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Synthesis and pillaring of a layered vanadium oxide from V_2O_5 at ambient temperature

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Abstract

The synthesis and structural characterization of an amine-intercalated layered vanadium oxide and its silica-pillared derivative are described. The amine-intercalated vanadium oxide was prepared by reacting V_2O_5 with a mixture of alkylamine and a small amount of water at ambient temperature. The layer structure was examined by means of various analytical techniques, such as X-ray powder diffraction, thermal analysis, IR, UV–Vis and NMR spectroscopy, as well as elemental analysis. The alkylammonium ion-formed bilayers in the interlayer were ion-exchangeable with alkali ions. Moreover, ESR spectra showed that vanadium retained pentavalence through the intercalation reaction, although a small portion of vanadium was found to be reduced after the compound was stored in air for longer than 24 h. By reacting the amine-intercalated layer vanadia with a solution of tetraethyl orthosilicate, amine and acetone, followed by calcination, a silica-pillared derivative of microporous structure and high surface area was obtained.

Keywords: Layered; Vanadium oxide; Pillaring; Amine-intercalation; Microporous

1. Introduction

Layer compounds of transition metal oxides have attracted much attention in the past decades because they behave as versatile host structures for the intercalating of ionic and molecular species and give anisotropic coatings on substrate surfaces. Their potential applications include catalysis, humidity sensors, electrochromic devices and active materials for batteries. Vanadium oxides of pentavalent ions tend to adopt layered structures. The layered vanadium pentoxide sols with interlayer water molecules were first prepared by Ditte [1] in 1885 by a sol-gel process. A more thorough study of the layered structure was reported by Lemerle and coworkers [2,3], where vanadium oxide gels were synthesized by polymerization of decavanadic acid with a tedious and time-consuming procedure. A portion of V(V) in the oxide layers was found to reduce to V(IV) by water, and the layers carried negative charges. These charges were balanced by interlayer hydronium ions. The interlayer distance was reported to vary from 40 to 8.8 Å, depending on the water content and the number of reduced V(IV) ions [4]. Later, several studies concerning the

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[1] The corresponding author dedicates this paper to Prof. Abraham Clearfield on the occasion of his seventieth birthday.

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intercalation of these vanadium pentoxide gels with polar organic solvents and ion-exchange with organic and inorganic ions were reported [5–8].

Vanadium pentoxide gels of layered structures were also made directly from the oxide, but the reaction conditions were relatively vigorous. Hydrogen peroxide was reported to react vigorously with crystalline V_2O_5 and to give rise to a red gelatinous product [9]. Muller [10] obtained the gels by pouring the molten oxide (heated to around 800°C) into water. In the past few years, several new vanadium oxide compounds of layered structures were synthesized by hydrothermal reaction in the presence of either alkali metal ions [11], tetramethyl ammonium ions [12,13] or diamine [14]. The common point in all the layered vanadium oxide materials reported up to now is that the negative charges have been introduced into the basal vanadia layers by reducing a portion of V(V) to V(IV) during the preparation procedures. The negative charges are then balanced by cations present in the interlayer.

Pillaring of layered compounds with inorganic oligomers is one way to prepare porous materials of high thermal stability for sorption and catalysis. The research was originated from pillaring reactions with smectite clays and was stimulated by the crisis of the oil embargo in 1973 [15]. In comparison with zeolite catalysts, pores of relatively large diameters were obtained from pillared clays, and they were expected to be the active sites for the cracking of large molecules into heavy crude oil [16]. Although the usage of pillared clays in cracking processes has never been in practice due to their low hydrothermal stability, the development of the pillaring technique and its applications to other layered compounds has led to new materials of diverse chemical properties [17–23].

In the present study, a new layered vanadium oxide with alkylamine intercalation was prepared from a simple mixture of crystalline vanadium pentoxide, *n*-alkylamines and small amount of water at ambient temperature. Different from the layered vanadium oxide compounds reported previously, the V(V) was not reduced during the intercalation process. The resultant layered compound was then used as a precursor for the preparation of silica-pillared derivatives. The preparation condition and chemical properties of the layered and pillared vanadium oxides were examined.

2. Experimental methods

All chemicals were reagent grade, and were used as received without further purification.

2.1. Synthesis of amine-intercalated layered vanadium oxide

The mentioned compounds were synthesized based on the substrate weight composition of V_2O_5: 0.6 H_2O: 15 *n*-alkylamine. To a good mixture of alkylamine (Janssen) and deionized water, dehydrated V_2O_5 powder (Janssen) was added, followed by vigorous stirring for 48 h. The resultant solids were separated by filtration, washed with acetone several times, and dried under a 0.1 Torr vacuum. The as-synthesized solids are termed BA–V_2O_5, HA–V_2O_5 and OA–V_2O_5 for products of V_2O_5 reacting with butyl-, hexyl- and octylamine, respectively.

2.2. Synthesis of silica-pillared layered vanadium oxide

A 0.5 g portion of amine-intercalated vanadium oxide powder had a mixture of 15 g *n*-octylamine, 1.5 g acetone and 1.5 g tetraethyl orthosilicate (briefly termed TEOS, Janssen), added. After stirring for 75 h, the solids were filtered, washed with acetone and dried under a 0.1 Torr vacuum. The silica-pillared derivatives were obtained by calcination of the solids at 360°C.

2.3. Characterization techniques

The V contents of the resultant samples were analyzed with an ICP-AES (Allied Analytical System, Jarrell–Ash, Model IC AP 9000) using HCl-dissolved solutions. The C, H and N compositions were analyzed with a Perkin Elmer 2500 elemental analysis system. TGA was performed in an N_2 environment on a du Pont 951 thermogravimetric analyzer. The powder XRD patterns were recorded with a Philips PW 1840 automated powder diffractometer, using Ni-filtered Cu Kα radiation. FT-IR spectra were taken with a Bomem MB 100 FTIR spectrometer. The ESR spectra were recorded with a Bruker ESP 300 X-band first derivative instrument and DPPH was used as an external standard. Wideline and MAS ^{51}V

solid-state NMR were performed at 157.7 MHz on a Chemagnetics CMX Infinity spectrometer. The MAS NMR spectra were also obtained at 94.7 MHz on a Chemagnetics CMX2 spectrometer for comparison. The MAS spectra obtained at 157.7 MHz used a 90° pulse of 0.2 μs length and 0.1 s relaxation delay, and those at 94.7 MHz used a 2.5 μs pulse length and 0.5 s relaxation delay. The wideline spectra were obtained with a quadruple echo program, using a 1.5 μs pulse length, 30 μs delay between pulses, 25 μs delay after the 2nd pulse and 0.2 s relaxation delay. Chemical shifts were referenced to $VOCl_3$. The BET surface area and pore-size distribution were determined from the N_2 adsorption–desorption isotherms measured at liquid N_2 temperature with a gravimetric system (Cahn TG-121 microbalance).

3. Results and discussion

3.1. Amine-intercalated layered vanadium oxide

When crystalline V_2O_5 powders were added into the solutions of *n*-alkylamine and water, the color of the solids changed gradually from brown orange to olive green, and finally to white. The color change is clearly demonstrated by the diffuse reflectance UV–Vis spectra of the solid products isolated after different reaction periods (Fig. 1). V_2O_5 has a broad absorption band extending from 200–500 nm. The absorption around 500 nm is attributed to the n $\rightarrow$ π^* transition centered on the V=O group. That accounts for the brown orange color of crystalline V_2O_5 observed from the compensatory frequencies. Fig. 1 shows that the intensity of the 500 nm band decreases gradually and almost disappears completely after 1 h of reaction. The remaining absorptions in the 200–385 nm region are attributed to $O^{2-} \rightarrow V(V)$ charge transfer [3]. These results imply that the V=O double bond was destroyed during the reaction.

Fig. 2 shows the X-ray diffraction patterns of the as-synthesized solids using *n*-alkylamines of different carbon chain lengths. The patterns predominantly consist of a series of peaks which have d-spacings of the type d_{00l}/l, where l is an integer, and that is a strong indication of the occurrence of lamellar structures. The d-spacings of the diffraction peaks at lowest 2θ increases from 13.8 to 16.4 to 19.6 Å as the

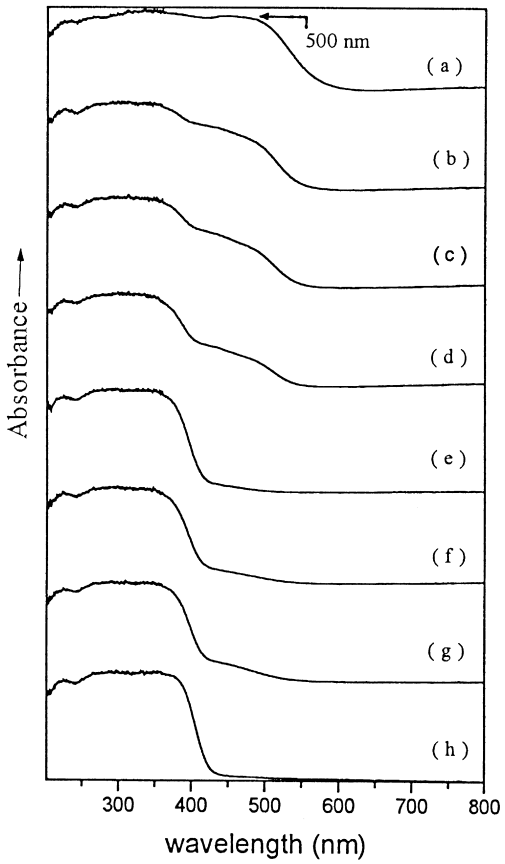


Fig. 1. UV–Vis spectra of V_2O_5 after reacting with *n*-octylamine and H_2O for: (a) 0 min; (b) 5 min; (c) 10 min; (d) 30 min; (e) 1 h; (f) 3 h; (g) 24 h; and (h) 48 h.

carbon chain length increases through butyl-, hexyl- and octylamine, respectively. When plotting these d-spacings versus number of carbon atoms in *n*-alkylamines, a straight line with a gradient of 1.45 Å/carbon atom, was obtained. Since alkyl chains grow by ca. 1.27 Å per added carbon, the gradient suggests that the *n*-alkylamines form bilayers in between the sheets. There are some differences in the increments, and a similar phenomenon was also observed by Bouhaouss and Aldebert [5] on amine-intercalated $V_2O_5.nH_2O$ gel. They proposed that the interlayer alkylamines of shorter (five to seven carbons) chains were tilted to a larger angle from the perpendicular to the sheet surface than those of longer carbon chains.

The samples prepared with different *n*-alkylamines also show very similar infrared spectra (Fig. 3). Absorptions below 1100 cm^{-1} are attributed to lattice

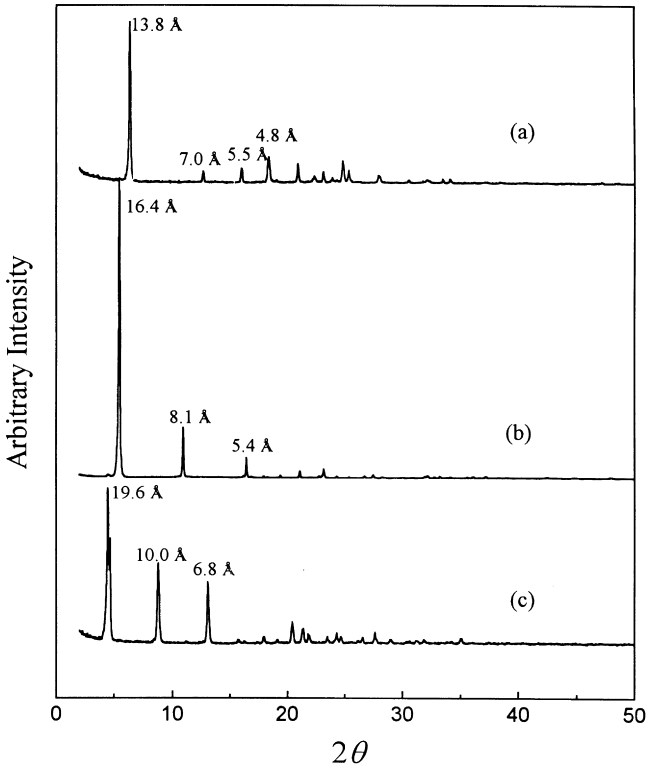


Fig. 2. XRD patterns of V_2O_5 intercalated with: (a) *n*-butyl-; (b) *n*-hexyl-; and (c) *n*-octylamine.

vibration of the vanadium oxide. It is noticed that the absorption around 1020 cm^{-1}, corresponding to the V=O double bond, is negligible in the spectra. These results are consistent with those of the UV–Vis data. The alkyl groups of amines give rise to strong absorption in the regions of 2850–3000 cm^{-1} and 1400–1600 cm^{-1}, which are assigned to C–H stretching and bending vibrations, respectively. The relative intensity of these peaks versus that of the lattice vibration decreases as the carbon number of the amines decreases. On the other hand, a broad band at ca. 3040 cm^{-1} overlapping over the uCH band is assigned to ammonium ions [24], implying that the *n*-alkylamines are present in the interlayer as alkylammonium ions instead of neutral molecules. Another broad absorption around 3500 cm^{-1} of relatively weak intensity is apparently attributed to hydrogen bonded O–H groups.

Fig. 4 shows the ESR spectra of the as-synthesized *n*-octylamine-intercalated V_2O_5 and that after standing in air for 24 h in the presence of dpph standard. The as-synthesized sample has no ESR signal, while that standing in air for a while has ESR signals composed of complicated hyperfine structures. These results imply that the vanadium is not reduced during the intercalation process, but a small portion may be reduced when the samples are exposed to air. Vanadium of lower oxidation states give dark colors. Since the stored samples remain white or turn into pale yellow, the amount of V(IV) present in the amine-intercalated samples should be small. The ESR spectra of V(IV) ions in an isotropic environment exhibit eight lines of equal peak-to-peak width due to the hyperfine coupling of one unpaired electron (S = 1/2) with the nuclear spin (I = 7/2) of ^{51}V. The spectrum in Fig. 4(b) shows that both parallel and perpendicular features can be seen. That implies that V(IV) ions are in a low symmetric ligand field [3].

Fig. 5 shows the wideline and MAS ^{51}V solid-state NMR spectra of octylamine-intercalated V_2O_5 in comparison with those of pristine crystalline V_2O_5. The wideline spectrum of V_2O_5 shows ^{51}V nuclei in

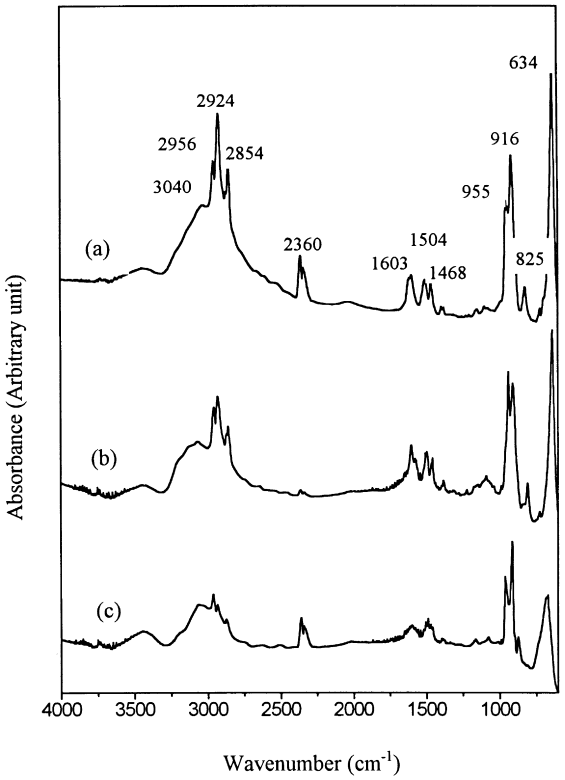


Fig. 3. IR spectra of V_2O_5 intercalated with: (a) *n*-octyl-; (b) *n*-hexyl-; and (c) *n*-butylamine.

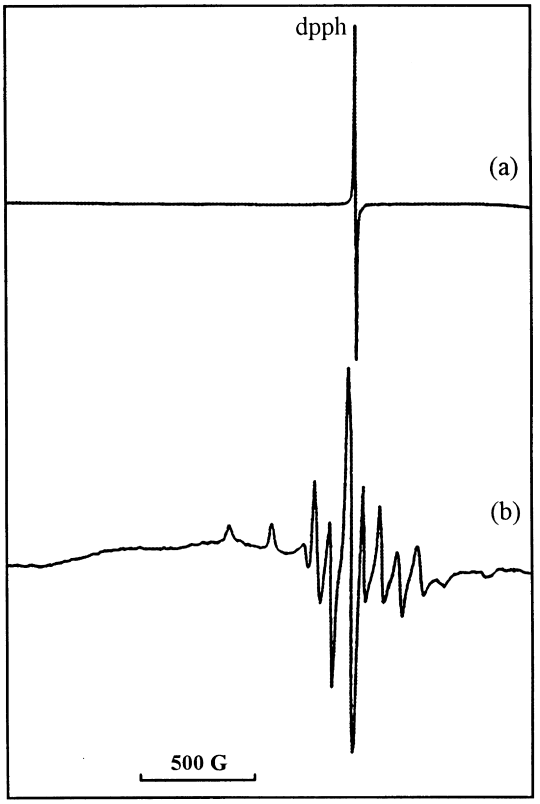


Fig. 4. EPR spectra of: (a) as-synthesized *n*-octylamine-intercalated V_2O_5; and (b) that after standing in air for 2 days, in the presence of dpph standard.

an axially distorted coordination environment with δ_1 and δ_2 at –320 ppm and δ_3 at –1210 ppm. The line shape of central transition (1/2, –1/2) is broadened by higher order transitions, such as (–3/2, –5/2), (–1/2, –3/2), (3/2, 1/2) and so on [25]. The MAS spectra show that the isotropic chemical shift, which appeared at – 615 ppm, is the average of the anisotropic chemical shifts observed in the wideline spectrum. The broadening of the central peak and the spin side-bands with the decrease in magnetic field strength from 157.7 to 94.7 MHz is attributed to the second-order quadrupolar perturbation. For the amine-intercalated compound, the wideline NMR spectrum has a narrower bandwidth than that of V_2O_5, implying that the first-order quadrupolar perturbation on the ^{51}V nuclei in the amine-intercalated compound is not as strong as that in the pristine V_2O_5. However, the line shape with symbols δ_1, δ_2 and δ_3 around –374, –508 and –800 ppm, respectively, indicates the loss of axial symmetry. The relatively weak signal to noise ratio is a result of suppression of the NMR signals by the paramagnetism of V(IV). Since the sample used for NMR studies was stored in air for some time, this observation is consistent with the ESR results that a portion of vanadium was reduced. The MAS spectrum obtained with a 157.7 MHz magnetic field shows a well-defined set of three peaks with chemical shifts at –545, –550 and –570 ppm, while that obtained with 94.7 MHz magnetic field shows a set of single peaks with chemical shift at approximately –550 ppm. The three peaks indicate a probable presence of three distinct vanadium sites in the intercalated compound. These sites however cannot be distinguished with the spectrometer of lower magnetic field due to the broadening of the peaks by second-order quadrupolar perturbation.

The chemical compositions of the as-synthesized samples were determined with ICP-AES and C, H,

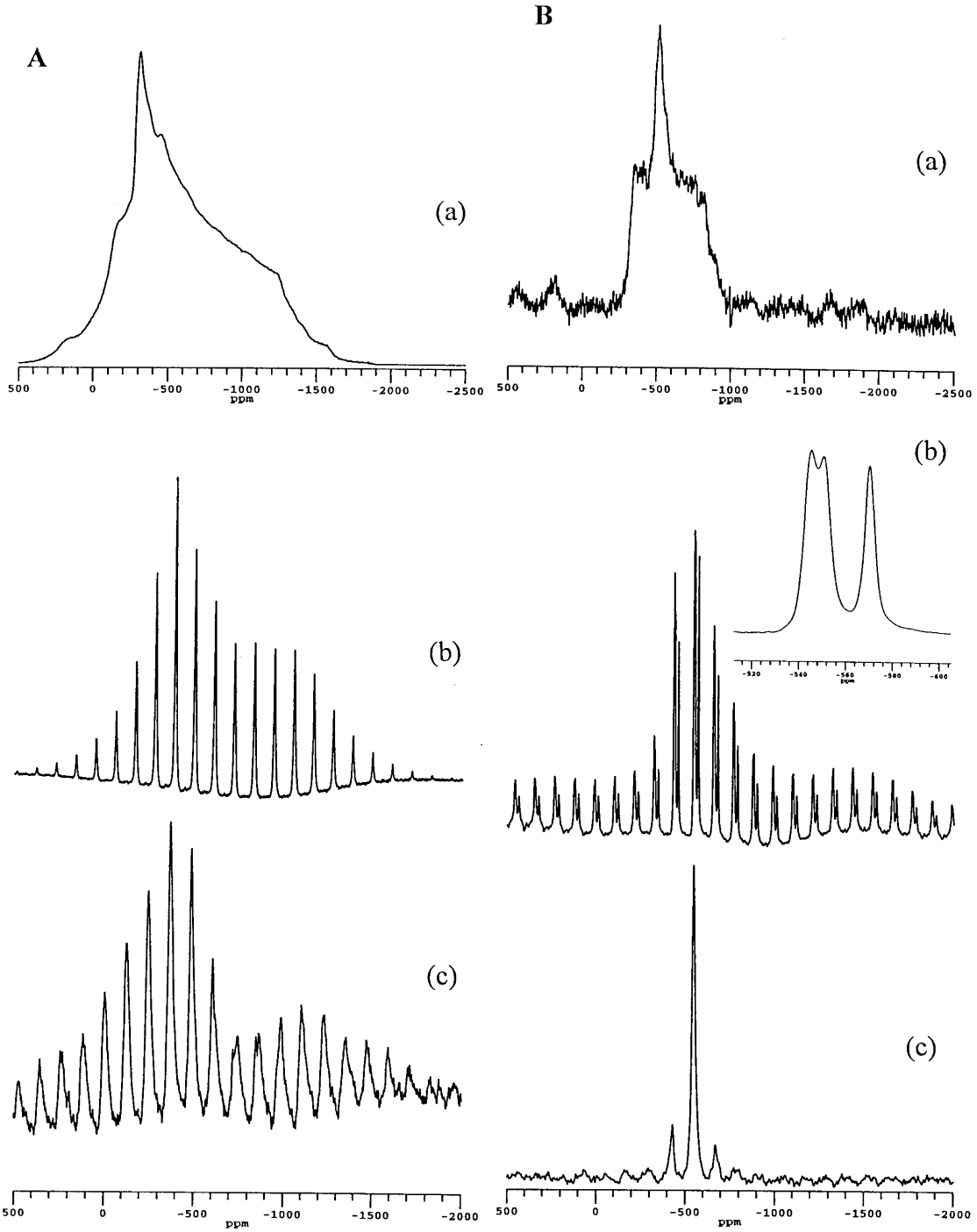
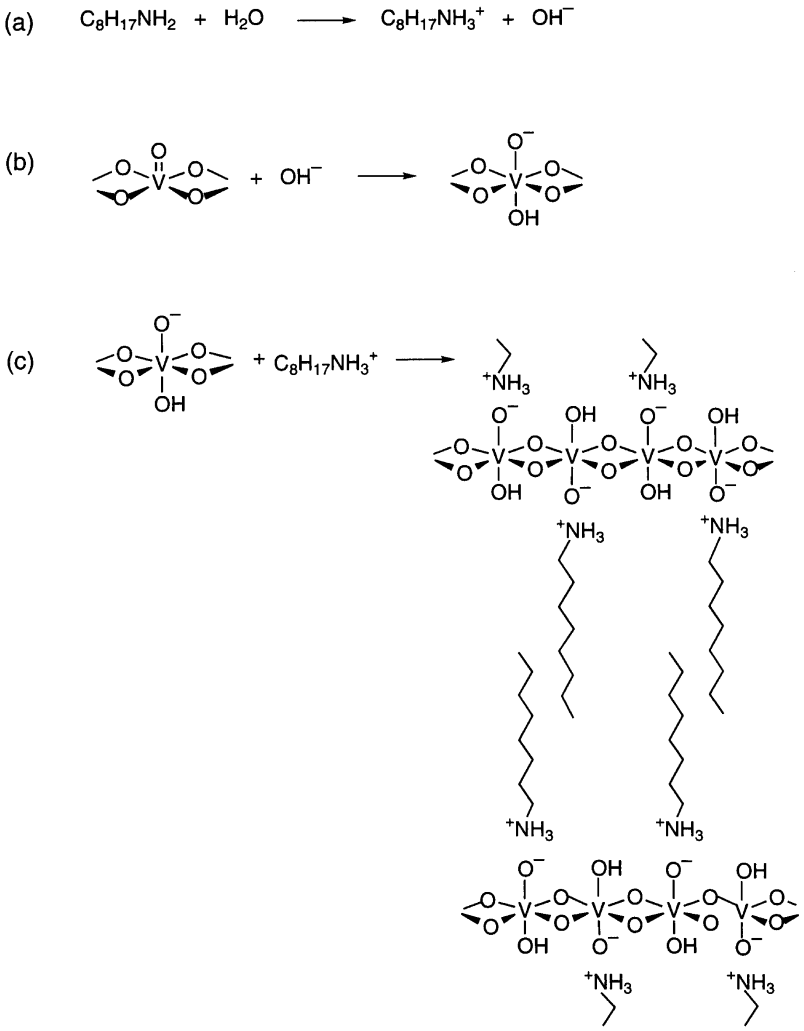


Fig. 5. ^{51}V solid state NMR spectra of (A) V_2O_5, and (B) octylamine-intercalated V_2O_5: (a) wideline spectra at 157.7 MHz; (b) MAS spectra at 157.7 MHz; spin rate of 17 kHz; and (c) MAS spectra at 94.7 MHz, spin rate of 11 kHz.



Scheme 1. Proposed reaction mechanism of V_2O_5 intercalated with *n*-octylamine in the presence of small amount of water.

Table 1
Elemental analysis data and the proposed formula of amine-intercalated V_2O_5

Sample		C	H	N	V_2O_5 residue E.A.	TGA[a]	Theoretical	Formula
BA–V_2O_5	wt %	26.3	6.7	7.7	59.3	44.2	56.3	$V_2O_5(H_2O)_{1.00}$
	Molar ratio	4.0	12.2	1	0.593			$(C_4H_9NH_2)_{1.69}$
HA–V_2O_5	wt %	35.7	8.0	6.9	49.4	47.4	47.2	$V_2O_5(H_2O)_{1.09}$
	Molar ratio	6.0	16.2	1	0.550			$(C_6H_{13}NH_2)_{1.82}$
OA–V_2O_5	wt %	41.7	8.8	6.0	43.5	40.1	41.7	$V_2O_5(H_2O)_{1.26}$
	Molar ratio	8.0	20.4	1	0.557			$(C_8H_{17}NH_2)_{1.80}$

[a]TGA was carried out in air.

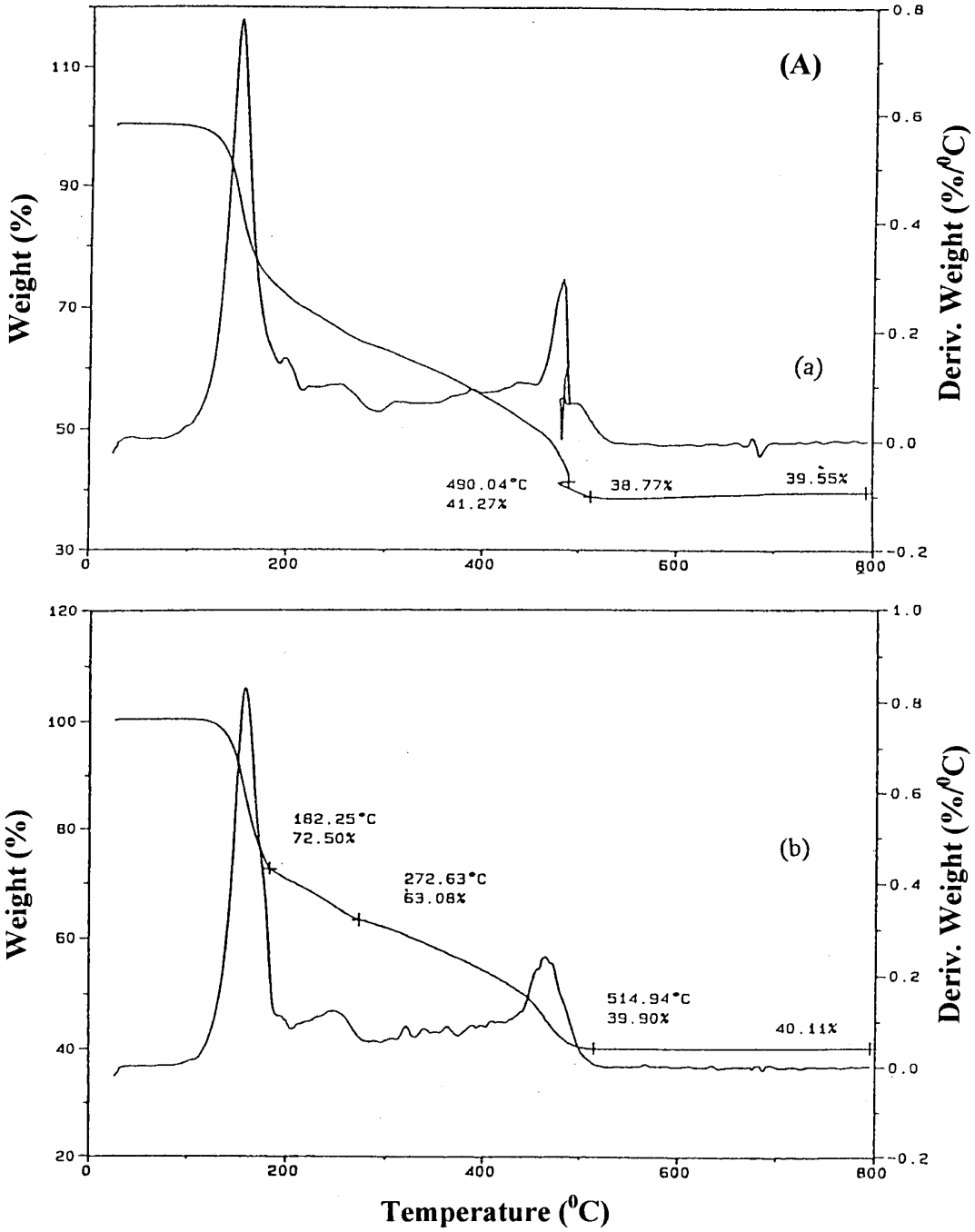


Fig. 6. Thermal analysis results of octylamine-intercalated V_2O_5: (A) TGA; and (B) DSC profiles in: (a) air; and (b) N_2 environment.

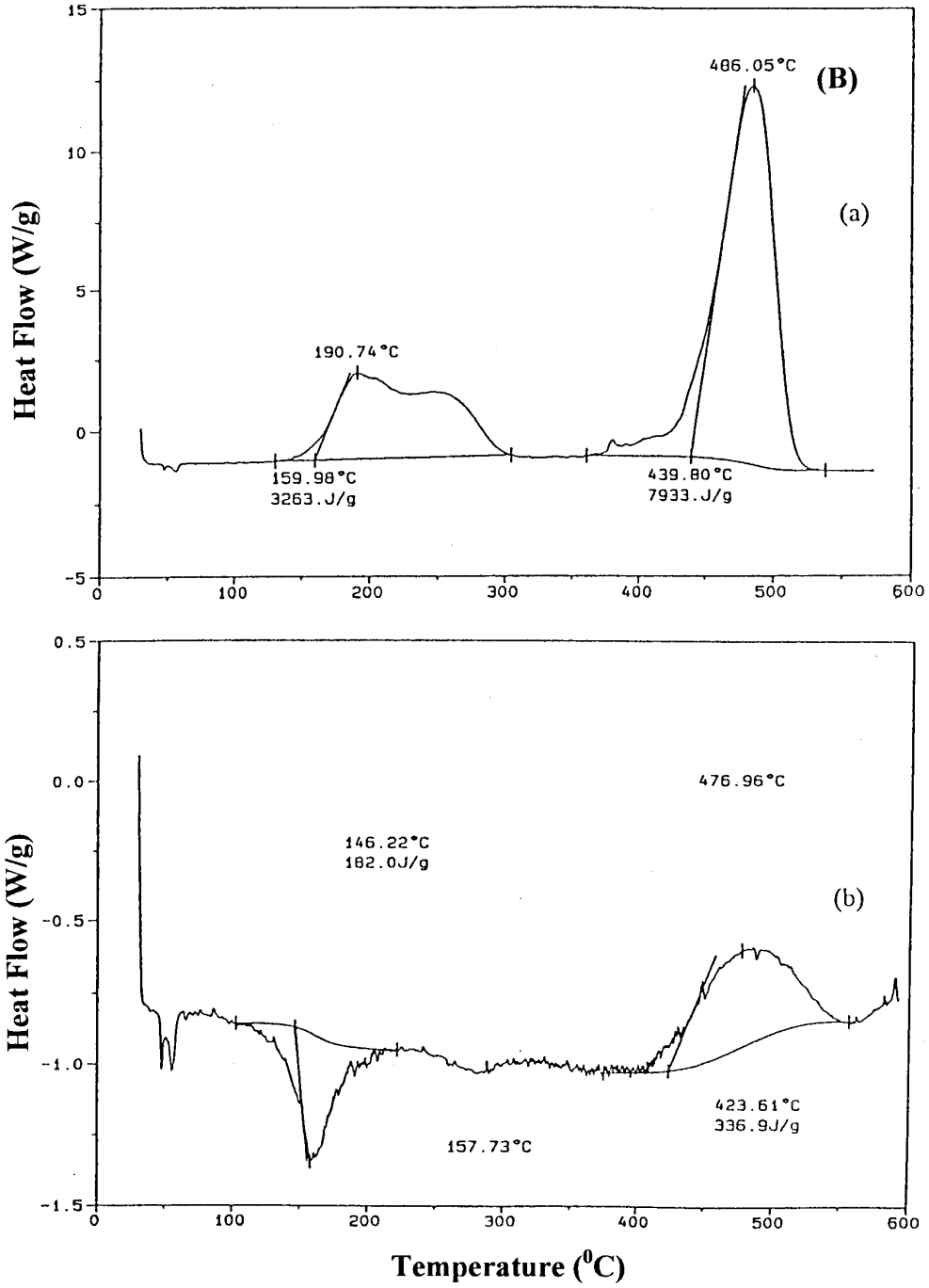


Fig. 6. *continued*.

N analysis. Based on the analytical data, the empirical formulae are in the form close to $V_2O_5(H_2O)(NH_2C_nH_{2n+1})_2$, where n is the carbon number on butyl-, hexyl- and octylamines (Table 1). It is noticeable that the N:V atomic ratios are all close to the value of 1:1. In comparison with other amine-intercalated compounds synthesized by the hydrothermal method, the N:V atomic ratios of 1:2 [14] and 1:3 [13], respectively, were observed on diamine-intercalated and tetramethyl ammonium-incorporated vanadates. Their nitrogen contents were considered to be proportional to the amount of reduced V(IV). Since ESR results showed that vanadium in our amine-intercalated compounds was not reduced during the intercalation procedure, the formation mechanism and structure of our amine-intercalated vanadia compound must be different from those reported in the literature. Table 1 also demonstrates that the V_2O_5 residues obtained from elemental analysis and from TG analysis are quite consistent with each other. The relatively great deviation observed on the TGA result of butylamine-intercalated V_2O_5 is probably due to its relatively high hydrophilicity, therefore a larger amount of water was absorbed on this intercalated sample.

The addition of a small amount of water in the preparation mixture was found to be essential for the amine-intercalation reaction to be complete. If crystalline V_2O_5 powders were reacted with only n-alkylamine, the resultant products examined by X-ray diffraction and IR spectroscopy were a mixture of intercalated compound and the pristine V_2O_5. Because both reactants,V_2O_5 and alkylamines, were hygroscopic to some extent, a slight amount of water might be present in the system even though no water was added on purpose. Hence, the intercalation is proposed to have water involved in the reactions. On the other hand, the IR spectroscopic results show the presence of alkylammonium ions and the absence of V=O groups in the intercalated product. The V_2O_5 intercalation reaction with alkylamines is therefore proposed to proceed through reaction paths depicted in Scheme 1. In the first step, amines are hydrolyzed by water to form ammonium ions and hydroxide ions. The hydroxide ion as a Lewis base shall attack vanadium on V_2O_5 through the open space of square pyramidal coordination, and the π-electrons on V=O transfer to oxygen as a lone-pair. Each negative charge on the $V-O^-$ terminal attracts an alkylammonium ion through electrostatic forces. As the alkylammonium ions form bilayers and prop open the V_2O_5 layers, the vanadium becomes six-coordinated and retains its pentavalent oxidation state. If the reaction is complete, the formula of the amine-intercalated compound would be $V_2O_5(OH)_2(NH_3C_nH_{2n+1})_2$, or $V_2O_5(H_2O)_2(NH_2C_nH_{2n+1})_2$, and the molar ratio of V: H_2O: n-alkylamine shall be 1:1:1. The large discrepancy in the H_2O content in the formulae derived from elemental analyses in Table 1 is attributed to the fact that a portion of OH^- groups may recombine with alkylammonium ions to form water, which is evaporated from the samples and leaves alkylamine molecules in the interlayer when the samples are dried by evacuation. Based on the formulae listed in Table 1, the molar ratios of amine molecule: ammonium ion in the intercalated samples are around 1: 2. That may explain the three sites observed on the ^{51}V solid-state MAS NMR spectrum of the amine-intercalated V_2O_5.

The thermal stability of the amine-intercalated compound was studied by carrying out TG and DSC analysis with either air or N_2 as the carrier gas (Fig. 6). Both TGA profiles of octylamine-intercalated V_2O_5 show an abrupt weight loss of ca. 27.5%, which started at temperatures a little bit higher than 100°C, with the maximum around 182°C. The weight losses, which reach a total of 60%, extend smoothly with temperature up to ca. 500°C. Both TGA profiles obtained in air and in N_2 are similar, except for a small interruption of the temperature at the end of the weight loss that appears on the profile obtained in air. On the other hand, the DSC profiles obtained in different gaseous environments are obviously different. In N_2, an endothermic peak appeared at 158°C and an exothermic peak appeared at 477°C. In air, two exothermic peaks were seen around 191°C and 486°C, and both areas were about twenty times greater than those observed in N_2. The huge exothermic peak in air at 486°C is apparently due to the combustion of interlayer organic species. The corresponding peak in N_2 is much smaller because the oxidation has to use lattice oxygen. On the other hand, since the boiling point of octylamine is 179.6°C, the abrupt weight loss at 182°C corresponds to the release of free octylamine molecules. The endothermic peak observed in N_2 is therefore due to heat absorption for evaporation of amines.

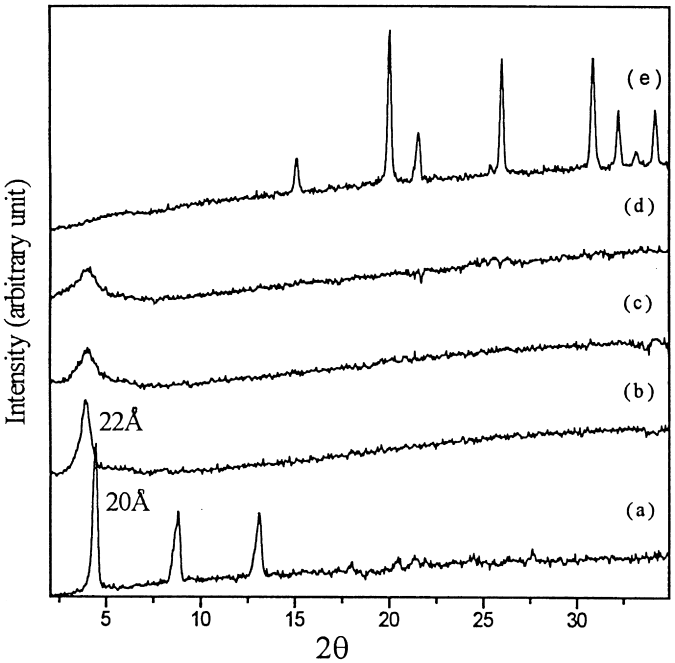


Fig. 7. XRD patterns of *n*-octylamine-intercalated V_2O_5: (a) as-prepared; and after calcination at (b) 200°C; (c) 300°C; (d) 400°C; and (e) 600°C.

However, that cannot explain the exothermic peak around 191°C observed in air.

Fig. 7 shows the structural changes of octylamine-intercalated V_2O_5 as a function of calcination temperature. The d-spacing increases from 20 to 22 Å with an apparent decrease in crystallinity after the sample was calcined at 200°C. The d-spacing at 22 Å is retained and the crystallinity further decreases as the calcination temperature rises up to 400°C. After 600°C, the crystalline phase of V_2O_5 was obtained. These results imply that the layered structure is retained up to ca. 400°C.

Fig. 8 shows the IR spectra of OA–V_2O_5 after calcination at various temperatures. The samples calcined at 200°C and 400°C were black, indicating the presence of coke, while that calcined at 550°C was white with a crystalline structure of V_2O_5. The IR spectra of the black samples still show C–H stretching peaks, although the intensity decreases with calcination temperature. Moreover, although the lattice vibration peaks at 955 and 916 cm^{-1} shifted toward higher wavenumbers upon calcination, the 1022 cm^{-1} peak of V=O bond did not appear until a calcination temperature of 550°C. Therefore, the d-spacing of 22 Å observed on the calcined samples is attributed to the rearrangement of interlayer alkylammonium ions accompanying the disordering of the vanadia sheet. The evaporation of amine molecules is endothermic, while the structural transformation is exothermic. Hence, both an endothermic peak and an exothermic peak are expected in the DSC profile around the boiling point of the amine. These two peaks in opposite directions, however, may cancel each other. That cancellation effect results in only an endothermic peak at 182°C being observed in the DSC profile obtained in N_2 and an exothermic peak around 191°C on the DSC profile taken in air.

The presence of alkylammonium ions in the interlayer was further proved by studying the ion-exchange behavior of the amine-intercalated compounds. Thus, 0.5 g portions of the amine-intercalated compounds were stirred with 50 mL of 4 M CH_3COONa or CH_3COOK solution for 2 days, followed by washing with alcohol and drying under vacuum. The interlayer alkylammonium ions were found to be exchangeable with alkali ions, and the interlayer distance varied with the sizes of the cations. Fig. 9 shows that the d-spacings shrink to 7.9 and 7.0 Å, respectively, for Na^+ and K^+-exchanged products, and these results are independent of the amines originally incorporated in the vanadium oxide layers. The diameters of Na^+ and

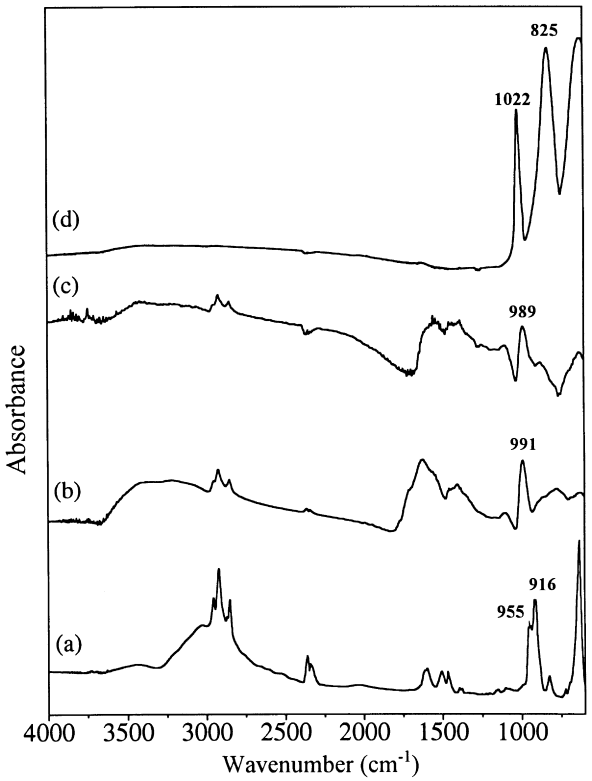


Fig. 8. IR spectra of *n*-octylamine-intercalated V_2O_5: (a) as-prepared; and after calcination at (b) 200°C; (c) 400°C; and (e) 550°C.

K^+ ions are 2.3 and 3.0 Å, respectively. The larger d-spacing of Na^+-exchanged products in comparison with that of K^+-exchanged ones implies that the cations exchanged with alkylammonium ions are hydrated alkali ions instead of plain alkali ions. The elemental analysis of the Na^+-exchanged products show the Na: V atomic ratio to be around 1: 1. When the Na^+-exchanged products were heated at temperatures higher than 200°C, the structure was found to transform to β-$NaVO_3$ with the strongest X-ray diffraction peaks appearing at $2\theta = 5.01$, 3.54 and 2.95°. These results support our model of the intercalated structure and confirm that the interlayer alkylammonium ions are completely exchanged by sodium ions. Besides, the interlayer amine molecules seem to be hydrolyzed by water again during the exchange reaction.

3.2. Silica-pillared layered vanadium oxide

The silica-pillared derivatives of V_2O_5 were prepared by utilizing the amine-intercalated compounds as precursors. Due to the hydrophobic nature of the interlayer alkyl chains, the amine-intercalated compounds were found soluble in TEOS. In order to obtain solid products, the addition of a proper amount of acetone and alkylamine into TEOS was found to be essential. Fig. 10(a) shows the XRD pattern of the amine-intercalated V_2O_5 after interacting with the TEOS solution. There is only one broad peak at d-spacing of 37 Å observed on the as-prepared sample. The d-spacing is much larger than those of amine-intercalated precursors, indicating that the interlayer distance is enlarged by the dissolved TEOS molecules. After calcination at 400°C in order to convert TEOS to silica, the resultant compound was nearly amorphous (Fig. 10(b)). Similar to the amine-intercalated precursors, the V_2O_5 phase was observed when the compound was heated at temperatures higher than 600°C. However, the V_2O_5 phase was much less crystalline than that obtained from calcination of amine-intercalated vanadia. In the amine-intercalated precursor, amines can be

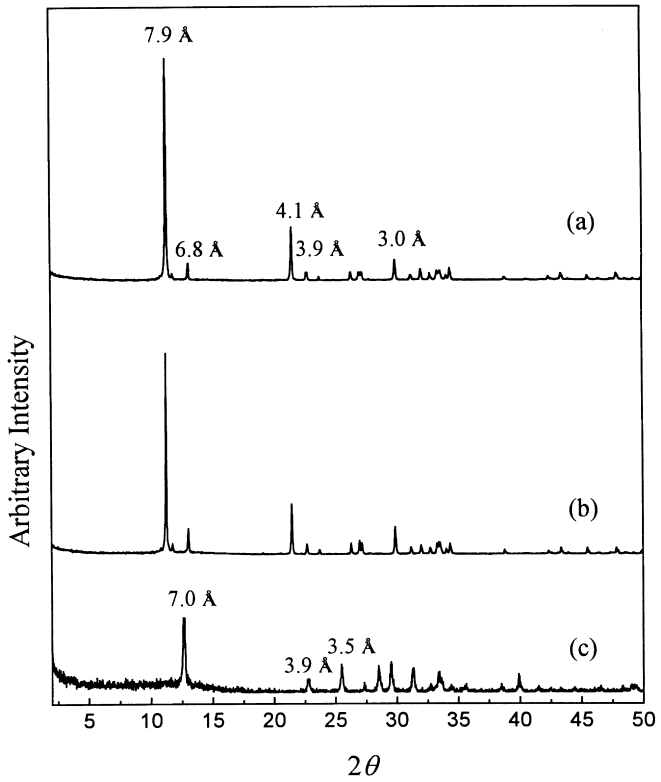


Fig. 9. XRD patterns of alkali ion-exchanged alkylamine-intercalated V_2O_5: (a) Na^+–BA–V_2O_5; (b) Na^+–OA–V_2O_5; and (c) K^+–OA–V_2O_5.

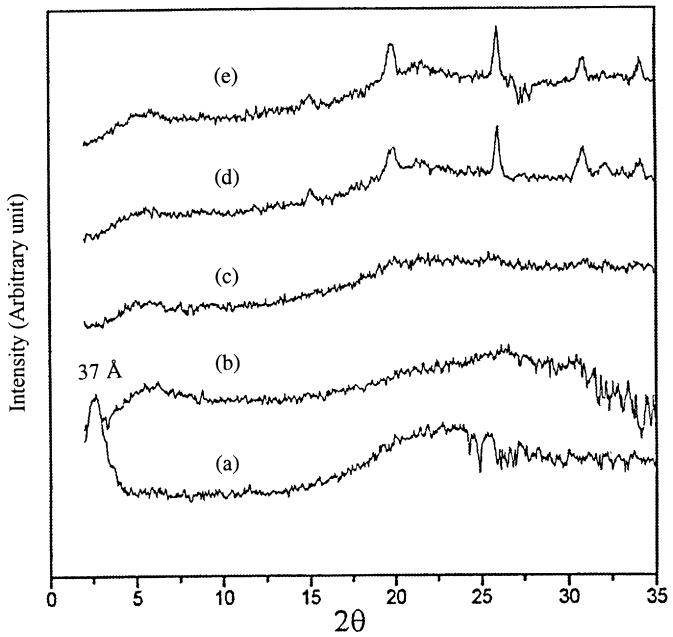


Fig. 10. XRD patterns of amine-intercalated V_2O_5: (a) after interacting with TEOS; and after calcination at (b) 400°C; (c) 500°C; (d) 600°C; and (e) 1000°C.

Table 2
Variation of surface area as a function of TEOS reaction period

Rxn period (h)	24	48	60	75	80	125
BET S.A. (m^2g^{-1})	457	393	429	618	533	389

completely removed after calcination at temperatures higher than 550°C. But, silica will remain in the product even upon calcining the silica-pillared sample at high temperature. Therefore, it is more difficult to crystallize V_2O_5 into large particles with silica pillars present in the structure.

Although the silica-pillared compound obtained after calcination at 360°C is X-ray amorphous, the N_2 adsorption-desorption isotherm shows that the compound contains mainly micropores (Fig. 11). The steep increase in N_2 adsorption volume at low N_2 pressure is a result of microporous condensation. Besides, the small hysteresis observed at P/P_0 greater than 0.45 is an indication that a small amount of mesopores is also present in the sample. These mesoporous structures are due to inter-particle defects and are often observed on pillared layer materials.

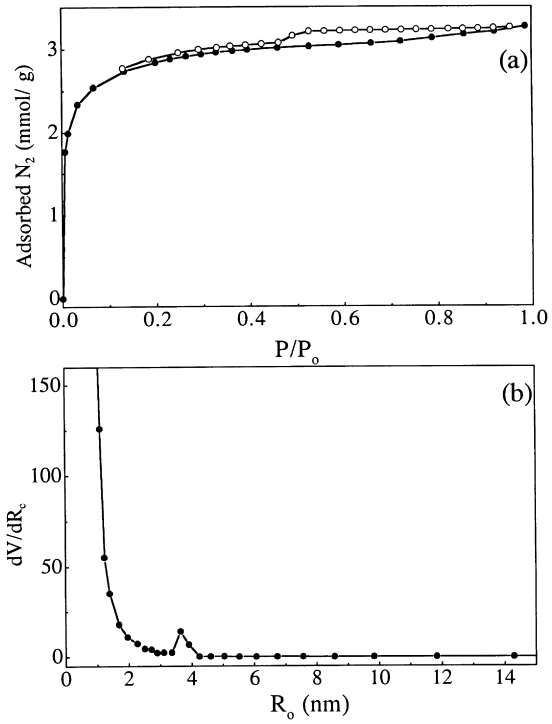


Fig. 11. (a) N_2 adsorption-desorption isotherm, and (b) pore radius distribution of silica-pillared V_2O_5.

The surface area of the silica-pillared derivatives was found to vary significantly with the reaction period of the amine-intercalated precursor in TEOS solution. Table 2 shows that the highest surface area was obtained with a 75 h reaction period. When the reaction period is too short, there are probably not enough TEOS molecules to diffuse into the deep interior of the interlayer space. After calcination, the silica pillars which aggregate on the outer rim cannot effectively support the interior space between the layers from collapse. As a result, the surface area is low. In contrast, when the reaction period is too long, there is probably too much TEOS dissolved in the interlayer. After calcination, the large silica pillars will occupy most of the interlayer space and leave small void spaces for gas molecules to be adsorbed. Similar correlation was also observed on silica-pillared magadiite [26].

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