

Structure of molybdenum dispersed in mesoporous titania

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The mesoporous titania prepared using a primary amine template has shown the BET surface area more than 1200 m²·g⁻¹ and uniform pore channels from 2.3 to 3.4 nm.[1] The bulk phase of titania is amorphous and approximately 37 % of the titanium atoms are 5-fold coordinated.[2] These features in the local structure have been found neither in rutile or anatase, which are composed of 6-fold coordinated Ti. Such anomalous valence of Ti will provide a unique coordination environment of catalytic active species when it is used as a support.[3] Since the catalyses of molybdenum oxide are also sensitive to the valence and coordination of the Mo (VI) ions, mesoporous titania possibly has extraordinary properties as a support material for molybdenum catalysts. We have investigated the structure of Mo (VI) incorporated into the support oxide as well as the catalytic performance.

The catalysts were prepared either by direct incorporation or by post-synthesis impregnation [3] using Mo(OC₂H₅)₅. The catalysts were decomposed and oxidized at 473 K, 573 K and 673 K. Mo K-edge XANES spectra were measured in BL-10B.

The Raman spectrum of 4.0 wt % Mo/meso TiO₂ (mesoporous titania supported molybdenum catalyst prepared by impregnation) showed the characteristic scattering of rutile at 153, 276, 412, 524, 612 and 821 cm⁻¹. On the other hand, those of 3.9 wt % Mo-meso TiO₂ (mesoporous titania supported molybdenum catalyst prepared by direct incorporation) showed peaks at 146, 318, 399, 517 and 637 cm⁻¹, which is assigned to the pattern of anatase. We have observed no significant pattern in Raman scattering in mesoporous titania. No bulk crystalline phase was observed in X-ray diffraction of these catalysts likely mesoporous titania. These observations in Raman spectroscopy and XRD imply that the crystallization of titania is promoted by impregnation or incorporation of Mo species, though the degree of extension is still too small to be detected by XRD, and post synthetic impregnation prompt the phase transfer into rutile phase while direct incorporation promotes the rearrangement of structure into anatase phase.

All Mo-K edge XANES spectra were normalized to compensate the difference in concentration and some of them for Mo/P-25 are shown in the figure. A peak appeared at ca. 1992 eV in the pre-edge region, which was attributed to 1s-4d transition, whose intensity has been used to estimate the deviation from the O_h structure. To evaluate the intensities of the pre-edge peak and compare them with the known structure, we subtracted backgrounds from normalized spectra to extract the peaks and integrated their areas.

The areas were distributed between those for K₂MoO₄ and MoO₃, implying the average symmetry molybdenum species of these catalysts are lower than O_h but higher than T_d. The degree of distortion was considered the same

between Mo-meso TiO₂ and Mo/meso TiO₂ in vacuum, which was higher than in Mo/P-25. Interestingly, the area for the impregnated catalysts, Mo/mesoTiO₂ and Mo/P-25, did not differ between the environments of powder while it decreased by the air exposure in the Mo-meso TiO₂. The increase of the symmetry is likely due to the adsorption and reaction of water. This result demonstrated that a significant amount of the molybdenum is exposed to the surface (not occluded into the framework) in Mo-meso TiO₂ and the distortion of them can be more easily relaxed than Mo/meso TiO₂. These two mesoporous catalysts are different in the catalytic nature even though the active element is supported on the same mesoporous oxide. The coordination environment of Ti (rutile-like or anatase-like) in mesoporous titania, which is inevitably accompanied with abnormality in the chemical bond, is possibly related to the difference in these Mo catalysts.

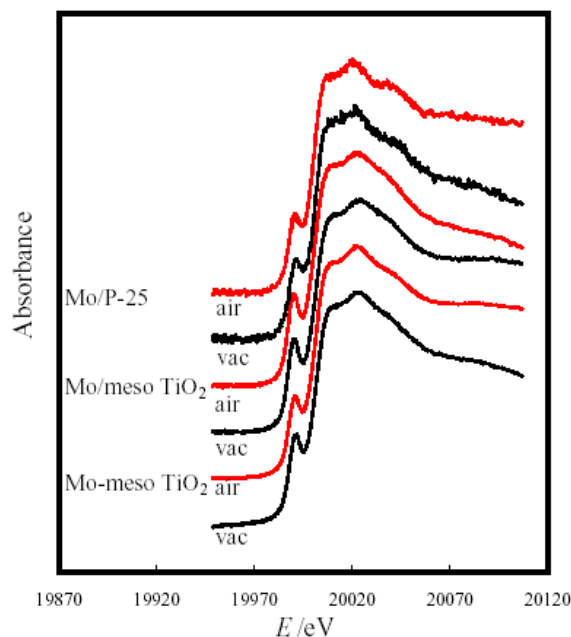


Figure Mo K-edge XANES spectra of P-25 and mesoporous titania-supported molybdenum catalysts.

References

- [1] H. Yoshitake et al., *Chem. Mater.* 14, 1023 (2002).
- [2] H. Yoshitake et al., *PCCP* 5, 767 (2003).
- [3] H. Yoshitake and T. Tatsumi, *Chem. Mater.* 15, 1695 (2003).

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