UV-Raman Characterizations of MoO_3/ZrO_2 Catalysts with Extremely Low MoO_3 Loadings

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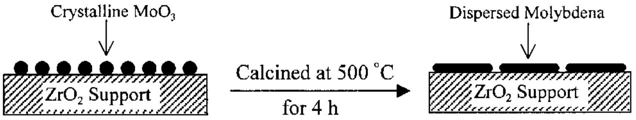
UV-Raman spectroscopy was first used and proved to be a powerful tool for the characterization of the surface molybdenum oxide species supported on ZrO_2, especially for samples with extremely low MoO_3 loadings due to the Raman bands of the surface molybdenum oxide species are greatly enhanced by this method. Only one kind of molybdenum oxide species was detected in samples with very low to near a mono-layer coverage of MoO_3 loading, and it is suggested that the structure of the highly dispersed molybdenum species is inevitably related to the structure of the support.

Supported molybdena catalysts are widely used in various catalytic processes, and the structure of the surface molybdenum oxide species on different oxide supports (particularly on Al_2O_3 and SiO_2) have been extensively investigated by using various techniques in the past decade.[1–5] In comparison to the MoO_3/Al_2O_3 and MoO_3/SiO_2 catalyst systems, relatively few studies have been carried out on the structure of the molybdenum oxide on ZrO_2.[6–8] Although ZrO_2, as a potential support, has been used to prepare supported transition metal oxide catalysts for oxidative reactions, the structure of the dispersed molybdenum oxide species are still not well characterized, which might because of the fact that the Raman signals of the surface molybdenum oxide species as compared to that of ZrO_2 support are rather weak, especially in the low-frequency region and for the catalysts with extremely low MoO_3 loadings.

A powerful tool for the characterization of the surface molybdenum oxide species will be helpful in clarifying the confusions on the surface structure of the supported molybdenum oxide species and its dependence on the structure of the supports.

UV-Raman spectrograph is a sensitive tool for these purposes as it can significantly improve the quality of the Raman signals of the supported molybdena species.[9, 10] In this letter, UV-Raman results of the MoO_3/ZrO_2 catalysts with extremely low MoO_3 loadings have been presented for the first time. In comparison to the conventional Raman, it has been proved that the resonance bands due to the stretching of the terminal Mo=O were greatly enhanced when the charge-transfer transition was excited by a UV laser source.

UV-Raman spectra were recorded on a homemade UV-Raman spectrograph with a continuous-wave (CW) UV line at 244 nm as the source. The UV line was from a Coherent Innova 300 Fred CW UV laser equipped with an intracavity frequency-doubling system based on a β-barium borate (BBO) crystal. A spectrograph system was set up with a UV sensitive CCD (Spex) and a triplemate. The MoO_3/ZrO_2 catalysts were prepared analogously to the reported procedure of MoO_3/CeO_2 preparation;[11] catalyst B, 0.05 mmol MoO_3/100 m^2 ZrO_2; catalyst C, 0.6 mmol MoO_3/100 m^2 ZrO_2.



UV-Raman spectra of the MoO_3/ZrO_2 samples with different MoO_3 loadings are shown in Figure 1. Raman bands for the crystalline MoO_3 are essentially featureless due to the strong ultraviolet absorption of MoO_3. Peaks below 700 cm^{-1} corresponding to the tetragonal zirconia (t-ZrO_2) support [12] are shown in Figure 1A. The spectrum of the sample (catalyst B) with an extremely low MoO_3 loading, i.e., 0.05 mmol MoO_3/100 m^2 ZrO_2 (~0.5 wt% MoO_3) is shown in Figure 1B. The relative intensities of the t-ZrO_2 peaks are decreased obviously with the increase of MoO_3 loading, which implies that the surface of t-ZrO_2 are gradually covered by the molybdenum oxide species highly dispersed on it. The peaks 910 and 840 cm^{-1} are assigned to the symmetric and asymmetric stretching of the terminal Mo=O bonding, respectively. And the peak at 1820 cm^{-1} is apparently the double frequency band of 910 cm^{-1}. One can see from Figure 1, the intensity of the 910 cm^{-1} is increased when the MoO_3 loadings from 0.05 to 0.6 mmol MoO_3/100 m^2 ZrO_2. Our complementary XRD results have proved the absence of the crystalline MoO_3 in these two samples, thus the above results suggest that the molybdenum oxide is highly dispersed on the surface of ZrO_2 and more importantly there is only one kind of the highly dispersed species existed. Noteworthy, as reported in the literature, the 910 cm^{-1} band used to be attributed to the isolated surface MoO_4 species by direct comparison to the spectrum of MoO_4^{2-} species in solu-

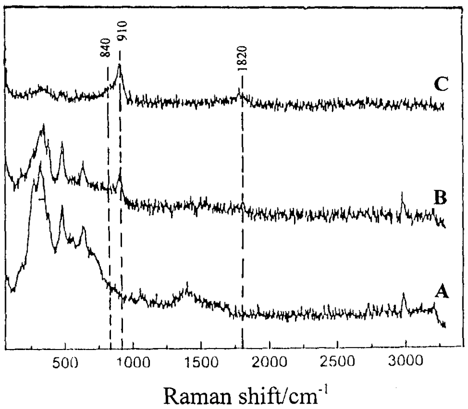


Figure 1. UV-Raman spectra of MoO_3/ZrO_2 catalysts with different MoO_3 loadings. (A) ZrO_2; (B) 0.05 mmol MoO_3/100 m^2ZrO_2; and (C) 0.6 mmol MoO_3/100 m^2ZrO_2.

tion, and it was argued that the polymerization of MoO_4 species will occur with the increase of MoO_3 loading (to a similar loading amount used in this study) [13]. Our result is apparently in contrast to these conclusions, as if the polymerization happened there should be at least two kinds of different species on the surface, i.e., at least two corresponding UV-Raman peaks should have been detected.

Along these lines and in connection with our result on the dispersion of MoO_3 on other supports, such as on γ-alumina and on ceria, it is suggested that the structures of the surface dispersed molybdenum oxide species are strongly related to the structure of the support. Accordingly, the structure of the surface dispersed molybdena species on t-ZrO_2 is tentatively assigned to a highly distorted 7-coordinated molybdenum oxide species, as shown in Figure 2, formed by the incorporation of Mo^{6+} ions into the surface vacant sites on the preferentially exposed (111) plane of t-ZrO_2[14,15] as described by the incorporation model reported previously.[16,17] Due to the distorted structure of t-ZrO_2, the four lattice O^{2-} ions of t-ZrO_2 are not completely equal (Zr–O_I = 2.065 Å, Zr–O_{II} = 2.455 Å),[14,15] the influence of O_{II} ion on Mo^{6+} is significantly weaker than those of the other three O_I ions. Therefore, this structure is more or less similar to the 6-coordinated molybdenum oxide species formed by the incorporation of Mo^{6+} in the tetrahedral sites of γ-Al_2O_3.

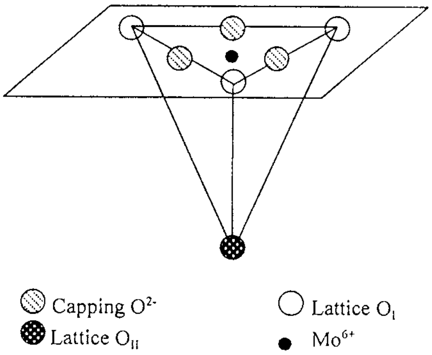


Figure 2. The schematic diagram for the incorporated Mo^{6+} ions in the surface vacant sites on the (111) plane of t-ZrO_2.

The above results lead to the conclusion that in comparison to the conventional Raman, UV-Raman is more sensitive and unique in characterizing the structure of the highly dispersed molybdenum oxide species on ZrO_2, in particular with samples of extremely low MoO_3 loadings. And there is no polymerization between the highly dispersed MoO_3 occurred at least in loading range of 0.05 to 0.6 mmol MoO_3/100 m^2ZrO_2.

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