Thermal Stability of Alumina Modified Silica Fiber

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Alumina modified silica fibers were prepared by covering with alumina fibrils. The modification induced the thermal stability under a stream of water at 1273 K without α-alumina formation. The morphology of alumina fibrils anchored on silica surface play an important role for the thermal stability in the presence of steam.

Alumina is an essential material for a catalyst support and is used widely to generate good catalytic performances. It is known that the specific surface area of alumina decreases due to the phase transition to α-alumina on heating over 1273 K. In addition, the decrease of specific surface area(sintering) is also induced by treatment at high temperatures under the steam, explaining that the phase transition of alumina is accelerated by the presence of steam. Since the sintering of alumina is correlated to the formation of α-alumina, most of the studies are focused to how to suppress the α-phase formation during heat treatment at high temperatures. Generally, the stabilization of alumina is achieved by the addition of foreign elements such as alkaline-earth metal, Zr,[1] La[2] and silicon-containing compounds.[3]

The present author has been investigating the thermal stability of alumina layer coated on silica fibers.[4] In brief, the surface of silica fibers showed homogeneously flat after the alumina layer was coated on the silica fiber. However, when the alumina-coated silica fibers were aged under deionized water at 373 K, the morphology of alumina layer changed from the flat surface to crude assemblies of alumina particles, and the alumina particles were composed of alumina fibrils with 6 nm in diameter and 100–150 nm in length. The specific surface area, based on the weight of alumina, of the samples calcined at 1473 K for 30 h in the air were 84 m^2·g^{-1}, indicating that the alumina modified silica fiber was thermally stabilized under dry conditions. In the present paper, effect of steam on the thermal stability of the alumina modified silica fibers was reported.

The alumina modified silica fibers have been prepared using a high purity silica filter (ADVANTEC QR-100, 45 mm in diameter and 0.35 mm thick.), where the silica fibers of 0.1–2 μm diameter and 1 mm long intertwined with each other. Alumina layer(denoted as SF-1) on the silica fiber was prepared by impregnating the fibers in a solution of aluminum nitrate dissolved in 1,3-butanediol, and was calcined at 773 K for 5 h. The modified alumina layer(SF-2) was obtained by immersing SF-1 into deionized water at 373 K for 2 h, and drying at room temperature. Powder alumina samples(denoted as P-1 and P-2) corresponding to SF-1 and SF-2, respectively, were also prepared for comparison. P-1 was prepared by the evaporation of aluminum nitrate solution, followed by calcination at 773 K for 5 h. P-2 was also prepared from P-1 by the treatment described above. The samples were aged under N_2 flow with and without 10 vol% steam at various temperature. The characterization of samples was carried out using X-ray diffraction(XRD), scanning electron microscope(SEM), transmission electron microscope (TEM) and energy dispersive X-ray spectrometer (EDS). BET surface areas were also measured.

Effect of steam on the thermal stability was observed clearly when the deposited alumina was treated by deionized water. Table 1 depicts the BET surface area based on the weight of alumina and crystallite structure of alumina aged at 1273 K for 30 h with and without 10% steam. SF-2 aged under 10% steam gave BET surface area as high as 156 m^2·g^{-1}, and no α-alumina formation was detected. On SF-1, although α-alumina was formed, the BET surface areas were nearly 50m^2·g^{-1} regardless of aging conditions. On the other hand, the powder samples, P-1 and P-2, show the BET surface area as low as 10 m^2·g^{-1} after aging at 1273 K, and most of alumina was transformed to α-phase.

Table 1. Specific surface area and crystalline phases after aging treatment.

Preparation method	1273 K 30 h in air		1273 K 30 h in 10% steam	
	S.A. / m^2·g^{-1}	XRD observation	S.A. / m^2·g^{-1}	XRD observation
SF-1	49	α + θ or δ	47	α + θ or δ
SF-2	160	γ	156	θ or δ
P-1	10	α	10	α
P-2	17	α + θ or δ	11	α

In order to evaluate the difference between SF-1 and SF-2 in the thermal stability, SEM measurements were carried out. The result shows in Figure 1. The crude assemblies of alumina fibrils were present on the surfaces of SF-2 (Figure 1(b)). The length of alumina fibrils was estimated to be 100–150 nm, and the diameter of fibrils was determined to be 6 nm from TEM observations. In addition, the surface morphology of SF-2 did not change even after aging at 1273 K under the steam flow as shown in Figure 1(d). On SF-1, when the sample was calcined at 773 K, the surface of silica fibers was homogeneously flat (Figure 1(a)) and the traces of melting were observed on the surface after aging at 1273 K shown in Figure 1(c).

Figure 2 shows TEM photograph of SF-2 aged at 1273 K for 30 h under the steam flow. The alumina fibrils were clearly observed on the silica fiber, indicating that the morphology of alumina does not change even at 1273 K under the steam flow. This means that alumina fibrils anchored on silica fiber are thermally stabilized even under the steam condition at 1273 K.

Figure 3 exhibits the Si/Al ratios in alumina layers of SF-1 and SF-2 after the aging at various temperatures in the air. The

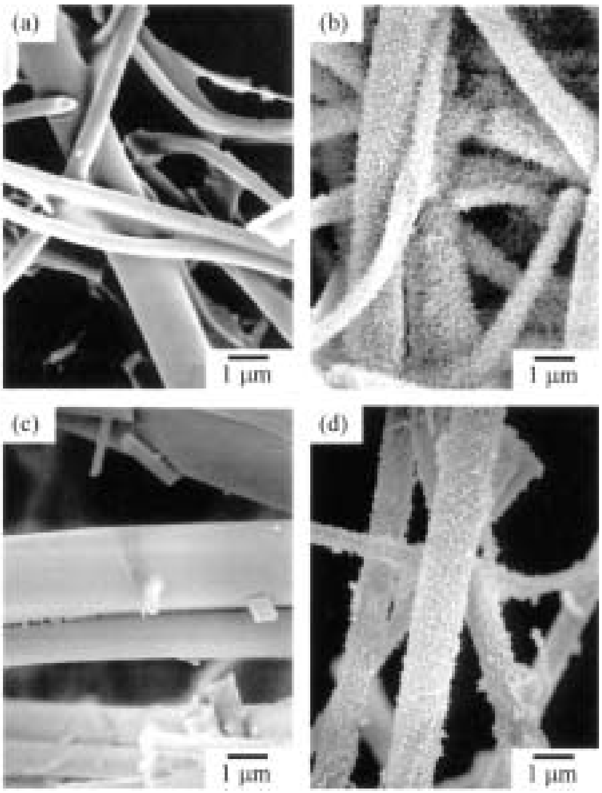

Figure 1. SEM photographs of alumina modified silica fibers.
(a) SF-1 and (b) SF-2: calcined at 773 K for 5 h in air.
(c) SF-1 and (d) SF-2: calcined at 1273 K for 30 h in the presence of steam.

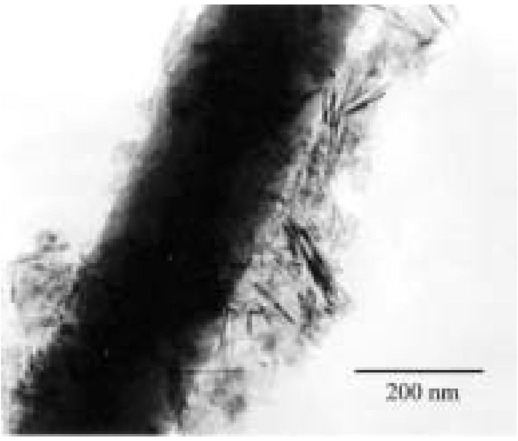

Figure 2. TEM photograph of SF-2 aged at 1273 K for 30 h under the steam flow.

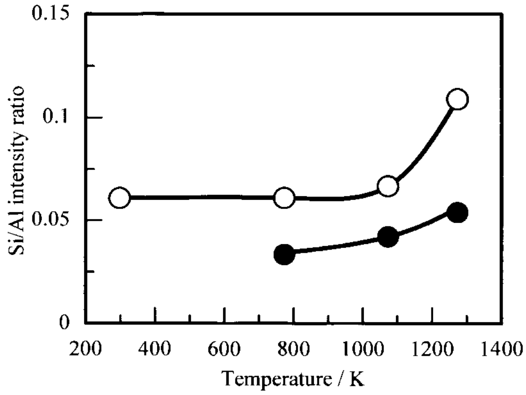

Figure 3. Changes in Si/Al ratio at various aging temperatures. ●:SF-1, ○:SF-2.

ratios were estimated by TEM-EDS. Most of SF-2 treated below 1273 K gave apparently high Si/Al ratios compared with those of SF-1. This means that the Si species of the silica fiber slightly migrate onto the alumina fibrils on immersing into deionized water at 373 K. The rapid increase of the Si/Al ratio at 1273 K on SF-2 seems to suggest that the alumina surface is covered with Si species. The behavior of Si species on alumina at high temperatures was investigated by Amato et al.[5] They have reported that the addition of silica to the γ-alumina was effective for the thermal stability because of a glass layer formed on the alumina surface. Beguin et al.[6] has also reported that the replacement of alumina surface by silanol group was a favorable method to inhibit the sintering and phase transition of alumina. Therefore, Si species on alumina observed in SF-2 might assist to inhibit the phase transition to the α-alumina because Si species locate vacant sites in the alumina fibrils. Furthermore, the morphology of alumina fibrils also contributes for the depression in the sintering of alumina compared with the typical alumina powder due to small contact area among the alumina fibrils.[7] In conclusion, both the morphology and the presence of Si species might synergistically act to improve the thermal stability of the alumina modified silica fiber in the presence of steam.

References and Notes

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