Thermochimica Acta, 37 (1980) 307—314
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STUDY OF RICE-HUSK ASH SILICA BY INFRARED SPECTROSCOPY

D.M. IBRAHIM, S.A. EL-HEMALY and F.M. ABDEL-KERIM
National Research Centre, Dokki, Cairo (Egypt)

(Received 15 October 1979)

ABSTRACT

Transformation of rice-husk white ash silica fired at temperatures between 500 and 1400°C was followed by IR spectroscopy. The ratio of the absorbancy bands corresponding to the Si—OH and Si—O groups occurring at 810 cm^{-1} gave the amount of Si—OH left undestroyed at each firing temperature. The results obtained were compared with those of silica gel. Silica gel lost its OH group above 1200°C while rice-husk silica lost it at about 700°C.

A plot of the ratio of the absorbancies of the two bands occurring at 470 and 810 cm^{-1} vs. temperature gave some idea of the sequence of transformation which took place in three steps at 700, 900 and 1200°C, respectively. No crystalline phase was detected by X-ray diffraction analysis at 700°C and this step was attributed to the destruction of the silanol group. X-ray diffraction analysis showed that cristobalite started to appear at 900°C and was responsible for the second step. The unordered cristobalite phase was found up to 1200°C. Ordered cristobalite and tridymite were detected by X-ray at 1300 and 1400°C and were responsible for the third step.

The results showed that rice-husk ash silica is similar in nature to silica gel. It follows the sequence of transformation suggested by Flörke for the different crystalline forms of silica. No quartz was detected at any firing temperature.

INTRODUCTION

The nature of white rice-husk ash silica, obtained from burning rice-husk, is still a matter of study. The ash is a slightly impure silica. The silicon occurs in the husk as a hydrated amorphous form of silica; whether this is opal or a silica gel is a question still not completely answered, although the evidence for the opaline form is rather strong [1].

There is fairly general agreement that the silica is predominantly in inorganic linkages. The formation of tridymite and cristobalite, then the predominance of tridymite at the expense of cristobalite in high-temperature fired ash, is dependent on the intensity and duration of combustion [2].

The aim of the present work is to follow the phase transformation of this ash when burned at different firing temperatures in the range 500—1400°C. The different groups in which silicon exists, e.g. siloxane Si—O and silanol Si—OH, are best observed by IR spectral analysis, while the transformation phases are studied by X-ray diffraction analysis. The results obtained are compared with those of a silica gel fired at selected temperatures.

EXPERIMENTAL

Rice-husk ash silica

Green rice-husk was boiled, washed, and dried to remove any impurities, then fired in an atmosphere of air to obtain the ash. White ash was obtained at a relatively low firing temperature by this treatment. Ash was fired between 500 and 1400°C with a 100°C temperature interval, soaked for 3 h at each firing temperature, then quenched in air. Firing at 500°C was also prolonged for 24 h to see the effect of time of combustion at this particular low temperature.

Silica gel (Merck)

Silica gel granules were crushed in a porcelain mortar, then ground to pass a 100-mesh sieve. Samples were fired at the following selected temperatures: 500, 700, 900, 1100, 1300 and 1400°C, and soaked for 3 h at each firing temperature, then quenched in air in the usual way.

IR spectroscopic analysis

The potassium bromide disc technique was used in the present study. Two mg of the fine substance (less than 100 μ mesh sieve) were mixed with 200 mg of spectroscopically pure KBr powder by shaking for 15 sec in a vibrator. The mixture was then pressed in a special die under vacuum at about 150 kg cm^{-2} by means of a hydraulic press. The measurements were carried out using a Beckmann recording double beam IR spectrophotometer, which was calibrated using a polystyrene film. The maximum of the absorption bands occurred in the region 250—200 cm^{-1}. The base-line technique was adopted for the determination of the absorbancies. The results obtained are shown in Table 1. The IR pattern of selected samples are shown in Figs. 1 and 2.

X-ray diffraction analysis

X-ray diffraction analysis was carried out for the different samples using a Philips X-ray diffractometer. Powder samples were analyzed by Cu$K\alpha$ radiation at 1.54 Å. The scanning rate was 2°C min^{-1}. The patterns obtained are shown in Figs. 3 and 4.

RESULTS AND DISCUSSION

The IR patterns of rice-husk ash silica samples fired between 500 and 800°C showed the following bands: 470, 810, 1100, 1640, 3400 cm^{-1} and a shoulder occurring at 1200 cm^{-1}.

The samples fired from 900°C onwards showed a more complicated spectrum. A band at 600 cm^{-1} started to appear, and developed with increase of firing temperature. The broad band occurring at 3400 cm^{-1} diminished

TABLE 1

Relationship between firing temperature and the ratio of silanol to siloxane adsorbancy bands at 470 and 810 cm^{-1}

Sample	Firing temp. (°C)	Ratio of $\frac{470\ cm^{-1}}{810\ cm^{-1}}$	Ratio of bands at 810 cm^{-1}	Ratio of bands $\frac{810\ cm^{-1}}{470\ cm^{-1}}$
Silica gel		1.40	0.53	0.81
	500	1.24	0.46	0.71
	700	1.07	0.38	0.64
	900	1.20	0.46	0.71
	1100	0.82	0.17	0.27
	1300	0.65		
	1400	0.67		
Rice-husk ash	500	1.72	0.38	0.41
	600	1.23	0.20	0.20
	700	1.27	0.10	0.10
	800	0.98	0.047	0.049
	900	1.00	0.072	0.07
	1000	0.74		
	1200	0.94		
	1300	0.96		
	1400	0.97		

in size until it disappeared in the sample fired at 1200°C.

X-ray diffraction analysis of the rice-husk ash silica samples, as shown in Fig. 3, revealed that crystallization become conspicuous in the samples fired at 900°C. The X-ray pattern of low form cristobalite was obtained at 1000°C. The peaks were broadened but sharpened with increase of firing

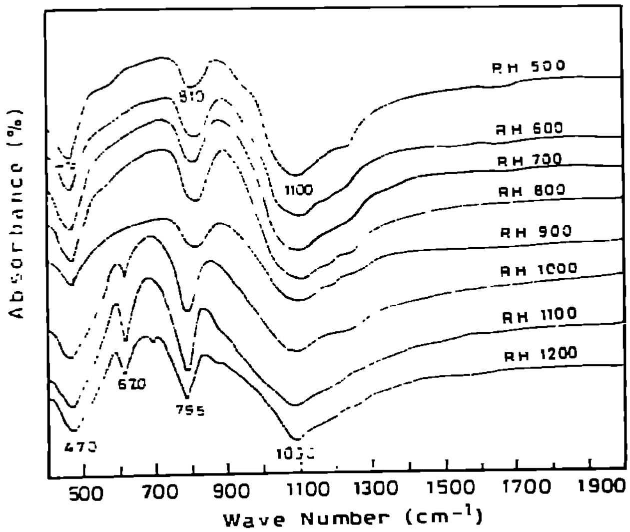

Fig. 1. IR spectral analysis of rice-husk ash (RH) fired at different temperatures.

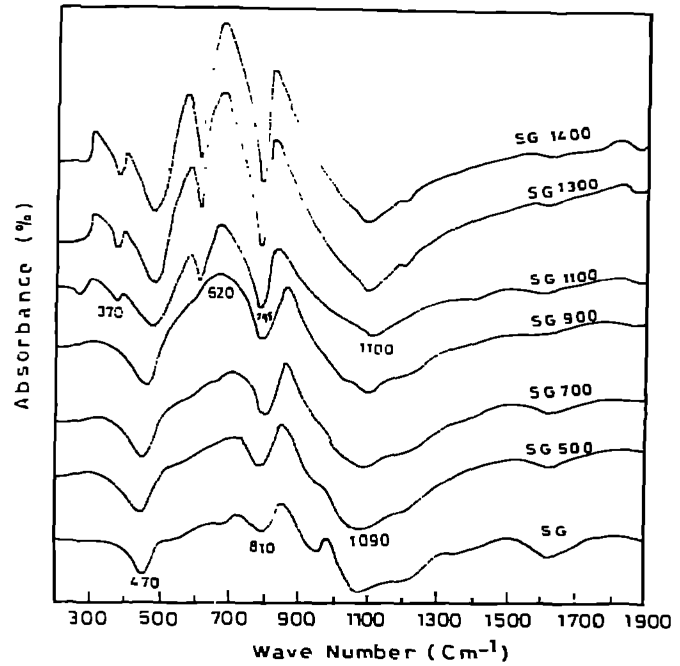

Fig. 2. IR spectral analysis of silica gel (SG) fired at different temperatures.

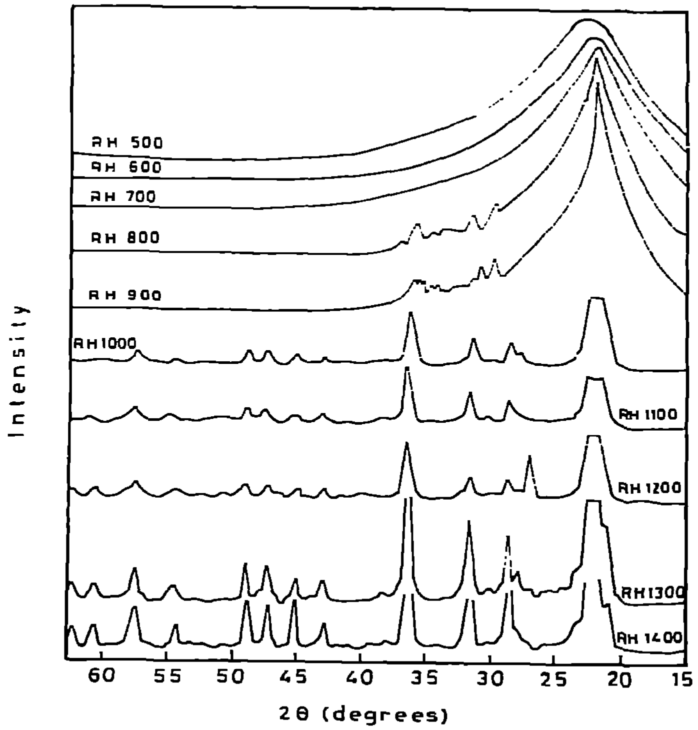

Fig. 3. X-ray diffraction analysis patterns of rice-husk ash (RH) fired at different temperatures for 3 h.

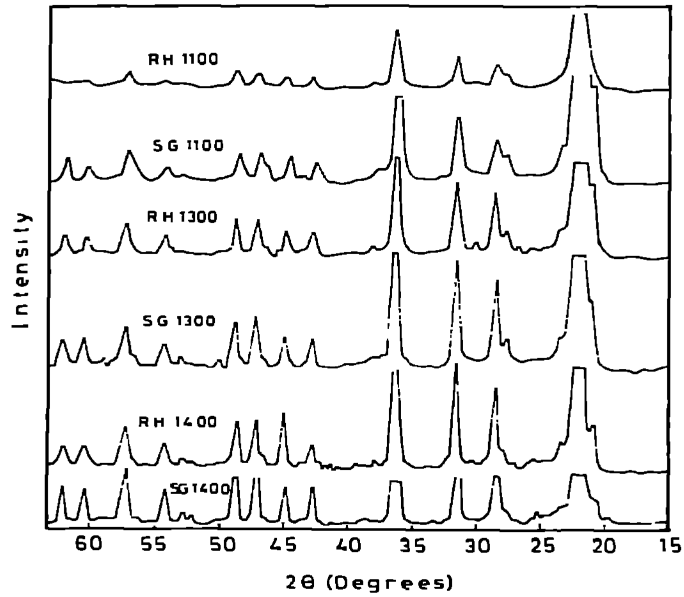

Fig. 4. X-ray diffraction analysis patterns of silica gel (SG) and rice-husk ash (RH) treated at different temperatures for 3 h.

temperature. Low form cristobalite was the dominant phase in all samples fired up to 1400°C. At 1200°C the peaks of tridymite were detected as shoulders around the 111 peak of cristobalite. The samples fired at 1300 and 1400°C showed small peaks of tridymite.

The IR patterns of silica gel showed the following bands: 470, 800, 950, 1100, 1640 cm^{-1}, and a broad one at 3400 cm^{-1}. The pattern displayed by silica gel fired at 1100°C showed a complicated spectrum. The bands were sharp; the broad band at 3400 cm^{-1} nearly disappeared. It is similar to that obtained for rice-husk ash fired at the same temperature.

X-ray diffraction patterns of silica gel (Fig. 4) showed the presence of low form cristobalite at 900°C. Peaks of tridymite were detected in samples fired at 1100°C, and were more developed here than rice-husk ash silica.

Two forms of bonding are possible in silica gel [3]. The Si—O bond gives characteristic absorption bands due to bending vibrations at 400—500 cm^{-1} and stretching vibrations between 800 and 1000 cm^{-1} [3]. If the silica tetrahedra are connected to form a chain, rings, or a more complicated structure, they give rise to adsorption bands occurring at 600 and 800 cm^{-1}.

The Si—OH bands occur mainly as a shoulder at 870 and 1200 cm^{-1}, water may occur partly as constitutional water and/or as adsorbed water with their bands appearing at 1640 and 3400 cm^{-1}, respectively; therefore an increase in the number of absorption bands mean crystallization is taking place [4,5].

Samples fired below 900°C show a broadening in the band at 815 cm^{-1}; this is probably due to the overlapping of the Si—O and Si—OH vibrations [3], the Si—OH stretching vibrations lie in this region.

The bands due to the Si—O vibration occurring at 815 cm^{-1} was shifted to 795 cm^{-1} in the samples fired between 1000 and 1400°C. It appeared as a sharp band, thus confirming the above assignment.

On examining the relation between the different absorption bands, it is obvious that the band width of the absorbancy bands occurring at 470 cm^{-1} increases with increase of treatment temperature; therefore the absorbancies of both bands were measured using the base-line technique. The ratio of the absorbancies of these two bands was calculated and the results obtained are shown in Table 1. Figure 5 shows the relationship for the different samples fired at the various temperatures.

The broad band at 810 cm^{-1} is considered as representing two overlapping bands corresponding to the silanol and siloxane groups occurring in this region. From the literature [3], it is obvious that silica gel loses its OH group at about 1200°C. It is believed, therefore, that the sample fired at 1300°C contains no Si—OH groups. The ratio of the two bands occurring at 470 and 810 cm^{-1} for the sample fired at 1300°C could be taken as representing the ratio of the siloxane group in the respective source of silica. By comparing the ratio of these two bands for the samples fired at different temperatures with that of the sample fired at 1300°C, each with its corresponding ratio, i.e. silica gel and rice-husk ash silica, it was possible to calculate the absorbancy related to the Si—OH group alone at 810 cm^{-1} in both cases. A new ratio (see a in Fig. 6) was obtained for the absorbancy band representing the Si—OH at 810 cm^{-1} to the absorbancy band at 470 cm^{-1} that gave the degree of transformation of silanol to siloxane. The ratio of the absorbancy bands corresponding to Si—OH and Si—O groups at 810 cm^{-1} (b in Fig. 6) gave a similar relation. The ratio decreases with rise of temperature, which indicated the loss of OH groups. The loss was rather sluggish in the case of silica gel and prevailed up to 1100°C, whilst rice-husk white ash silica readily lost its OH at ~700°C. The material obtained at 700°C was amorphous as no crystalline phase was detected by X-ray diffraction analysis.

Reorientation and connection between the tetrahedra to form a crystalline phase started to take place in the second step (Fig. 5) at 800—900°C.

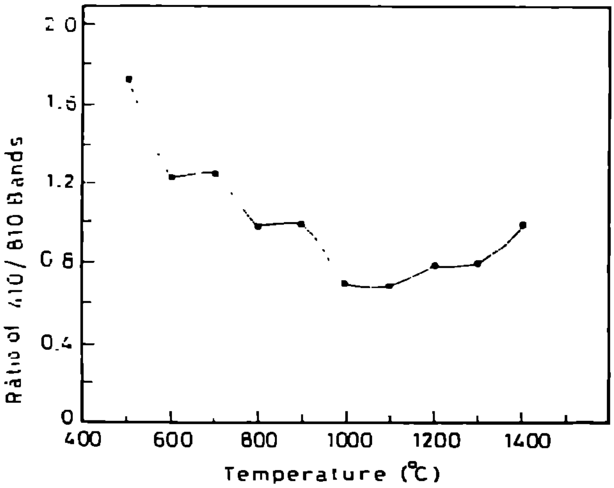

Fig. 5. Relation between the ratio of absorbancy of IR bands for rice-husk ash and temperature.

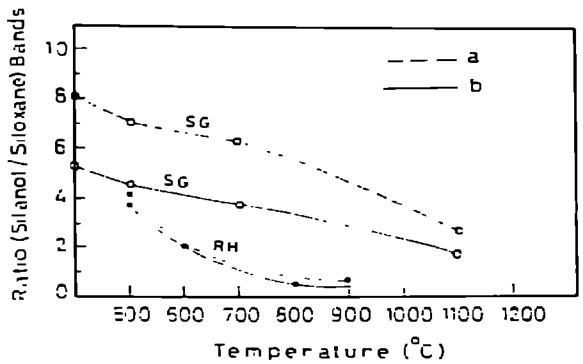

Fig. 6. Ratio of silanol/siloxane bands at (a) 810 cm^{-1} and (b) 810/470 cm^{-1} for silica gel (SG) and rice-husk ash (RH) silica.

A crystalline phase readily occurred at 1000° C, accompanied by the appearance of an absorption band at 600 cm^{-1}. This crystalline phase predominated at 1100 and 1200° C. An increase in the ratio was recorded, denoting a structure instability taking place which was confirmed by the appearance of an absorbancy band at 375 cm^{-1}.

The above results were confirmed by the X-ray findings. Thus, the X-ray diffraction pattern of rice-husk ash fired at 500° C showed a curve resembling that of silica gel without any characteristic peak. The curve sharpened with rise of treatment temperature. Cristobalite was the crystalline phase which started to appear at 900° C in both samples. At 1200° C tridymite was detected, which may be responsible for the change in the ratio of absorbancy of the IR bands.

The sequence of transformation of rice-husk ash silica is similar to that taking place in silica gel. Thus, in both cores, cristobalite is the crystalline phase first to appear at 900° C. According to Flörke [6] the sequence of transformation of silica depends on the degree of purity of the starting material. Pure silica is readily transformed to cristobalite without the intermediate stage of tridymite. The presence of tridymite is governed by the kind and amount of impurities. Flörke [6] believed that they form a kind of solid solution which stabilizes tridymite. He also concluded that tridymite has no thermodynamic existence in the silica diagram. This is a view opposing Fenner's postulation [7], that tridymite readily forms from silica at 870°C and becomes the predominant phase up to 1470°C then cristobalite is formed.

From the above findings it is clear that the of transformation sequence of rice-husk ash silica supports the view of Flörke. Rice-husk ash silica is similar in nature to silica gel.

CONCLUSION

The IR absorption patterns for white rice-husk ash silica obtained by firing rice-husk in an atmosphere of air at different temperatures ranging between 500 and 1400°C were examined. A relation between the ratio of the two main absorption bands occurring at 470 and 800 cm^{-1} gave some idea of the sequence of transformation into the different forms of silica. The curve showed three steps: the first corresponds to the destruction of Si—OH groups at 700°C, the second at 900°C, is due to the formation of unordered cristobalite, and the third is attributed to the crystallization of cristobalite and tridymite. X-ray diffraction analysis confirms the above assignment.

The ratio of the bands characteristic of silanol and siloxane groups at 810 cm^{-1} gave some idea of the degree of transformation of silanol to siloxane. Rice-husk ash silica lost its OH at about 700°C compared with silica gel which lost it above 1200°C.

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