

RESEARCH NOTE

Surface Coordination Structure of Molybdate with Extremely Low Loading on γ -Alumina Characterized by UV Resonance Raman SpectroscopyGuang Xiong, Can Li,¹ Zhaochi Feng, Pinliang Ying, Qin Xin,¹ and Jianke Liu*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China*

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The extremely low loading of molybdate on γ -Al₂O₃ (0.1 wt% MoO₃/ γ -Al₂O₃) is characterized by UV resonance Raman spectroscopy. Thanks for the resonance Raman effect, the surface coordination structure of molybdate is well identified. For the first time, the surface octahedral molybdate and the tetrahedral species are detected, even with molybdate loading down to 0.1 wt%. This study suggests that the octahedral molybdate is formed on γ -Al₂O₃ at all molybdate loadings. © 1999 Academic Press

INTRODUCTION

Molybdate supported on γ -alumina with high loadings has been extensively characterized by conventional Raman spectroscopy (1, 2), as this is an important catalyst or catalyst precursor for a variety of reactions (3–5). Two kinds of surface molybdate species, tetrahedral and octahedral, are believed to exist on the support (6, 7). It is assumed that the tetrahedral species is formed at all loadings, while its octahedral counterpart begins to appear only when the loading exceeds a limit, and then the amount of octahedral species increases as the loading increases. The crystalline MoO₃ phase is usually detectable when the molybdate loading is about or higher than one monolayer (6–8).

However, past Raman spectroscopic studies on supported molybdate mainly concentrated on high loading catalysts. For the low-loading ones, it is hard to get the Raman spectra because of strong fluorescence interference and the low sensitivity of conventional Raman spectrometers. Obviously, a study on low-loading molybdate will provide more definitive information about the initial coordination structure of the supported species and the interaction between the surface species and the support, while the study with high loadings gives information mainly of the supported molybdate phase itself. Hence, the study on molybdate with low loadings will supply the knowledge of

how the molybdate species first interacts with support and then evolves with increasing loading, and about any other factors governing the synthesis process of the supported molybdate. In this paper, we report the characterization of γ -alumina-supported molybdate catalysts with low loadings, using a new technique, UV Raman spectroscopy. For the first time, the surface species of extremely-low-loading molybdate (down to 0.1 wt% MoO₃) on γ -alumina are well identified.

Recently, a UV resonance Raman spectrometer, specially designed for the characterization of catalytic materials, was set up in this laboratory. Fluorescence interference from the catalyst surface can be avoided successfully using this technique (9–11). Since the Raman scattering cross section is larger using a laser line with a shorter wavelength, the sensitivity of UV Raman spectroscopy is higher than that of visible or near-IR Raman spectroscopy. Moreover, when the UV laser line is close to an electronic absorption band of the material, the resonance or preresonance effect will enhance the Raman intensity by several orders of magnitude. As a result, the intensity of the UV Raman signal is greatly enhanced compared with that of the visible Raman ones. Owing to the high sensitivity and the absence of fluorescence of UV Raman spectroscopy, it is possible for us to obtain the vibrational spectra of low-loading molybdate species, which are usually difficult to achieve by conventional Raman spectroscopy.

To distinguish the coordination structure of the low-loading molybdate based on the resonance selective enhancement of the Raman bands of tetrahedral and octahedral species, the laser line for Raman spectroscopy is chosen to excite the electronic absorption of the species. The Mo=O bond of tetrahedral molybdate and Mo–O–Mo bridge bond of the octahedral species possess electronic absorptions at 220–250 and 320 nm, respectively. Accordingly, the laser lines at 244 and 325 nm are chosen as the excitation sources to record the UV resonance Raman spectra. The 488-nm line is also used to get normal Raman spectra as a reference.

¹ To whom correspondence should be addressed. Fax: 86-411-4694447 or 4691570. E-mail: canli@ms.dicp.ac.cn.

METHODS

A low-loading molybdate catalyst, denoted as $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ (0.1 wt% MoO_3), was prepared by incipient wetness impregnation as follows: $\gamma\text{-Al}_2\text{O}_3$ ($S_{\text{BET}} = 242 \text{ m}^2/\text{g}$, Phôe-Poulence) was impregnated with an aqueous solution of ammonium heptamolybdate (AHM), and the wet sample was dried at 393 K and then calcined at 773 K.

UV Raman spectra were recorded on a homemade UV Raman spectrometer which has four main parts: a UV cw laser, a Spex 1877 D triplemate spectrograph, a CCD detector, and an optical collection system. The 244.0- and 488.0-nm lines from Innova 300 FRED and a 325.0-nm line from a He-Cd laser were used as the excitation sources. The 244-nm line is generated by frequency doubling of the 488-nm line via a cw intracavity frequency doubling crystal. The laser powers at the sample were kept below 2.0 mW for 244.0 nm, 2.0 mW for 325.0 nm, and 100 mW for 488 nm, respectively. A triplemate spectrograph (SPEX 1877 D spectrograph 0.6 m, $f/6.3$) was used with a manually set prefiller stage and a computer-controlled spectrograph grating. A 180° collection geometry was used to collect the scattered Raman light. Samples were mounted into a spinning holder to avoid thermal damage during the scanning. The spectral resolution was estimated to be 1.0 cm^{-1} . The acquisition time is 10 min. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV-365 UV-VIS-NIR recording spectrophotometer, and a pure alumina support was used as a reference.

RESULTS AND DISCUSSION

Figure 1 shows the UV-visible diffuse reflectance spectrum of 0.1 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$. Two broad bands centered at 220 and 290 nm are observed. In general, three bands at 220–250, 280, and 320 nm are detected in the UV-visible diffuse reflectance spectrum of supported molybdate (12). The bands at 220–250 nm are commonly attributed to the tetrahedral molybdate, while the band at 320 nm is assigned to the Mo–O–Mo bridge bond of the octahedral molybdate. The band at 280 nm has been assigned to monomer, dimer, and polymerized molybdate species, respectively, but the assignment is not well clarified yet (13–15). The band at 290 nm in Fig. 1 is quite broad; its tail extends to 350 nm. The broad band at 280–350 nm can be considered as an overlap of the two bands at 280 and 320 nm. Therefore, the laser sources, 244- and 325-nm lines, are just in the regions of the absorption bands of tetrahedral and octahedral molybdate respectively.

Figure 2 shows the Raman spectra of 0.1 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ excited by 244-, 325-, and 488-nm lines, respectively. The visible Raman spectrum of the sample shows no Raman signal except for the strong fluorescence background. This is the same as most reports in the literature. However, using

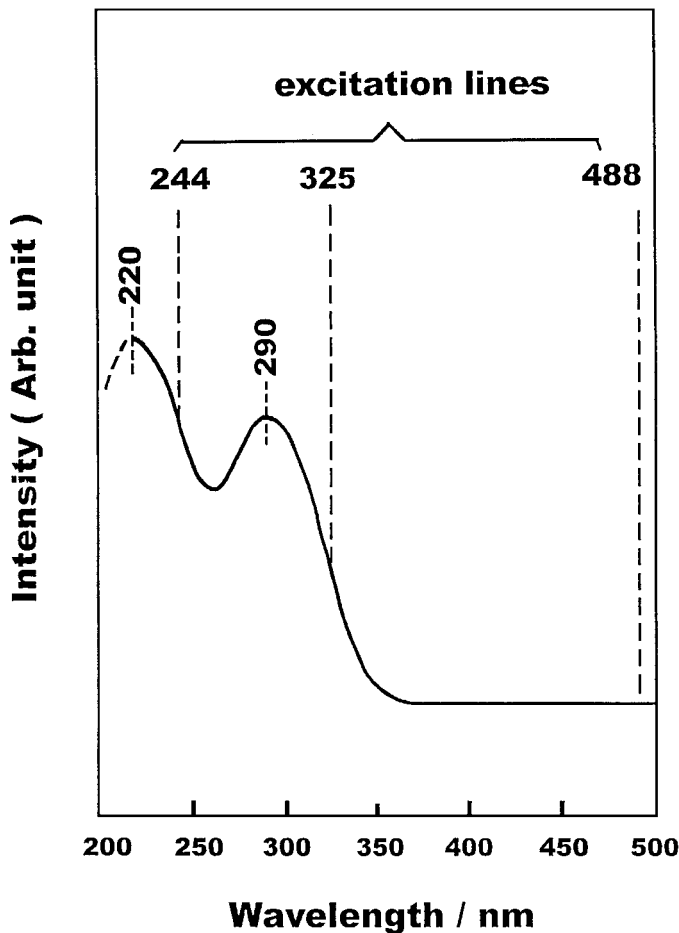


FIG. 1. UV-visible diffuse reflectance spectrum of 0.1 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$.

UV Raman spectroscopy, the sample excited by the 244- and 325-nm lines exhibits nice spectra with strong Raman signals.

The UV Raman spectrum excited by a 244-nm line gives the Raman bands at 325, 910, 1802, and 2720 cm^{-1} (Fig. 2a). The 325- and 910-cm^{-1} bands are attributed to the bending and symmetric stretching modes of the Mo=O bond of the tetrahedral molybdate, respectively. The bands at 910, 1802, and 2720 cm^{-1} are respectively the fundamental-, double-, and triple-frequency bands of the tetrahedral Mo=O bond because the frequencies of the latter two are approximately the double and triple of the band at 910 cm^{-1} . The 1802- and 2720-cm^{-1} bands were never detected in visible Raman spectra for supported molybdate because there is no resonance effect in the visible region. It is the resonance effect that makes the overtone bands greatly enhanced since the 244-nm line is located in the electronic absorption band of the tetrahedral Mo=O bond.

Figure 2 shows that for the low-loading molybdate the Raman signals of surface molybdate species cannot be detected by conventional Raman spectroscopy. The 244- and

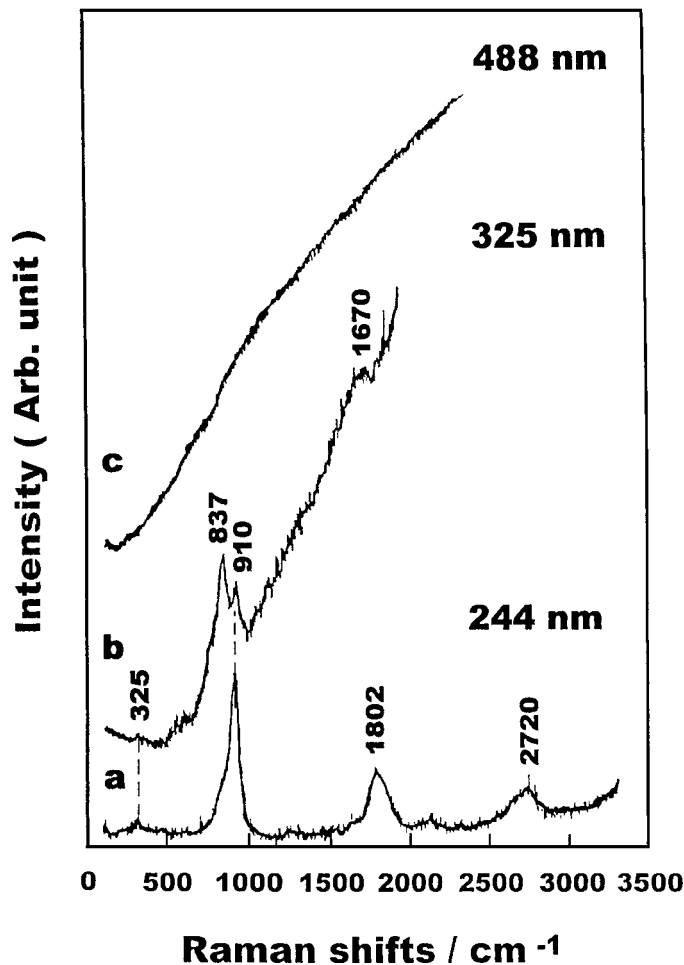


FIG. 2. Raman spectra of 0.1 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ using 244-nm (a), 325-nm (b), and 488-nm (c) lines as the excitation sources.

325-nm lines are just in the electronic absorption regions of tetrahedral and octahedral species, respectively. Accordingly, the Raman intensities of the tetrahedral and octahedral species are enhanced greatly. The UV resonance Raman effect makes it possible to characterize the coordination structure of the extremely-low-loading molybdate species.

As shown in Fig. 2b, there are four Raman bands at 325, 837, 910, and 1670 cm^{-1} detectable for the 0.1 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ excited by the 325-nm line. The 325- and 910- cm^{-1} bands are assigned to the bending and symmetric stretching modes of the $\text{Mo}=\text{O}$ bond of the tetrahedral molybdate. Compared with the Raman spectrum excited by 244 nm, two new bands at 837 and 1670 cm^{-1} are detected. The two bands are assigned to the fundamental- and double-frequency bands of the asymmetric stretching mode of the $\text{Mo}-\text{O}-\text{Mo}$ bond of the octahedral species. Obviously, these bands are enhanced because the 325-nm laser line accesses the electronic transition absorption of the $\text{Mo}-\text{O}-\text{Mo}$ bridge bond. An additional band at 220 cm^{-1}

due to the deformation mode of the $\text{Mo}-\text{O}-\text{Mo}$ bond is not observed in this spectrum because the band is relatively weak or it is not resonance enhanced. It is clearly shown that not only the tetrahedral molybdate but also the octahedral molybdate species (polymolybdate) are detected for molybdate supported on a $\gamma\text{-Al}_2\text{O}_3$ catalyst, even with the loading down to 0.1 wt%. This is inconsistent with the general conclusion that only tetrahedral species are formed on the $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst with low-loading molybdate.

Wachs has proposed a model to predict the molecular structure of surface metal oxide supported on the high surface area oxide support (2). Under ambient conditions, the molecular structures of a hydrated surface metal oxide are found to be determined by the net pH at the pzc (point of zero charge) of the supported metal oxides. The surface molybdate with extremely low loading cannot change this pH value a lot. The pH value at pzc of the $\gamma\text{-Al}_2\text{O}_3$ support is 8.0 (16). Both isolated tetrahedral MoO_4^{2-} and polymerized octahedral $\text{Mo}_7\text{O}_{24}^{6-}$ appear in the solution at pH 8.0 (17). Therefore, it is reasonable that the octahedral molybdate is detected at the loading down to 0.1 wt%. In Fig. 2b only tetrahedral Raman bands at 325 and 910 cm^{-1} are detected if there is no resonance Raman effect. This indicates that the amount of octahedral molybdate is rather small at extremely low loading. It is consistent with the fact that the tetrahedral molybdate species predominates in the solution at pH 8.0.

CONCLUSION

UV resonance Raman spectroscopy is a powerful technique for the characterization of supported oxide catalysts. On the basis of the resonance Raman effect, the supported molybdate species with extremely low loading can be detected, and the coordination structure of the surface molybdate species can be well determined as well. The surface-polymerized octahedral species as well as the tetrahedral molybdate is detected by UV resonance Raman spectroscopy even for $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ with a loading of 0.1 wt%. This suggests that the octahedral molybdate species is formed at all loadings, including tetrahedral molybdate species for $\gamma\text{-Al}_2\text{O}_3$ support.

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