

UV-Raman Characterizations of MoO₃/ZrO₂ Catalysts with Extremely Low MoO₃ Loadings

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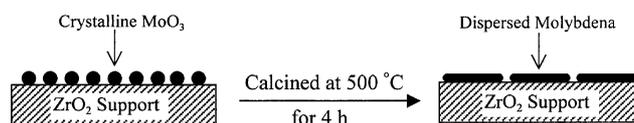
UV-Raman spectroscopy was first used and proved to be a powerful tool for the characterization of the surface molybdenum oxide species supported on ZrO₂, especially for samples with extremely low MoO₃ loadings due to the Raman bands of the surface molybdenum oxide species are greatly enhanced by this method. Only one kind of molybdenum oxide species was detected in samples with very low to near a mono-layer coverage of MoO₃ 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 Al₂O₃ and SiO₂) have been extensively investigated by using various techniques in the past decade.¹⁻⁵ In comparison to the MoO₃/Al₂O₃ and MoO₃/SiO₂ catalyst systems, relatively few studies have been carried out on the structure of the molybdenum oxide on ZrO₂.⁶⁻⁸ Although ZrO₂, 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 be because of the fact that the Raman signals of the surface molybdenum oxide species as compared to that of ZrO₂ support are rather weak, especially in the low-frequency region and for the catalysts with extremely low MoO₃ 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 MoO₃/ZrO₂ catalysts with extremely low MoO₃ 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 MoO₃/ZrO₂ catalysts were prepared analogously to the reported procedure of MoO₃/CeO₂ preparation;¹¹ catalyst B, 0.05 mmol MoO₃/100 m² ZrO₂; catalyst C, 0.6 mmol MoO₃/100 m² ZrO₂.



UV-Raman spectra of the MoO₃/ZrO₂ samples with different MoO₃ loadings are shown in Figure 1. Raman bands for the crystalline MoO₃ are essentially featureless due to the strong ultraviolet absorption of MoO₃. Peaks below 700 cm⁻¹ corresponding to the tetragonal zirconia (t-ZrO₂) support¹² are shown in Figure 1A. The spectrum of the sample (catalyst B) with an extremely low MoO₃ loading, i.e., 0.05 mmol MoO₃/100 m² ZrO₂ (~0.5 wt% MoO₃) is shown in Figure 1B. The relative intensities of the t-ZrO₂ peaks are decreased obviously with the increase of MoO₃ loading, which implies that the surface of t-ZrO₂ 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 MoO₃ loadings from 0.05 to 0.6 mmol MoO₃/100 m² ZrO₂. Our complementary XRD results have proved the absence of the crystalline MoO₃ in these two samples, thus the above results suggest that the molybdenum oxide is highly dispersed on the surface of ZrO₂ 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 MoO₄ species by direct comparison to the spectrum of MoO₄²⁻ species in solu-

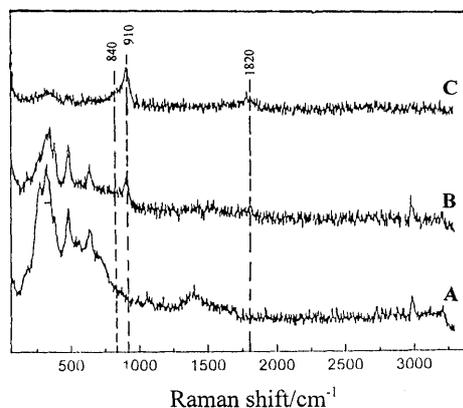


Figure 1. UV-Raman spectra of MoO₃/ZrO₂ catalysts with different MoO₃ loadings. (A) ZrO₂; (B) 0.05 mmol MoO₃/100 m²ZrO₂; and (C) 0.6 mmol MoO₃/100 m²ZrO₂.

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 ($\text{Zr}-\text{O}_I = 2.065 \text{ \AA}$, $\text{Zr}-\text{O}_{II} = 2.455 \text{ \AA}$),^{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 $\gamma\text{-Al}_2\text{O}_3$.

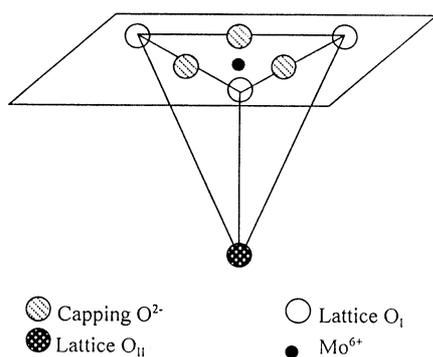


Figure 2. The schematic diagram for the incorporated Mo^{6+} ions in the surface vacant sites on the (111) plane of t- ZrO_2 .

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 $\text{MoO}_3/100 \text{ m}^2\text{ZrO}_2$.

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