Direct spectroscopic evidence for vanadium species in V-MCM-41 molecular sieve characterized by UV resonance Raman spectroscopy

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Vanadium species in tetrahedral and octahedral coordination in V-MCM-41 molecular sieve are characterized by UV resonance Raman bands at 1070 and 930 cm^{-1} respectively.

Vanadium-substituted molecular sieves have been found to be excellent catalysts for many selective oxidation reactions.[1–3] In particular, V-MCM-41 has drawn much interest owing to its large pore diameter which is suitable for selective oxidation of large organic compounds.[4–6]

The catalytic activity and selectivity of vanadium-substituted molecular sieves are directly related to the coordination structures of the vanadium species in the molecular sieves. In general, three forms of vanadium species, isolated tetrahedral, two-dimensional octahedral species and crystalline V_2O_5, are believed to be present.[4,5,7,8] The coordination structure of vanadium species in V-MCM-41 has been investigated by ^{51}V NMR, UV–VIS absorption spectroscopy and many other techniques,[4,5,8] but identification of vanadium species in tetrahedral or octahedral coordination environments is not straightforward. Raman spectroscopy is a potentially viable technique for the study of the structure of vanadium species in V-MCM-41, since it has been used to characterize supported vanadium oxides with both tetrahedral and octahedral coordination structures.[9,10]

However, there have been relatively few Raman studies on vanadium-substituted MCM-41,[8] mainly because of fluorescence interference and the low sensitivity of conventional Raman spectroscopy. The limited amount of substituted vanadium atoms also hinders the application of Raman spectroscopy in characterization of vanadium atoms in V-MCM-41.

UV Raman spectroscopy has been proved to be a powerful technique for the study of catalysts and other solids,[11,12] especially, for the identification of isolated transition metal atoms substituted in the framework of molecular sieves[13] or grafted on metal oxides.[14] An increase in the intensity of Raman signal and decrease in the intensity of fluorescence background help to increase the sensitivity of the Raman spectra. Moreover, the resonance Raman effect will selectively enhance the intensity of the Raman signal by several orders of magnitude when the excitation laser line is close to the electronic transition absorption of the samples.

In this work, for the first time, we study the different vanadium species in V-MCM-41 using UV resonance Raman spectroscopy. Based on the UV resonance Raman effect the vanadium species in tetrahedral and octahedral environments in V-MCM-41 can be successfully identified by UV resonance Raman spectroscopy.

MCM-41 and V-MCM-41 were synthesized according to the method reported in the literature.[4] V-MCM-41 samples which possess Si/V ratios of 250, 125 and 60 are denoted V-MCM-41 (250), V-MCM-41 (125) and V-MCM-41 (60), respectively. The as-synthesized samples show XRD patterns matching well with these reported in the literature.[4,5,15] UV Raman spectra were recorded on a homemade UV Raman spectrometer.[12] 244 and 488 nm lines from a Innova 300 FRED (Coherent) laser were chosen as the excitation sources. The laser power at the samples were kept below 2.0 mW for the 244.0 nm line and 100 mW for the 488 nm line. The spectral resolution is estimated to be 2.0 cm^{-1} for UV Raman spectra and 1.0 cm^{-1} for visible Raman spectra.

Fig. 1 shows Raman spectra of V-MCM-41 and MCM-41 samples excited by the 488 nm line. The signal to noise ratio of visible Raman spectra is very poor because of both fluorescence interference and the inherently low sensitivity of visible Raman spectroscopy. The MCM-41 sample excited by the 488 nm line showed weak Raman bands at 490, 610, 810 and 970 cm^{-1}. Bands at 490 and 610 cm^{-1} are attributed to the 3 and 4 Si siloxane rings, respectively,[10] while the bands at 810 and 970 cm^{-1} are assigned to the siloxane bridges (Si–O–Si) and surface silanol groups of MCM-41.[8,10] The visible Raman bands of V-MCM-41 are similar to that of MCM-41 in that no additional bands of V-MCM-41 due to vanadium species are observed. This means that the Raman bands associated with vanadium species in MCM-41 are too weak for detection by visible Raman spectroscopy.

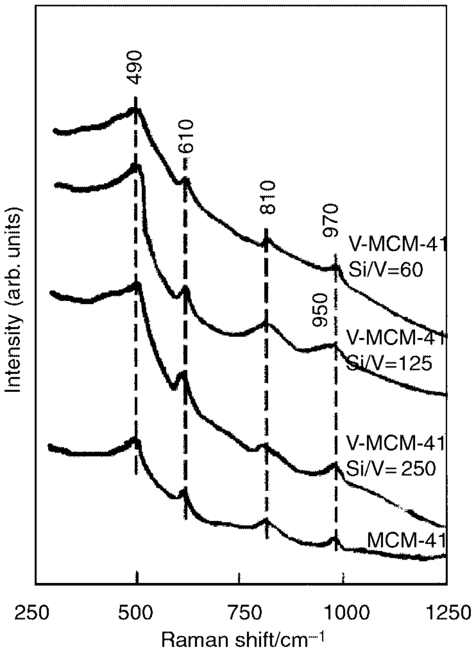

Fig. 1 Visible Raman spectra of V-MCM-41 and MCM-41 excited by 488 nm line radiation.

Compared with visible Raman spectra, UV Raman spectroscopy gives significantly different spectra, (Fig. 2). Besides the Raman bands at 490, 610 and 810 cm^{-1} which appear in the visible Raman spectra, Raman bands in the region 900–1200 cm^{-1} are present in the UV Raman spectra of MCM-41 and V-MCM-41 samples. The band at 970 cm^{-1} of MCM-41 is assigned to surface silanol stretching vibrations while weak bands in the region 1000–1200 cm^{-1} of MCM-41 are attributed to the asymmetric stretching modes of Si–O–Si bridges. These

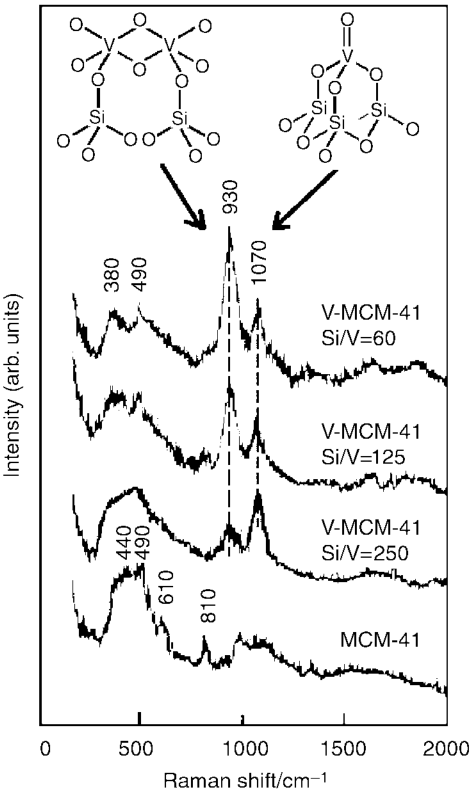

Fig. 2 UV Raman spectra of V-MCM-41 and MCM-41 excited by 244 nm line radiation.

bands become observable owing to reduced fluorescence interference when the excitation is changed from 488 to 244 nm. It is significant that two new bands at 930 and 1070 cm^{-1} are detected in UV Raman spectrum of V-MCM-41. Taking into account that the laser line at 244 nm is close to the charge transfer absorption of the vanadium species in V-MCM-41, the high intensity of the 930 and 1070 cm^{-1} bands must be a result of enhancement by the resonance Raman effect.

Two main absorptions bands are present at 275 and 340 nm in the UV–VIS diffuse reflectance spectrum of V-MCM-41.[15] These bands are assigned to low energy charge-transfer (CT) associated with framework vanadium species in tetrahedral coordination.[8,15] The band centered at 275 nm is very broad covering the range 230–300 nm. Thus the 244 nm laser line is within the electronic transition band of tetrahedral vanadium species. The UV–VIS absorption bands also appear in a similar region for polymerized vanadium oxides supported on SiO_2.[16] A band at 250 nm together with a shoulder at 320 nm is observed in the UV–VIS absorption spectrum of vanadium oxide. Therefore, the 244 nm laser line can excite both the band centered at 275 nm associated with the isolated vanadium species and the band centered at 250 nm of polymerized vanadium oxides. In other words, the 244 nm laser line can excite the electronic absorptions of vanadium species in tetrahedral and octahedral coordination simultaneously. Obviously the 488 nm laser line (visible Raman spectroscopy) lies outside of the UV–VIS absorption region for vanadium species in V-MCM-41.

The absence of a typical band at *ca.* 1000 cm^{-1} of V_2O_5 in Fig. 1 and 2 implies that no crystalline V_2O_5 is formed in V-MCM-41. This suggests that the vanadium species in V-MCM-41 are isolated or, at least, are highly dispersed on the surface. The Raman bands in the 900–1000 cm^{-1} region of supported vanadium oxides are usually attributed to hydrated polymerized vanadium oxides.[9,17] Thus the band at 930 cm^{-1} can be attributed to the V=O symmetric stretching mode of polymerized vanadium oxides.[9] The band at *ca.* 1030 cm^{-1} has been assigned to the V=O stretching vibration of monometric vanadyl species bound directly to the support. [8,9,10] The V=O stretching frequencies of VOF_3, $VOCl_3$ and $VOBr_3$ occur at 1053, 1035 and 1028 cm^{-1}, respectively.[18–20] Therefore the band at 1070 cm^{-1} is reasonably assigned to a tetrahedral V=O group bonded to the MCM-41 host. It should be noted that the band position (1070 cm^{-1}) of V-MCM-41 is higher than that of tetrahedral vanadate in the literature (*ca.* 1030 cm^{-1}).[10] An empirical relationship between V–O bond lengths and Raman stretching frequencies has been assumed based on vanadium oxides.[21] According to this assumption, a higher frequency position corresponds to shorter V–O bonds; the highest frequency position at 1070 cm^{-1} thus corresponds to the shortest V=O bond distance. This result provides evidence for the isolated mono–oxo vanadate species in V-MCM-41 molecular sieve being of tetrahedral structure with strong structural tension. This structure is metastable and aggregates into the octahedral vanadium species at high temperature as indicated by the disappearance of the band at 1070 cm^{-1} and the growth of the band at 930 cm^{-1} after calcination at high temperatures.

In summary, UV resonance Raman bands of V-MCM-41 at 1070 and 930 cm^{-1} are detected for the first time. These bands provide direct spectroscopic evidence for vanadium species in tetrahedral and octahedral environments, respectively. The vanadium species in tetrahedral coordination is an isolated species with strong structural tension, while that in the octahedral form corresponds to highly dispersed polymerized oxides. This study also demonstrates that UV resonance Raman spectroscopy is a powerful technique to selectively identify transition metal species in molecular sieves or on supports.

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