Thermochimica Acta, 37 (1980) 347—351

Note

THERMAL TREATMENT OF RICE-HUSK ASH: EFFECT OF TIME OF FIRING ON PORE STRUCTURE AND CRYSTALLITE SIZE

D.M. IBRAHIM and S.A. EL-HEMALY

National Research Center, Cairo (Egypt)

S.A. ABO-EL-ENEIN and S. HANAFI

Faculty of Science, Ain Shams University, Cairo (Egypt)

M. HELMY

Petroleum Research Institute, Cairo (Egypt)

(Received 15 October 1979)

Pore structure characteristics from nitrogen adsorption were fully described earlier for the thermally treated silica gel [1] and rice-husk ash [2]. Detailed information about the previous studies regarding the forms of bonding in silica [3,4], crystal structure [5] and physical state [6,7] were fully discussed in an earlier study [2].

In the present paper, the effect of time of firing of rice-husk ash at various temperatures on the pore vacation and crystal growth processes is discussed. The factors affecting the structure of the silicas produced could also be related to each other.

EXPERIMENTAL

A fresh sample of green rice-husk was first boiled with water, washed, and then dried. The dried sample was then fired at temperatures of 500, 700, 900 and 1100°C in an atmosphere of air to obtain the ash, and the resulting rice-husk ash silicas are designated as RH500, RH700, RH900 and RH1100, respectively. The process of firing at each temperature was carried out for various time intervals of 3, 6, 9, 12 and 24 h. Firing was continued to the prescribed time intervals and then quenched in air.

X-ray crystallographic analysis was used for the determination of the crystallite size of the silica produced upon the thermal treatment of rice-husk ash.

Nitrogen adsorption was used for investigating the surface area and pore structure of the various samples. Each sample was outgassed at 100°C for 1 h in the BET-volumetric apparatus prior to any adsorption—desorption cycle.

RESULTS AND DISCUSSION

The values of crystallite size (particle diameter), as determined from X-ray crystallographic analysis, are shown in Fig. 1 as a function of time of thermal treatment of the rice-husk ash samples RH500, RH700, RH900 and RH1100. The results obtained clearly indicate that firing of rice-husk ash at 500 and 700°C produces no change in the particle size of the resulting silica; the effect of thermal treatment is only restricted to the pore vacation through the conversion of silanol groups into siloxane bridges, as discussed in an earlier publication [2]. However, firing at 900 and 1100°C is associated with marked variations in the crystallite size of the silica phase produced at these temperatures; the extent of crystal growth is enhanced at the higher temperature (1100°C).

From the nitrogen adsorption isotherms obtained for the rice-husk ash silicas, fired at various temperatures for different times, the V_l—t plots could be constructured using the t-values of Mikhail et al. [8] for the low-heat adsorbent—adsorbate interactions. The V_l—t plots obtained for RH500 and RH1100 were taken as representations for all silica samples fired at the lower and higher temperatures, respectively; the plots are shown in Figs. 2 and 3.

Evidently, the V_l—t plots obtained for the RH500 sample, fired for various time intervals, clearly indicate a sort of increasing accessibility of nitrogen molecules into the pore system of these adsorbents by increasing time of firing at 500°C. Such a pore-opening process, via the conversion of silanol groups into siloxane bridges, is indicated by the decrease in the relative vapour pressure at which the upward deviation in the V_l—t plots is started with the increase in the time of firing at 500°C (cf. Fig. 2). The appearance of the upward deviation in the V_l—t plot at lower relative vapour pressure of the adsorbate is a good criterion for the increased extent of pore vacation.

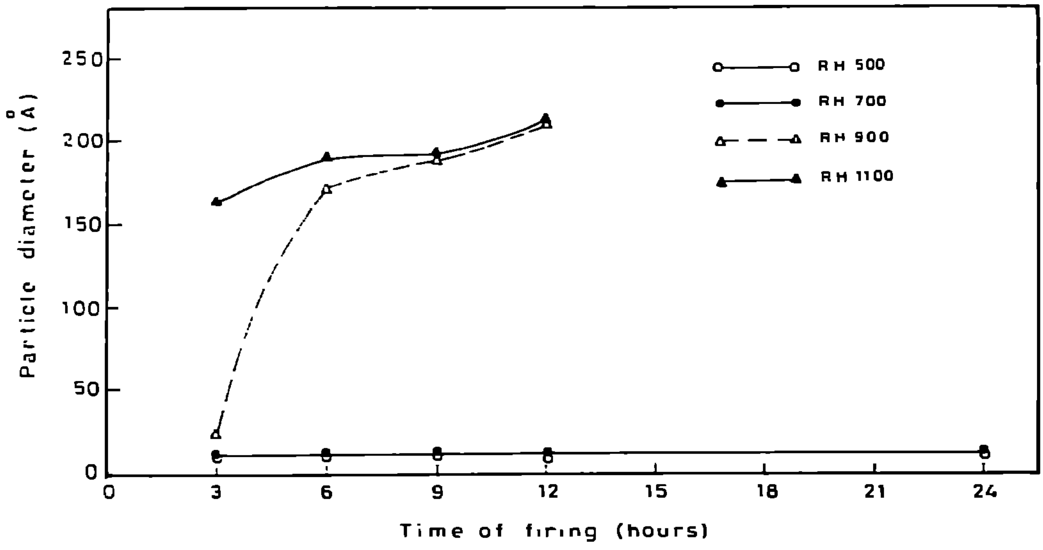

Fig. 1. Variation of particle size (diameter) of rice-husk ash silica with time of firing at various temperatures.

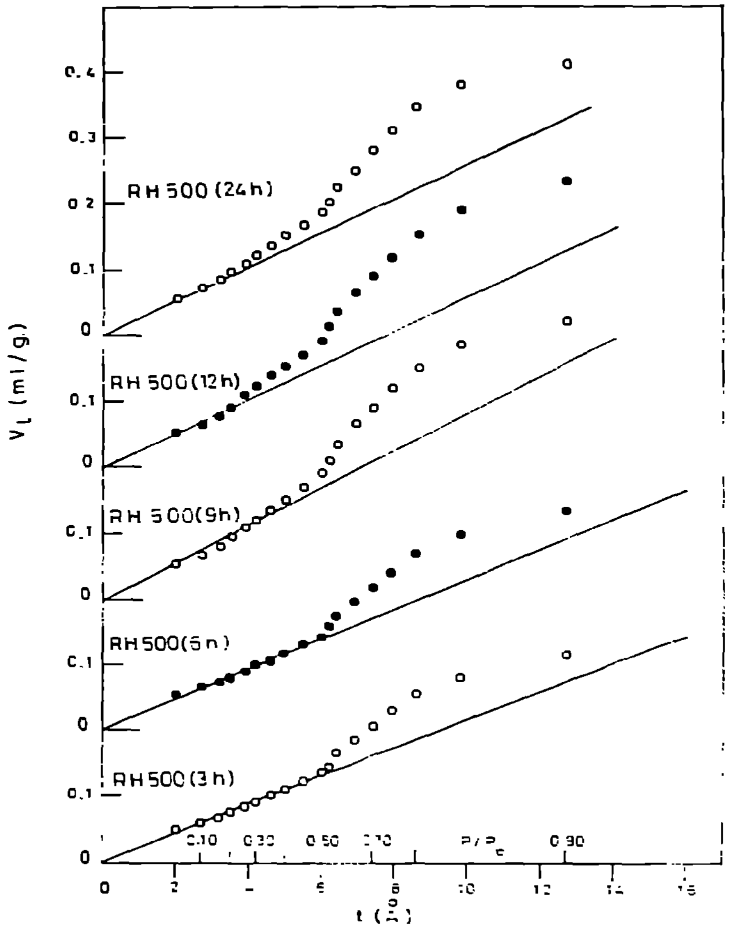

Fig. 2. V_l—t plots for the adsorption of nitrogen on the RH500 silica fired at various time intervals.

However, there appeared a decreased accessibility of nitrogen molecules toward the pore system, as indicated by the increase in the pressure at which the upward deviation in the V_l—t plots is started, with increasing time of firing at 1100°C (cf. Fig. 3); the same indication is also derived for RH900. In these samples the increase in the grain size of the formed silica crystallites is responsible for the marked decrease in surface area and porosity of the RH900 and RH1100 silica samples with increasing time of firing (vide infra).

The variations in the BET surface areas, S_{BET} (m^2 g^{-1}), and the total pore volume, V_p (ml g^{-1}), as a function of time of firing are shown in Fig. 4.

Obviously, there appeared a continuous increase in both the specific surface area and total pore volume of the RH500 sample with increasing time of firing to 12 h, where constant values of surface areas and pore volumes were obtained between 12 and 24 h; this result is mainly attributed to the pore vacation process discussed above.

In the case of the RH700 silica sample, only slight variations in the surface area and pore volume were detected with increasing time of firing; this

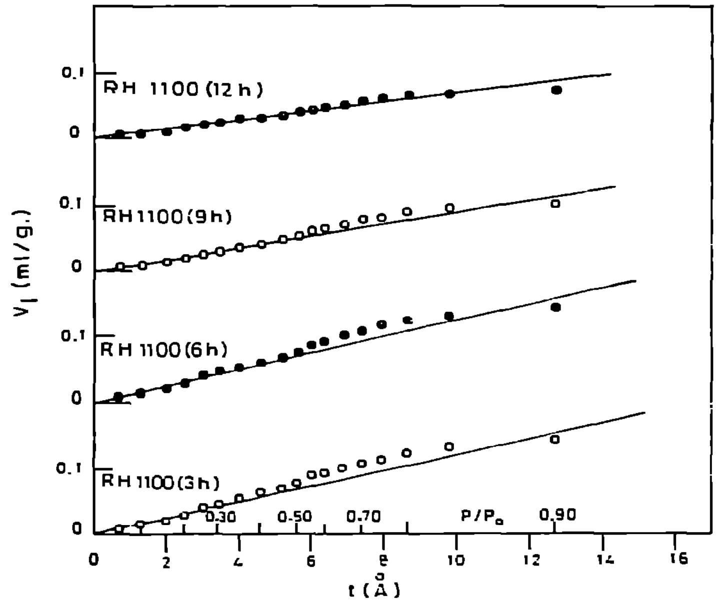

Fig. 3. V_l—t plots for the adsorption of nitrogen on the RH1100 silica fired at various time intervals.

indicates a compensating effect between the pore vacation process, which leads to an increase in both surface area and pore volume, and the beginning of the nucleation process which leads to a decrease in both surface area and pore volume.

In the temperature range 900—1100°C, a continuous decrease in both surface area and total pore volume, with increasing time of firing, was

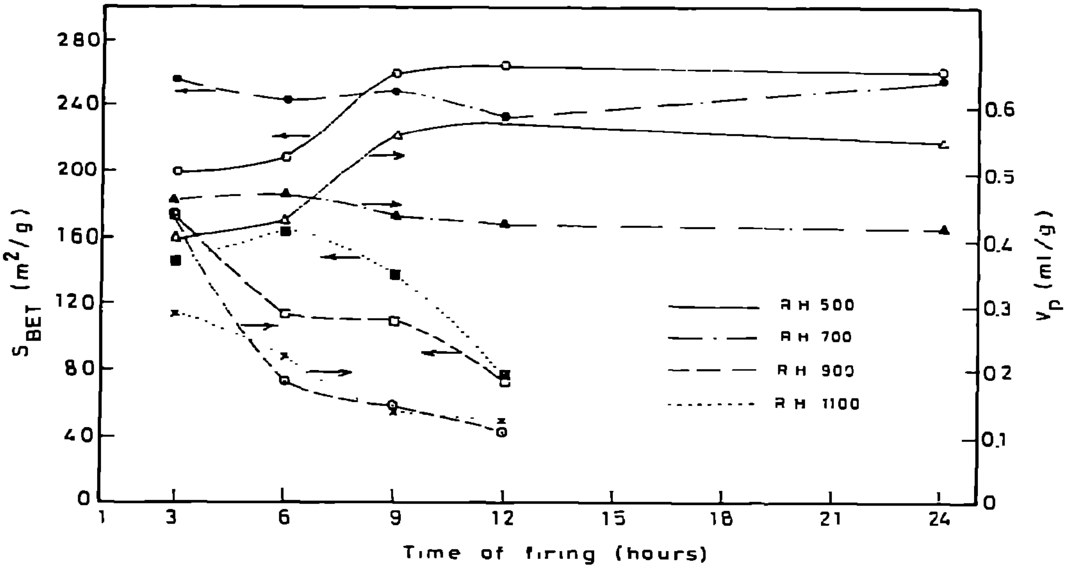

Fig. 4. Variation of the nitrogen surface area and total pore volume with time of firing at various temperatures.

obtained (Fig. 4). This result is mainly due to the increased extent of crystal growth with increasing time of firing at 900—1100°C (Fig. 1).

Despite variations in the pore structure characteristics of these rice-husk ash silicas, the pore size is always limited, whether pore-opening or crystal growth processes are occurring. The limited pore size of these adsorbents is indicated by the reversibility of the adsorption—desorption isotherms and the limiting upward deviations in the V_l—t plots.

REFERENCES

1 S.A. Abo-El-Enein, S. Hanafi, D.M. Ibrahim and S.A. El-Hemaly, Thermochim. Acta, 36 (1980) 299.
2 S. Hanafi, S.A. Abo-El-Enein, D.M. Ibrahim and S.A. El-Hemaly, Thermochim. Acta, 37 (1980) 137.
3 H.A. Benesi and A.C. Jones, J. Phys. Chem., 63 (1959) 179.
4 J.M. Hunt, M.P. Wisherd and L.C. Bonham, J. Anal. Chem., 22 (1950) 1478.
5 V.C. Farmer, in H.F.W. Taylor (Ed.), Chemistry of Cement, Vol. II, 1964.
6 F.C. Lanning, J. Agric. Food Chem., 11 (1963) 435.
7 N.D.F. Houston, Rice Chemistry and Technology, American Association of Cereal Chemists, 1972, Chap.12.
8 R.Sh. Mikhail, N.M. Guindy and S. Hanafi, J. Chem. U.A.R., 16 (1973) 53.