
	42.4	2.126	-
	50.2	1.814	-
	59.9	1.541	-

Table 4: Interplanar Spacings of Contributing Phases in Oxalato - Doped Silica

Crystalline Phase	$2\theta^{\circ}$	d-spacing in Å°	hkl
Montmorillonite	17.3	5.112	003
Quartz	20.8	4.253	100
	26.5	3.354	101
	39.3	2.287	102
	40.3	2.233	111
	45.0	2.008	200
	45.7	1.979	201
	50.1	1.818	112
	54.9	1.667	103
	59.9	1.541	211
Alanite	27.8	3.204	113
	52.6	1.736	220
KCr_3O_8	29.8	2.992	112
Cr_5O_{12}	21.9	4.048	002
	23.4	1.941	512
	28.7	3.096	221
	32.3	2.767	122
	34.7	2.574	131
	38.1	2.353	322
	42.2	2.134	223
	43.7	2.067	040
Cr_2O_3	24.3	3.654	012
	33.7	2.654	104
	36.3	2.469	110
	57.3	1.604	122

Table 5 : Chromatographic Fractions (%) of 2g QP Using Different Adsorbents

Sample	Solvents				Loss
	n-hexane $d\pi^*$ (31)	Toluene $d\pi$ (33.9)	Dichloride Methelen $d\pi$ (41.1)	Ethanol $d\pi$ (51.9)	
Natural Silica	1.47	0.12	0.10	0.22	0.09
Selenato - doped Silica	1.28	0.19	0.05	0.38	0.10
Oxalato - doped Silica	1.44	0.20	0.03	0.23	0.10
Amorphous Silica	1.07	0.49	0.01	0.42	0.01
Selenato - doped Amorphous silica	1.31	0.10	0.02	0.41	0.16
Oxalato - doped Amorphous silica	1.25	0.39	0.05	0.25	0.06

*Polarity unit

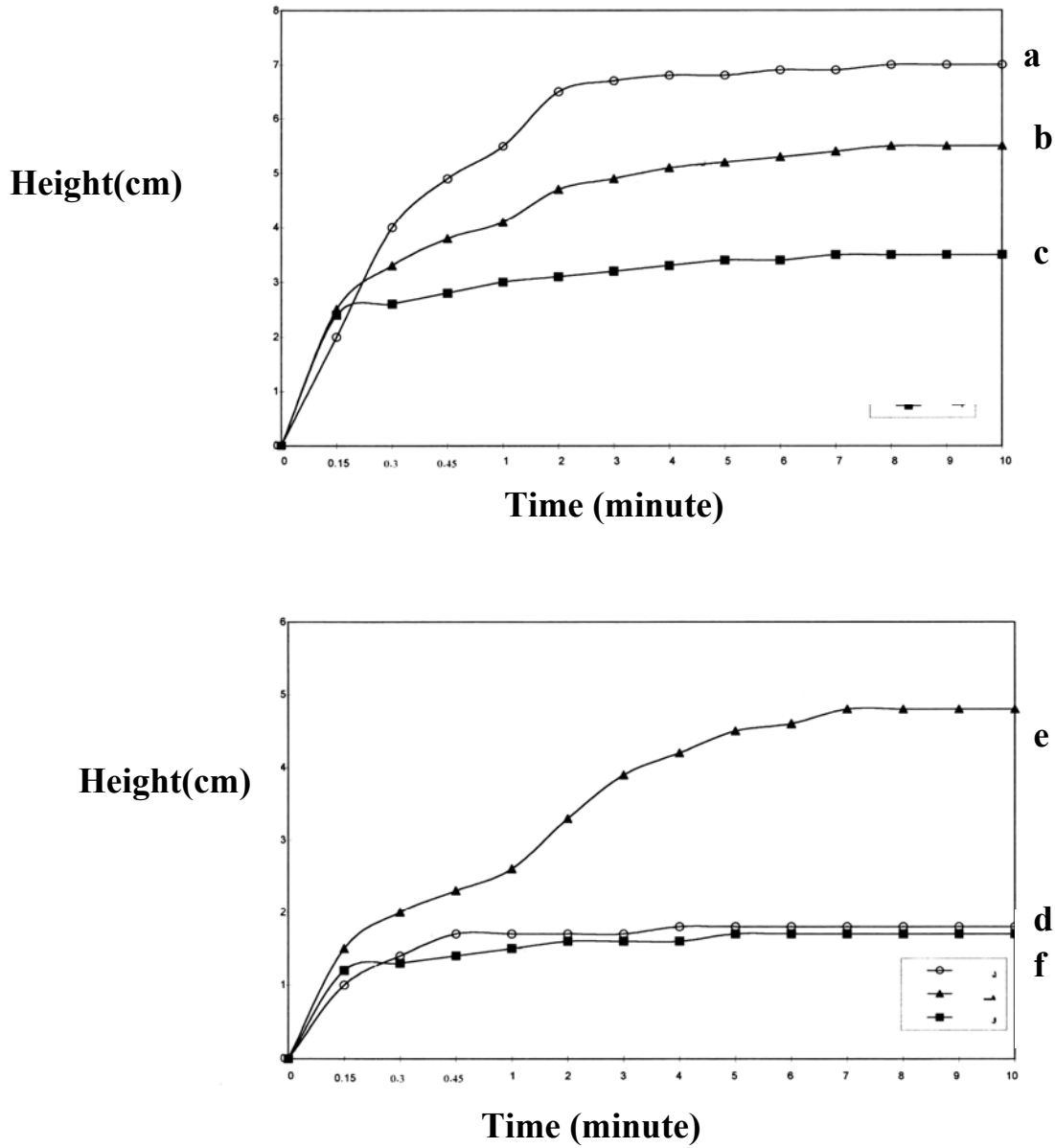


Fig.1 : Capillary Action Curves of :

- a-Natural Silica.
- b-Selenato - doped Silica.
- c-Oxalato - doped Silica.
- d-Amorphous Silica.
- e-Selenato - doped Amorphous silica.
- f-Oxalato - doped Amorphous silica.

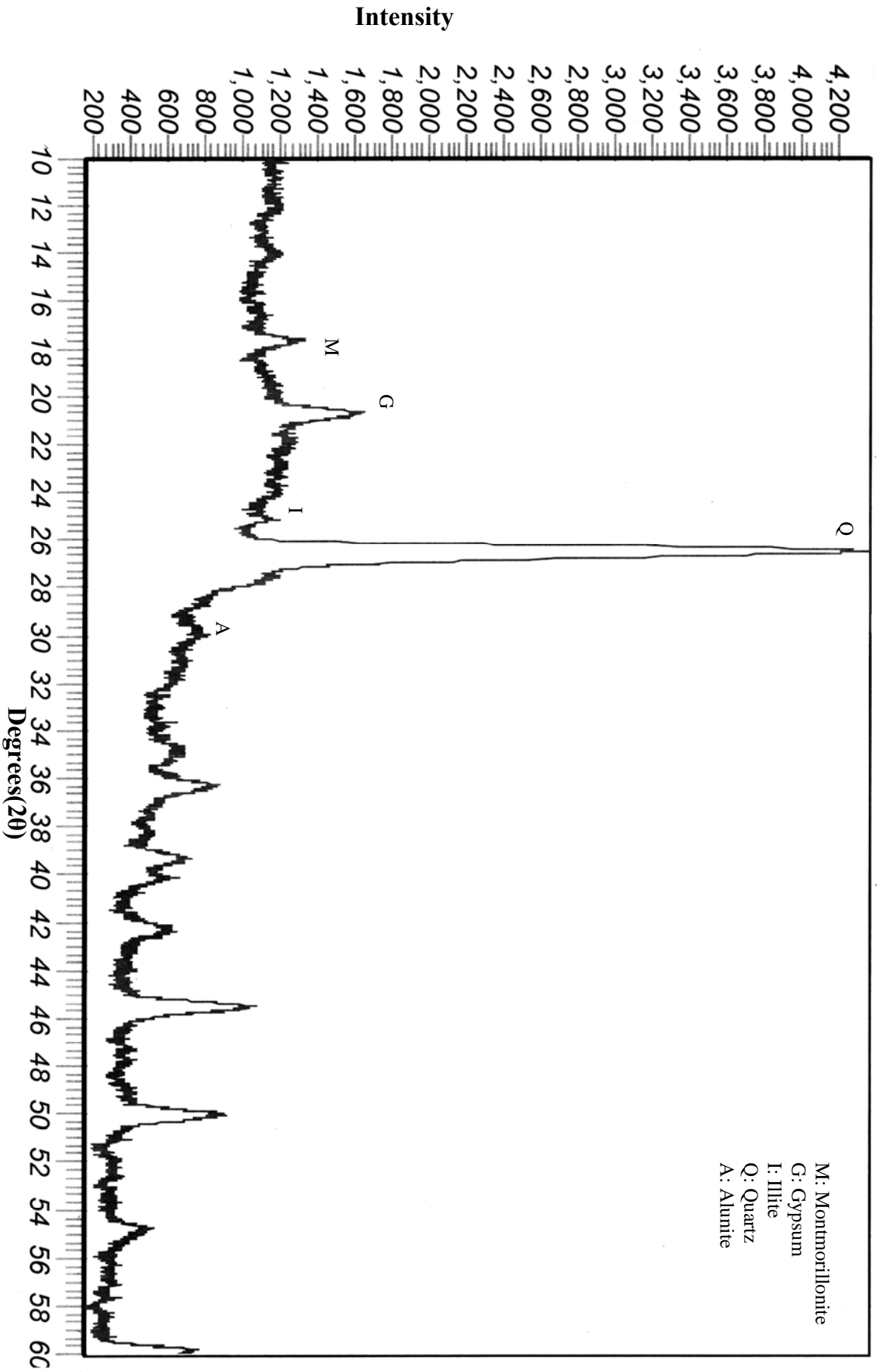


Fig. 2: Powder X-Ray Diffraction Pattern of Natural Silica Samples

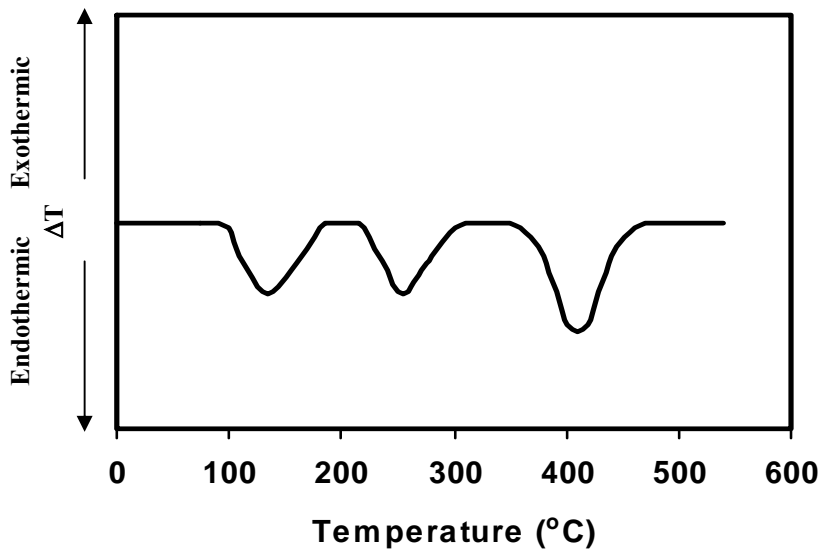


Fig. 3: Differential Thermal Analysis Curve of Natural Silica Sample (Buker and Taher, 2006)

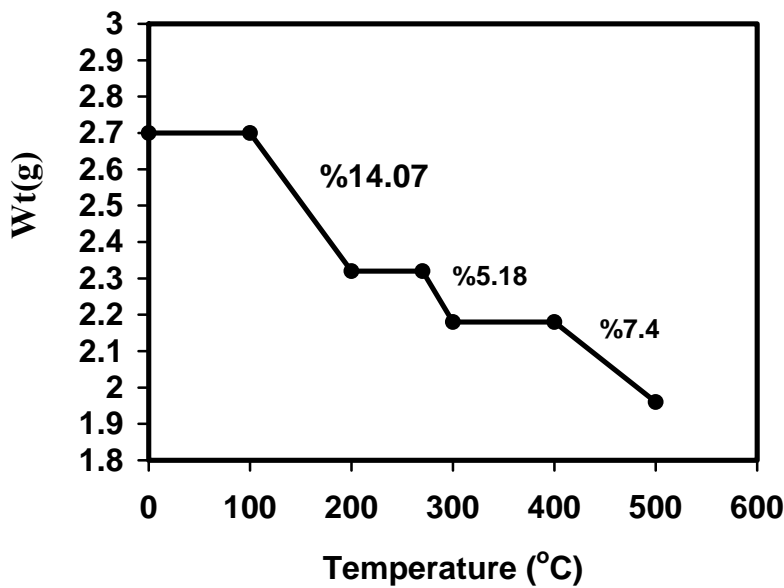


Fig. 4: Thermogravimetric Curve of Natural Silica Sample (Buker and Taher, 2006)

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