

Identification of vanadium species in VAPO and VAPSO aluminophosphate by UV resonance Raman spectroscopy

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A sensitive UV resonance Raman spectroscopy has been used to characterize VAPO-5 and VAPSO-5 aluminophosphate. UV-Raman spectra of VAPO-5 suggest that three different vanadium species are existed in VAPO-5, but the framework vanadium species are not observed. However, the framework vanadium species are existed in VAPSO-5 and located in the matrix of framework silica.

1. INTRODUCTION

Vanadium analogues of aluminophosphate have attracted much attention recently due to their potential catalytic oxidations on various hydrocarbons.¹ The location and structure of the vanadium ions are of considerable importance for understanding the catalytic properties of such materials. In general, three forms of vanadium species, isolated tetrahedral, two-dimensional octahedral species and crystalline V₂O₅, are believed to be present.² The coordination structure of vanadium species in VAPO molecular sieves has been investigated by ⁵¹V NMR, UV-Vis absorption spectroscopy and many other techniques.³ However, the identification of vanadium species in tetrahedral or octahedral environments is not yet straightforward.

Raman spectroscopy can provide helpful direct information about identification and structure of zeolitic framework. This makes Raman

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spectroscopy being an efficient and rapid technique for directly probing the framework and other compounds in the porous system of molecular sieves. However, high-quality Raman spectra of molecular sieves are difficult to obtain because of the weak Raman cross-sections of the vibrational motions and the intense fluorescence background under laser excitation. This confines the application of Raman spectroscopy in characterization of molecular sieves. Moreover, the limited amount of substituted vanadium atoms also hinders the application of Raman spectroscopy in characterization of vanadium species in VAPO molecular sieves.

UV-Raman spectroscopy has been proved to be a powerful technique for the identification of isolated transition metal atoms substituted into the framework of molecular sieves.⁴ 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. More important, the resonance Raman effect can selectively enhance the intensity of the Raman signal by several orders of magnitude when the excitation laser is close the electronic transition absorption of the samples.

In this work, VAPO-5 and VAPSO-5 molecular sieves were studied by UV resonance Raman spectroscopy. Based on the UV resonance Raman effect, the vanadium species of the framework and extraframework are identified unambiguously.

2. EXPERIMENT

VAPO-5 and VAPSO-5 molecular sieves were synthesized hydrothermally. Phosphoric acid (85%), pseudoboehmite (78.18% Al_2O_3), colloidal silica (25.5%wt) and $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ were used as sources for phosphorus, aluminum, silicon and vanadium, respectively. AlPO_4 -5 and SAPO-5 were synthesized simultaneously using the same method only without adding the vanadium source. XRD patterns demonstrate that the synthesized molecular sieves are the typical AFI type structure and without any impure phases are observed. Also, the main peaks of vanadium pentoxide at $2\theta=15.5^\circ$, 20.3° , 21.9° and 31.0° that can be clearly distinguished from the AlPO_4 -5 peaks are not present in the diffractogram of VAPO-5 and VAPSO-5. UV-Raman spectra were recorded on a home-made UV Raman spectrometer.¹⁵ A 244 nm line from an Innova 300 FRED (Coherent) laser was used as excitation sources. The spectral resolution is estimated to be 2.0 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. UV-Raman Spectra of AlPO₄-5 and SAPO-5

We first studied the samples of AlPO₄-5 and SAPO-5 by UV resonance Raman spectroscopy. The spectra are shown in figure 1. In the spectrum of AlPO₄-5, several Raman bands at 273, 407, 500, 643, 1060 and 1139 cm⁻¹ are observed. The Raman bands of aluminophosphate molecular sieves can be assigned as following: (1) 200~300 cm⁻¹, the breathe mode of channel opening; (2) 400~600 cm⁻¹, the region of bending vibration; (3) 600~900 cm⁻¹, the symmetric stretching mode of TO₄ tetrahedra and (4) 1000~1200 cm⁻¹, asymmetric stretching modes of individual PO₄ and AlO₄ tetrahedra.⁵ Thus the Raman bands at 1139, 500 and 273 cm⁻¹ in the spectrum of AlPO₄-5 and SAPO-5 are attributed to T-O stretching, T-O-T bending and ring breathing vibrational mode, respectively. They are the typical vibration of aluminophosphate molecular sieves. Comparing with that of AlPO₄-5, three other Raman bands at 600, 1077 and 1100 cm⁻¹ are observed in the spectrum of SAPO-5, The band at 1077 and 1100 cm⁻¹ are assigned to asymmetric stretching vibration of Si-O bond in Si-O-Al and Si-O-Si units, respectively. The band at 600 cm⁻¹ can be assigned to the bending vibration of Si-O-Si units. These results suggest that some domains of silica exist in the framework of SAPO-5. Namely, the silicon atoms are coordinated not only in Si(4Al) mode but also in Si((4-n)Al, nSi) (n=1-4) mode in the framework of SAPO-5. This is also confirmed by ²⁹Si MAS NMR spectra (not show), in which the chemical shift of Si(4Si) in ~110 ppm is intensive.

3.2. UV resonance Raman spectra of VAPO-5 and VAPSO-5

UV resonance Raman spectra of VAPO-5 and VAPSO-5 are shown in figure 2. Contrasting the UV-Raman spectrum of VAPO-5 with that of AlPO₄-5, VAPO-5 gives significantly different bands. In the asymmetric stretching region, three new Raman bands at 930, 984 and 1038 cm⁻¹ are observed. These three Raman bands are all concerning to the vanadium species in the molecular sieves. It has been reported that the isolated vanadium species, two-dimensional vanadium clusters (thin films) and nanoparticle V₂O₅ in supported vanadium oxide give the V=O stretching mode at Raman bands of 1042, 1039 and 997 cm⁻¹, respectively.¹⁹ Thus, the band at 1038 cm⁻¹ in the spectrum of VAPO-5 is reasonably attributed to V=O asymmetric stretching mode of two-dimensional vanadate clusters. The band at 983 cm⁻¹ is caused by nanoparticle V₂O₅.

The Raman bands in the 900-1000 cm⁻¹ region of supported vanadium

oxides are usually attributed to hydrated polymerized vanadium oxides.⁶ Thus the band at 930 cm^{-1} in the spectrum of VAPO-5 can be assigned to V=O asymmetric stretching mode of polymerized vanadium oxides outside the framework. Therefore, two-dimensional vanadate clusters, polymerized vanadium oxides and/or nanoparticle V_2O_5 crystallites are recommended to be the dominant vanadium species in VAPO-5.

As far as the spectrum of VAPSO-5 is concerned, three new bands at 1028 , 930 and 557 cm^{-1} are observed compared to that of SAPO-5. The band at around 1040 cm^{-1} has been assigned to the V=O stretching vibration of monomeric vanadyl species bound directly to the SiO_2 support.⁷ The V=O stretching frequencies of VOF_3 , VOCl_3 and VOBr_3 occur at 1053 , 1035 and 1028 cm^{-1} , respectively.⁸ The Raman band at 1035 cm^{-1} has also been assigned by Chao *et al.* to the stretching frequency of a terminal of V=O group bonded to the silicate MCM-41 host.⁹ Therefore, the band at 1028 cm^{-1} in the spectrum of VAPSO-5 is reasonably assigned to isolated tetrahedral V=O group bonded to the silica host. This is a direct evidence for that the isolated mono-oxo vanadate species which fixed in the silica domain of the framework of VAPSO-5. It is worth noting that the intensity of the band at 1028 cm^{-1} is much stronger than that of other bands. The high intensity of this band is assumed to be resulted from the resonance Raman effect. The laser line at 244 nm is close to the frequency of the electronic absorption band of isolated vanadium species in VAPSO-5. Based on the Kramers-Heisenberg Equation, when the energy of the excitation laser is closed to the electronic absorption state, the resonance effect will take place. In Raman spectroscopy, the resonance effect will cause Raman scattering increased greatly. It is thus evident that vanadium ions are isolated dispersed in the framework of VAPSO-5. The band at 557 cm^{-1} in the spectrum of VAPSO-5 corresponded to the bending vibration of Si-O-V unit. This indicates that the isolated vanadium atoms are connected with the silicon atoms in the framework. The band at 930 cm^{-1} is also observed and suggested that the polymerized vanadium species also exist in VAPSO-5.

UV-Raman spectrum of purely crystalline V_2O_5 is also shown in Fig. 2. The main bands of crystalline V_2O_5 are around 430 , 950 and 1183 cm^{-1} . The absence of the bands of crystalline V_2O_5 in the spectra of VAPO-5 and VAPSO-5 implies that no crystalline V_2O_5 is formed in VAPO-5 and VAPSO-5.

3.3. UV-Raman spectra of VAPO-5 with different vanadium contents

UV-Raman spectra of VAPO-5 with different vanadium contents are

shown in Figure 3. It shows that quite similar spectra are obtained for every sample except for the intensity of the bands at 930 and 984 cm^{-1} . The intensity of the bands at 930 and 984 cm^{-1} increases gradually with the increasing of the vanadium content in VAPO-5. This suggests that the amounts of polymerized vanadium species and bulk V_2O_5 crystallites increase. It should be noted that the Raman band of isolated vanadium species is not observed despite the vanadium content is high. It reveals that vanadium can not be substituted into the framework of VAPO-5 even though the contents of vanadium precursor added in the synthesis gel are high.

UV-Raman spectra of VAPSO-5 with different vanadium content are shown in Figure 4. It can be seen that the intensity of the band at 1042 cm^{-1} becomes relatively stronger with increasing the vanadium contents, the intensity of the bands at 930 cm^{-1} , while that of the band at 1028 cm^{-1} remains unchanged. This suggests that, when the vanadium contents are low, most of the vanadium atoms in VAPSO-5 are isolated tetrahedral species in the framework, whereas when the vanadium contents are high, most of the vanadium will be formed polymerized vanadium oxide and aggregated outside

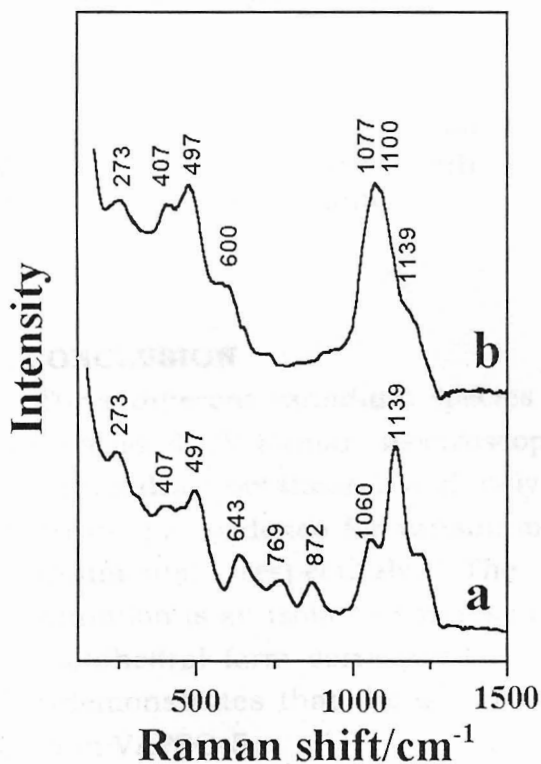


Fig. 1. UV-Raman spectra of (a) $\text{AlPO}_4\text{-5}$, (b) SAPO-5

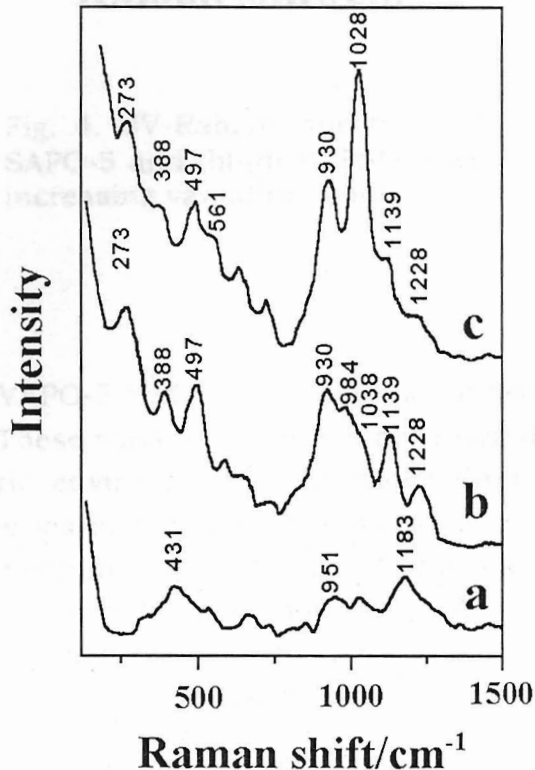


Fig. 2. UV-Raman spectra of (a) V_2O_5 , (b) VAPO-5 and (c) VAPSO-5

the framework. The content of framework vanadium is limited to a certain amounts. If the vanadium contents are beyond this limit, the vanadium species will be formed mainly the polymerized vanadium oxide.

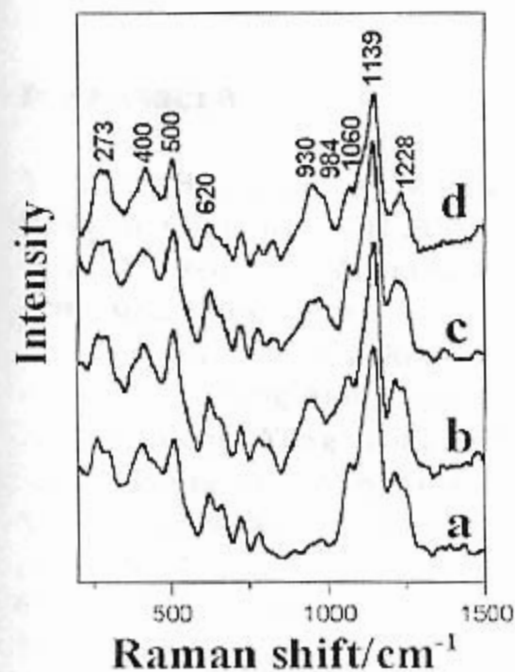


Fig. 3. UV-Raman spectra of (a) $\text{AlPO}_4\text{-5}$ and (b)-(d) VAPO-5 with increasing vanadium contents

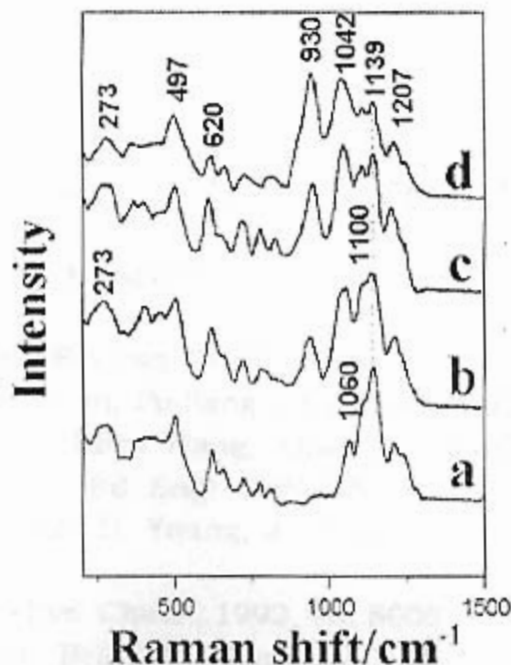


Fig. 4. UV-Raman spectra of (a) SAPO-5 and (b)-(d) VAPSO-5 with increasing vanadium contents

4. CONCLUSION

Three different vanadium species in VAPO-5 and VAPSO-5 are identified using a novel UV-Raman spectroscopy. These vanadium species are existed in tetrahedral, octahedral and polymeric environment. It provides direct spectroscopic evidence for vanadium species in tetrahedral and octahedral environments, respectively. The vanadium species in tetrahedral coordination is an isolated species in strong structural tension, while that in the octahedral form corresponds to highly dispersed polymerized oxide. It also demonstrates that the isolated vanadium is located in the domain of silica in VAPSO-5.

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