Catalysis Letters Vol. 96, Nos. 1–2, July 2004 (© 2004)

Potential of UV–Raman spectroscopy for characterization of sub-monolayer MoO_x model catalysts at ambient pressure

B.L. Mojet*,**, L. Coulier, J. van Grondelle, J.W. Niemantsverdriet, and R.A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 3 March 2004; accepted 8 April 2004

UV–Raman spectroscopy is demonstrated to be a valuable tool to study molybdenumoxide model catalysts at ambient pressure while visible light Raman yields no information. UV–Raman offers the possibility to characterize $MoO_x/Al_2O_3/Si$ and $MoO_x/SiO_2/Si$ model systems with sub-monolayer loading of MoO_x even though the surface area of a Si-wafer is much lower than that of a bulk support. Anchoring of MoO_x onto Al_2O_3/Si and SiO_2/Si results in similar molybdenum oxide compounds as for bulk catalysts.

KEY WORDS: UV–Raman; model catalysts; molybdenum oxide; catalyst characterization.

1. Introduction

Supported molybdenum oxides are widely known as catalysts for selective oxidation, oxidative coupling, or methathesis reactions, and as precursors for hydrodesulfurization catalysts [1,2]. Over the years, molybdenum catalysts have been extensively characterized by conventional Raman spectroscopy revealing different types of MoO_x phases depending on the support material, as recently reviewed by Mestl *et al.* [3,4]. In general the detected species are a mixture of monomers, (MoO_4^{2-}), oligomers ($Mo_7O_{24}^{6-}$), other polymeric species, and crystalline MoO_3. The final structure appears to depend upon an inherent chemical interaction between the support material and precursor state of the molybdenum. It was shown recently that UV–Raman spectroscopy of low-loading $MoO_3/\gamma\text{-}Al_2O_3$ could successfully be used to investigate the structure of the MoO_x phase [5,6]. Due to a resonance effect both tetrahedral and octahedral molybdate species were detected even at a loading of 0.1 wt% MoO_3.

In general, application of UV–Raman ($\lambda < 300$ nm) to study inorganic materials has been shown to successfully circumvent the problem of fluorescence and heat radiation interfering with the Raman signals [7]. Furthermore, when the laser energy is close to an electronic absorption band of the investigated material resonance effects may enhance the Raman intensity by several orders of magnitude [8]. Recently, a comparison was published of ultraviolet and visible Raman spectra of supported metal oxide catalysts, including MoO_x [9]. The authors concluded that only a modest resonance enhancement is observed in UV-excited Raman spectra, since the UV-excited spectra are similar to the visible excited spectra.

In addition to bulk catalysts, model catalyst systems are investigated to better understand the real active phase in catalysts. Model systems of molybdenum oxide catalysts have been extensively studied with techniques as XPS and infrared emission spectroscopy [10,11,12,13] which have to be performed under ultra-high-vacuum conditions. Although Raman spectroscopy showed to be an indispensable tool to study the different phases and coordination of Mo-species in catalysts the extremely low loading of active phase in model systems makes it very difficult to obtain Raman spectra with conventional Raman spectroscopy. Thus far only a limited number of studies has been published on Raman spectroscopy applied to supported thin metal oxide films [13]. Since anchoring of the active species onto the support has been shown to be vital for catalysis it is essential to identify the supported MoO_x species in model catalyst systems to assure a similarity between the model and the "real catalysts."

We demonstrate that UV–Raman offers the possibility to characterize $MoO_x/Al_2O_3/Si$ and $MoO_x/SiO_2/Si$ model systems with sub-monolayer loading of MoO_x. The data show that anchoring of MoO_x onto Al_2O_3/Si and SiO_2/Si results in similar molybdenum oxide compounds as for bulk catalysts.

2. Experimental

2.1. Sample preparation

Alumina model support was prepared by evaporation of Al_2O_3 onto a Si(100) wafer, resulting in a 5 nm layer of $\gamma\text{-}Al_2O_3$ as determined by XPS. A silica model

---

*To whom correspondence should be addressed.
E-mail: B.L.Mojet@utwente.nl

**Present address: University of Twente, Faculty of Science and Technology, P.O. Box 217, NL – 7500 AE Enschede, The Netherlands.

1011-372X/04/0700–0001/0 © 2004 Plenum Publishing Corporation

support was prepared by oxidizing a Si(100) wafer with a diameter of 75 mm in air at 750 °C for 24 h (sample SiO_2/Si). Rutherford backscattering experiments indicated that the SiO_2 layer was 90 nm thick. Atomic Force Microscopy measurements indicated that the roughness of the SiO_2 surface was below 5 Å. After oxidation the wafer was cleaned in a solution of ammonia and hydrogen peroxide at 65 °C for 10 min. The surface was rehydroxylated by boiling in water for 30 min.

Molybdenum was added by spin coating the wafers at 2800 rpm in N_2 with an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; Merck); pH 5–6. The concentration of Mo in the aqueous solution was adjusted to result in a loading of 6 or 25 Mo atoms/nm^2 after spincoating [14]. Calcination was carried out in a glass reactor under a 20% O_2/Ar flow at 1.5 bar. The catalyst was heated to 500 °C at a rate of 5°C/min and kept at the desired temperature for 30 min.

Samples are designated $MoO_x(x)/SiO_2/Si$ and $MoO_x(x)/Al_2O_3/Si$ with (x) denoting the number of metal atoms per nm^2. The samples were exposed to ambient air while Raman spectra were taken.

2.2. Visible light Raman spectroscopy

Visible light Raman experiments were performed on a Confocal Raman Microscope (Instruments SA Inc. – Olympus BX 40 microscope] in 180° backscattering geometry operated at $\lambda = 532$ nm. Data were collected in four spectra of 16 s (averaged into one data set) with a 10 × enlargement. Laser power was approximately 20 mW at the sample.

2.3. UV–Raman spectroscopy

The UV–Raman spectrometer was built based on improved concepts published before [7]. The focusing and collecting system consists of a set of flat mirrors and lenses instead of an ellipsoidal mirror. All optical parts are made of very pure quartz to limit the absorbance of UV-light. The spectrometer is equipped with a Lexel 95-SHG frequency doubled Argon$^+$ laser operated at $\lambda = 244$ nm. The detecting system is a T64000 triple-stage spectrometer of Jobin Yvon S.A. equipped with two 24,000 cm^{-1} gratings and a specially coated UV-sensitive CCD detector. Spectra were taken in air using 90° scattering geometry on a static sample with laser powers between 1 and 3 mW at the sample (spot size ~100 μm^2) to avoid heating of the surface. Each spectrum was collected for 300 s; four spectra were averaged to increase S/N ratio. All spectra have been calibrated using the gas phase N_2 stretching frequency at 2330 cm^{-1}. Reproducibility of data for all samples was checked by taking spectra at different spots on the same wafer and by examining freshly prepared samples.

3. Results and discussion

3.1. $MoO_x/Al_2O_3/Si$

The visible light Raman spectra of an oxidized Si-wafer, Al_2O_3/Si and $MoO_x(6)/Al_2O_3/Si$ are shown in figure 1. The spectra are practically identical, even between 900 and 1050 cm^{-1} where characteristic Mo=O stretching frequencies were expected. The sharp peak at 520 cm^{-1} can be attributed to Si–Si stretching, while the Raman scattering between 900 and 1100 cm^{-1} can be assigned to silicon overtones from the wafer. Alumina signals cannot be observed, since γ-Al_2O_3 is Raman inactive between 100 and 1200 cm^{-1}[3]. The data clearly show that visible light Raman is not an option to detect sub-monolayers of molybdenum oxide on Al_2O_3/Si wafers, since the Mo–O signals seem to be obscured by the Raman spectrum of the plain wafer.

Figure 2 shows the spectra of Al_2O_3/Si and $MoO_x(6)/Al_2O_3/Si$ obtained with UV–Raman. The difference in the spectra compared to those taken with visible light (figure 1) is striking. Although a small Si–Si signal was observed at 520 cm^{-1} hardly anything was visible in the 900 – 1100 cm^{-1} range for Al_2O_3/Si. After deposition of molybdenum clear molybdenum–oxygen stretching vibrations were observed between 800 and 1000 cm^{-1}, with overtones present between 1700 and 1900 cm^{-1}.

The observed broad Raman bands indicate that the supported particles consist of a mixture of different molybdenum oxides. The maximum of the Raman signal of $MoO_x(6)/Al_2O_3/Si$ is located around 947 cm^{-1}, and can be attributed to Mo=O stretching in a hydrated tetrahedral molybdenum oxide structure on Al_2O_3 [4]. Since no bands were observed above 1000 cm^{-1}, no molybdenum aluminate phase has been formed ($Al_2(MoO_4)_3$ is around 1030 cm^{-1}). The broad

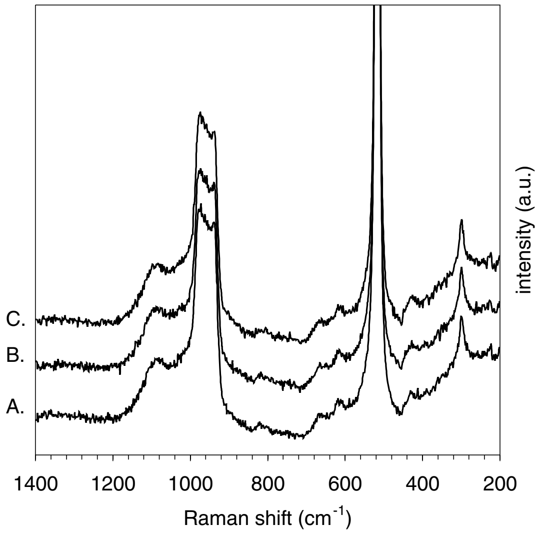

Figure 1. Visible light Raman spectra ($\lambda = 532$ nm) of (a) oxidized Si-wafer, (b) Al_2O_3/Si and (c) $MoO_x/Al_2O_3/Si$ (spectra are arbitrarily shifted along y-axis for clarity).

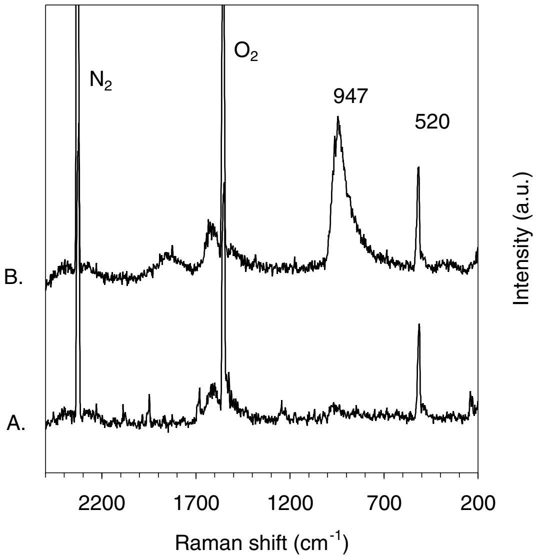

Figure 2. UV–Raman spectra ($\lambda = 244$ nm) of (a) Al_2O_3/Si and (b) MoO_x(6)/Al_2O_3/Si (spectra are arbitrarily shifted along y-axis for clarity).

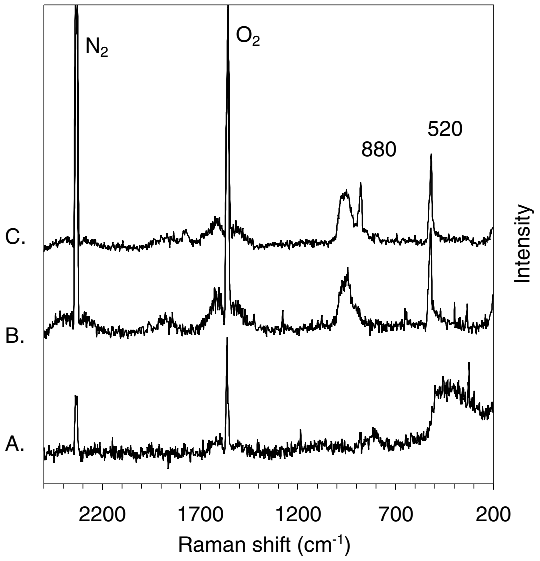

Figure 3. UV–Raman spectra ($\lambda = 244$ nm) of (a) SiO_2/Si, (b) MoO_x(6)/SiO_2/Si and (c) MoO_x(25)/SiO_2/Si (spectra are arbitrarily shifted along y-axis for clarity).

tailing between 900 and 800 cm^{-1} can be attributed to polymolybdate structures.

Recently, Xiong *et al.* reported on a resonance effect observed for low-loading MoO_x–γ-Al_2O_3 [5]. Spectra were presented with specific Raman signals at 910 and 1802 cm^{-1}, attributed respectively, to Mo=O stretching in an isolated tetrahedral MoO_4^{2-} species and its overtone. In the present study the sharp signals from isolated tetrahedral MoO_4^{2-} were not observed. Thus, low loading MoO_x on bulk alumina has a different structure compared to sub-monolayer MoO_x on Al_2O_3/Si, which exhibits a Raman spectrum similar to a bulk catalyst.

3.2. MoO_x/SiO_2/Si

Since the type of support material affects the final type of molybdenum oxide, model catalysts of MoO_x on SiO_2/Si were prepared as well. SiO_2/Si showed a weak Raman scattering intensity for UV-light below 500 cm^{-1} since most of the UV-radiation was absorbed by the amorphous silica (figure 3a). MoO_x(6)/SiO_2/Si showed only a broad band from molybdenum oxide species was detected between 900 and 1050 cm^{-1} as well as its overtones between 1800 and 1900 cm^{-1} (figure 3(B)). Increasing metal oxide loading to 25 atoms/nm^2 resulted in an additional band at 880 cm^{-1} (figure 3c). For MoO_x(6)/SiO_2/Si the maximum of the broad band shifted to higher wavenumbers (~956) compared to MoO_x(6)/Al_2O_3/Si. This can be attributed to Mo=O stretching vibrations from to surface polymolybdate species on SiO_2 as reported in literature [4,15]. The relatively sharp peak at 880 cm^{-1} present at high molybdenum oxide loading can be assigned to hydrated polymolybdate species [16]. None of the spectra showed characteristic bulk MoO_3 vibrations (996, 820, 667 cm^{-1}) even at a high loading of 25 atoms/nm^2.

Remarkably, all samples except SiO_2/Si showed Si–Si stretching from the Si-wafer (520 cm^{-1}) reproducibly. It is well known that oxidation of a Si-wafer yields a fully covered SiO_2 layer on top of the Si wafer. However evaporation of Al_2O_3 onto Si(100) can result in small pinholes, causing a contribution of the Si-wafer to the Raman spectrum. Further, the SiO_2/Si wafers were modified using ammonia and hydrogen peroxide at 65 °C, followed by boiling water before molybdenum was added. This extra treatment may also result in defects in the SiO_2 layer.

3.3. General discussion

The difference in sensitivity between visible light Raman and UV-excited Raman for these MoO_x model catalysts can be explained by the resonance Raman effect. UV-absorbance spectra clearly show a UV-absorption band for supported molybdenum oxide, pointing to an enhancement of Raman signals [9]. Moreover, although UV-light penetrates the sample deeper due to its shorter wavelength than visible light, most of the UV-radiation is absorbed by the sample because of the high UV-absorbance capacity of amorphous SiO_2 and Al_2O_3. Consequently, only Raman scattering from surface species is detected. The data also show that the scattering intensity is lower for SiO_2 supported molybdenum oxide than for Al_2O_3 supported samples. This might be explained by stronger interaction of molybdenum oxide with Al_2O_3 than with SiO_2 in agreement with earlier observations on bulk samples [17]. As a result, Al_2O_3 supported samples have a higher metal oxide dispersion with more uniform structure, resulting in more intense Raman scattering.

The results of this study clearly demonstrate the possibility of UV–Raman spectroscopy for investigating sub-monolayer coverage of molybdenumoxide on SiO_2/Si or Al_2O_3/Si-wafers, opening up a new area of characterization of model systems at atmospheric pressure. For the first time the similarity in molybdenum oxide species is revealed for MoO_x model and bulk catalysts with UV–Raman spectroscopy. Further, the MoO_x structures vary in a similar way as a function of support material (Al_2O_3 versus SiO_2) for model systems as for bulk catalysts.

Acknowledgment

The National Research School Combination – Catalysis by Chemical Design is gratefully acknowledged for financial support.

References

[1] J. Haber, Stud. Inorg. Chem. (1994) 477.
[2] H. Topsøe, B.S. Clausen and F.E. Massoth, *Hydrotreating Catalysis* (Springer-Verlag, Berlin, 1996).
[3] I.E. Wachs, Catal. Today 27 (1996) 437.
[4] G. Mestl and T.K.K. Srinivasan, Catal. Rev.-Sci. Eng. 40(4) (1998) 451 and references therein.
[5] G. Xiong, C. Li, Z. Feng, P. Ying, Q. Xin and J.J. Liu, J. Catal. 186 (1999) 234.
[6] G. Xiong, Z. Feng, J. Li, Q. Yang, P. Ying, Q. Xin and C. Li, J. Phys. Chem. B 104 (2000) 3581.
[7] P.C. Stair and C. Li, J. Vac. Sci. Technol. A 15(3) (1997) 1679.
[8] B. Schrader and D. Bougeard, *Infrared and Raman Spectroscopy: Methods and Applications* (VCH, Weinheim, 1995).
[9] Y.T. Chua, P.C. Stair and I.E. Wachs, J. Phys. Chem. B 105 (2001) 8600.
[10] A.M. de Jong, H.J. Borg, L.J. van Ijzendoorn, V.O.M.F. Saudant, V.H.J. de Beer, J.A.R. van Veen and J.W. Niemantsverdriet, J. Phys. Chem. 97 (1993) 6477.
[11] J.C. Muijsers, Th. Weber, R.M. van Hardeveld, H.W. Zandbergen and J.W. Niemantsverdriet, J. Catal. 157 (1995) 698.
[12] A. Jimenez-Gonzalez and D. Schmeisser, J. Catal. 130 (1991) 332.
[13] P.A. Spevack and N.S. McIntyre, J. Phys. Chem. 97 (1993) 11020.
[14] R.M. van Hardeveld, P.L.J. Gunter, L.J. van IJzerdoorn, W. Wieldraaijer, E.W. Kuipers and J.W. Niemantsverdriet, Appl. Surf. Sci. 84 (1995) 339.
[15] T. Ono, M. Anpo and Y. Kubokawa, J. Phys. Chem. 90 (1986) 4780.
[16] H. Jeziorowski and H. Knozinger, J. Phys. Chem. 83 (1979) 1166.
[17] T. Fransen, P.C. van Berge and P. Mars, in: *Preparation of Catalysts* (Elsevier, Amsterdam, 1976) p. 405.