



Synthesis and Spectroscopic Characterization of Vanadium incorporated V-AIMCM-41 Molecular Sieves

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Received May 30, 2006

Abstract : A solid-state reaction of V_2O_5 with AIMCM-41 followed by calcinations generated V^{5+} species in the mesoporous materials. Dehydration results in the formation of a vanadyl species, VO^{2+} , that can be characterized by electron spin resonance (ESR). The chemical environment of the vanadium centers in V-AIMCM-41 was investigated by XRD, EDX, diffuse reflectance UV-VIS, ESR, ^{29}Si , ^{27}Al , and ^{51}V NMR. It was found that the vanadium species on the wall surface and inside the wall of the hexagonal tubular wall of the V-AIMCM-41 were completely oxidized to tetrahedral V^{5+} and transformed to square pyramidal by additional coordination to water molecules upon hydration. The oxidized V^{5+} species on the wall surfaces and inside the wall were also reversibly reduced to VO^{2+} species or lower valences by thermal process.

Key words : MCM, Vanadium, Molecular Sieve, ESR, Solid State NMR

INTRODUCTION

Vanadium-substituted molecular sieves have attracted great interest as efficient catalysts.¹⁻³ However, most vanadium-doped microporous solids have micropore channel less than 10 Å which restricted the oxidation of large organic molecules.

The hexagonal tubular silica MCM-41 materials have uniform mesoporous channels varying from 15 to about 100 Å, which allow the faster diffusion of large organic molecules than the smaller channels of the microporous molecular sieves do.^{4,5} The properties open an

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opportunity for the preparation and characterization of vanadium-containing mesoporous molecular sieve materials.¹ The pure silica MCM-41 framework has limited use for applications as catalysts and adsorbents due to the lack of acid sites and ion exchange capacity.⁶ Aluminum can be incorporated into the framework of MCM-41 during synthesis.^{7,8} Ryoo *et al.* showed that the ion exchange levels for AlMCM-41 have been increased by 36~ 41 % compared to the pure silica type MCM-41. Luan *et al.* synthesized V-containing mesoporous MCM-41 materials. The Vanadium species located inside the walls remain stable upon calcinations and hydrations.^{1,6} They reported that only mobile vanadyl VO^{2+} ions are detected in the VAlMCM-41 with either low or high vanadium loading from combined studies of ESR and diffuse reflectance UV-visible spectroscopy.¹ In this work, vanadium-doped V-AlMCM-41 samples were prepared successfully by a high-temperature solid-state reaction between AlMCM-41 and V_2O_5 . The paramagnetic V(IV) species were characterized by EPR, diffuse reflectance UV-Visible and solid state NMR.

EXPERIMENTAL

Materials

Sodium silicate solution (27 wt% silica and 14 wt% NaOH, Aldrich) and fumed silica (Sigma) were used as silicon sources. The $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NOH/Cl}$ (CTACL/OH) solution was prepared by batch exchange of a 25 wt % aqueous solution of $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NCl}$ (Aldrich) using an IRA-26(OH) ion-exchange resin (Aldrich).⁹ A 25 wt% aqueous solution of tetramethylammonium hydroxide (TMAOH) was obtained from Aldrich. Aluminum sulfate was used as an aluminum source for synthesizing AlMCM-41.

MCM-41 Synthesis

Siliceous MCM-molecular sieves was synthesized from sodium silicate and $\text{C}_{16}(\text{CH}_3)_3\text{NBr}$ surfactant according to the processes reported by Beck *et al.*¹⁰ Each $\text{C}_{16}(\text{CH}_3)_3\text{NBr}$ surfactant (0.046 mol) was dissolved in 88-100 g of water to make an 11 wt% solution, and 20.4 g of sodium silicate was added slowly with stirring. This silicate-surfactant mixture was stirred for 30 min, and then the pH was adjusted to 10 by adding

dilute sulfuric acid slowly. The mole composition of the final gel mixture was 1 SiO₂: 0.50 surfactant:0.39 Na₂O:60 H₂O. The resultant gels were crystallized in Teflon-lined autoclaves at 150 °C for 6 days. After cooling to room temperature, the solid products were centrifuged, filtered, washed with distilled water, and dried in air at 100 °C. The product were then calcined at 550 °C for 24 h in flowing air.

AIMCM-41

The synthetic procedure for AIMCM-41 was as follows.¹¹ Tetramethylammonium hydroxide (TMAOH) solution (5 g) was combined with 2.95 g of sodium silicate dispersed in 25 g of water with stirring, and then 17.15 g of CTACl / OH solution and 2.26 g of silica were added and stirred for 2 h. The required amount of Al₂(SO₄)₃ was dissolved in water and slowly added to the gel. The pH was adjusted to 11 by adding dilute sulfuric acid slowly. The composition of the final gel mixture was 1 SiO₂ : 0.27 CTACl / OH : 0.13 Na₂O : 0.26 TMAOH : 60 H₂O : 0.017 - 0.033 Al₂O₃. The resultant gels were treated as described above. The samples are designated as AIMCM-41-(x), where x is the Si / Al ratio in the gel.

Characterization

X-ray powder diffraction (XRD) patterns of all MCM-41 samples were recorded on a Philips 1840 powder diffractometer using Cu K α radiation with a wavelength 1.541 Å, a 0.0025° step size, and 1 s step time over the range 1.5° < 2 θ < 15°. Nitrogen adsorption and desorption isotherms of all the MCM-41 were measured by the BET (Brauner-Emmett-Reller) method with N₂ physisorption at 77 K using a Quantachrome Monosorb analyzer. The diffuse reflectance (DR) UV-vis spectra were recorded using a Varian model Cary 1C spectrometer with an integrating sphere accessory.

ESR spectra were recorded with 300 MHz spectrometer (Jeol model JES-FA) at 77 K and 298 K. Each spectrum was obtained by multiple scan to achieve a satisfactory signal-to-noise-ratio. The magnetic field was calibrated with a Jeol model E-500 ESR field meter. Solid-state NMR spectra were recorded at 9.4 T using a 400 MHz Bruker model DSX spectrometer at Daegu Korea Basic Science Institute. ²⁹Si MAS spectra were measured at 79.45 MHz with 60 ° pulses and 600 s cycle delays using zirconia rotors 7.5 mm in diameter spun at 3 kHz. ⁵¹V MAS spectra were acquired 105.1 MHz with very short (< 7 °)

pulses and 1 s recycle delays using zirconia rotors 4 mm in diameter with spinning at 12 kHz. Spinning rates were changed to identify isotropic ^{51}V resonances. The chemical shifts are given in ppm from external tetramethylsilane (TMS) for ^{29}Si and from external NaVO_3 (Aldrich) for ^{51}V . ^{27}Al spectra were measured at 104.3 MHz with 0.3 s recycle delays. Short $\pi/20$ radio frequency pulses were used to ensure that they are quantitative reliable. External $\text{Al}(\text{H}_2\text{O})_6^{3+}\text{Cl}_3$ was used as a reference. The elemental composition of the resultant solid products was analyzed by EDX method using an Oxford energy dispersive X-ray analyzer. It is analyzed the elemental composition from the X-ray intensity resulting in the specific element.

RESULT AND DISCUSSION

XRD

XRD patterns of siliceous MCM-41, AIMCM-41(30) and V-AIMCM-41 in both as-synthesized and calcined forms are shown in Figure 1. The MCM-41 gives a well-resolved XRD patterns (Figure 1a) typical of hexagonal structure as describe previously by Beck *et al*^{4,5} with a d-spacing of ca. 33.5 Å. The hexagonal unit cell parameter (a_0) is calculated as $2d_{100}/\sqrt{3}$ from d_{100} which is obtained from 2θ of the first peak in the XRD pattern by Bragg's equation¹² ($2d\sin\theta = \lambda$, $\lambda = 1.541$ Å for the Cu $K\alpha$ line). The value of a_0 is equal to one internal pore diameter plus one pore wall thickness. For as-synthesized AIMCM-41 and calcined-hydrated V-AIMCM-41 materials, some decrease of the XRD intensities was observed as shown in Figure 1b and 1c. This indicates the reduction of crystal size along the a and b axis after incorporation of Al into the structure as indicated by Z. Luan *et al*.¹³ Table 1 summarizes the structural properties of the mesoporous materials studied in this work.

It was observed that the intensity of (100) peak decreases at very low levels of aluminum incorporation (Figure 1b). The peaks are shifted towards to higher angle for AIMCM-41 and V-AIMCM-41 samples. These data are very similar to those of the literature.⁹ For extra-framework incorporation of vanadium into of the AIMCM-41, vanadium was dispersed using high-temperature solid-state ion-exchange method. XRD

shows that vanadium is homogeneously distributed throughout the AIMCM-41 solid products. Practically no loss in crystallinity was observed when an as-synthesized sample was heated at 823 K for 24 h to remain the surfactant. The chemical composition of AIMCM-41 was estimated by the characteristic X-ray intensity of specific element analyzed on a number of crystals. The ratio for Si/Al is found to be 30.

Table 1. Structural properties of siliceous as-synthesized MCM-41, as-synthesized AIMCM-41, and calcined-hydrated V-AIMCM-41.

sample	$d_{100}(\text{\AA})$	$a^a(\text{\AA})$	pore size ^b	Bet surface area(m ² /g)	Si/Al	Si/V
MCM-41	33.5	38.7	28.7(27.3) ^c	1460.9		
AIMCM-41	34.9	40.3	30.3		30	
V-AIMCM-41	37.8	37.8	27.8		19	52

^a $a_0 = 2d_{100}/\sqrt{3}$. ^bPore sizes are obtained by subtracting 10 Å from the a_0 values assuming the pore wall thickness is ~ 10 Å.¹⁴ ^cArea is determined by BET isotherm.

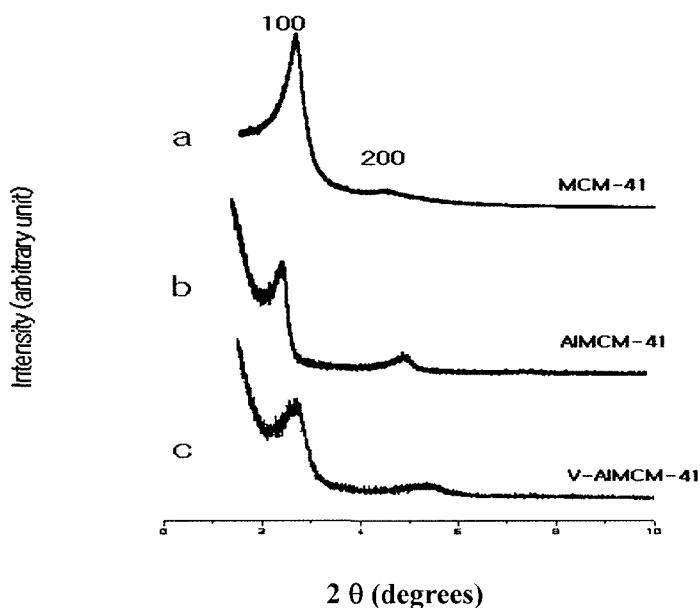


Fig. 1. XRD patterns of (a) as-synthesized MCM-41, (b) as-synthesized AIMCM-41 and (c) calcined-hydrated V-AIMCM-41.

^{27}Al MAS NMR

^{27}Al MAS NMR spectrum of as-prepared sample gives a single sharp resonance at 53.5 ppm from 4-coordinate Al (Figure 2a). This means that Al from the synthesis gel is incorporated exclusively into the framework when TMAOH is used as the source of aluminum(Figure 1a). Z. Luan *et. al* reported that ^{27}Al MAS NMR spectrum of as-synthesized AIMCM-41 gives a single peak at 53.0 ppm from 4-coordinate Al.⁹ ^{27}Al MAS NMR spectrum of the calcined, hydrated V-AIMCM-41 (Figure 2b) gives a broad line at 1.5 ppm in addition to line at ca. 51 ppm, indicating that some of the aluminum has been expelled from the MCM-41 structure upon heat treatment as indicated by Z. Luan *et al.*¹³

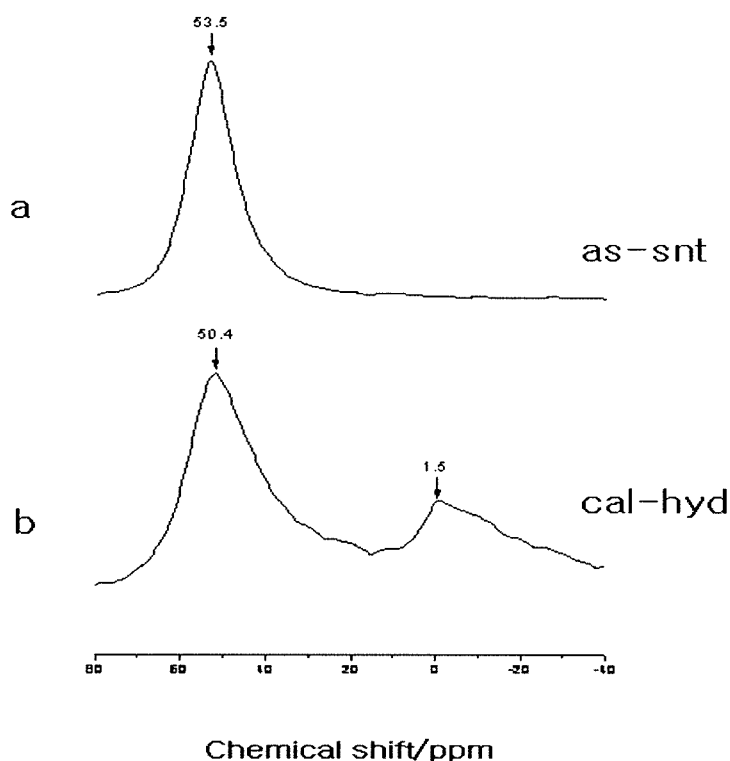


Fig. 2. (a) ^{27}Al NMR spectra for as-synthesized AIMCM-41 (b) calcined V- AIMCM-41 fully hydrated after equilibrated with room air.

^{29}Si MAS NMR

Typical ^{29}Si MAS NMR spectrum of purely siliceous MCM-41 was illustrated in Figure 3. A signal centered at -110 ppm attributal to Q_4 , $\text{Si}(4\text{Si})$, environment and a shoulder at ca. -100 ppm from Q_3 silicons on $\text{Si}(\text{OSi})_3\text{OH}$ site were observed.^{9a} It would be confirmed that aluminum has been inserted into the framework from a well-developed peak at -112 ppm coming from $\text{Si}(3\text{Si}, 1\text{Al})$ sites and ^{27}Al spectrum. The peak at -102 ppm is due to Q_3 silicons on $\text{Si}(\text{OSi})_3\text{OH}$ sites. Maria D. Alba et. al reported that ^{29}Si MAS spectrum gives the appearance of a line centered at -116 ppm, which has been assigned to the Si-O-Ti linkage.¹³

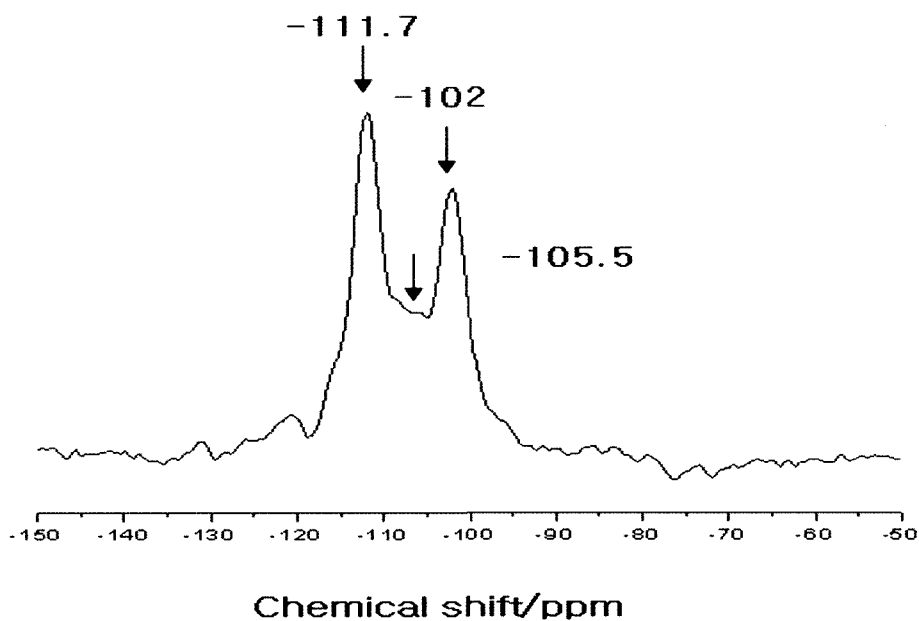


Fig. 3. ^{29}Si MAS NMR spectrum of calcined V-AlMCM-41 followed by hydration.

⁵¹V MAS NMR

Typical spectrum for a distorted octahedral V⁵⁺ species shows a nearly axially symmetric spectrum with the most intense chemical shift at δ_{\perp} in the range of -200 to -500 ppm relative to VOCl₃, while a distorted tetrahedral V⁵⁺ species typically shows a rhombic anisotropic spectrum with the most intense chemical shift at δ_{\perp} in the range of -500 to -800 ppm relative to VOCl₃.¹⁴

⁵¹V NMR spectrum was recorded at 9.4 T for MAS condition. Since NMR spectral features are not much affected by the overall vanadium content, only the spectrum with the highest signal-to-noise from V-AIMCM-41(30) is presented in Figure 4. A well-defined spinning sideband pattern centered at -373 ppm was observed. The relatively narrower envelope of the resonance line at -373 ppm in the MAS spectrum indicates that the chemical shift anisotropy of V⁵⁺ is somewhat averaged by MAS. The strong spinning side bands imply the significant chemical shift anisotropy and somewhat square pyramidal environment of the V⁵⁺ species.

UV-Vis

Calcined-hydrated V-AIMCM-41 sample exhibits strong UV-Vis absorption bands with overlapping maxima at about 275 and 410 nm as illustrated in Figure 5. The 275 nm band is assigned to the low-energy charge transfer transitions between tetrahedral oxygen ligands and a central V⁵⁺ ions.¹

Upon calcinations in air, the V-AIMCM-41 samples change from green to white due to oxidation of the small amount of VO²⁺ to V⁵⁺ ions. After exposing these calcined samples to hydrated air, the sample color changes rapidly to bright yellow and then orange. This indicates an additional coordination of water molecules to V⁵⁺ ions. A charge transfer transition near 410 nm is generally observed for yellow V⁵⁺ species with square pyramidal coordination.^{1,15,16}

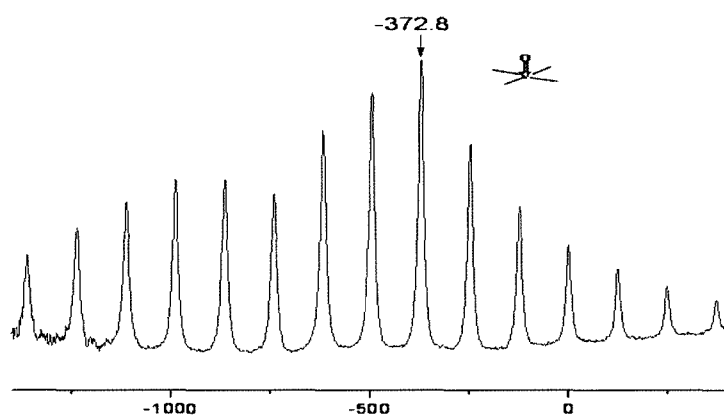


Fig. 4. ^{51}V MAS NMR spectrum of calcined V-AlMCM-41 after fully hydrated and equilibrated with room temperature.

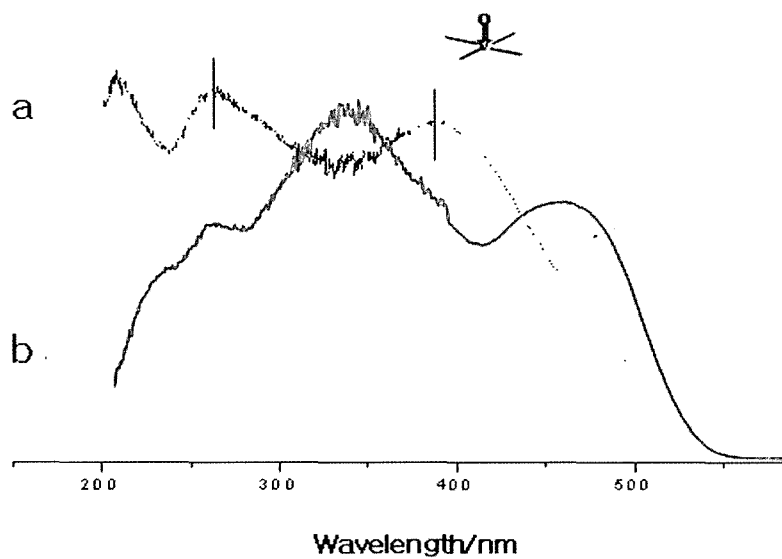


Fig.5. Diffuse reflectance UV-Vis spectra of (a) calcined-hydrated V-AlMCM-41 (b) reference, V_2O_5 .

ESR

The thermally reduced V-AIMCM-41 samples give similar ESR signals at room temperature. The example is illustrated in Figure 6a. The spectrum can be characterized by two axially symmetric sets for eight lines originating from vanadyl VO^{2+} species coupled to its own nuclear spin (^{51}V , $I_n = 7/2$, natural abundance 99.8%). The well-resolved hyperfine structure supports a high dispersion of the VO^{2+} ions in AIMCM-41. Moreover, no broad background signals were observed due to polynuclear oxidized vanadium, which is normally present in samples prepared with high vanadium contents.

V-AIMCM-41 does not show any signals immediately after calcinations in dry oxygen, suggesting the complete oxidation of VO^{2+} to V^{5+} during calcinations. A calcined sample was generally hydrated by the exposure to room temperature humidity before evacuation and dehydration treatment. This calcined, hydrated sample does not show ESR signal. The calcined sample after oxidation treatment at 673 K for 3 h also does not show ESR signal as well as a calcined, hydrated sample (Figure 6b and 6c). On the other hand, ESR spectrum of V-AIMCM-41 after dehydration at 873 K at 18 h using previously oxidized sample shows an axially symmetric signal with hyperfine structure (Figure 6a). In addition, parallel set of lines shows doubling which indicates presumably two different sites for the VO^{2+} species. The spin Hamiltonian parameters are $g_{\perp} = 2.015$, $A_{\perp} = 50.3$ G, where A_{\perp} is the hyperfine coupling. The parallel components overlap each other and have same values for $g_{\parallel} = 1.910$, $A_{\parallel} = 208$ G. The signals for VO^{2+} species appear to be isolated and well dispersed because of no superimposed broad singlet. These g values and the hyperfine coupling constants are typical for vanadyl VO^{2+} complexes with square pyramidal coordination¹⁷ that have been observed in several molecular sieves¹⁸ and are so assigned here. The occurrence of one vanadyl complex also indicates one local environment in V-AIMCM-41.

N_2 Adsorption Isotherms

The most reliable information about the mesoporous structure of solids could be obtained from nitrogen adsorption isotherms at low temperature, which is useful for the calculation of the specific area, pore volume and mesopore size distribution.¹⁹

Figure 7 represents the N_2 adsorption isotherm for purely siliceous MCM-41 at relatively low pressure ($p/p_0 < 0.1$). This isotherm accounts for monolayer adsorption of N_2

on the walls of the mesopore, and does not imply the presence of the micropore.

Pore size distribution

The BJH(Barrett-Joyner-Halenda) plot of N_2 physisorption on the purely siliceous MCM-41 was shown in Figure 8. The pore size distribution curve shows a remarkably narrow distribution with a pore size of 27 Å and an exceptionally high mesopore surface area of $1461 \text{ m}^2 \text{ g}^{-1}$ (can be seen in Table 1). This aspect can give a further confirmation for the structural uniformity of purely siliceous MCM-41. The approximate pore size calculated by nitrogen physisorption is smaller than that determined by XRD which includes the thickness of the pore wall as similar to that of Z. Luan.¹³

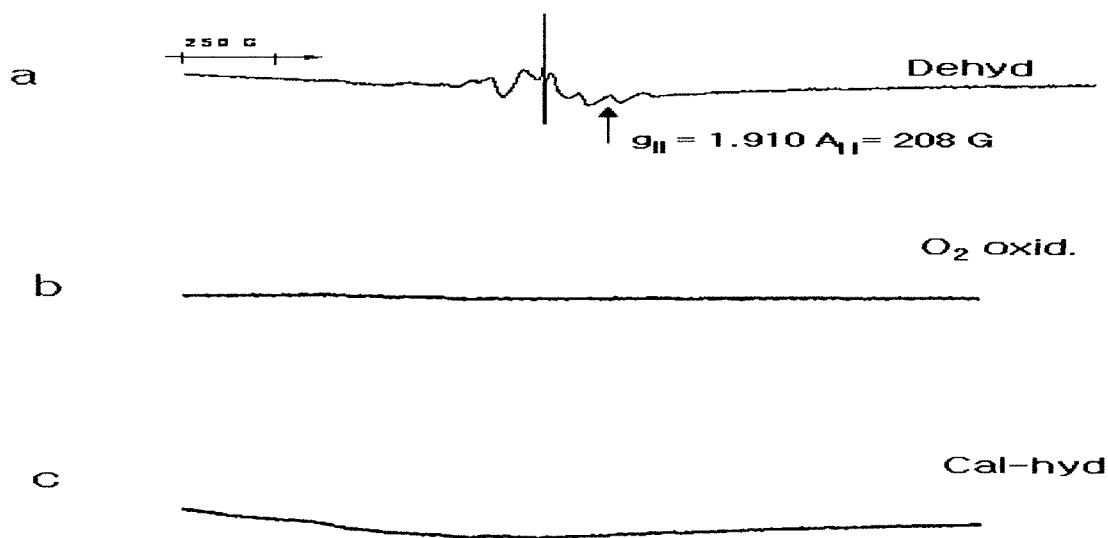


Fig. 6. ESR spectra (a) at 77K of V-AlMCM-41 after O_2 oxidation at 673 K for 5 h followed by dehydration at 873 K for 18 h (b) calcined-hydrated V-AlMCM-41 followed by O_2 oxidation at 673K for 5 h (c) calcined-hydrated V-AlMCM-41.

CONCLUSIONS

Vanadium-substituted mesoporous V-*Al*MCM-41 molecular sieves has been successfully synthesized. The molecular sieves have atomically dispersed vanadium centers located at the extra-framework. UV-Vis, ESR and ^{51}V NMR show that vanadium was observed as species with one oxidation state and coordination structure in V-*Al*MCM-41, namely as a square pyramidal VO^{2+} species. The single vanadium species suggests that vanadium is incorporated into an extra-framework site, one on the wall surface. The vanadium ions on the exterior wall and inside wall were found to occupy multiple coordination site (> 4) and perform reversible redox cycle.

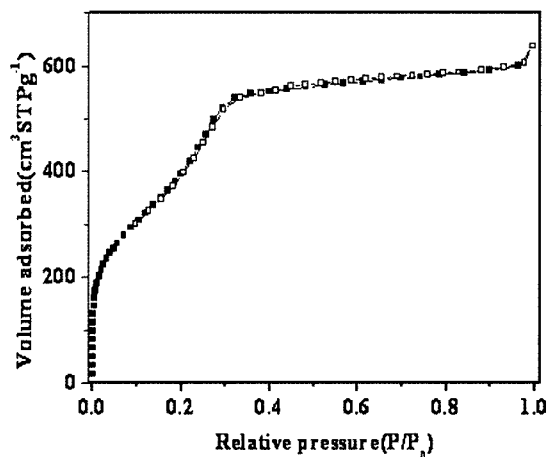


Fig. 7. Adsorption isotherms of nitrogen at $-196\text{ }^\circ\text{C}$ for purely siliceous MCM-41.

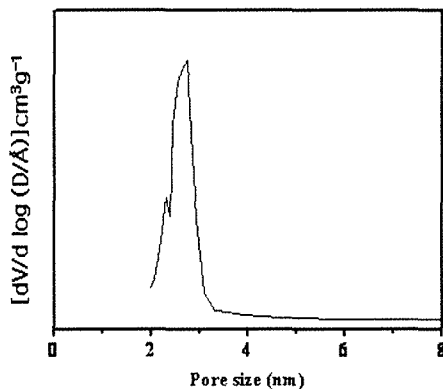


Fig. 8. Pore size distribution curve for purely siliceous MCM-41.

Acknowledgements

JSYu thanks to KEMC for financial support.

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