ADSORPTION EFFECT MECHANISM OF SODIUM OLEATE ON FELDSPAR AND QUARTZ①

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ABSTRACT

A study about the adsorption mechanism of sodium oleate on feldspar and quartz is briefly introduced. The investigation works found that the active silicon on quartz surface has some reaction with oleate ions. Based on the data from XPS analysis, the thickness of the adsorption layer on feldspar was calculated.

Key words: feldspar quartz sodium oleate adsorption XPS analysis

1 INTRODUCTION

Fatty acid like oleate and their soaps are commonly used collectors for the flotation of oxide ores. Many research works have been done on the principal effect mechanism, on which some mature views have been developed. Generally, it is considered that the anions formed in the discomposition of the oleate is the main constituent[1-3]. The main adsorption mechanism is that the polar radical of the anion reacts with the metal ions on the mineral surface. As a result, an unsoluable compound is formed[4-5]. The oleate ions and molecula can adsorb on the mineral surface with physical effect, too[6-7]. Quartz as well as feldspar has no suitable condition for a large amount of oleate radicals to adsorb chemically, so these two minerals can not be floated by oleate collector only. Anyway, some oleate still can adsorb on these two minerals, about which the author's previous work had proved already. IR analysis and s-potential determination had been used for the investigation on the adsorption mechanism research, and by which some valuable knowledge had been got: one is that the oleate anions adsorb on the partial positive charged area of the minerals with electrostatic effect, the other is that oleate molecula adsorb on the minerals as molecule ion assemble or by hydrogen bond. Besides these two ways, on feldspar surface there is chemical adsorption existing between the oleate ions and Al ions. In order to further confirm these understandings, the authors apply XPS(X-ray photoelectron spectroscopy) analysis technique to investigate the energy states of the continent atoms on the mineral surface before and after the treatment with reagent. Combined with IR analysis result, it is hoped that the effect mechanism between oleate and minerals will be understood in more detail.

2 TEST METHOD AND SAMPLE PREPARATION

XPS analysis was done on a Model MICRO-LAB-MK Ⅱ multipurpose surface determination apparatus. Angular resolved method was used in the analysis, which means that at different inlet angle, the energy state of the photoemission electron will be determined for the crystal. From the energy posi-

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tion variation of the photoemission electron, it is possible to realize whether the chemical environment of the atom has changed or not and to further judge the property of the effect between the reagent and the mineral surface. The variation of chemical environment for an atom has two meanings: one is the change of the element and its amount; the other is that the atom has different valence.

The principle of the angular resolved method is described in Ref. [8].

The test sample is a d 1 mm × 1 cm crystal disc pealed off from the mineral crystal. The crystal was first cleaned in deionized water for 1 h and then treated in oleate solution for 15 min. The oleate concentration of the solution is 30 mg/L, its pH is 5.0. After exposed in air until the surface was dry, the sample was dried in a vaccumn dryer for 10 h, then used for XPS analysis.

3 XPS ANALYSIS TO QUARTZ SURFACE TREATED WITH SODIUM OLEATE

The combination energy of the Si, C and O main peaks for the quartz treated with sodium oleate is shown is Table 1.

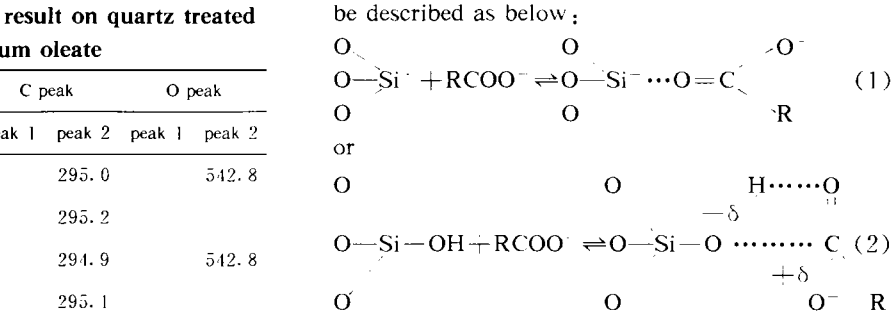
Peak 1 of C energy peak comes from the C atom of the oleate carbon chain, so called adsorption C peak. Peak 2 comes from the trace impurity C in the mineral crystal, so called base C peak.

Table 1 XPS analysis result on quartz treated with sodium oleate

Inlet Angle/(°)	Si peak		C peak		O peak	
	peak 1	peak 2	peak 1	peak 2	peak 1	peak 2
90		113.5		295.0		542.8
80		113.5		295.2		
35		113.4		294.9		542.8
20		113.6		295.1		
10	110.4	113.6	292.5	294.5	539.7	513.1

The results in Table 1 show that when the inlet angle gets down to 10°, the adsorption C peak appears, and its intensity is very low, which indicates that the oleate adsorption layer on quartz is quite thin. From the spectrum figures (omitted), we can also find that with 5° inlet angle, the base C peak is still very strong, which means the oleate adsorbed area is very small. If the adsorbed area is large, with a small inlet angle, the emission electrons should go mainly through the adsorption layer, and the information about the layer should be more too. On the other hand, with a thin and small adsorption layer, the information about it have to be very weak.

From Table 1, we can also find that when the inlet angle is 10°, double peaks appear for both Si and O, which show that Si and O on quartz surface have two different existing forms: one is in crystal structure, the other is that reacted with ions. This means that besides the elecrostatic adsorption on the partial positive charged area and radical aggromeration, there is some other effect between the oleate and the quartz surface, by which the chemical environment for Si atom changed. Although IR analysis results show that no chemical adsorption product had formed, but some other combination form should exist between oleate and Si or O. When quartz crystal is crushed forcedly, a large amount of Si—O bonds will be broken, these Si and O exposed on the surface both can be unsaturated active points. With 3d free track, Si ions have a chemical property like metal cationic ion. Refering the effect between oleate and other metal ions[9], it can be considered that the O atom on the carboxide of the oleate radical has some bonding effect with the Si ions on quartz surface. The reaction pattern can be described as below:



(1)

or

(2)

The split of the O peak is possiblly caused by the Si ions connected with. Because of the change of its chemical environment, Si atom has enforced absorbing the electrons on outside track. The thinning of the outside electronic cloud affects the energy position. According to the charge potential model[10], supposing the atom in the molecule can be

represented by a hollow, unoverlapped electrostatic spherical shell which surrounds a central charge. The valency electrons consist the outside charge shell. This shell affects the combination energy of the electrons on the inner track. The reason for the change of the charge concentration is that when the atom emitting photoelectrons reacts with other ions, there will be an electron transformation, in other words, the variation of the valency electron structure is also one of the reasons for the shift of the energy position. The energy position variation for O element is caused by Si bonded with it.

4 XPS ANALYSIS TO FELDSPAR SURFACE TREATED WITH SODIUM OLEATE

The variations of combination energy of Si, C, O and Al with the photoelectron inlet angle are shown in Table 2.

Table 2 XPS analysis result on feldspar treated with sodium oleale

Inlet angle(°)	Si peak	O peak	Al peak	C peak		Intensity of C peak	
				peak 1	peak 2	peak 1	peak 2
90	108.4	537.7	80.0		288.9		
80					288.9		
70				284.7	289.1	111	705
50				284.7	288.6	251	562
35	106.6	535.9	78.2	284.6	288.5		
30				284.7	289.0	396	263

It can be seen that at 70° inlet angle, the adsorption C peak appears, which indicates that the adsorption layer on feldspar is much thicker than that on quartz. With dropping of the inlet angle, the adsorption C peak goes up gradually. When inlet angle reaches 30°, the adsorption C peak gets over base C peak, which means that the percentage of the covered surface on feldspar is higher than that on quartz too. Comparing the positions of Si, Al and O peaks at 90° inlet angle with that at 35°, it is found that the processing of oleate has caused the combination energy of theses elements to shift to lower position, which shows that there is a chemical adsorption effect between the reagent and the mineral surface. Refering the results from IR analysis, we know that the variation of Al's energy position is caused by the reaction between Al^{3+} and oleate ion; The change of Si's energy position is possiblly caused by two reasons; one is the effect of the energy position variation of Al, O connected with it; the second is like that on quartz, the active silicon from the broken Si—O bond reacts with O from the polar radical of the oleate.

5 CALCULATION OF THICKNESS OF OLEATE ADSORPTION LAYER ON FELDSPAR

Comparing the reagent adsorption capacity from analysis with that calculated out on the base of forming a monolayer which consist of a close molecula arrangement, the thickness of the reagent layer can be worked out[7]. This is a traditional way. In fact, the reagent is not evenly and closely arranged on the mineral surface, so the thickness got by this way is theoretical one.

For an adsorption layer not so thick, the thickness can be calculated with the following formula:

$$d = \lambda\left(\ln\frac{H}{\sin\alpha_2} - \ln\frac{W}{\sin\alpha_1}\right) \Big/ \left(\frac{1}{\sin\alpha_1} - \frac{1}{\sin\alpha_2}\right) \quad (3)$$

where d — thickness of adsorption layer; α_1, α_2 —photoelectron inlet angle; I_s —the peak intensity of the specific atom in base with the reagent layer whose thickness is d; I_0 —the peak intensity of the specific atom in the reagent layer whose thickness is d; λ —the mean free path of the photoelectron of the specific atom.

From Table 2, when $\alpha_1 = 50°$, $I_{s1}^d = 562$, $I_{01}^d = 251$; $\alpha_2 = 30°$, $I_{s_2}^d = 263$, $I_{02}^d = 396$

then $W = 2.24$; $H = 0.634$

The mean free path of C's photoelectron is 16.95 Å. Taking W, H, λ into formula (3), we obtain $d = 20.39$ Å

The length of the oleate molecula is 23.8 Å. By comparison, it can be known that the thickness of the oleate layer on feldspar is not as thick as that on molecular layer.

The adsorption layer of oleate on quartz is

very thin, and the covered area is small too, so calculating the thickness has no actual meaning.

6 CONCLUSIONS

The XPS analysis results have not only confirmed the adsorption of oleate and its ions on minerals, but also indicated that oleate ions can react with Si ion and adsorb on the mineral surface, by which causes the energy position of Si and O on feldspar and quartz to shift. Si and O on feldspar have only one existing form, which means the amount of the oleate reacted with Al^{+} on feldspar is much larger than that on quartz. The XPS analysis results and the calculation results of adsorption layer's thickness have also proved that the oleate layer on feldspar is thicker than that on quartz.

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(*From page 48*)

i. e., $Y = 44.85$. As $X + Y + Z = 100$, $Z = 50.65$. Therefore, the ammonium molybdate mixture dehydrated from the absorbed water contains 4.50% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 44.85% $(NH_4)_4Mo_5O_{17}$ and 50.65% $(NH_4)_2Mo_4O_{13}$ + β-$(NH_4)_2Mo_4O_{13}$ as well.

Similarly, the weight loss of the initial mixture of the above composition at the third stage due to the decompostion of $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ into MoO_3 is evaluated to be 8.06% which is 0.75% larger than the actual weight loss of 7.31% in the TG measurement. This difference in weight loss may be caused by the impurities in the mixture or the $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ which do not decompose completely.

3 CONCLUSIONS

(1) When heated, the ammonium molybdate mixture will decompose and give off NH_3 and H_2O with MoO_3 being the final product. During the decomposition, several intermediate phases are formed in which the content of molybdenum increases with the rise of temperature. The whole process proceeds at three different temperatures of 110, 220 and 290 ℃ according to the following five steps:

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \longrightarrow (NH_4)_4Mo_5O_{17} \longrightarrow (NH_4)_2Mo_4O_{13}$;

$(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13} \longrightarrow (NH_4)_2Mo_{14}O_{43} \longrightarrow (NH_4)_2Mo_{22}O_{67} \rightarrow MoO_3$

(2) From the weight losses in the TGA curve, the weight percentage of each component in the mixture dehydrtated from absorbed water is evaluated.

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