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Evolution of Surface Area of Clay Treated with Sulphurous Acid and its Subsequent Activation

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Clay sample (composition: Al_2O_3 23.6%, SiO_2 52.9%, CaO 0.24%, K_2O 0.05%, Na_2O 0.07%, Fe_2O_3 6.3%) was mixed with water and treated with various amounts of sulphur dioxide gas generated by reacting known amounts of sodium sulphite with dilute hydrochloric acid. The value of Fe_2O_3 in the clay sample was reduced by as much as 95% by the SO_2 treatment. The surface area of the clay sample was treated with SO_2 and subsequently activated (boiled in 0.8M HNO_3 and heated at 573°K).It was observed that treatment with SO_2 markedly enhanced the surface area of the clay samples, the surface area values of clay samples were compared with untreated clay samples and silica-alumina gels of comparable silica/alumina ratios. The practical applications of clay as adsorbents, decolourising agent, catalyst support etc. depend on the physico-chemical activity at the clay surface. However, acid and heat treatments of clay may produce changes which are responsible for the physico-chemical activity of clay. The use of acid treated clays as a solid source of protons in a number of novel and industrially significant reactions is now well documented, (Mills *et al.* 1950; Thomas *et al.* 1950; Novak and Gregor 1969; Fernandez-Alvarez 1970; Atkins *et al.* 1983; Ballantine 1986; Adams 1987). It was thought that a reduction in the iron content of clay might be accompanied with the development of large surface area upon activation by acid and heat treatments. Clay sample was obtained from the local deposit (Uhonmora, Owan West) and purified as described previously (Okieimen *et al.* 1991) and treated with SO_2 prepared by reacting sodium sulphite with HCl. The amount of SO_2 generated was varied by using different amounts of NaS_2. The iron content of the clay sample before and after treatment was determined (Jeffrey *et al.* 1989) using UV spectrophotometer, Unicam SP 500. Then the clay sample was boiled in HNO_3 solution (0.8M) for 1h and then heated at 573°K for 10h. Silica-alumina gels were prepared using the stepwise precipitation method described by Sinhamahaparta *et al* (1978).

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The surface areas of the clay and silica-alumina samples were determined by the iodine and methylene blue adsorption methods (Hang and Brindley 1970).

Clay suspensions containing different amounts of methylene blue were prepared by adding various volumes of 1mg mL^{-1} methylene blue stock solution to give a range ($4.2x10^{-7}$ to 4.0×10^{-6} mol L^{-1} mixtures). All solutions were prepared using plastic containers. The mixture was allowed to stand for 1h to obtain optimum flocculation and the absorbance of the supernatant was measured using Unicam SP 500 spectrophotometer at 665nm.

Table 1 shows that the level of iron in the clay is quantitatively reduced (95%) from 43.0mg g^{-1} to 2.0mg g^{-1} by the SO_2 treatment. The iodine number of the untreated clay sample is highest followed by that of the activated clay sample. The iodine numbers of the silica-alumina samples (except for Si-Al(B) are the lowest and are generally about 30% lower than the values obtained for the clay samples. A reduction in the iron content of the clay sample is accompanied by an increase (generally less than 20%) in the surface area of the samples.

The values of the specific surface area of the samples obtained by the methylene blue method (Kalousek and Blahniz 1950) are shown in Table 1. It would be observed that SO_2 treatment improves the evolution of surface area of clay (up to 70% increase) the variation in the surface area of the samples are similar to the trend observed from the iodine adsorption

Table 1
Surface area of clay and silica - alumina samples

Sample	Iron content (mg g^{-1})	Iodine number	Specific surface area (m^2 g^{-1}) sample	X*
a. Clay		Clay		
Untreated*	43.0	4.03	48	0.31
Activated (0.8M;573°K)		3.97	67	0.31
SO_2 treated and activated (0.8M;573°K)	30.0	3.91	69	0.31
	22.9	3.90	72	
	7.2	3.76	75	
	4.6	3.61	76	
	2.0	3.42	80	
b. Silica – alumina				
Si – Al (B)	0.0	1.85	114	0.52
Si – Al (B)	0.0	5.56	38	0.71
Si – Al (B)	0.0	2.47	86	0.36

*X, Al_2O_3 / (Al_2O_3 + SiO_2), 0.31.

method. Silica-alumina samples generally show higher surface area value than the clay samples even when the silica/alumina ratios are comparable.

The study shows that clay treated with sulphurous acid and subsequently activated by acid and heat treatments results in enhanced surface area.

Key words: Surface area, Clay, Sulphurous acid.

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