Preparation of Niobia/Silica Mixed Oxide Model Thin Films

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Model thin films of niobia/silica (Nb_2O_5/SiO_2) were prepared by radio-frequency sputtering and, subsequent to different calcination conditions, found to have structures which are similar to their high-surface-area counterparts.

There are many catalytic materials which consist of either one oxide deposited onto the surface of another or two oxides distributed homogeneously in the bulk.[1] The study of how the structures of these materials are influenced by oxide–oxide interactions is important in understanding the catalytic properties. One approach to obtaining this type of information is to use model thin films which can be directly observed with transmission electron microscopy (TEM), as demonstrated by recent studies involving Nb_2O_5 on SiO_2[2] and MoO_3 on Al_2O_3.[3] In this paper, we show that the same approach is

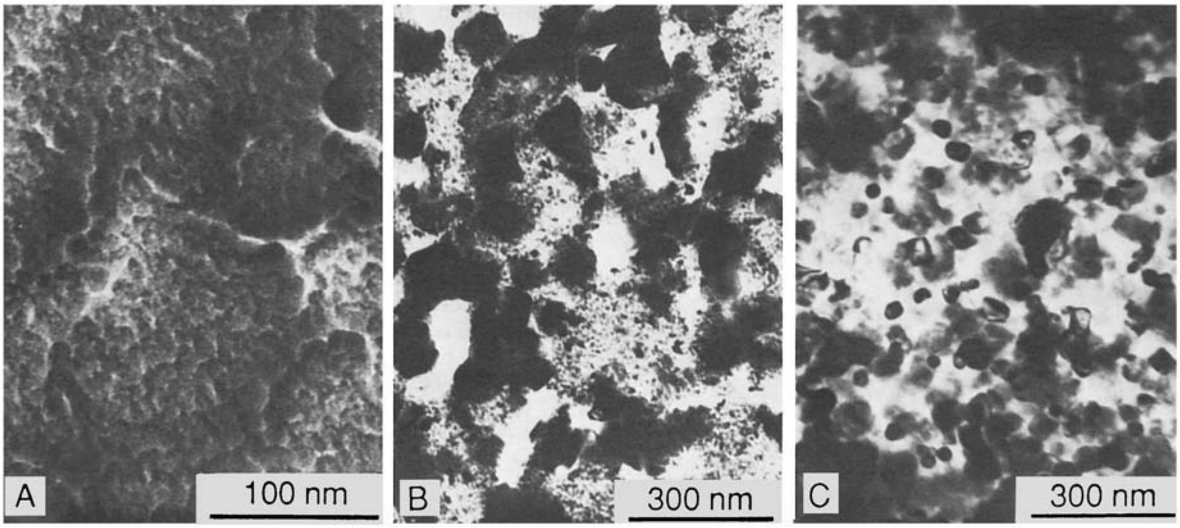

Figure 1. Transmission electron micrographs of niobia/silica mixed oxide thin film containing 68 wt % niobia, after calcining at; A: 500 °C for two hours, B: 800 °C for two hours, C: up to 1 000 °C.

Table 1. Phases observed in mixed oxide samples.[a]

Calcination conditions[b]	High surface area NS50[c]	NS75[c]	Nb_2O_5[c]	Thin film NS68[d]
(500,2)	A	A	T	A
(800,2)	T	T	T	T
(1000,-)	T	T	T	T

[a] Letters refer to; A: amorphous, T: T–Nb_2O_5. [b] Given as (temperature in °C, time in hours). [c] Identified by *X*-ray diffraction. [d] Identified by selected-area electron diffraction.

also applicable to bulk mixed oxides. Specifically, we have established the same structure–temperature relationship for low- and high-surface-area samples of Nb_2O_5/SiO_2 mixed oxides.

High-surface-area Nb_2O_5/SiO_2 mixed oxides containing 50 and 75 weight % of Nb_2O_5, were prepared by a conventional co-precipitation method. Briefly, ammonium hydroxide was added to a well-stirred methanol solution of $NbCl_5$ and $SiCl_4$ to a pH of 7. The resulting precipitate was repeatedly washed to remove all traces of chlorine. A model thin film, containing 68 weight % of Nb_2O_5, was prepared by inertly co-sputtering from elemental targets of niobium and silicon disks in a radio-frequency sputtering apparatus. A disk of silicon was placed on top of a larger disk of niobium in such a way that the ratio of the exposed area of the two metals determined the composition of the final product. The metals were co-deposited onto thin carbon films supported by 200 mesh stainless steel TEM grids. The carbon was removed by oxidation after deposition. The as-deposited thickness was measured by a quartz crystal thickness monitor to be about 90 nm. The notation NSX is used to represent these samples, where X denotes the weight percent of Nb_2O_5.

The as-prepared samples, both high-surface-area and thin film, were calcined at 500 °C for two hours to fully oxidize the materials. They were subsequently oxidized at 800 °C for two hours and heated to 1 000 °C from room temperature with a heating rate of 10 °C/min. Phases formed after heat treatment were measured by *X*-ray diffraction for the high-surface-area samples and by selected-area electron diffraction for the thin film. These results are summarized in Table 1, which also includes the corresponding data of pure Nb_2O_5 for comparison.[4] Electron micrographs of the thin film sample after the three heat treatment steps are given in Figure 1.

Observation of high-surface-area samples by electron microscopy is difficult owing to the irregular topology and extreme changes of contrast within the sample. The micrographs of Figure 1 show that the mixed oxide thin film is ideally suited for this type of observation, as morphological details within the sample are clearly discernible. Figure 1A has only thickness contrast, as the sample was amorphous after being calcined at 500 °C, while Figures 1B and 1C show increasing degrees of crystallinity. The darker regions of Figure 1B were identified as polycrystalline aggregates of T–Nb_2O_5 separated by amorphous regions, while the larger crystals visible in Figure 1C were T–Nb_2O_5, separated by smaller crystals of T–Nb_2O_5 contained within an amorphous matrix.

These results are significant in two ways. First, they are similar to previous observations for Nb_2O_5 overlayer on SiO_2 in that the presence of SiO_2 inhibits the crystallisation of T–Nb_2O_5 at a calcination temperature of 500 °C. This suggests that interactions between niobia and silica may be of the same fundamental nature in the surface and mixed oxides. Second, the phases identified in the model thin films were exactly those found under similar conditions in the high-surface-area samples. Since there are many known forms of Nb_2O_5,[5] this excellent agreement establishes the thin films as a valid model for studying the structure-temperature relationship of high-surface-area samples.

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