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Transmission electron microscopy of supported molybdenum and vanadium oxides

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Transmission electron microscopy has been used to characterize dispersions of molybdena and vanadia on titania and silica supports. When silica spheres of controlled morphology were used as support, the dispersed "monolayer" phase of both oxides could be imaged due to characteristic changes in contrast. In addition to the dispersed phase, we could detect three-dimensional crystallites of V_2O_5 but in the case of MoO_3 only two-dimensional islands were seen. On Degussa P-25 titania, there was no observable contrast change due to the presence of a monolayer of these dispersed oxides. However, exposure to the electron beam caused dramatic changes in the surface texture of the support. Such changes were not seen when blank TiO_2 was similarly irradiated. These e-beam induced changes were more pronounced in the vanadia/titania catalysts leading to formation of 1–3 nm clusters of reduced VO_x. However, on the MoO_3/TiO_2 sample, e-beam exposure caused only a pronounced change in texture but no well defined clusters could be detected.

Keywords: Transmission electron microscopy (TEM) characterization; supported molybdenum; vanadium oxides

1. Introduction

Dispersions of transition metal oxides on a support constitute an important class of catalysts for applications such as selective oxidation [1], pollution control [2] and hydrotreating [3]. The properties of an oxide when dispersed on another support are quite different from the same oxide used as an unsupported powder. For instance, unsupported titania yields only acid catalyzed products during methanol oxidation while titania supported on silica yields partial oxidation products with high selectivity [4]. In these catalysts, the suported oxide can result in the following morphologies: (1) "molecularly" dispersed species anchored to the support, no more than a *monolayer* in thickness, sometimes also referred to as a dispersed phase; (2) a two-dimensional island; (3) a three-dimensional crystalline phase or (4) incorporated into the bulk or surface region of the support forming a compound. The distinction between (2) and (3) is the thickness of the oxide in a direction normal to the support: a crystalline phase will consist of particles whose three dimensions are roughly equal (isotropic) whereas two-dimensional islands would have a thickness much smaller than in the other two dimensions. The upper limit of the loading of the dispersed phase, i.e. the monolayer capacity, can be estimated from that of a low index plane of the supported oxide. However, the actual monolayer capacity is dictated by the interaction between the dispersed phase and specific surface sites on the support oxide. Thus, if each hydroxyl group on a support oxide can immobilize one transition metal atom, we will be able to calculate a monolayer capacity based on the number of hydroxyl groups per cm^2. Dispersed oxides are often characterized by methods such as IR or Raman spectroscopy, ESR, solid state NMR and EXAFS. Information on three-dimensional order is obtained from X-ray diffraction (XRD) which, however, loses sensitivity due to line broadening when the particles become smaller than about 4 nm. Since none of the above techniques provides direct information on the morphology of the dispersed oxide, transmission electron microscopy (TEM) is increasingly being used. Wallenberg and co-workers studied the V_2O_5/TiO_2(B) catalyst system using high resolution TEM [5,6] and Regalbuto and co-workers reported on the spreading of MoO_3 on silica [7,8].

TEM is essentially a bulk characterization technique, ideally suited for the study of defects in materials, therefore TEM has been used mainly to determine whether crystalline particles have formed from the dispersed phase oxide. The absence of crystalline particles is then used as evidence that the oxide phase is dispersed. For instance, Weissman et al. [9] found little difference in contrast even when three monolayers of niobia were present on their high surface area silica support suggesting that a dispersed phase had formed on the support. When these samples were calcined at 873 K, the presence of niobia was manifested by the appearance of crystallites of Nb_2O_5. One problem with the use of high surface area silica supports is that the oxide tends to charge, making examination difficult at high magnifications. The amorphous background from the silica also makes it difficult to detect small particles of the dispersed phase. To improve the detection of such small particles, specialized image processing methods such as those used by Sattler and O'Keefe [10] may be necessary.

Since the problem of detecting dispersed phase oxides is often one of obtaining enough contrast, we have found that use of a model support having controlled surface texture can result in improved detectability. In previous work, we have shown that "molecularly" dispersed titania on silica could be detected in TEM images since it led to an increase in apparent surface roughness of the silica support [4]. The known surface/volume ratio of these model silica supports allowed us to use the bulk analysis by EDS and convert weight loadings into a surface coverage. Concentrations as low as 3 Ti/nm^2 could be readily imaged. Since vanadia and molybdena are reported to have a monolayer capacity in excess this number [1], it would be of interest to determine whether TEM could be used to detect a "monolayer" phase of these oxides. Therefore, in this study, we have examined dispersions of oxides of vanadium and molybdenum both on model silica as well as commercial titania supports.

2. Experimental

The supports used were Degussa P-25 TiO_2 (65 m^2/g) and non-porous silica spheres (15–20 m^2/g) prepared by the method of Stober et al. [11]. Aqueous impregnation of ammonium heptamolybdate and ammonium metavanadate was used to deposit the oxides. The preparation technique consisted of dissolving the aqueous precursor in water and adding the support material and stirring it on a hot plate and then transferring to an oven kept at a temperature of 573 K for 2 h. Some of the vanadia and the molybdena tended to stick to the sides of the beaker resulting in the actual loading being somewhat lower than intended. On titania, the catalysts were prepared by calcining a physical mixture of V_2O_5 (or MoO_3) and the titania support at 773 K in laboratory air. Laser Raman spectroscopy was used to confirm that no crystalline V_2O_5 or MoO_3 was present in these samples after calcination. The nominal weight loading on these samples was 5 wt% of molybdena or 4 wt% of vanadia, both of which are below the monolayer capacity for titania but exceed the monolayer capacity of the silica support. Transmission electron micrographs were obtained on a JEOL 2000 FX microscope operated at 200 kV. The powders were supported on holey carbon films mounted on 200 mesh, 3 mm TEM copper grids. Elemental analysis was performed using a Tracor Northern 2000 EDS system using a Be window detector. The EDS spectra were analyzed using the standardless analysis program SMTF on the Tracor system.

3. Results and discussion

3.1. MOLYBDENA/SILICA

Fig. 1A shows a micrograph of the MoO_3/SiO_2 after 573 K calcination in air. The MoO_3 forms two-dimensional islands on the silica surface that are indicated by arrows. The higher magnification view in fig. 1B shows that the 2D islands are composed of smaller individual structures. These amorphous islands do not cover the entire surface of the silica. The presence of dispersed molybdena on the silica is best revealed after sulfiding this sample at 698 K in 10% H_2S/H_2. Higher magnification views of the surface of the silica spheres after sulfiding are shown in figs. 2A and 2B. The region marked M shows a two-dimensional patch of MoO_3 that has now transformed into hexagonal MoS_2 as identified by the characteristic dark lines (MoS_2 $d_{002} = 0.63$ nm). Pratt et al. [12] have concluded, based on a computer simulation of a through focus series

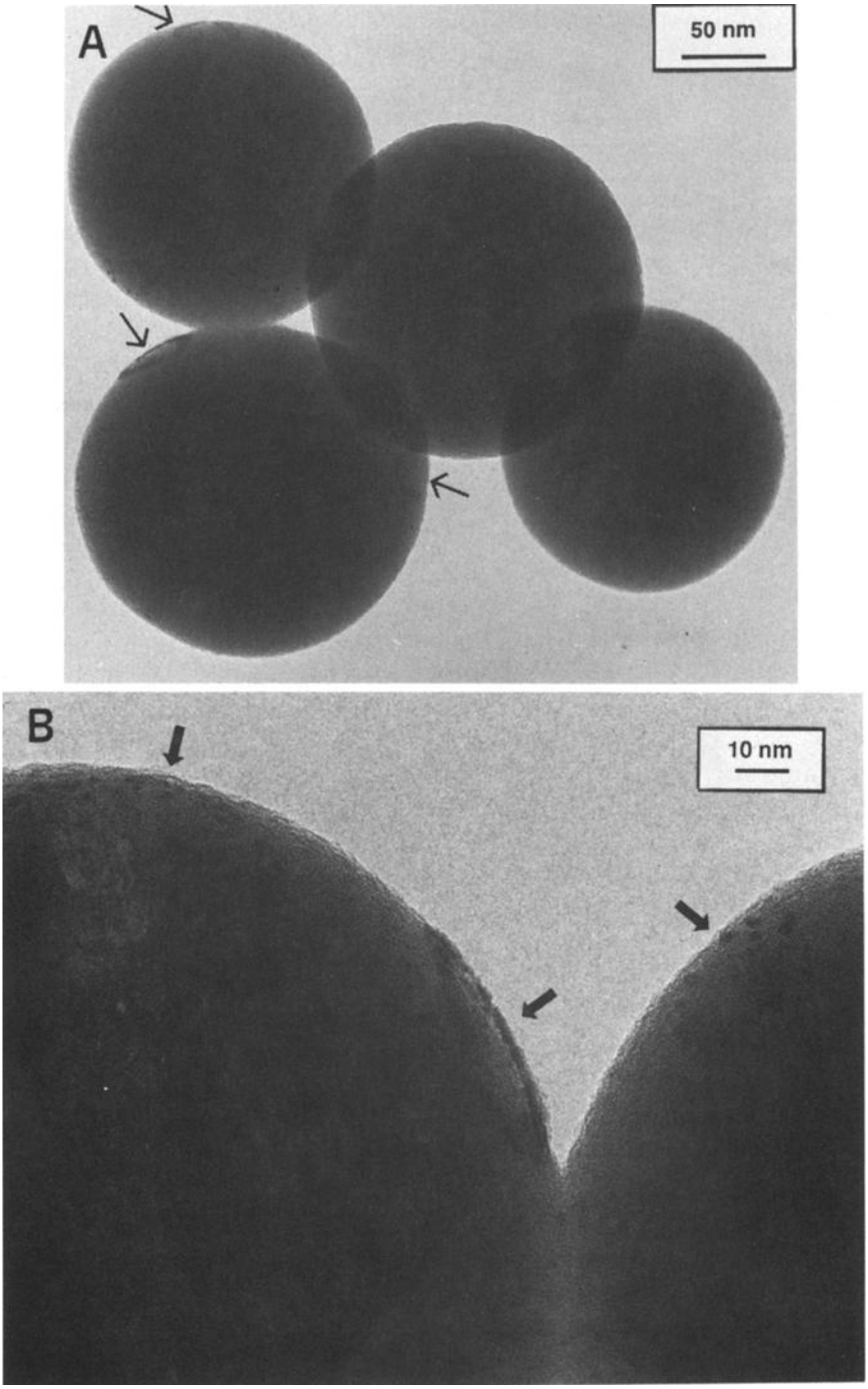

Fig. 1. (A) Low magnification view of MoO_3/silica spheres calcined in air at 573 K. Two-dimensional islands of molybdena are present in addition to a dispersed phase since the weight loading exceeds the monolayer capacity; a higher magnification view of these islands is shown in (B).

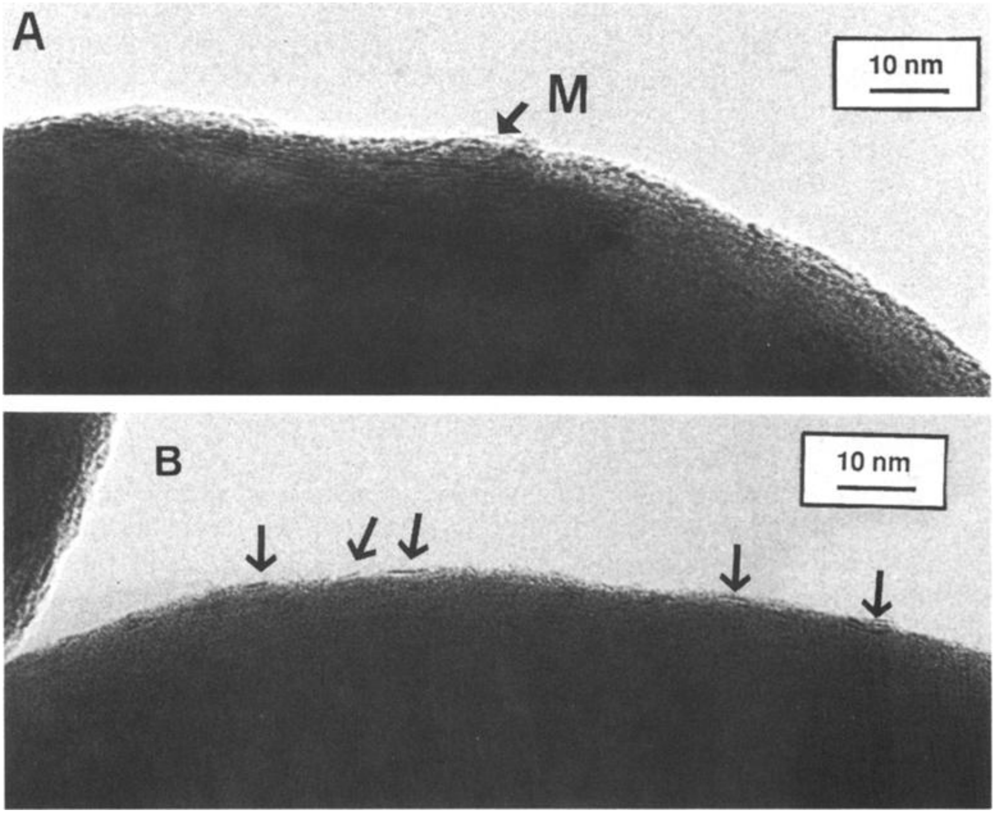

Fig. 2. (A) Micrograph of a silica sphere from the same sample imaged in fig. 1 but after sulfiding in 10% H_2S/H_2 at 698 K. The region marked M shows a higher concentration of MoS_2 which may arise from the two-dimensional islands of MoO_3 shown in fig. 1. Small segments of dark lines (arrowed) represent single layers of hexagonal MoS_2 (B).

of images, that a single sheet of MoS_2 will give a single black line image at a defocus of 50–60 nm for a tilt of about (±5°) to the electron beam. These characteristic dark lines in the image therefore correspond to single sheets of MoS_2. Besides the obvious concentrations of MoS_2 shown in fig. 2A, we also see small segments of dark lines all over the silica surface as pointed by the arrows in fig. 2B. These dark lines correspond to a single layer of MoS_2 with its basal plane parallel to the silica surface.

We conclude that under our preparation conditions, a dispersed phase of MoO_3 is formed in addition to two-dimensional islands. The two-dimensional islands of MoO_3 appear to be amorphous since no spots were seen in electron diffraction patterns. Since the sample was calcined at 573 K, no three-dimensional crystallites of MoO_3 appear to have formed. These observations are in agreement with previous studies of MoO_3/SiO_2 where it was suggested that a hexagonal phase of MoO_3 is formed on heating to 573 K [7]. The hexagonal

MoO_3 has been shown to be more amenable to dispersion and it transforms to the orthorhombic form of MoO_3 when calcined at 773 K [7]. The presence of a dispersed MoO_3 on these silica spheres may also be facilitated by the hydroxyl groups on the surface of the silica spheres. Our previous work shows that the model silica spheres are extensively hydroxylated and the hydroxyl groups exhibit considerable hydrogen bonding [4]. When studying dispersed molybdena we need to consider a possible interaction with Na since it has been shown that the MoO_3 preferentially reacts with sodium to form surface sodium molybdates [13]. However, we do not expect this to be a problem with our silica support since it was prepared by hydrolysis of TEOS with NH_4OH and the Na content is quite low (160 ppm by AAS).

3.2. VANADIA/SILICA

Fig. 3A shows a micrograph of the vanadia supported on silica spheres. The sample was calcined at 573 K in air after impregnation. Two crystalline particles of V_2O_5 are seen on the silica surface with a higher magnification view presented in fig. 3C. The particle on the right exhibits 3.4 Å lattice fringes that are consistent with the (110) plane of orthorhombic V_2O_5 (JCPDS file 9-387). In addition to the crystalline particles, we find that the silica sphere appears to have a rougher surface texture than the uncoated silica sphere shown in fig. 3B. The arrows in fig. 3A point to what appear to be small clusters on the surface. The "apparent" surface roughness of this silica is the only indication we have of the presence of a dispersed vanadia species. We have confirmed by elemental analysis the presence of V even on spheres that do not contain crystalline particles of V_2O_5 which proves that the hydroxylated silica surface in these Stober spheres is able to stabilize a dispersed vanadia monolayer phase.

3.3. MOLYBDENA/TITANIA

This sample was prepared by mixing together MoO_3 and Degussa P-25 TiO_2 in the desired proportion and calcining at 773 K in laboratory air for 2 h. The Mo was uniformly dispersed on the titania surface and there was no obvious contrast change due to the presence of the surface molybdena. Fig. 4 shows TEM images of the MoO_3/TiO_2 sample, before and after prolonged e-beam irradiation. The electron beam was focussed on the specimen for approximately 4 min and as seen in fig. 4B, there is a marked change in the contrast of the titania support. These changes in contrast were not seen if the samples were observed for prolonged periods under conditions normally used for recording images (with a defocussed beam). Closer examination suggests that clusters have formed on the surface, but they are so small that they do not stick out over the edges of the support. The overall effect is to make the surface of the titania appear more rough after exposure to the electron beam. The changes caused by

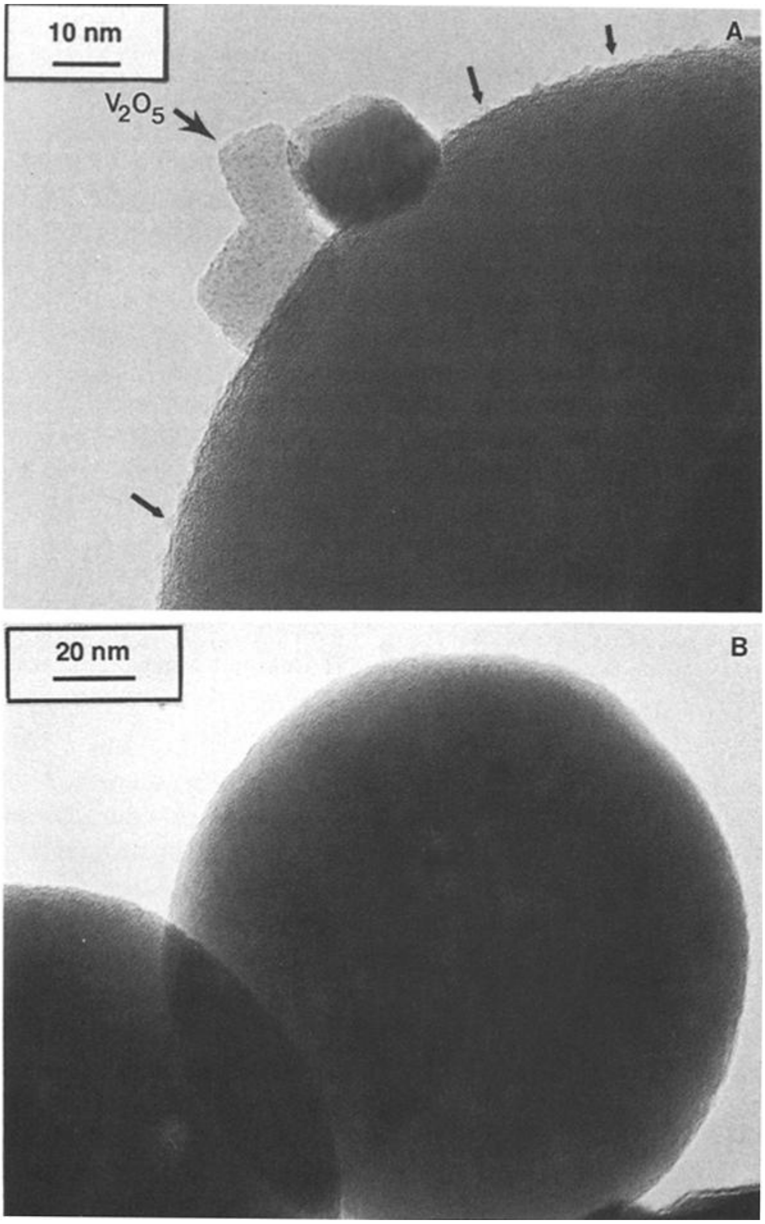

Fig. 3. (A) Micrograph of V_2O_5/silica spheres after calcination at 573 K in air. Besides the crystalline particles of orthorhombic V_2O_5, we also see evidence of a dispersed phase as indicated by arrows. The presence of the dispersed phase becomes more apparent when compared with the image of an uncoated silica sphere shown in (B). An enlarged view of the crystalline V_2O_5 particle is shown in (C).

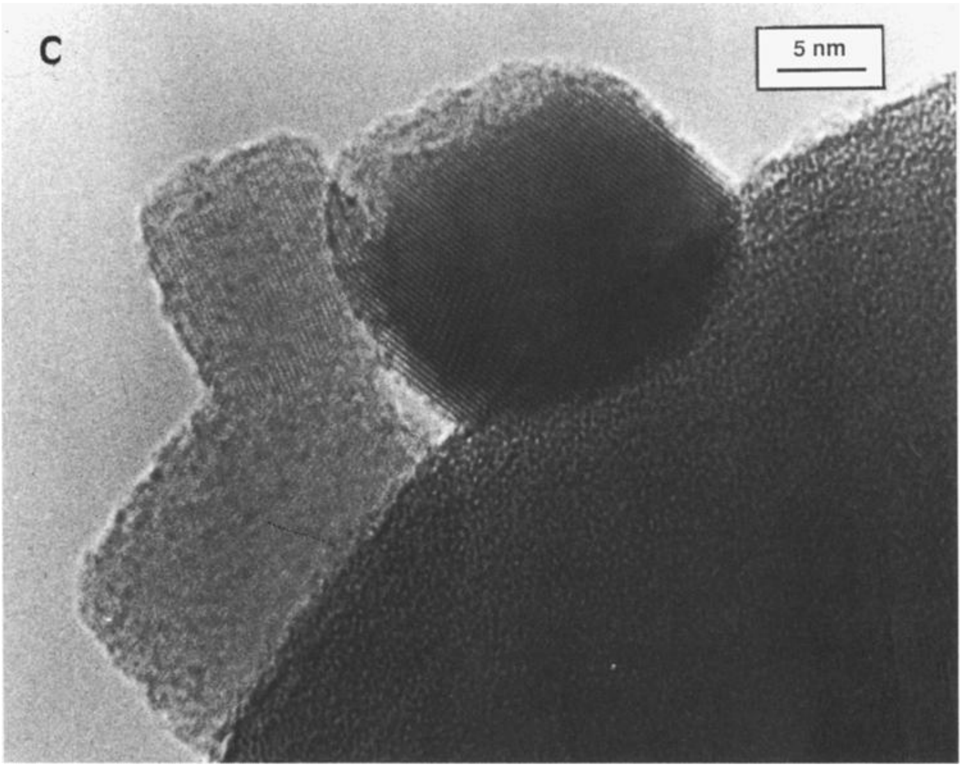

Fig. 3. (continued).

e-beam irradiation of the MoO_3/TiO_2 sample can be seen more clearly when we contrast these with the effect of similar e-beam exposure on the uncoated titania, as shown in fig. 5. It is clear that the changes in surface texture seen in fig. 4 are not seen in fig. 5. Again, the presence of the dispersed molybdena is revealed best after sulfiding the sample at 695 K in 10% H_2S/H_2. As shown in fig. 6, the sulfided molybdena sample shows small segments of black lines (arrowed) that represent monolayer patches of the hexagonal MoS_2 phase. The images of MoS_2/TiO_2 are very similar to those reported previously by Pratt et al. [12].

3.4. VANADIA/TITANIA

Fig. 7 shows micrographs of the vanadia/titania catalyst before and after prolonged e-beam irradiation. The electron beam was focussed on the sample for a few minutes before the image in 7B was recorded. While the presence of dispersed vanadia cannot be detected in fig. 7A, exposure to the focussed electron beam causes the appearance of small clusters (arrowed) that stick out

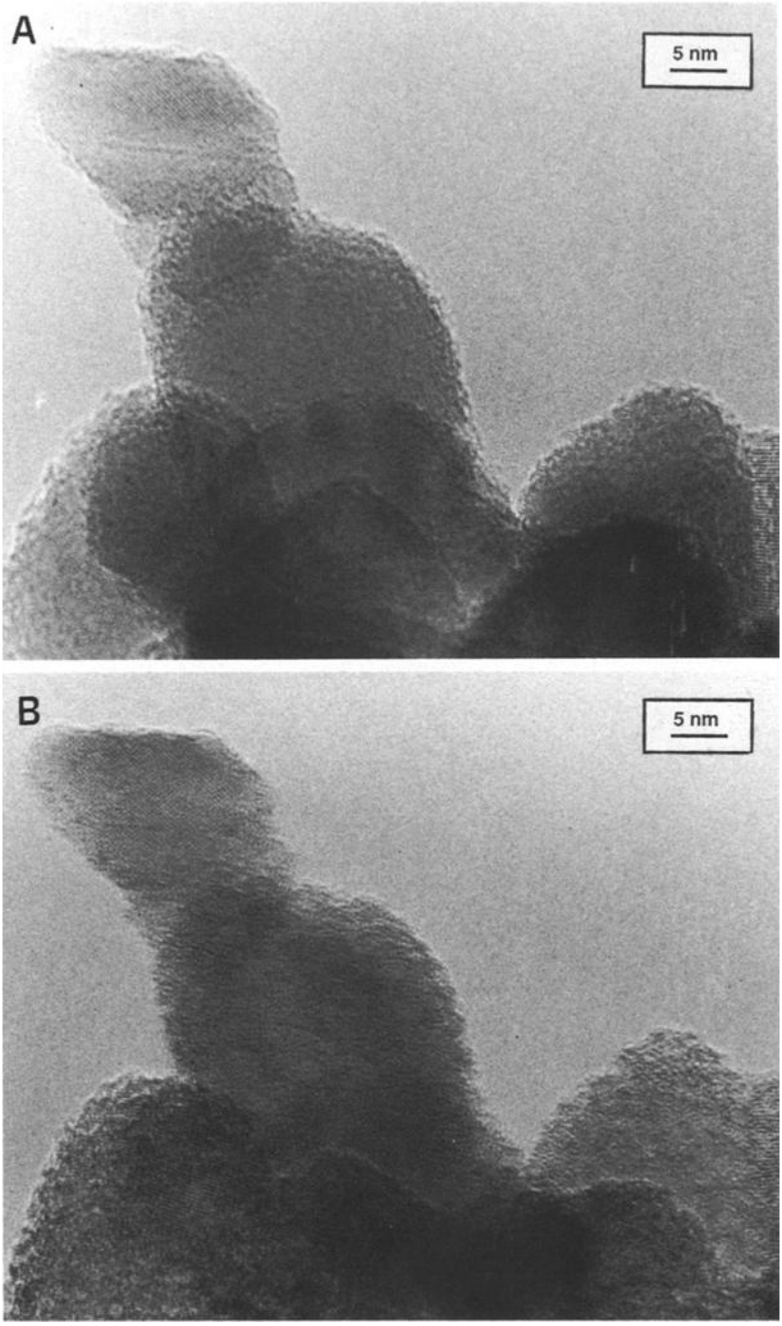

Fig. 4. Micrographs of a region of the MoO_3/TiO_2 sample that was calcined in air for 2 h at 773 K. The sample shown in (A) was exposed to a focussed electron beam for approximately 4 min before recording image (B). The e-beam exposure causes a marked change in contrast of the titania support.

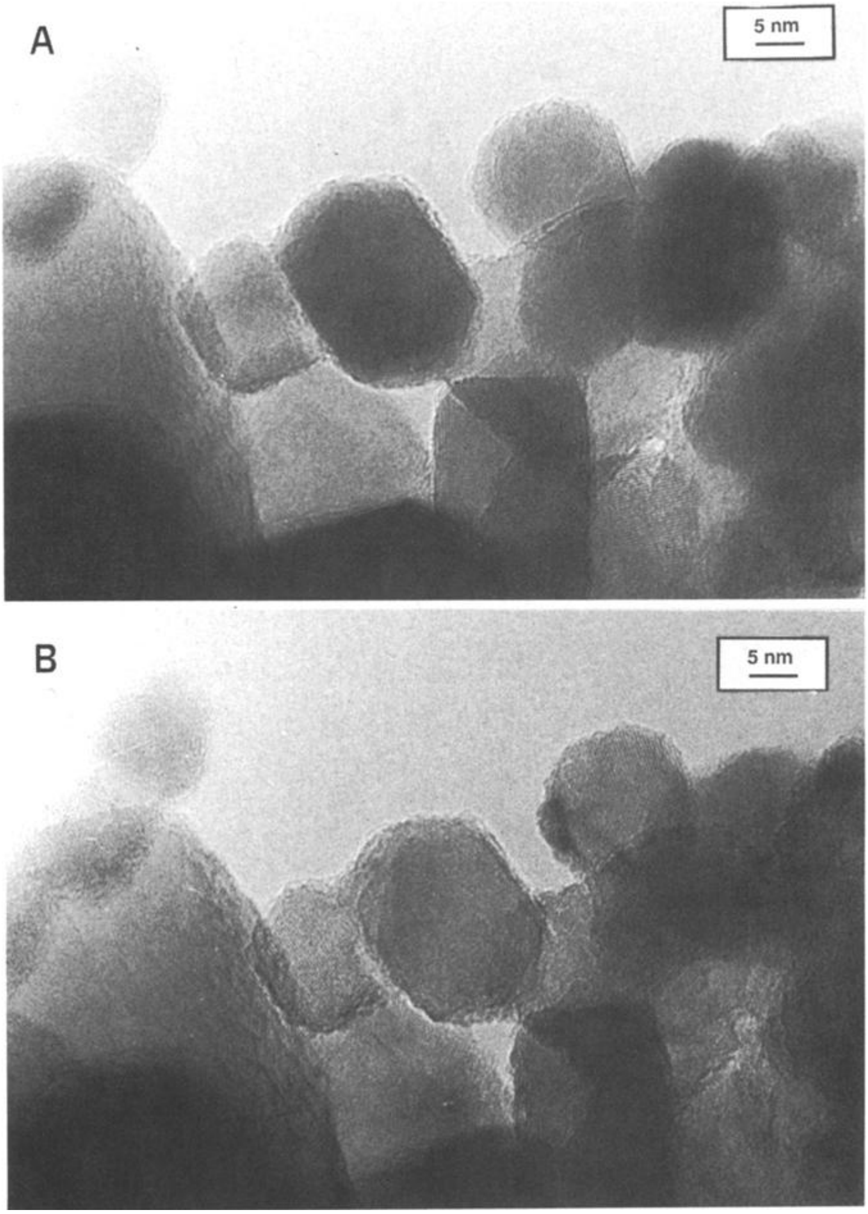

Fig. 5. Micrograph of blank TiO_2 (A) before and (B) after exposing the sample to a focussed electron beam for 4 min. There is no significant change in contrast due to the electron beam exposure of the uncoated titania.

over the edges of the titania support. These clusters are very similar to those reported previously by Sanati and co-workers [5] and are thought to be composed of VO_x formed by e-beam induced reduction of V_2O_5. Based on these

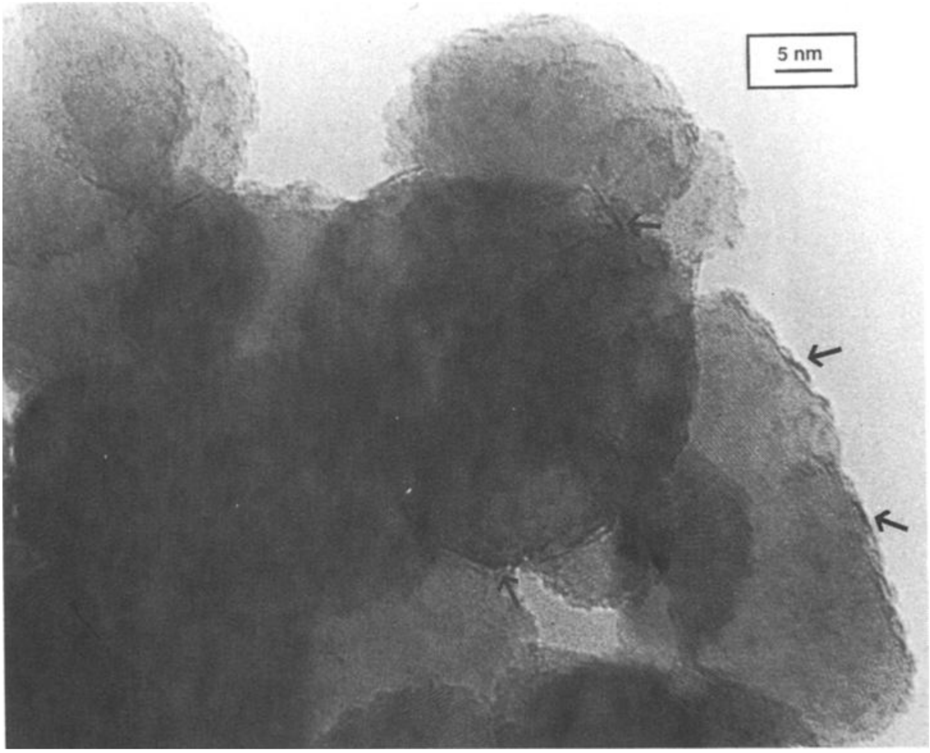

Fig. 6. Micrograph of the same sample imaged in fig. 4 after sulfiding in 10% H_2S/H_2 at 698 K. The dispersed MoS_2 can be imaged as small segments of black lines that are indicated by arrows.

results we can conclude that the reduced vanadia species are more mobile than the corresponding reduced molybdena leading to larger clusters on the titania surface after e-beam exposure.

4. Summary

Our study of dispersed oxides of vanadia and molybdena confirms that on titania supports, these oxides are "molecularly" dispersed and do not give rise to any observable contrast in TEM images. Exposure to a focussed electron beam causes significant changes in samples that contain the dispersed oxide. Small clusters (< 1 nm) appear to form on the MoO_3/TiO_2 sample while on V_2O_5/TiO_2 the clusters are much larger (1–3 nm). While the surface texture of commercial titania supports makes it difficult to detect any changes in contrast due to the "molecularly" dispersed oxide phase, e-beam irradiation causes clustering of the dispersed phase making it easier to observe the dispersed phase oxides. Model silica spheres, on the other hand, have a smoother surface texture

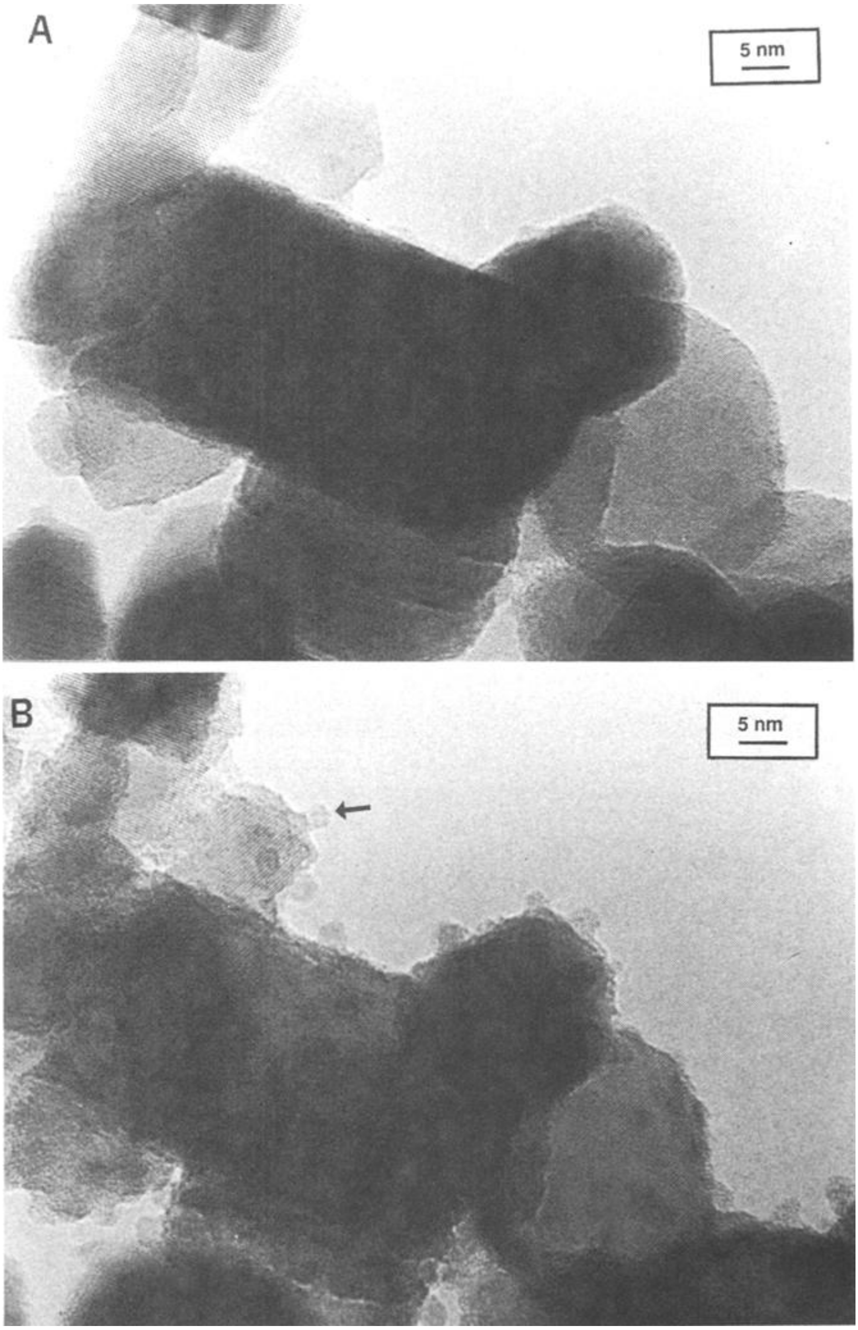

Fig. 7. Micrograph of the vanadia/titania sample after calcination in air at 773 K for 2 h. There is no evidence for the presence of a dispersed vanadia phase in (A) but exposure to a focussed electron beam for a few minutes (B) causes small clusters (arrowed) 1–3 nm in diameter to appear on the surface.

making it easier to detect the presence of a dispersed oxide phase. Since the loading of the dispersed phase was in excess of the monolayer capacity of silica, we see a dispersed phase in addition to three-dimensional crystallites of V_2O_5 and two-dimensional islands of what appears to be amorphous MoO_3. TEM observations are facilitated also by the fact that the silica spheres are stable in the microscope; similar observations would be very difficult on high surface area silica gel or fumed silica which tends to charge and become unstable when examined at a high magnification. On silica spheres, the only effect of e-beam irradiation is to cause necking of adjacent spheres. In conclusion, detection of "molecularly" dispersed phase by TEM appears possible due to the controlled surface texture of model oxide supports. These supports may therefore be of use in studies of dispersed transition metal oxides involving wetting and spreading.

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