BET Surface Area Determination of Calcium Oxide from Adamawa Chalk Mineral Using Water Adsorption Method, for Use as Catalyst.

Aminu H. Isa (Corresponding author)
Energy planning and analysis, Energy Commission of Nigeria,
Plot 701c, Central Area, P. M. B. 358, Garki, Abuja, Nigeria
Email-jaminh1177@gmail.com

Funke W. Abdulrahman
Department of Chemistry, University of Abuja, Nigeria
Email-funkabdul@yahoo.com

Haruna D. Aliyu
Department of Chemistry, University of Abuja, Nigeria

Abstract

This paper describes a test procedure for determining the total surface area of chalk mineral using the water adsorption method. The test involves saturating the thermally treated chalk sample with saturated salt solution of known relative humidity, until the water vapor forms a monomolecular layer on the treated chalk sample surface. The results of the test are expressed as Specific Surface Area (SSA), which describes the surface area/unit mass of dry treated sample with units of m^2g^{-1}. The test results presented demonstrate the BET isotherm of chalk samples after being thermally treated at 700, 900, 1100 and 1200^oC. Results for a number of different treated chalk samples are presented. The proposed method uses simple and inexpensive laboratory equipment, is relatively simple to perform, and allows for rapid determination of SSA.
Keywords: specific surface area, chalk mineral, water vapor, BET isotherm

Introduction

The surface of a solid particle is the dividing line between the solid particle and its surroundings such as liquid, gas or other solid particles, thus, the amount of surface area is an important factor in the behavior of solids, for example, it affects dissolution rates of solids, catalytic activities substance dissolution, adsorption capacity adsorbers, and the processing of most powders and porous materials. Any solid matter that is divided into smaller particles produces new other surfaces thereby increasing the surface area. Similarly, when pores are created within the particle interior (by dissolution, decomposition or some other physical or chemical means) the surface area is also increased. The true surface area, including surface irregularities and pore interiors, cannot be calculated from particle size information, rather, it is determined at the atomic level by the adsorption of an unreactive, or inert gas. In the past, two general approaches have been used predominantly to determine specific surface area of clays, they are: (1) measurement of external surface areas by the adsorption of simple molecules, such as nitrogen at low temperatures, with surface areas being derived from adsorption isotherm data and the application of BET theory (Brunauer et al., 1938), and (2) measurement of total surface area by means of adsorption of polar liquids, example, the work of Amy and Alan (2002), utilized Ethylene Glycol Monoethyl Ether (EGME) in their method of determining the surface area of fine grained soils. Another technique is using water adsorption method as in the studies of Shang-Li et al. (2002), Adefila, et al. (2003) and Salahudeen et al. (2012). Other techniques for determining surface area have ealier been suggested, e.g., Cetyl Pyridinium Bromide (CPB) (Greenland and Quirk 1964),p-Nitrophenol Adsorption (pNP) (Ristori et al., 1989) and Methylene Blue Adsorption (Hang and Brindley, 1970). Some of these methods produce similar surface area values as those obtained with theoretical soil structure equations, but are time-consuming or require expensive, specialized apparatus (Amy and Alan, 2002). This paper is aimed at determining the BET specific surface area of CaO produced from Adamawa chalk mineral, using water vapor adsorption method, especially for use as catalyst material. The techniques employed were: (a) resorption of water by the calcined product; (b) the sorption isotherm of the vapor on the calcined product; and (c) X-ray examination of the calcined product.

Material: The material, raw chalk samples were obtained from Adamawa state and beneficiated as described below.

Experimental: Sampling and processing

Beneficiation: Raw chalk samples were wet-beneficiated according to the work of Ahmed in 2008, in order to purify it from both physical and chemical impurities such as metallic oxides, soluble salts and grits (Ahmed, 2008). The raw samples were crushed then grounded using wooden mortar and pestle. The ground chalk samples were wet-beneficiated using an experimentally determined optimum mixing ratio of 0.1 kg of chalk material to 1 liter of water, and optimum settling time of 24 hrs. After soaking the chalk material for 24 h the mixture was blunged by vigorously stirring at 400 rpm for 3 hrs in order to separate all possible agglomerates of chalk particles, the mixture was left overnight to settle down. The blunge slurry settled into three clear layers; the bottom coarse particles; the middle fine particles and the top supernatant. The three layers were separated by siphoning. The top supernatant layer and the bottom coarse particles were discarded while the middle fine particles slurry layer was further processed. The fine particle slurry was sieved using Tyler sieve of mesh size 230 (63 μm aperture opening). The resulting fine particle slurry was allowed to settle and the supernatant layer was removed by siphoning in intervals of 2hrs until there was no reasonable quantity of top water layer. The drying process was done according to the work of Salahudeen et al., 2012, y pouring the thick slurry into an open clay-pot to ensure faster separation of the water through the micro-pores of the clay-pot surface and allowed for to stay for 6 days (Salahudeen et al., 2012). The slurry was kept in the clay-pot for open drying at room temperature for another 2 days, then finally, the solid chalk material cake was dried in an electric oven (AX 120, Carbolite Aston, England), at 300 °C for 3 hrs.

The dried chalk mineral samples were then calcined using thermogravimetric method, to remove water and carbon dioxide from the mineral particles, and converted into oxide (this is necessary to reveal basic sites on the surfaces of the raw materials). The TGA was done by measuring 1g portion of dried chalk mineral sample (less than 2mm mesh size), poured into cleaned and pre-weighed dried crucibles at each time and was heated at temperatures of 50°C intervals for 5 hours, up 1100°C, in an electric muffle furnace (Carbolite RHF 16/3, Aston, England), and the loss of weight was measured by static method. A desired temperature was set between 350-1100°C and the sample was removed from the furnace and weighed after every 10 min to constant weight, after which the sample was removed finally from the furnace and poured from the crucibles into a bath of ice cold water (this is to quench any further oxidation). Excess water from the samples was drained and samples were sundried and further dried in oven at 110°C for overnight. This process continued until substantial amount of calcined sample was obtained and kept in air tight desiccators.

Surface area determination: Surface areas of the samples were determined by water adsorption method. This was done after degassing the samples using an adopted BET surface area analysis method adopted by Adefila, et al. (2003). The method employed the establishment of the adsorbent's constant relative humidity (RH) as that of water vapor obtained from saturated salts solutions in water. This RH was proved to be equal to P/P_o in BET isotherm equation. The method was achieved by keeping in an air tight desiccator both the saturated salt solutions of the following four salts: $CaSO_4$, K_2SO_4, CH_3COONa and $MgCl_2$. After determining the value of P/P_o for each salt solution, one f each saturated solution of the salts was prepared and kept in an air tight desiccator with 1.0 g portion of the adsorbent (samples of chalk calcined at temperatures: 700, 900, 1100 and 1200°C), evenly spread on an Aluminium tare for 24hrs, maintaining the laboratory temperature at room temperature. The constant weight gained by each the samples determined at the end of the 24 hrs was used to represent X in the same BET isotherm equation, and the constant RH of the adsorbate was used to represent P/P_o of the same equation. Also, three samples of known BET surface area values were used as standards to establish the correction factor of this method.

Determination of RH: The RH of each saturated salt solution was determined by preparing two equal and separate saturated solutions of a particular salt, one was kept in an air tight desiccator while the other was left in the open, inside the laboratory, and both were left for 24hrs., noting their respective weights at the beginning and the end of 24hrs. The ratio of the weight differences as shown in Table 1 for both salt solutions in the desiccator [at initial point (wd1) and after 24h (wd2)], and left open in the laboratory [at initial point (wo1) and after 24 h (wo2)], was used to evaluate the RH of the saturated salt solution (Sand and Crowley, 1960). In this dissertation, calcium sulphate, potassium sulphate, sodium ethanoate and magnesium chloride were used for determining various RH values.

Structural characterization: The samples were structurally characterized using X-ray diffraction (XRD); X-ray diffraction patterns were recorded on a D/Max-3C X-ray powder diffractometer (Rigalcu Co., Japan); using a Cu-Kα source fitted with an Inel CPS 120 hemispherical detector for structural identification and degree of

crystallinity as well as true density measurement and Atomic Adsorption Spectroscopy (AAS) for catalysts' elemental analysis.

Results and Discussions

Elemental composition: The AAS analysis of the calcined chalk mineral sample (presented in Table 2) revealed the composition by mass percent of the following metal atoms: Ca, Mg, Zn, Fe and others in the sample. This indicated that the calcined chalk mineral sample presented here have very high content of Ca among others.

Surface Area Analysis: Surface area decisively plays a good role on the catalytic activities of solid particles. In this study, chalk samples calcined at 700, 900, 1100 and 1200°C were tested for BET surface areas using method adapted by Adefila et al., 2003, as shown in Table 3, (Adefila, et al., 2003). The samples were analyzed for surface area to determine BET surface area within 24hrs, and each sample was tested in triplicates to test for reproducibility. All samples exhibited relatively low specific surface areas (below $10 m^2/g$), ranging between $3.04-9.73 m^2/g$, as shown in Table 6. A particular decrease was observed when the sample was calcined outside the temperature of 1100°C, confirming the attainment of relatively large surface at 1100°C. The BET surface areas obtained showed improvement over some literature studies such as the work of Domka et al. in 2001.

The BET method used gave average error of +9.0667 % of the actual BET surface area values expected due to some inherent error introducing factors associated with the method, such as; ideal situation assumption, efficiency of the desiccators used, purity of the salts used, etc.

Sample characterization: The diffractorgramm patterns of CaO from the sample cailcined at 1100°C are shown in Figure 1. A series of reflections at 32.2, 37.4, 53.9 and 67.4 are consistent with X-ray diffractorgrams of CaO being similar to those from previous reports (Zhu et al., 2006; Granados et al., 2007; Kouzu et al., 2008; Ngamcharussrivichai et al., 2008). Minor reflections from the X-ray diffractograms: 18.1, 28.6, 34.2, 47.2, 50.8, 53.9 and 64.2 are attributed to $Ca(OH)_2$ phase, which indicated that the hydration of fresh CaO cannot be avoided during the calcination activities (Klug and Alexander, 1954). No peak of calcium carbonate was observed in the XRD patterns, which indicated total expulsion of CO_2 from the carbonates of the fresh chalk mineral sample. It can be seen that the diffraction peaks corresponding to the CaO phase showed well degree of crystallinity.

Conclusion

1. The natural chalk from Adamawa State is mainly calcium based, with some deposit of magnesium, zinc and iron metals.
2. The XRD of the sample confirmed total conversion of the carbonates in the chalk to oxide can be attained at a temperature of 1100°C, and also confirmed that the hydration of the oxide cannot be avoided during calcination.
3. The surface area obtained though low but showed little improvement over some literature studies.
4. The sample calcined at 1100°C exhibited relatively high BET surface area

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Note 1:   RH $= \dfrac{Wd_2 - Wd_1}{Wo_2 - Wo_1} = \left(P \middle/ P_O \right)$

1

Where, Wd_1 and Wd_2 = Initial and final weights of salt solutions inside desiccators, respectively.

Wo$_1$ and Wo$_2$ = Initial and final weights of salt solutions left open to room condition, respectively.

Note 2: The expression: $\dfrac{P/P_O}{V\left(1 - P/P_O\right)}$ from BET equation is represented by Y in Tables 3 and 4,

where 'X' in Tables 3 & 4 represent V in the expression.

Table 1: Data for determination of RH of salts solutions

Salts	$CaSO_4$	K_2SO_4	CH_3COONa	$MgCl_2$
Wd_1	39.8427	50.6254	57.0574	41.9625
Wd_2	39.6880	50.2909	56.7850	41.6087
Wo_1	35.8986	47.7108	65.1647	42.1894
Wo_2	39.1339	42.4947	64.0124	40.9293
RH (P/Po)	**0.0325**	**0.0641**	**0.2364**	**0.2808**

Table 2: Percentage composition by mass of the chalk mineral sample calcined at 1100°C

Sample	Ca	Mg	Zn	Fe	Others
	%				
Calcined chalk mineral	85	11	0.3	2.40	< 1%

Table 3: BET isotherm of chalk mineral samples calcined at 700, 900, 1100 and 1200°C

Sample	$CaSO_4$		K_2SO_4		CH_3COONa		$MgCl_2$	
Temp. (°C)	$X(g)$		$Y(g^1)$	$X(g)$	$Y(g^1)$	$X(g)$	$Y(g^1)$	$X(g$
700	0.0006	55.0684	0.0007	104.2467	0.0010	305.7118	0.0012	320.8166
900	0.0005	62.9059	0.0008	84.2438	0.0013	234.5350	0.0016	245.7104
1100	0.0005	79.9803	0.0007	90.1187	0.0022	147.4220	0.0025	151.9198
1200	0.0005	68.5546	0.0008	82.5183	0.0021	150.2845	0.0025	155.5513

Table 4: BET isotherm of standard samples used

Standard	$CaSO_4$		K_2SO_4		CH_3COONa		$MgCl_2$	
	$X(g)$	$Y(g^1)$	$X(g)$	$Y(g^1)$	$X(g)$	$Y(g^1)$	$X(g)$	$Y(g^1)$
A	0.1378	0.2632	0.0960	0.8580	0.0706	4.3221	0.0360	0.6052
B	0.2470	0.1468	0.1590	0.5180	0.0640	5.0023	0.0130	29.3683
C	0.0091	4.0032	0.0066	12.5180	0.0030	102.3951	0.0019	205.2624

Table 5: Measured BET surface area (S_t) of standard samples used to determine correction factor for the test method
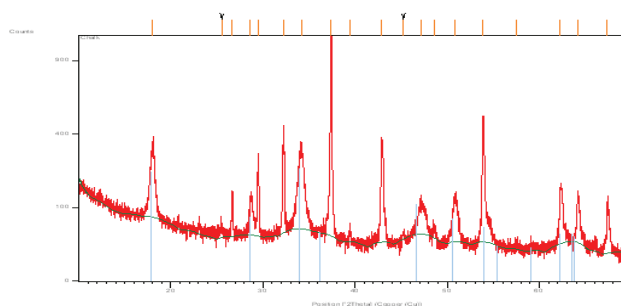
Sample	Actual surface area $\left(m^2/g\right)$	Obtained surface area $\left(m^2/g\right)$	Percentage Error (%)
Standard A	168.15	195.21	16.1
Standard B	155.20	161.1	8.9
Standard C	5.04	5.15	2.2

Average Error = + 9.0667 %

Correction factor = 1- 0.0907 = 0.9093

Table 6: Measured BET surface area (S_t) for Chalk sample obtained at 700^OC, 900^OC, 1100^OC and 1200^OC

Temp. (^{O}C)	Surface Area $\left(m^2/g\right)$
700	3.04
900	4.31
1100	9.73
1200	8.36

Figure 9: Diffractorgrams of intensity Vs 2θ showing XRD pattern of CaO from chalk sample calcined at 1100^oC