

Chapter 2

Phase Transformation of Amorphous Rice Husk Silica

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Abstract This work aims at assessing the crystallization process of amorphous silica from rice husk (RH) by in situ X-ray diffraction, upon heating up to 1450 °C in a high-temperature chamber. The study includes microstructural characterization by transmission electron microscopy. The work was conducted on rice husk ash (RHA), obtained by combustion of RH at 650 °C with and without leaching in 1 N HCl solution, obtaining samples with variable impurity content. The results showed that crystallization of RHA amorphous silica upon continuous heating occurred at higher temperatures compared to the isothermal one, considering the sample purity. The type of polymorph silica identified in the samples during continuous heating consisted of cristobalite or a combination of cristobalite and tridymite depending on the impurity levels in the samples. The study revealed silica crystallites with spherical shape nucleated by a dominant homogeneous mechanism. The size of crystallites ranges from around 2 nm to 20 nm. Larger particles nucleated on impurities and constituted by combinations of P, Ca, K, Mg, and Na were also observed.

Keywords Nanosilica • Amorphous silica • Rice husk ash • Crystallization

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1 Introduction

Rice is the primary agricultural product of Ecuador, estimated in 1.6 million tons of rice paddy produced per year [1], which roughly originates 320.000 tons of RH annually. The RHA obtained from the combustion of RH is mainly SiO_2 (87–97%) [2] in an amorphous state. In this regard, amorphous silica from RH could be an alternative material for a wide variety of applications, such as production of SiC [3], SiN [4], and zeolites [5, 6]. It is a promising source of raw material for ceramics [7], polymer and aluminum composites [8–11], solar cell [12], concrete [13], and steel industry [14]. Previous to combustion, RH is usually subjected to a chemical treatment (leaching) to reduce the impurity content [15, 16]. In the case of special applications such as the production of nitrides, carbides, and other inorganic materials, it is fundamental to use pure silica in the amorphous state [5]. However, amorphous silica becomes crystalline when heated. Studies [17–19] have shown that trydimite and cristobalite are the phases present after crystallization of RHA, promoted by the presence of alkaline impurities [20]. Even though some research works have been carried out to study the transition from amorphous to crystalline silica in RHA, none of the revised literature has assessed the dynamic crystallization process of RHA silica upon in situ heating. Moreover, rather few of these studies have evaluated the microstructural characteristics at the nanometric scale [21, 22]. The increasing interest in RHA demands additional studies to evaluate the effect of heat treatment on its transition from amorphous to crystalline state and microstructure. Thus, the main focus of this study is on the assessment of dynamic and static crystallization behavior of amorphous silica from RHA of rice produced in Ecuador. The study includes microstructural characterization of crystallites in terms of size and shape, as well as the effect of impurity levels on phase transformation behavior.

2 Methods

2.1 Sample Preparation and Chemical Analysis

Samples of RH were collected from a pile in the region of Taura, Ecuador, and prepared with and without leaching. The as-received material was thoroughly washed with distilled water and dried in oven at 60 °C. Afterward, 100 gr. of samples were subjected to leaching at room temperature for 16 h in 1.5 L of 1 N HCl solution, to reduce the amount of impurities, followed by washing with distilled water and dried. In order to combust the organic components (calcination), such leached sample together with other sample without leaching, in portions of 20 gr, was placed in a graphite crucible and calcinated in oven during 3 h at 650 °C, obtaining RHA rich in amorphous silica. The calcinated sample without leaching

was labeled as Sample 1, and the other leached and calcinated was labeled Sample 2. The chemical composition of the samples was determined by X-ray fluorescence.

2.2 X-Ray Diffraction (XRD) Analysis

Dynamic studies of crystallization behavior of amorphous silica of the 2 calcinated samples were conducted by in situ XRD during continuous heating from room temperature up to 1450 °C, at a rate of 20 °C/min. A HTK 16 Anton Paar high-temperature chamber with a platinum filament and sample holder was employed in these studies. Drops of samples suspended in alcohol were placed on a platinum stage until it was covered with a fine layer of silica powder. XRD patterns were recorded every 100 °C during heating and 200 °C during cooling, according to the experimental procedure followed by Cornejo et al. [23]. XRD diffraction analysis was performed on a Panalytical X'Pert (40 kV, 30 mA) X-ray diffractometer. Scans were taken with a 2θ , step size of 0.017°, and a counting time per step of 0.1 s using a Cu-K α radiation source ($\lambda = 1.542 \text{ \AA}$).

2.3 Transmission Electron Microscopy (TEM) Analysis

TEM analysis was performed on a Field Emission JEOL TEM 2100F operating at 200 kV accelerating potential. For this technique, samples 1 and 2 were analyzed after isothermal annealing at 800 °C for 6 h. Small portions of each sample were dispersed in ethanol, and some drops of the suspension were pipetted onto a copper grid covered with a carbon amorphous film. The samples were then analyzed under diffraction contrast mode, documented in bright- and dark-field images and also in analytical mode using energy-dispersive X-ray spectroscopy (EDX), thereby allowing measuring particle size and shape, chemical constituent of phases, and evaluating crystallization mechanism.

3 Results and Discussion

3.1 Chemical Analysis

The chemical composition of samples in the calcinated condition is presented in Table 1. RHA without leaching (Sample 1) has a silica content of 87.39% and K, P, and Ca as the major impurities in percentages of 5.42%; 2.95%, and 2.77%, respectively. The total amount of the other impurities combined sum 1.35% altogether. After leaching, the content of silicon has raised above 96% mainly due to the

Table 1 Chemical constituents of Sample 1 and Sample 2 via X-ray fluorescence

Component Weight (%)	Wt. (%)	
	Sample 1	Sample 2
Si as SiO ₂	87.39	96.94
K as K ₂ O	5.42	0.09
P as P ₂ O ₅	2.95	1.94
Ca as CaO	2.77	0.67
S as SO ₃	0.48	–
Mn as MnO	0.28	0.02
Fe as Fe ₂ O ₃	0.24	0.14
Mg as MgO	0.22	–
Al as Al ₂ O ₃	0.09	0.20
Cl	0.10	–
Zn as ZnO	0.03	–

removal of K, constituent that was reduced in more than 98% after 16 h of leaching. In contrast, data reported in Table 1 show that the chemical treatment applied to the samples was less efficient to reduce the contents of P, Ca, and Fe. These impurities after leaching for 16 h were reduced to 66%, 76%, and 42%, respectively. The content of RHA silica from Sample 1 (without leaching) is in the range of the silica values found worldwide (87–97%) [2], with unusually high level of K₂O, when compared with other published data [24–27]. Nonetheless, the chemical composition of RHA can be quite different from distinct paddy sources. K and P compounds are micronutrients of plants, commonly used in fertilisers as an inorganic component, to increase land yields. Their amounts may vary depending on the crop. Even though a high K content was detected in this work, similar results could also be found in other studies as well [22, 27–29].

3.2 X-Ray Diffraction

The progressive transition from amorphous to crystalline state observed by in situ XRD in samples 1 and 2 upon continuous heating is shown in Figs. 1 and 2, respectively. Up to 800 °C, both samples remain amorphous. The first trace of silica crystallization appears at 900 °C in Sample 1, distinguished by the presence of a weak cristobalite peak, centered around 21.9°. In the case of Sample 2, higher temperatures are required to start crystallization of silica. Figure 2 exhibits the beginning of structural transformation in this sample at 1100 °C, as evidenced by a very low intensity peak in the XRD pattern that emerges around 21.9° at this temperature. According to the XRD profile of both samples with respect to temperature, the rate of crystallization is faster in Sample 1. Moreover, at 1200 °C, the transformation from amorphous to crystalline phase is fully completed in Sample 1. At this temperature, a new peak located at around 20.9° appeared, which

Fig. 1 X-ray diffraction of Sample 1 at different temperatures, during continuous heating

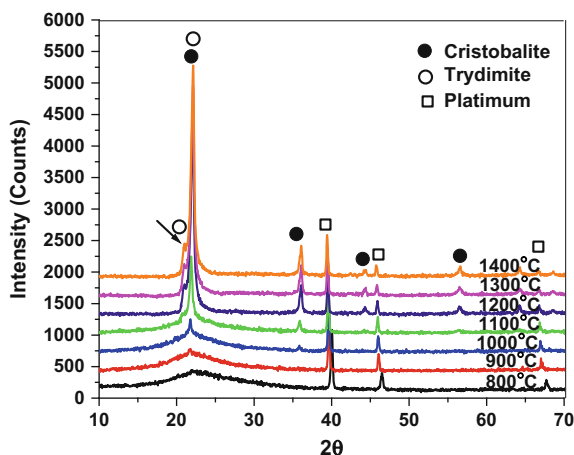
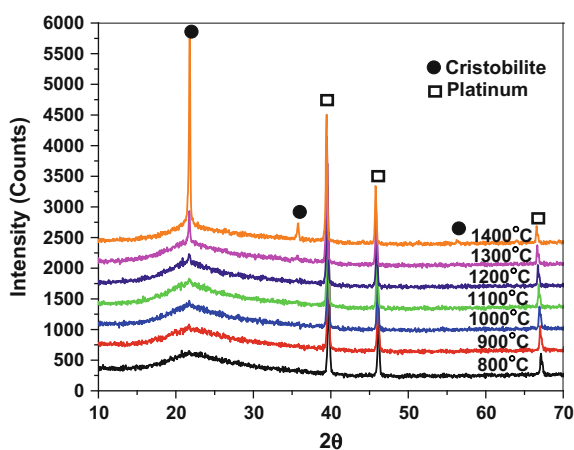


Fig. 2 X-ray diffraction of Sample 2 at different temperatures, during continuous heating



corresponds to trydimite. At 1200 °C, Sample 2 still remains, in great extent, amorphous and undergoes complete crystallization at temperatures beyond 1400 °C. Another noticeable characteristic that differentiates both samples is the type of polymorphs formed. For Sample 1, two phases were identified, cristobalite and trydimite, with noticeable predominance of cristobalite. On the other hand, Sample 2 only displays cristobalite, while trydimite did not form. The cristobalite has a tetragonal structure, and trydimite is monoclinic.

The results have shown that Sample 1 has a significant amount of K, constituent that was mostly removed by leaching in sample 2. These differences in chemical composition may account for the particularities in the crystallization behavior observed in the investigated samples. Alkaline oxides such as K_2O decompose at low temperatures and may produce low-melting eutectic compounds with silica

promoting crystallization. Particle size of amorphous silica could also contribute to a lower crystallization temperature of silica [18]. Considering that K and other impurities lower the crystallization temperature of silica, the results obtained upon continuous heating are consistent with those expected. Sample 1 with higher amount of impurities exhibited a transition from amorphous to crystalline phases at much lower temperatures than Sample 2. The transformation of amorphous silica in both samples proceeds with the formation of cristobalite, accompanied with a small fraction of tridymite in Sample 1. It is important to notice that in Sample 2, tridymite does not form during continuous heating. Tridymite phase forms preferentially when K is present in high amount [18, 30]. Moreover, at high temperatures, the content of low-melting-point impurities such K may decrease, prevailing the formation of cristobalite. In both samples, cristobalite was the dominant crystalline phase.

3.3 Transmission Electron Microscopy

Figure 3 shows bright-field TEM images of a RHA sample in the amorphous condition (Sample 2), as corroborated by the inserted electron diffraction pattern, displaying characteristic diffuse scattering. It consists of an aggregate of globular amorphous silica nanoparticles with sizes in the 50 nm range or smaller.

Figure 4 shows a set of bright-field (BF) and centered dark-field (CDF) TEM images, taken from Sample 1 anneals for 6 h at 800 °C. Figure 4a, b show a BF/CDF pair, while Fig. 4c shows a CDF image of the same sample under different diffraction conditions. One can clearly identify the formation of spherical crystalline nanoparticles in an amorphous matrix. These nanoparticles, however, appear in two size ranges: one larger, on the 20 nm in average, and other smaller with around 5 nm in average size. The shape and sizes of the particles suggest that the crystallization from amorphous silica takes place by homogeneous nucleation and growth processes, throughout the bulk material. The set of larger particles in the 20 nm size can be interpreted as resulting from a coarsening phenomenon.

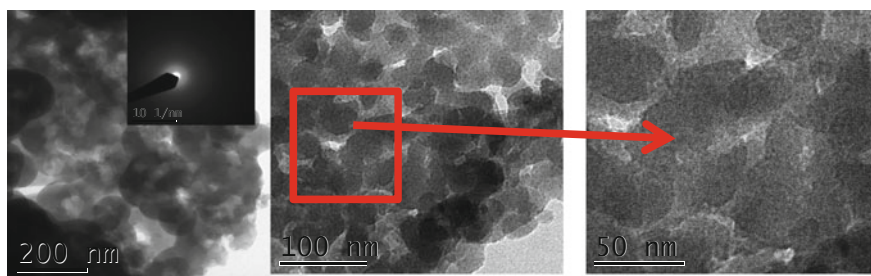


Fig. 3 TEM bright-field images and select area diffraction pattern (inserted) of sample in the amorphous condition

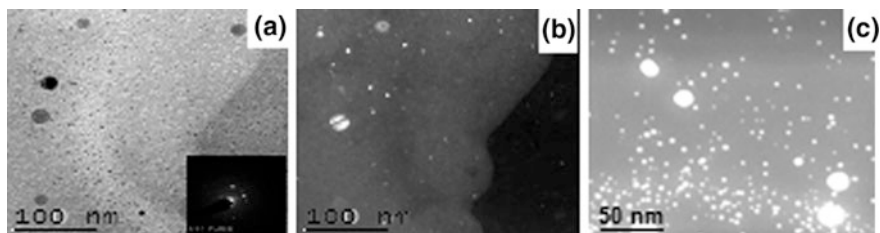


Fig. 4 Sample 1 heated for 6 h at 800 °C. **a** TEM bright field and corresponding selected area diffraction pattern (inserted); **b** a centered dark field of same area as **(a)**; **c** Dark-field TEM image of other area in same sample

Figure 5 displays a bright-field TEM image of a large, 250-nm particle, with EDS mapping of different elements present in this complex particle. The larger part of this particle, on light gray contrast, exhibits a spherical cap-type shape. The elemental mapping reveals its heterogeneous chemical nature, constituted predominantly by silicon and oxygen, which suggests a silicon dioxide compound with some amount of iron dissolved in it. This particle seems to be nucleated on a phosphorous calcium oxide compound, appearing in this image with a darkest contrast. As indicated by the intensity of P and Ca elemental mapping, these two

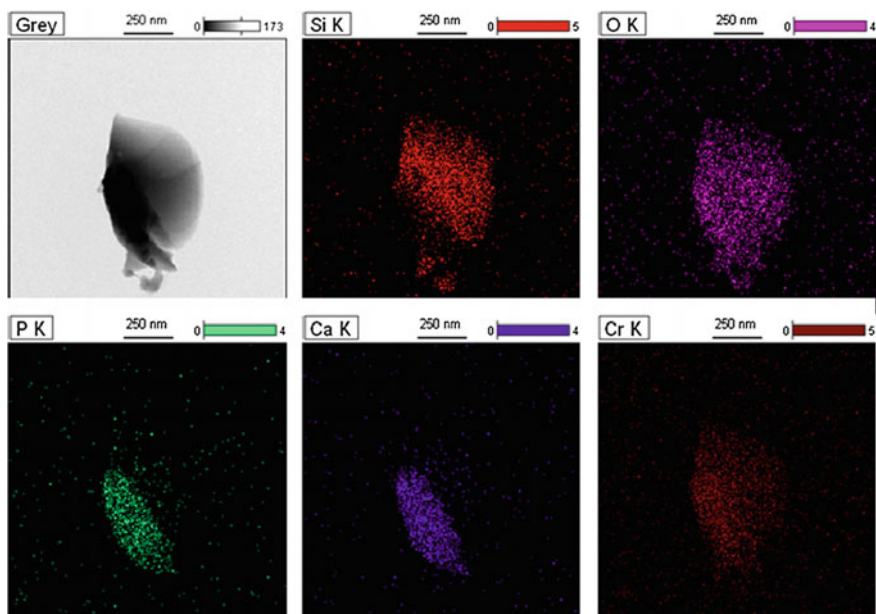


Fig. 5 TEM bright field of a silica and phosphorous calcium particles and characteristic X-ray intensity elemental mapping of Si, O, P, Ca, and Cr

elements are not dissolved as a spinel, but rather separated as a second phase in the sample. The particle morphology, together with the substrate, constitutes a typical case of heterogeneous nucleation.

The results presented here show that crystallization of amorphous silica occurs by processes controlled by nucleation and growth. Nucleation occurred homogeneously throughout the bulk of amorphous silica and heterogeneously at the P-Ca oxide substrate and also at oxides that contain K and Na. It is well known that unlike a heterogeneous process, homogeneous nucleation proceeds in the interior of the parent phase, in this case here amorphous silica, without the intervention of preexisting surfaces.

The energy barrier for homogeneous nucleation is larger than that required for heterogeneous nucleation. However, depending on the system conditions, the rate of homogeneous nucleation can be higher than the rate for heterogeneous one, prevailing the former in the entire system. Sample 1 has a considerable amount of impurities to act as substrates for heterogeneous crystallization, as shown in TEM images (Fig. 5). Nonetheless, the formation of small crystallites from amorphous silica at 800 °C occurred by a homogeneous nucleation mechanism. Therefore, the probability of homogeneous nucleation appears to be competing with that of a heterogeneous mechanism. For nucleation of a crystalline phase to occur in an amorphous matrix, atoms in the matrix rearrange themselves toward a short-range order as crystallite clusters. The amorphous matrix has a nature random array of atoms with some eventual local order. By statistical fluctuations of atomic movements, in some locations in the matrix, this local order configuration characteristic of amorphous solids could coincide with the long-range order of the crystal. The probabilities of finding these local atom arrangements are higher as smaller are the clusters. If the energy fluctuation in the system is sufficient to overcome the activation barrier, that means the continuous addition of atoms from the amorphous matrix to these clusters, the local random array of “clusters” reaches a supercritical size, leading to the nucleation and growth of a new stable crystalline phase. As the rate of homogeneous nucleation increases with undercooling, a copious small-size crystallites nucleate and subsequent growth and, eventually, coarsening occurs, a phenomenon known as Ostwald ripening. The sequence of above-presented events, documented at the micro- and nanostructural level, supports the mechanism of crystallization as controlled by nucleation processes; the driving force could be so high for homogeneous nucleation of crystallites take over the entire amorphous system. In fact, micrographs in Fig. 4 show in the same sample evidence for copious homogeneous nuclei together with coarsen spherical crystallites, while the remaining of the matrix maintains its amorphous structure. On the other hand, experimental evidence for heterogeneous nucleation, in virtue of impurity oxide particles containing K, P, Ca, and other elements, is presented. Such events of heterogeneous nucleation do not prevent homogeneous nucleation to dominate the crystallization process of amorphous silica from (RH).

4 Summary/Conclusion

The transformation from amorphous to crystalline state in RHA is affected by the purity of the samples, the heating conditions, temperature, and annealing time. Continuous heating yields to higher transition temperatures from amorphous to crystalline state in samples with low impurities contents. The main product of crystallization consists of tetragonal cristobalite and secondly trydimite with a monoclinic structure. Trydimite formation can be prevented by reducing the level of impurities of RHA. The crystallization of silica occurred by a combinations of homogeneous and heterogeneous nucleation of crystallites. Impurity compounds, mainly constituted by oxides containing combinations of K, Ca, P, and other elements, act as substrates for heterogeneous nucleation of crystallite upon heating. The homogeneous nucleation of spherical crystallites appears, however, to dominate the crystallization throughout the amorphous matrix.

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