Thermochimica Acta, 37 (1980) 137—143
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SURFACE PROPERTIES OF SILICAS PRODUCED BY THERMAL TREATMENT OF RICE-HUSK ASH

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(Received 27 August 1979)

ABSTRACT

Silica samples were prepared by firing rice-husk ash at various temperatures ranging from 500 to 1400°C for a period of 3 h. Adsorption of nitrogen was used to study the surface properties of the silica obtained at each firing temperature. The parameters derived were related to the pore structure and the degree of crystallinity of the silica samples. X-Ray diffraction analysis was also used for the identification of the silica phases produced by thermal treatment of rice-husk ash.

INTRODUCTION

The crystal structure and physical state of the silica produced from the combustion of rice-husk has been the object of certain studies [1,2]. Other investigators have studied the forms of bonding in silica, namely the silanol and siloxane bonds, by means of infrared spectroscopy [3,4]. Moreover, the formation of any crystalline modification was found to be associated with an increase in the number of absorption bands in the infrared spectra [5].

Nitrogen surface areas and pore structure characteristics of thermally treated silica gel were fully described in an earlier publication [6] in which the details of the previous studies on this subject were fully discussed.

In the present paper, the nitrogen adsorption technique was used to investigate the pore structure of the silica produced by firing rice-husk ash at various temperatures. The parameters derived could be related to the crystalline modifications as detected by X-ray diffraction analysis.

EXPERIMENTAL

A sample of green rice husk was boiled with water, washed, dried, and then fired at various temperatures in an atmosphere of air to obtain the ash. The temperatures used were 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, and 1400°C and the resultant rice-husk ash silicas are designated as

RH 500, RH 600, RH 700, RH 800, RH 900, RH 1000, RH 1100, RH 1200, RH 1300, and RH 1400, respectively. At each firing temperature, the ash was soaked for a period of 3 h and then quenched in air.

X-Ray diffraction analysis was used for the identification of the crystalline modifications produced by thermal treatment. Differential scanning calorimetric (DSC) analysis was also used on the RH 1200 sample in the temperature range 20—600° C.

Surface properties were investigated by the adsorption of nitrogen at liquid nitrogen temperature using a BET volumetric apparatus of the conventional type. Each sample was outgassed at 100° C for 1 h prior to any adsorption run.

RESULTS AND DISCUSSION

The nitrogen adsorption—desorption isotherms obtained for the rice-husk ash silica samples, fired at various temperatures, are shown in Fig. 1. All isotherms show common characteristics and are similar in shape to type II of Brunauer's classification. The isotherms obtained for the samples treated within the temperature range 500—900° C are characterized by being irreversible with closed hysteresis loops, whilst the isotherms obtained for the samples treated above 900° C are completely reversible over all ranges of relative vapour pressures.

The plots of the volume of liquid absorbate adsorbed, expressed in millilitres per gram of the adsorbent (V_l ml g^{-1}), versus the statistical (multilayer) thickness of the adsorbed layer (t Å) are shown in Fig. 2. The values of t reported here as those obtained by Mikhail et al. [7] for the low-heat adsorbent—adsorbate interactions. Pronounced upward deviations from the initial straight lines appeared in the V_l—t plots obtained for the samples heated at up to 900° C. These upward deviations demonstrate the existence of mesopores. However, the V_l—t plots obtained from the adsorption of nitrogen on the rice-husk ash samples fired above 900° C are characterized by the presence of only micropores and/or mesopores with limited sizes. This result will be explained later from the mean hydraulic radii calculated for the total pore systems measured by nitrogen molecules.

From the results of nitrogen adsorption, the BET surface areas, the total pore volumes and the average hydraulic radii of the total pore systems of these thermally treated rice-husk samples could be evaluated and the values derived are given in Table 1. These parameters are also plotted as a function of the temperature of thermal treatment in Fig. 3.

The results shown in Fig. 3 indicate that the average width of the total pore system measured by nitrogen molecules (the hydraulic radius, r_h) decreases on heating the rice-husk samples from 500 to 600° C. This leads to an increase in the surface area and the total pore volume at 600° C as a result of increasing accessibility of nitrogen molecules towards major parts (narrower hydraulic radius) of the total pore system. The destruction of silanol groups is enhanced between 500 and 600° C thus leading to a more open pore system as measured by nitrogen molecules.

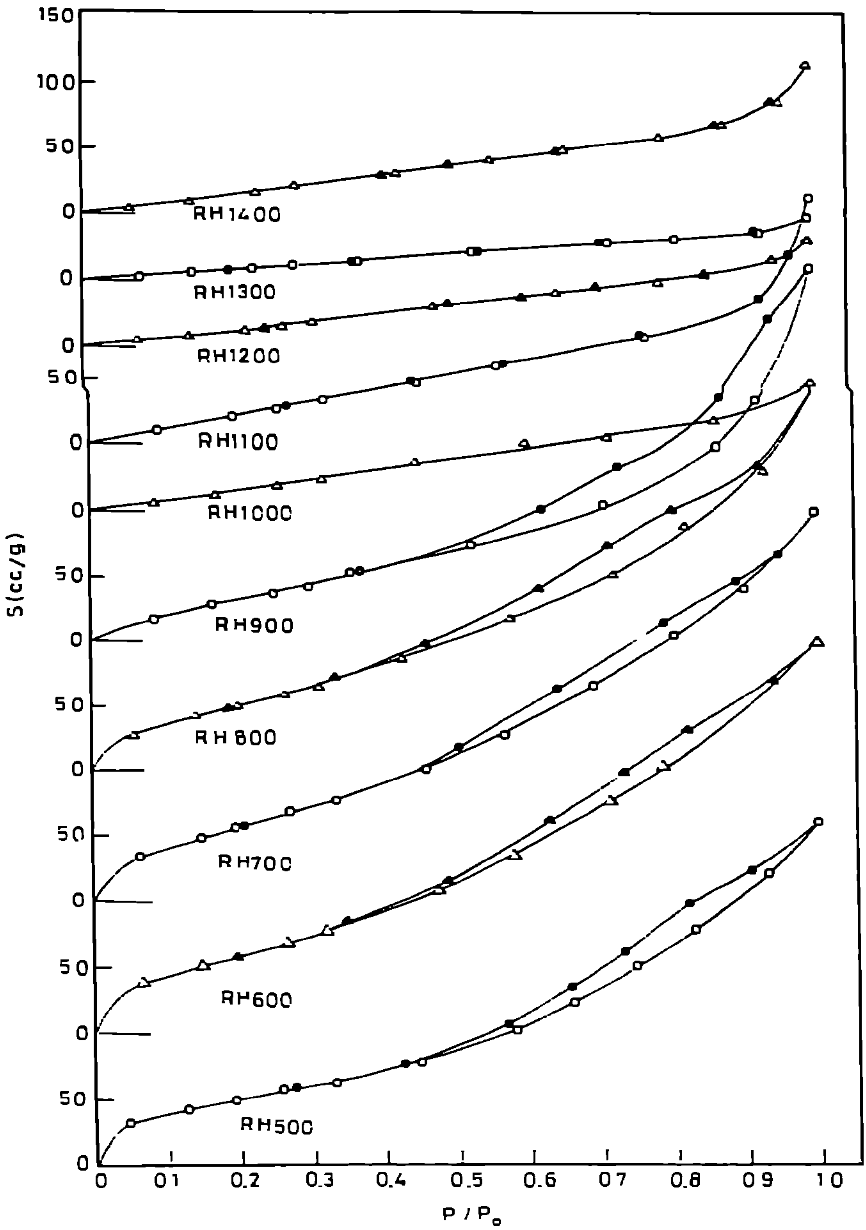

Fig. 1. Adsorption isotherms of nitrogen on the thermally treated rice-husk ash silicas.

In the temperature range 600—900°C, there appeared a continuous increase in the mean hydraulic radius of the pore system measured by nitrogen. This leads to a decrease in the surface area and total pore volume with increasing temperature of thermal treatment of the rice-husk silica. The results of X-ray diffraction analysis showed that no crystalline modification was detected on heating the rice-husk up to 800—900°C; at 900°C, the nucleation process for the formation of the low-form crystobalite phase was pronounced (Fig. 4). Therefore, the decreased accessibility of nitrogen molecules towards the pore system of these adsorbents, as a result of increasing

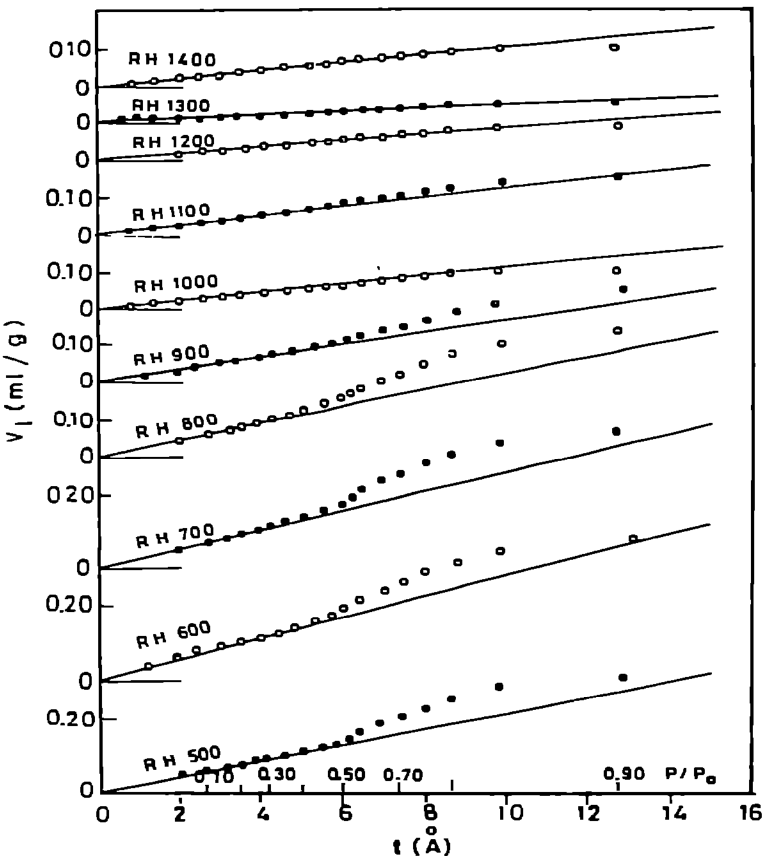

Fig. 2. V_l—t plots for the adsorption of nitrogen on the thermally treated rice-husk ash silicas.

the temperature of thermal treatment up to 900°C, is mainly due to the minor increase of crystallite size of the silica particles, thus making a sort of agglomeration, as calculated from X-ray analysis (Fig. 5).

TABLE 1

Nitrogen surface areas, S_{BET}, total pore volumes, V_p, and hydraulic radii, r_h, of the rice-husk ash silica samples fired at various temperatures

Sample	S_{BET} ($m^2 g^{-1}$)	V_p (ml g^{-1})	r_h (Å)
RH 500	200.1	0.3972	19.86
RH 600	274.2	0.4680	17.07
RH 700	256.4	0.4586	17.89
RH 800	214.7	0.4462	20.78
RH 900	171.6	0.4368	25.45
RH 1000	112.6	0.1498	13.30
RH 1100	146.8	0.2856	19.46
RH 1200	88.0	0.1217	13.83
RH 1300	51.0	0.0661	12.96
RH 1400	145.5	0.1700	11.68

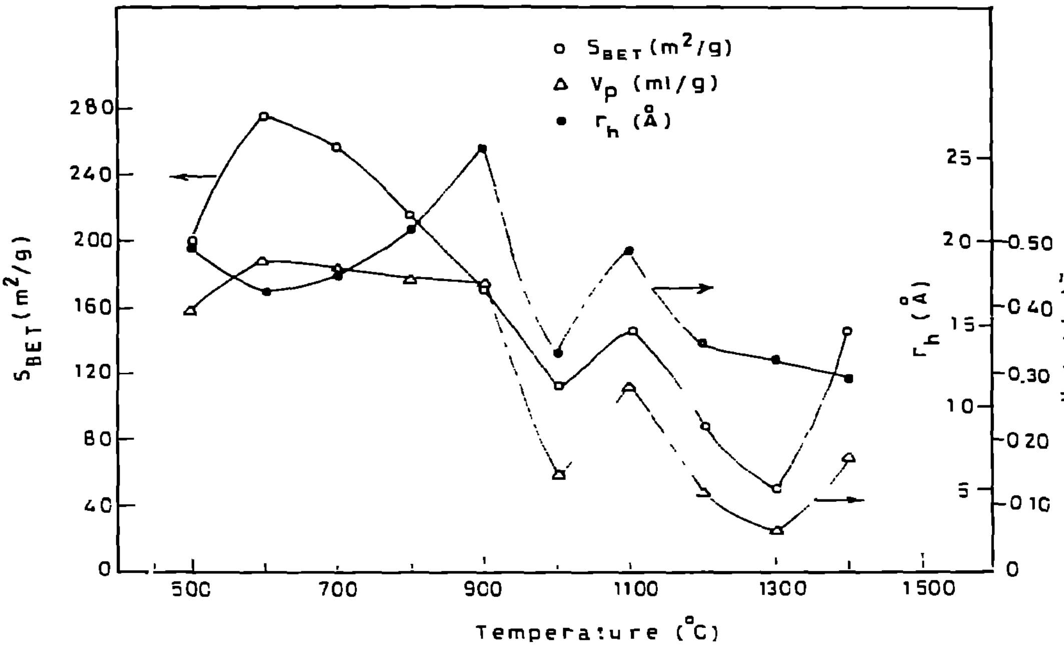

Fig. 3. Variation of the nitrogen surface areas, total pore volums and hydraulic radii with temperature of thermal treatment of the rice-husk ash

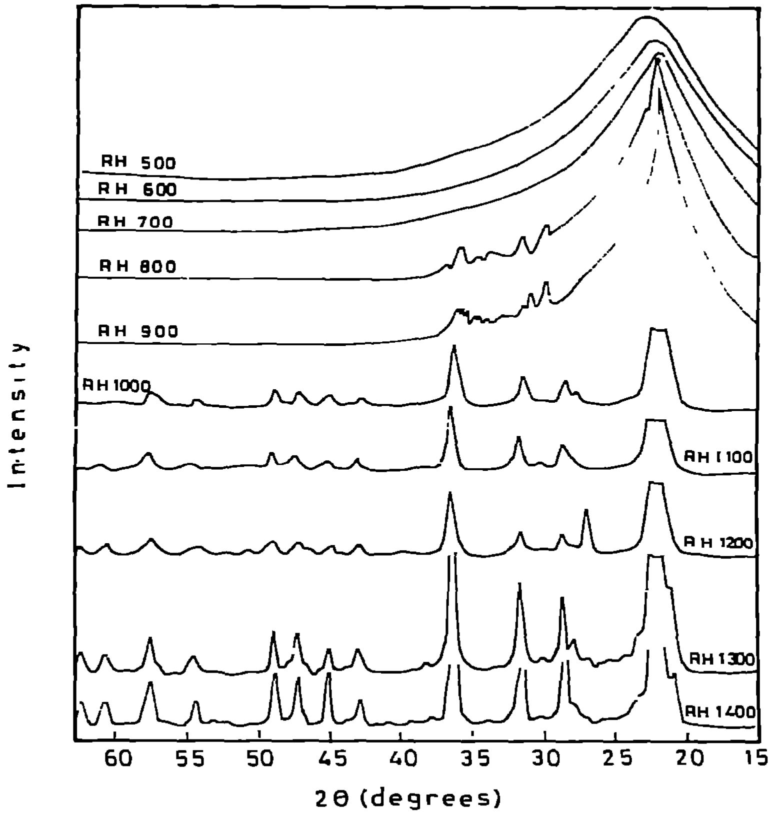

Fig. 4. X-Ray diffraction patterns of rice-husk ash silicas prepared at various temperatures.

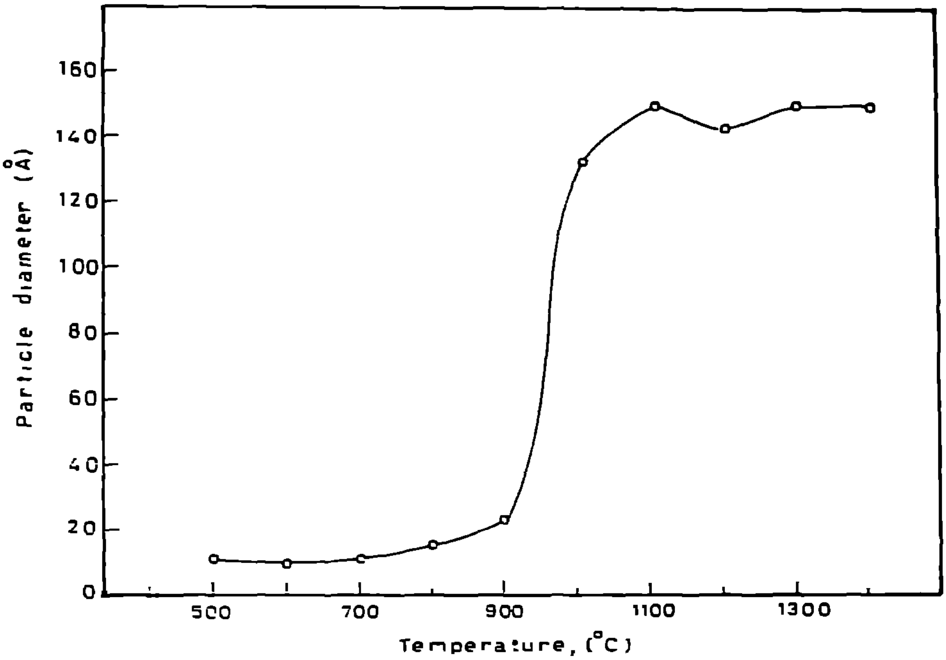

Fig. 5. Variation of the particle size (diameter) of the rice-husk ash silica with temperature of thermal treatment.

Heating of rice-husk ash at 1000°C is accompanied by the crystallization of the low-form crystobalite phase as indicated from X-ray diffraction analysis (Fig. 4); the formation and later crystallisation of this phase at 1000°C accounts for the marked decrease in the surface area, the total pore volume as well as the mean hydraulic radius of the total pore system. A sharp increase in the crystallite size of the silica grains was observed after thermal treatment at 1000°C as can be seen from Fig. 5. At 1100°C, however, the initial formation of tridymite phase in an amorphous (disordered) state accounts for the increase in surface area, pore volume and the hydraulic radius of the pore system measured by nitrogen (Figs. 3 and 4).

Tridymite phase begins to crystallise on heating rice-husk at 1200°C, whereas at 1300 and 1400°C the well-ordered hexagonal form of tridymite makes its appearance beside the crystobalite phase (Fig. 4). The beginning of the crystallisation of tridymite is associated with a minor decrease in the crystallite size of the silica grains produced at 1200°C (Fig. 5). However, the ordered hexagonal form obtained at 1300 and 1400°C is accompanied by an increase in the crystallite size to a characteristic value. The hydraulic radius of the total pore system of the silica produced was found to decrease in the temperature range 1200—1400°C. In fact, the tridymite phase produced on thermal treatment of rice-husk is less developed than that obtained by thermal treatment of silica gel [6].

The DSC thermogram obtained for the RH 1200 sample is shown in Fig. 6. It demonstrates the existence of an exothermic peak at 135°C, which represents the transformation of the tridymite phase ($T_\beta \rightarrow T_\alpha$), and four

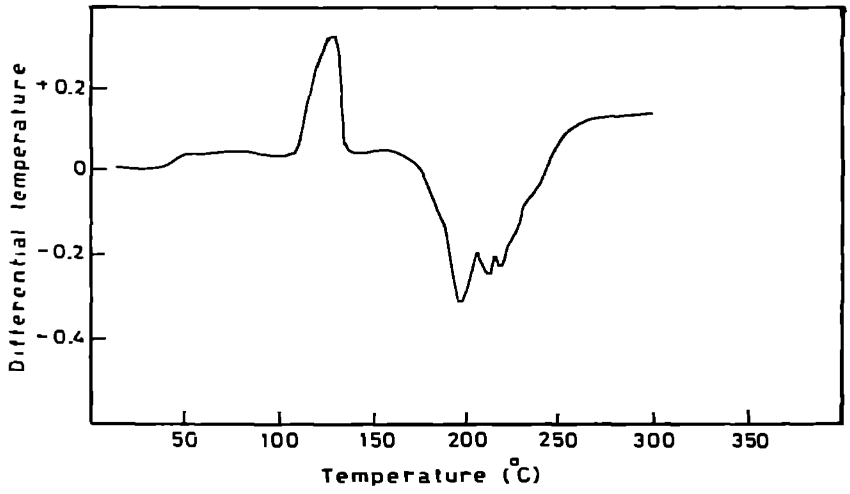

Fig 6. Differential scanning calorimetric (DSC) analysis of the rice-husk ash fired at 1200°C for 3 h (sample RH 1200).

endothermic peaks located at 190, 220, 235 and 250°C representing the transformation of the crystobalite phase ($C_\alpha \rightarrow C_\beta$). The three endotherms located at 190, 220 and 235°C represent the transformation of the low-form (unordered) crystobalite, whereas the endotherm located at 250°C represents the transformation of the well-ordered crystalline form. However, the DTA studies by Florke showed that the dominant phase changes are restricted to the transformation of the unordered (low-form) crystobalite into the well-ordered form [8].

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