Monitoring of molybdenum H-ZSM5 catalyst preparation by *in situ* ultraviolet Raman spectroscopy

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Received 26 January 2001; accepted 14 March 2001

In situ ultraviolet Raman spectroscopy was used to follow the preparation of Mo/H-ZSM5 catalysts by thermal treatment of a physical mixture of MoO_3 and H-ZSM5. The Raman spectra recorded from 300 to 1800 cm^{-1} during the thermal treatment showed that MoO_3 spread over the zeolite support to form dispersed molybdenum oxide species. Curve-fitting analysis of the overall spectral profile for the samples after treatment at 600 °C in O_2 showed the presence of three spectral components at 962, 868 and 815 cm^{-1}. The band at 815 cm^{-1} was assigned to the zeolite support. The most intense band at 962 cm^{-1} could be attributed to terminal Mo=O groups of isolated tetrahedrally coordinated monomers and the weaker band at 868 cm^{-1} to bridging Mo–O–Mo groups of dimeric species. These last two assignments are not definitive and may be due to other unique structures of oxides of molybdenum on the zeolite framework.

KEY WORDS: UV Raman spectroscopy; molybdenum oxide; ZSM5

1. Introduction

Supported molybdenum oxide is widely used as a catalyst or a precursor in various catalytic processes: metathesis, oxidation and hydrogenation of hydrocarbons, water–gas shift, CO hydrogenation, hydrodesulfurization and hydrodenitrogenation. More recently, Wang et al. [1] showed that molybdenum oxide supported on H-ZSM5 is effective in the non-oxidative conversion of methane into liquid fuels. The objective of this contribution is to report results of *in situ* ultraviolet (UV) Raman monitoring of the process of catalyst preparation from a physical mixture of MoO_3 and H-ZSM5 via solid-state exchange at elevated temperatures. It is well known that the surface properties of molybdenum oxide species strongly depend on the oxide support and thus will influence its catalytic behavior. Raman spectroscopy has been a useful technique in the study of molybdenum oxide catalysts, as reviewed by Mestl and Srinivasan [2]. However, there have been very few Raman studies on zeolites probably because they show a strong fluorescence band, which is thought to originate from transition metal ions (Fe^{3+}, Cr^{3+} or Mn^{2+}) [3] or organic impurities absorbed from ambient air [4]. The strong fluorescence signal usually overwhelms the much weaker Raman signal. In contrast to conventional Raman spectroscopy where the excitation laser is in the visible region, the use of laser excitation in the UV spectral region provides a unique opportunity to avoid both fluorescence and interference of thermal emission at high temperatures. The conclusion of this contribution is that MoO_3 interacts strongly with the zeolite surface during preparation forming new molybdenum oxide structures.

2. Experimental

The Mo/H-ZSM5 samples were prepared from a mixture of MoO_3 (Johnson Matthey, Puratronic, 99.9995%) and H-ZSM5 powder by grinding the mixture in a mortar. The mixtures are reported by weight of MoO_3. Fully exchanged H-ZSM5 was obtained by ion exchange of a ZSM5 sample from UOP with a Si to Al ratio of 61 with NH_4NO_3 at 80 °C for 4 h. The exchange was repeated three times, followed by drying overnight at 110 °C and calcination at 500 °C for 4 h.

About 0.1 mg of the sample was pressed into a wafer of 1 mm thickness. The reactor cell was similar to the one described by Li and Stair [5]. The wafer was then placed into a quartz cell. The cell was heated with an external coiled heater and a gas flow could be established through the cell. The Raman signal could be collected while gas flowed through the cell at temperatures up to 600 °C.

Raman spectra of the zeolite-supported molybdenum oxide catalyst were collected on a setup similar to the one described by Li and Stair [6]. The excitation UV laser light was generated with an Ar-ion laser (Lexel model 95). The 244 nm excitation laser line in this laser is produced with a nonlinear BBO crystal (second harmonic of 488 nm), which is housed inside the laser resonance cavity. High efficiency rejection of Ar-ion laser plasma lines was ensured by a 240 nm blazed diffraction grating combined with an iris diaphragm. The laser beam power was kept at about 2 mW at the sample to prevent possible laser-induced local decomposition of MoO_3. The scattered light was collected

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in a back-scattered geometry arrangement using an Al mirror coated with MgF_2 and shaped in the form of an elliptical reflector. An objective and focusing lens directed the collected light into a Spex 1877 Triplemate triple spectrometer for rejection of Rayleigh scattering and imaging into a circular array of single-photon counting photomultipliers, model 2601B Mepsicron single-photon imaging detector (Quantar Technology Inc.). The detector was cooled thermoelectrically to about −28 °C to decrease thermal noise.

The Raman spectra were collected and recorded using OxfordWin Software (Oxford Instruments, Inc.). Second-derivative analysis and curve fitting of complex spectral profile were made with the use of GRAMS/32 Software package (Galactic Inc.).

The instrumental resolution and reproducibility was experimentally determined to be better than 5 cm^{-1}. All measurements were made starting at room temperature (RT) to a final temperature of 600 °C and under a continuous flow of dry O_2 at atmospheric pressure. The temperature was increased in 100 °C steps at a heating rate of 3 °C min^{-1}. The time of spectral accumulation was about 1 h at each temperature.

3. Results and discussion

The *in situ* UV Raman spectroscopy of crystalline MoO_3 and the H-ZSM5 support were measured to serve as standards. The reversible changes in their crystalline structures during the cycle of gradual heating from room temperature (RT) to 600 °C and back to RT in O_2 flow is shown in figure 1. In the Raman spectrum of pure MoO_3 the spectral band at 820 cm^{-1} is attributed to the asymmetric stretching vibration of the Mo–O–Mo bond and the band at 996 cm^{-1} is attributed to the symmetric stretching vibration of the Mo=O bond [2,7]. As the temperature is increased (figure 1) and also after cooling, a small decrease of intensity of the band at 996 cm^{-1} relative to the band at 820 cm^{-1} is observed suggesting the condensation of small crystallites to form larger ones upon heating. No prominent changes were detected in the Raman spectra of pure H-ZSM5. For both substances, the spectral band broadening and low-frequency shift are typical for vibrational spectra recorded at a high temperature.

The spectrum of MoO_3 at room temperature matches the ones reported before for crystalline MoO_3 with bands at 996 and 821 cm^{-1} [2,7]. However, Hu et al. [8], in contrast to our findings, reported that no spectrum was obtained for crystalline MoO_3 at the same laser excitation wavelength (244 nm) employed in our work. The authors explained their results by the strong absorption of light by the sample.

In contrast to the samples of pure molybdenum oxide and pure zeolite, the physical mixture of the compounds shows irreversible changes for the structure of MoO_3 when they undergo the same thermal treatment in O_2 (figure 2). At room temperature (RT), the Raman spectrum of the physical mixture exhibits characteristic bands of bulk MoO_3 at 996 and 820 cm^{-1}. As the temperature increases, the bands become weaker and wider and an increase in intensity for the band at 996 cm^{-1}, corresponding to Mo=O stretch mode, relative to that at 820 cm^{-1}, corresponding to Mo–O–Mo stretch mode, indicates the high mobility of molybdenum oxide species and their spread forming small particles possibly on the ex-

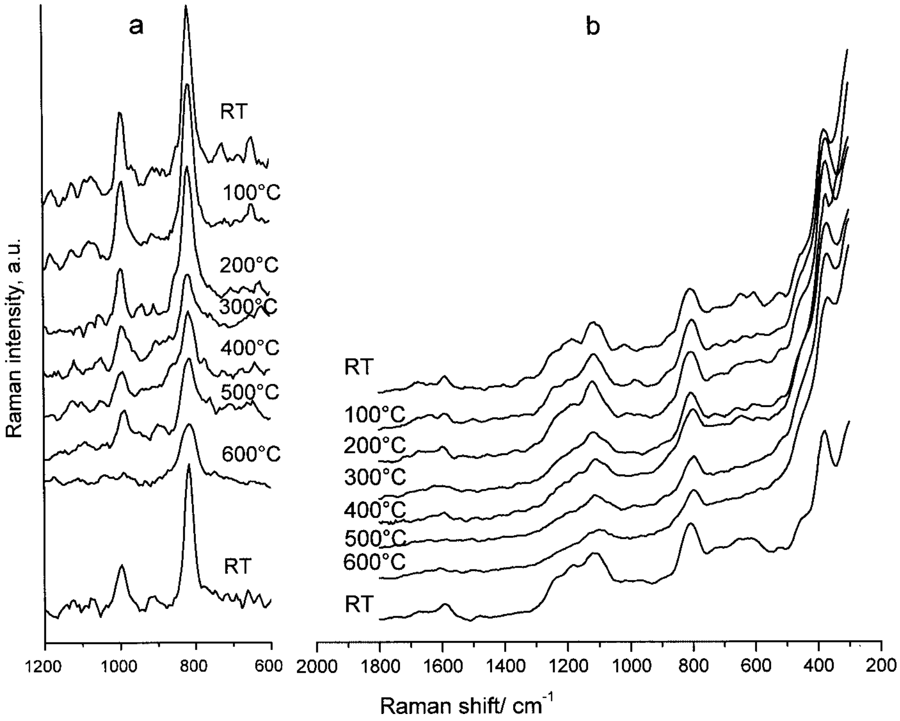

Figure 1. The UV Raman spectra of pure crystalline MoO_3 (a) and H-ZSM5 (b) recorded *in situ* in flowing O_2 during the heating cycle from room temperature (RT) to 600 °C and back to RT.

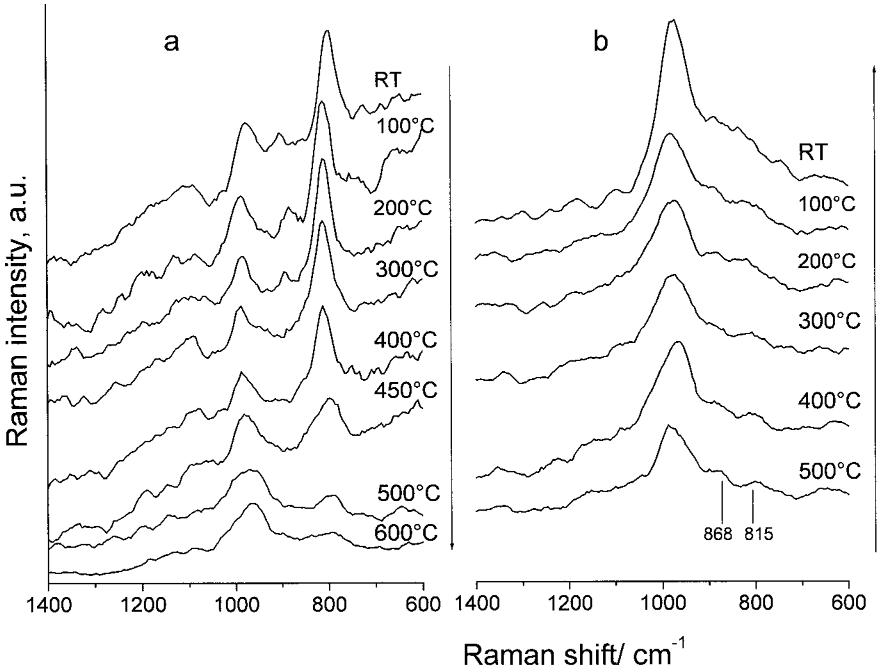

Figure 2. UV Raman spectra for the physical mixture of 2% MoO_3 and H-ZSM5 recorded *in situ* with dry O_2 flow. The sample was first heated (a) and then cooled (b) in steps lasting 1 h each.

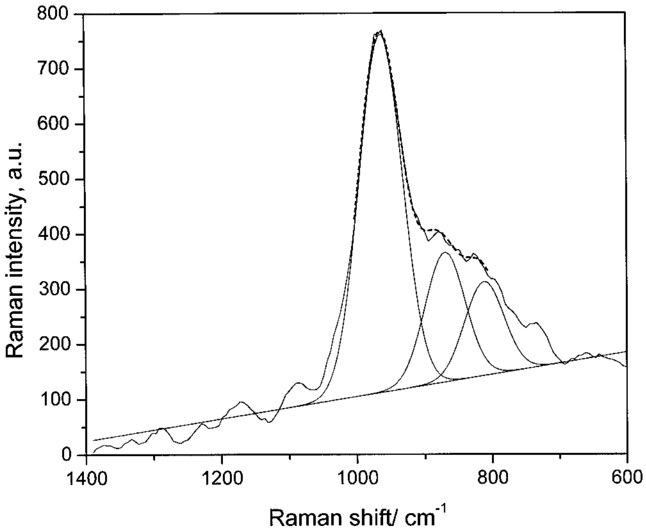

Figure 3. Curve fit of the Raman spectra from figure 2(b) (1) with three Gaussian lines at 962 (half-width 74 cm^{-1}), 868 (half-width 72 cm^{-1}) and 815 (half-width 71 cm^{-1}). Dotted line is the sum of the three fitting Gaussians.

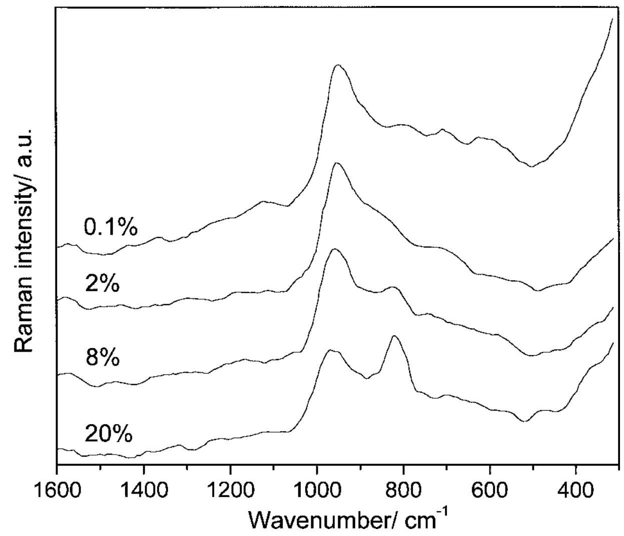

Figure 4. Raman spectra for Mo-ZSM5 samples as a function of MoO_3 loading after calcination at 500 °C for 12 h in ambient air. Spectra collected at ambient conditions. The intensities for each loading were not normalized.

ternal zeolite surface. After the temperature reaches 600 °C and is subsequently decreased, only one main peak at about 962 cm^{-1} remains in the Raman spectra. However, two shoulders at 868 and 815 cm^{-1} (marked in figure 2) appear on the low-frequency side of the main peak. The application of the second-derivative technique followed by a curve-fitting procedure shows the existence of at least three bands under the overall profile with the main peak at 962 cm^{-1}. The spectral profile recorded at room temperature and fitted with three Gaussian shape lines is shown in figure 3. The half-widths of the spectral components were determined to be almost about 70 cm^{-1} for the three bands. The relatively large half-width of these bands indicates that Mo–O coordination includes a high degree of nonuniformity.

Figure 4 shows a series of spectra as a function of MoO_3 loading. It is noted that the spectrum of the 0.1% sample does not differ significantly from the one for the 2% sample. The small differences observed are not significant since the signal to noise ratio in the 0.1% sample is lower and there is an interference from the ZSM5 band at 820 cm^{-1}. For the samples with higher molybdenum loading, the appearance of the 820 cm^{-1} band indicates the presence of leftover

MoO_3, which could not spread and react on the surface beyond its saturation point. The spectra of all these samples were acquired in ambient air to decrease accumulation time since it was observed that the spectra were the same as the ones taken in the *in situ* cell.

One can conclude that if MoO_3 were added to the zeolite support and no interaction occurred upon calcination, the resulting spectrum should be the sum of spectra taken from pure MoO_3 and H-ZSM5. The actual result, however, points to a strong chemical interaction between molybdenum oxide and the zeolite support as also verified by Li et al. [4]. The absence of bands at 996 and 820 cm^{-1} on the 2% Mo/ZSM5 sample, which are characteristic of crystalline MoO_3, reveals that after the cycle of thermal treatment the supported molybdenum oxide is present as a finely dispersed zeolite-supported phase.

The assignment of molybdenum species supported on an oxide by Raman spectroscopy is still debatable [2,4,9–12], particularly the significant difference between the spectra obtained under hydrated (ambient) and dehydrated conditions [9,13]. The main reason for the difficulty of identification is the fact that the adsorbed molybdenum species may form unique compounds on the surface with no well-characterized analogues available for comparison. In the case of our studies, this fact was compounded by our inability to record spectra in the fingerprint low frequency region of 200–300 cm^{-1}, caused by an overlap with the zeolite bands and high background from Rayleigh scattering. The molybdate is usually considered to be in the form of isolated monomers MoO_4^{2-} [14], dimers $Mo_2O_7^{2-}$ [15], oligomers $Mo_7O_{24}^{6-}$, or other polymeric species [9]. However, isolated monomeric species are believed to predominate at low MoO_3 loadings [9]. Borry et al. [16] and Li et al. [4] used a combination of techniques on a sample prepared in the same way as reported here to propose that molybdenum dimers are formed with two O-atoms located in the H-ZSM5 framework. In particular, Li et al. [4] reported three Raman bands at 970, 1000 and 1045 cm^{-1}, all assigned to Mo=O stretching modes. The one at 1000 cm^{-1} was assigned to isolated molybdate species external to the zeolite pores and the other two to a dimer structure inside the zeolite pores. These bands, however, are distinct from the ones reported in figure 3 (815, 868 and 962 cm^{-1}) although the samples were prepared by the same procedure in both studies. One explanation for the difference is that our ZSM5 sample had a Si : Al ratio four times higher than that of Li et al. [4], thus implying that it is more difficult in our case to find contiguous Al sites necessary for dimer formation. However, the Mo/Al ratios are similar in both cases, and in one instance in figure 4 (0.1%) even lower, to justify this explanation. Another possible explanation for the different spectra, pointed out by Xiong et al. [17,18] and Hu et al. [8], could be due to a resonance enhancement in the UV Raman. This effect may emphasize different bands in the UV than in the visible. However, the MoO_3 spectrum in the UV is the same as the one obtained with visible Raman and thus resonance-enhanced Raman does not seem to explain our results either. A comparison with the spectra of oxides of molybdenum on different supports using UV light at 244 nm is in order. Xiong et al. [17,18] studied MoO_3 on γ-alumina and identified a band at 910 cm^{-1} and for molybdenum on zirconia Hu et al. [8] have identified bands at 840 and 910 cm^{-1}. These are again quite distinct from the spectrum in figure 3 but it is known that the structures of the oxides of Mo are a strong function of the support and the fact that the results are distinct is not unexpected. Finally, it is important to add that the same samples used here for Raman were also used for the reaction of non-oxidative coupling with methane at atmospheric pressure. The rate and selectivity for the samples were similar to the ones reported in the literature [19] and thus these are representative samples.

Taking into account the data above, we can say with certainty (1) that the structure of the oxide on H-ZSM5 is quite distinct from crystalline MoO_3 and (2) also distinct from the structures reported before for various supports. We can not positively identify the bands but only state that there are many possibilities for the compounds on the surface. For example, the most intense Raman band at 962 cm^{-1} could be attributed to terminal Mo=O groups of isolated tetrahedrally coordinated monomers, MoO_4^{2-}, and the weaker band at 868 cm^{-1} to bridging Mo–O–Mo groups of dimeric species, $Mo_2O_7^{2-}$ [2]. The least intense band at 815 cm^{-1} should be assigned most likely to the band of zeolite framework positioned at about the same frequency in the Raman spectrum of pure H-ZSM5 (figure 1(b)). However, we cannot exclude the possibility that this band originates from leftover crystalline MoO_3 particles, since its position is close to the position of the most intense band at 820 cm^{-1} in the spectrum of pure MoO_3 (figure 1(a)) attributed to asymmetric stretching vibration of the Mo–O–Mo bond in bulk MoO_3.

Our assignment is in line with the generally accepted knowledge that the stretching modes of terminal Mo=O groups lay in the spectral region higher than that of bridging Mo–O–Mo groups. However, the Raman shift of the band of terminal Mo=O groups determined in the spectra of MoO_3/Al_2O_3 and MoO_3/SiO_2 catalysts obtained under dehydrated conditions was 990 and 976 cm^{-1}, respectively, for 1 wt% MoO_3 loading [9]. The lower Raman shift of the same band in the case of H-ZSM5 support may be explained by an influence of the zeolite framework structure. This assignment is consistent with the dimers suggested by Borry et al. [16].

4. Conclusions

In situ measurements with UV Raman at high temperature allowed us to follow the incorporation of MoO_3 into H-ZSM5 from an initial physical mixture. The use of UV laser excitation prevents the fluorescence from the zeolite support as well as the thermal emission at high temperatures from overwhelming the Raman signal. It was established that in solid-state exchanged samples, molybdenum oxide spreads over the H-ZSM5 surface and forms new structures with bands at 868 and 962 cm^{-1}. The most intense band at 962 cm^{-1} could be attributed to terminal Mo=O groups of isolated tetrahedrally coordinated monomers and the weaker band at 868 cm^{-1} to bridging Mo–O–Mo groups of dimeric species. These bands, however, could be due to another unique structure formed by an oxide of molybdenum on H-ZSM5.

Acknowledgement

We gratefully thank the National Science Foundation for funding through grant CTS-9702699 and the Cooperative Research Program at the Dow Chemical Company.

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