Novel Method for Preparation of High Surface Area SnO_2: Solvent Replacement by Alcohol

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A novel method named "solvent replacement" was proposed for the preparation of high surface area SnO_2 containing no additive ions. The surface areas of thus obtained dried gels were much higher than that of gel prepared by a conventional method. The superiority of the novel method remained even after the calcination at 773 K: The surface area of SnO_2 calcined under optimum condition was 108 $m^2 g^{-1}$.

Much attention has been paid to the preparation of SnO_2 having high surface area for gas-sensors, catalysts and so on, because the performance of these materials is expected to strongly depend on the surface area. One of the approaches is the retardation of sintering during the calcination process, because the surface area of SnO_2 is drastically decreased by calcination. This was successfully performed by adding the other elements, such as metal ions,[1] ammonium sulfate[2] and ammonium chloride,[3] to dried gel of $SnO_2 \cdot xH_2O$ before calcination. Another possible approach is the preparation of dry gel of $SnO_2 \cdot xH_2O$ having high surface area, such as drying gel in supercritical fluid.[4] In this letter, we report a novel method named "solvent replacement" for the preparation of dried gel of $SnO_2 \cdot xH_2O$ with high surface area.

SnO_2 hydrate was prepared by precipitation by adding aqueous ammonia solution (4 mol dm^{-3}) into an aqueous solution of $SnCl_4 \cdot 5H_2O$ (25g / 250ml) at pH 7. After the precipitate was settled for 2 h, 100 ml of the supernatant was removed by decantation, and then the equivalent volume of alcohol, such as methanol, ethanol and 2-propanol, was added. This operation, "solvent replacement", was repeated twenty times. The precipitate was dried at 383 K for 12 h after the supernatant was removed. The glassy gel thus obtained was calcined at 773 K for 3 h in flowing air or He.

XRD pattern of dried gel conventionally prepared without using alcohol showed weak and very broad lines at 27°, 34° and 52°, which can be attributed to cassiterite, indicating that the gel is mostly amorphous and/or consists of very fine particles. TG analysis showed that dried gel contained 8.3 wt% residue, which corresponds to $SnO_2 \cdot 0.76H_2O$. As shown in Table 1, BET surface area of dried gel was 197 $m^2 g^{-1}$ which agreed well those of SnO_2 gel prepared by the conventional method, i.e., 193 $m^2 g^{-1}$ for the gel dried at 373 K[5] and 179 $m^2 g^{-1}$ dried at 393 K.[6]

In comparison to these results, the solvent replacement method gave much higher surface area, 352-361 $m^2 g^{-1}$. XRD patterns agreed well with this result: Diffraction lines of dried gel prepared by the solvent replacement method were weaker and broader. It should be noted that all the alcohols gave much higher surface area than that prepared without alcohol, and that the surface area did not depend on the kind of alcohol. Although the mechanism of increase in the surface area is not clear, one of the possible explanations would be the effect of lower surface tension of alcohols. This is because it is widely accepted that the surface tension of solvent has a large effect on the structure change during drying process.[7]

Table 1. BET surface area of dried and calcined SnO_2

solvent [a]	surface area / $m^2 g^{-1}$ dried	surface area / $m^2 g^{-1}$ calcined	calcination procedure [b]
water	197	45	A
(72)		55	B
methanol	352	76	A
(22)		72	B
ethanol	358	60	A
(22)		108	B
2-propanol	360	71	A
(21)		88	B

a Numeral in parenthesis is surface tension of solvent in 10^{-5}N cm^{-1}.
b A: in air flow at a heating rate of 15 K min^{-1},
B: in He flow at a heating rate of 2 K min^{-1}.

The solvent replacement method remained superior over the conventional method after the calcination for which two procedures were tested. The surface area of SnO_2 prepared without using alcohol was 45 and 55 $m^2 g^{-1}$ after the calcination in air and in He, respectively. The former was close to and the latter was slightly higher than those reported.[8] As shown in Table 1, the novel method gave higher surface area in both cases: 60-76 $m^2 g^{-1}$ after the calcination in air and 72-108 $m^2 g^{-1}$ in He. XRD patterns supported the result: The solvent replacement method gave broader and less intense diffraction lines. The highest surface area, 108 $m^2 g^{-1}$, was obtained, when dried gel was prepared by using ethanol and calcined in He at 2 K min^{-1}. This value was higher than those prepared by using super critical fluid and calcined at the same temperature, 50-100 $m^2 g^{-1}$.[4]

References and Notes

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