

Hydrothermal crystallization and secondary synthesis of vanadium containing zeolites

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바나듐함유 제올라이트의 수열결정화 및 2차처리합성

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Abstract The substitution of vanadium atoms into the zeolite framework structure could be applied to the large pore zeolites by means of modified treatments as well as direct hydrothermal synthesis. The incorporation of V into the zeolite framework was demonstrated by instrumental analysis techniques. The result of X-ray diffraction analysis showed that the unit cell parameters increased after incorporation of vanadium into the zeolitic lattice, indicating that the replacement of Si by the larger V atoms could cause a slight expansion in the unit cell. In addition, the results of FTIR, Uv-Vis and Si-MAS-NMR spectra strongly support the incorporation of V into the zeolite framework. Acid leaching of aluminum in zeolites can provide a vacant position in the lattice for the insertion of vanadium by secondary hydrothermal treatment.

요약 약 직접 수열합성법과 변조된 처리법을 이용하여 세공경이 큰 제올라이트의 결정구조내에 바나듐원자가 치환되도록 하였다. 제올라이트 골격에 바나듐이 도입되었는지의 여부를 기기 분석을 통하여 시험하였다. X선회절분석의 결과, 바나듐이 제올라이트의 구조중에 도입되면 결정골격중의 실리콘원자 대신 치환되어 결정단위세포의 확장을 나타내었다. 또한 FTIR, UV-Vis 및 Si-MAS-NMR 스펙트럼결과는 제올라이트 골격내로의 바나듐의 도입을 강하게 뒷받침하였다. 제올라이트중의 알루미늄을 산처리로 용출시키면, 격자에 빈자리를 제공하여 2차수열처리법에 의한 바나듐의 도입을 가능케 하였다.

1. Introduction

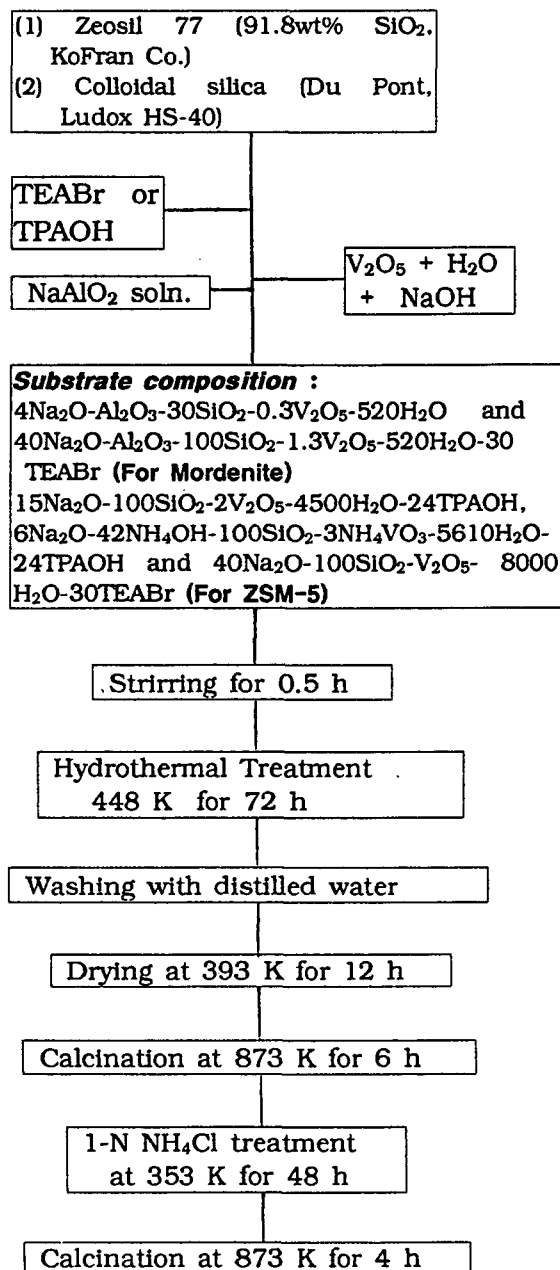
The crystal of vanadium incorporated molecular sieves are of particular interest because various oxidations of hydrocarbons are catalyzed selectively over these catalysts [1,2]. The synthesis of the vanadium-incorporated molecular sieves, VAPO-5, VAPO-11 and vanadium silicate with ZSM-11 structure, were reported recently. The catalytic activities of these crystals depend substantially on the oxidation state and redox properties of the catalysts. The direct hydrothermal synthesis is known as the unique method to obtain the vanadium-containing zeolites such as vanadium silicate with ZSM-5 or ZSM-11 structure [3-5]. However, Sulikowski and Klinowski [6] have shown that boron and aluminum can be isomorphously substituted for silicon in the framework of ZSM-5 and Y-zeolite by hydrothermal treatment of the dealuminated zeolite with aqueous solutions of strong bases at elevated temperatures, namely secondary synthesis. It is possible to introduce the elements such as B, V and Ti into zeolitic frameworks after the completion of hydrothermal synthesis. Kraushaar and Van Hooff [7] reported that titanium silicalite could be obtained from ZSM-5 by dealumination and subsequent treatment with TiCl_4 . Ferrini and Kouwenhoven [8] have reported on the secondary synthesis of Ti modified ZSM-5, zeolite Beta and Y by reaction with TiCl_4 or Ti-tetraisopropylate with dealuminated H-zeolite crystals. Even though suc-

cessful and consistent crystallization of a VS-1 has been relatively well established, the attempts to introduce vanadium into the Mordenite and ZSM-5 crystal and determining their physico-chemical properties are very limited. In this work, V-Al-Mordenite and V-ZSM-5 crystal were prepared by direct hydrothermal synthesis and by secondary hydrothermal treatment in the strong bases after dealumination. The incorporation of V into the zeolite framework was demonstrated by XRD, FTIR, ESR, UV-Vis and solid Si-MAS NMR techniques.

2. Experimental

Firstly, vanadium incorporated zeolites with Mordenite and ZSM-5 type structure can be obtained by direct hydrothermal synthesis. Vanadium containing Mordenites were synthesized hydrothermally from the substrate composition of $4\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2 \cdot 0.3\text{V}_2\text{O}_5 \cdot 520\text{H}_2\text{O}$ and $40\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 100\text{SiO}_2 \cdot 1.3\text{V}_2\text{O}_5 \cdot 520\text{H}_2\text{O} \cdot 30\text{TEABr}$ at 448 K. The starting batch compositions for the synthesis of vanadium containing ZSM-5 type zeolites were $15\text{Na}_2\text{O} \cdot 100\text{SiO}_2 \cdot 2\text{V}_2\text{O}_5 \cdot 4500\text{H}_2\text{O} \cdot 24\text{TPAOH}$, $6\text{Na}_2\text{O} \cdot 42\text{NH}_4\text{OH} \cdot 100\text{SiO}_2 \cdot 3\text{NH}_4\text{VO}_3 \cdot 5610\text{H}_2\text{O} \cdot 24\text{TPAOH}$ and $40\text{Na}_2\text{O} \cdot 100\text{SiO}_2 \cdot \text{V}_2\text{O}_5 \cdot 8000\text{H}_2\text{O} \cdot 30\text{TEABr}$ at 448 K, respectively. Fine amorphous silica powder (Zeosil 77 from KoFran Co. 91.8 % SiO_2 -8.2 % H_2O), Colloidal silica sol (Du Pont, Ludox HS-40), sodium aluminate (Junsei), V_2O_5 powder (Aldrich) and

(A) Hydrothermal crystallization



(B) Secondary Synthesis

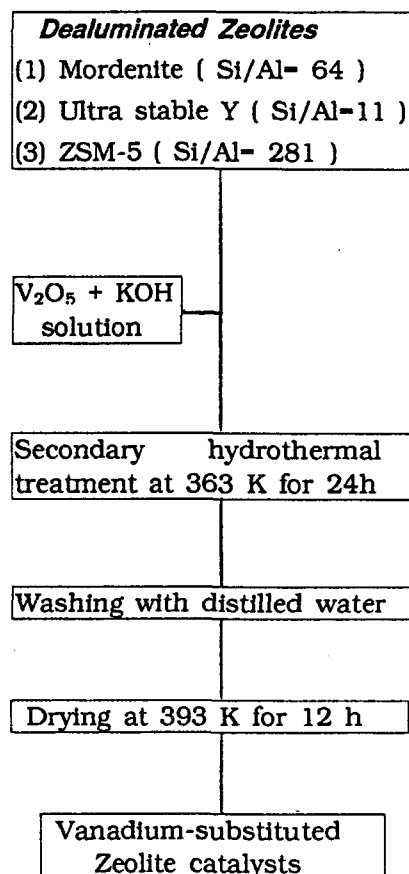


Fig. 1. Schematic diagrams for the preparation of vanadium containing zeolite catalysts.

sodium hydroxide (Junsei) were used in preparing the starting mixture. The hydrothermal synthesis reaction was carried out in a 250 ml stainless steel autoclave at 448 K, without agitation, for 3 days. Obtained samples were washed, filtered and dried at 393 K for 12 h. The organic material was removed by calcination in air at 873 K.

Secondarily, the substitution of vanadium into Mordenite and ZSM-5 also could be achieved by modified treatments of dealuminating zeolites in the V_2O_5 + KOH solution at 363 K (namely secondary synthesis). The parent zeolite was dealuminated Mordenite(Si/Al=64) and ZSM-5 (Si/Al=281). The secondary synthesis method has been described by Salikowski and Klinowski, and the complete experimental procedure is shown in Fig. 1(B). Because small amount of vanadium oxide could be present in the pore system after this treatment, the samples were washed subsequently with distilled water (V_2O_5 solubility in cold water = 0.8 g/100 cc). Conventional spectroscopic techniques were used for the characterization of vanadium modified Mordenite and ZSM-5. The incorporation of vanadium into the zeolites was demonstrated by the change in the X-ray diffraction (Philips, PW-1700) and FT-IR spectra (BIO RAD, FTS-40) pattern. UV-VIS diffuse reflectance spectroscopy was performed on a double beam spectrometer using $BaSO_4$ as a standard. ^{29}Si NMR spectra were obtained on a Bruker MSL-200 high resolution spectrometer

operating at a field of 4.7 T with a standard magic angle spinning (MAS) probe. The chemical shift was determined from TMS as an external reference. The samples were also characterized by ESR (Jeol Co.) spectroscopy. The elemental analysis was done by ICP analysis after dissolution in HF.

3. Results and discussion

3.1. X-ray diffraction

Figure 2 shows the XRD patterns of V-zeolites obtained by direct crystallization or by secondary synthetic treatment of dealuminated zeolites. The diffraction patterns of hydrothermally synthesized vanadium containing Mordenite and ZSM-5 were essentially similar to those of Al containing zeolites respectively. Other crystalline phases were not observed in the X-ray powder diffraction patterns of well washed products. There were no changes in the diffraction peaks after alkaline vanadia solution treatment of dealuminated samples, which indicates that crystallinity of zeolites are fully maintained during secondary synthesis. Pure Silicalite-I was monoclinic, while hydrothermally crystallized and secondarily synthesized V-ZSM-5 were orthorombic. The result of X-ray diffraction analysis also showed that the unit cell parameters decreased after dealumination of H-Mordenite and then increased again after subsequent re-

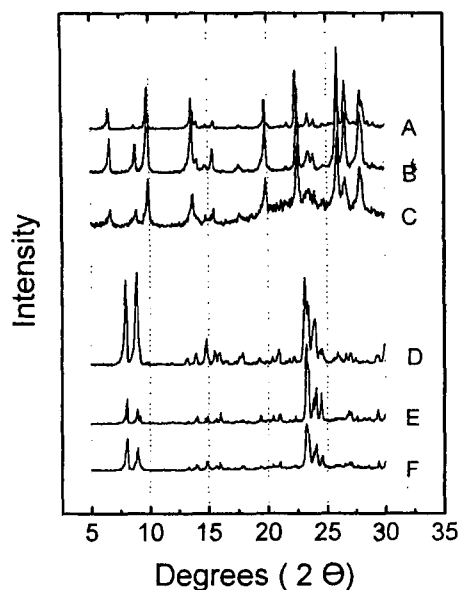


Fig. 2. X-ray diffractograms of (A) dealuminated Mordenite (Si/Al=64) (B) V-Al-Mordenite obtained by hydrothermal crystallization (C) V-Mordenite by secondary synthesis (D) Silicalite-I (E) V-ZSM-5 zeolite crystallized hydrothermally in TPAOH system and (F) V-ZSM-5 in TEABr system.

action in $V_2O_5 + KOH$ solution, indicating that the replacement of Si by the larger V atoms could cause a slight expansion in the unit cell parameters. This behavior is consistent with the presence of vanadium in the framework of zeolite, which is brought about by the difference between V-O and Si-O bond length. In the case of hydrothermally obtained samples, there was no change in the unit cell parameters as compared to those of Al-Mordenite. All the samples recovered after direct hydrothermal crystallization or secondary synthesis treatment were completely white indicating the presence of vanadium in the

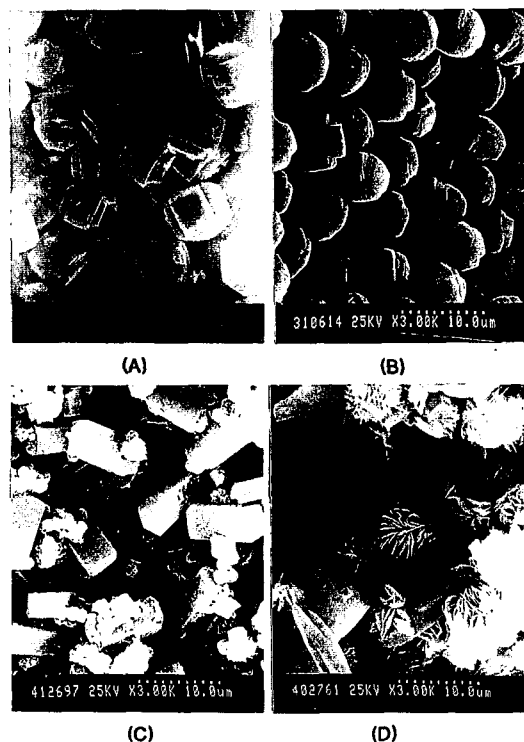


Fig. 3. Scanning electron microscope photographs of (A) ZSM-5 (Si/Al=21) (B) V-ZSM-5 zeolite crystallized hydrothermally in TPAOH system (C) V-ZSM-5 in TEABr system (D) V-Al-Mordenite obtained by hydrothermal crystallization without addition of template.

crystal structure.

3.2. Scanning electron microscopy

Figure 3 shows the morphologies of V-Al-Mordenite and V-ZSM-5 crystals obtained by hydrothermal synthesis. The organics used to make these zeolites were tetrapropylammonium (TPA) and tetraethylammonium (TEA) respectively. V-Al-Mordenite can be obtained without any or-

ganic template under the same synthesis conditions. Al containing ZSM-5 (Fig. 3-A) showed the typical twin crystals of 15 μm . Figure 3-B shows the morphology of V-ZSM-5 crystals obtained with TPA ions. Spherulites of 5 - 7 μm were formed in the TPA system. In TEA system, larger lath-shaped V-ZSM-5 crystals could be obtained (Fig. 3-C). However, small spherical aggregates also remained on the surface. Al-Mordenite crystals showed agglomerated discus-shape. The crystals of V-Al-Mordenite have a rough striated surface.

3.3. IR spectroscopy

Figure 4 shows the IR spectra of vanadia (V_2O_5), normal Al containing zeolites, dealuminated zeolites, V-zeolites obtained by direct crystallization and by secondary synthetic treatment of dealuminated zeolites. All the bands shifted to higher frequencies after dealumination of original zeolites. The absorption bands near 800, 1090 cm^{-1} shifted again slightly toward the lower frequency region after subsequent treatment of dealuminated zeolites in an alkaline V_2O_5 solution at 363 K or after incorporation of vanadium by direct hydrothermal crystallization, as compared with the absorption band of dealuminated H-zeolites. It is expected that the substitution of V for Si in the zeolite framework results in a band shift to a lower frequency region owing to the longer V-O bond distance as compared with

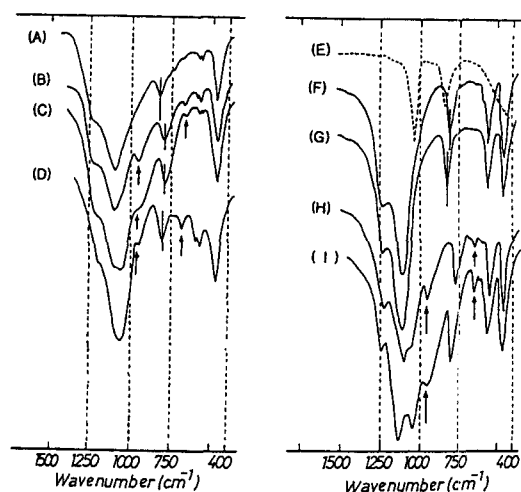


Fig. 4. FT-IR spectra of vanadium-containing zeolites. (A) dealuminated Mordenite (Si/Al=64) (B) V-Mordenite obtained by secondary synthesis (C) hydrothermally crystallized V-Mordenite (D) V-Mordenite by impregnation-calcination method (E) V_2O_5 powder (F) ZSM-5 (Si/Al=21), (G) dealuminated ZSM-5 (Si/Al=281) (H) V-ZSM-5 obtained by secondary synthesis (I) hydrothermally crystallized V-ZSM-5 zeolite (Si/V=62).

Si-O bond. As shown in this figure, the IR spectra of vanadium incorporated zeolites also exhibited an absorption band at 960 cm^{-1} , which was not found in vanadia powder and dealuminated H-type zeolites. A characteristic absorption band at about 970 cm^{-1} has been also observed in all the framework IR spectra of V-silicalite-II [5]. It was also reported that the intensity of 970 cm^{-1} band increased as a function of vanadium in the lattice and this band was absent in the IR spectra of pure Silicalite or vanadia powder [9]. This absorption band has been attrib-

uted to the stretching mode of metal-oxygen linkages [10]. It is expected that the substitution of V for Si in the zeolite framework results in the shift of absorption band to a lower frequency region owing to the longer V-O bond distance as compared with Si-O bond. In addition, vanadium containing zeolites have a weak band at 650 cm^{-1} , which can be assigned to the symmetric Si-O-V stretching band. Hong et al. [11] have reported that this peak also observed for vanadosilicate with ZSM-5 structure. The results in Fig. 4 may provide an evidence for the substitution of vanadium into the defective Mordenite type structure after secondary hydrothermal treatment.

3.4. ^{29}Si MAS NMR analysis

^{29}Si MAS NMR spectra were taken to investigate further evidences for the incorporation of vanadium species into the various crystal structures. ^{29}Si MAS NMR spectra of the dealuminated and V-modified samples are given in Fig. 5. In the zeolite system, each silicate is surrounded by four silicate or aluminate units. When one or more Si atoms are replaced by Al atoms, a shift in the spectra occurs. From the relative intensities of the ^{29}Si MAS NMR signals, information regarding the ordering of silicon and aluminum in the framework can be inferred. The areas under the peaks in the spectrum are directly proportional to the populations of the respective structural units in the sam-

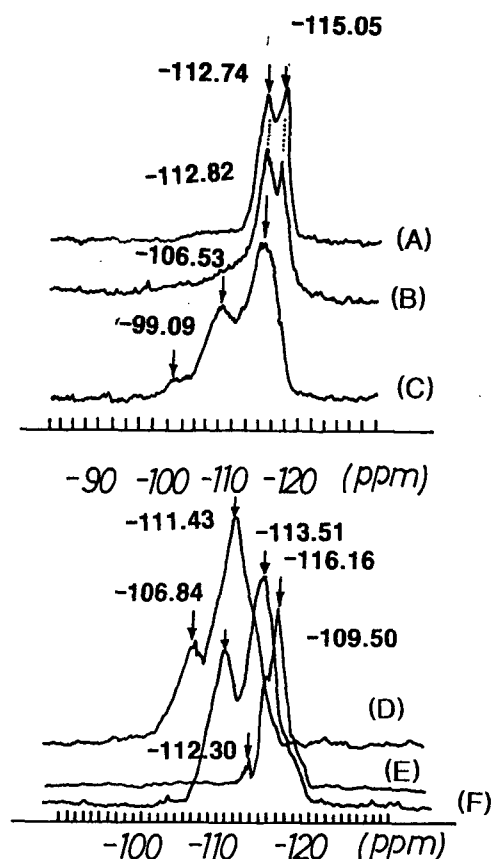


Fig. 5. ^{29}Si MAS NMR spectra of (A) dealuminated Mordenite ($\text{Si}/\text{Al}=64$) (B) V-Mordenite obtained by secondary synthesis (C) hydrothermally crystallized V-Mordenite (D) ZSM-5 ($\text{Si}/\text{Al}=16$) (E) Silicalite-1 (F) V-ZSM-5 obtained by hydrothermal crystallization (no Al, $\text{Si}/\text{V}=62$).

ple. Y type zeolite shows five peaks at -84.2 , -90.2 , -96.3 , -102.3 and -108.4 ppm and these peaks can be assigned to Si(4 Al), Si(3 Al), Si(2 Al), Si(1 Al) and Si(0 Al) structural unit, respectively [12]. In the ^{29}Si MAS NMR spectrum of Mordenite, three signals are observed and the largest signal, occurring at -115 ppm, is

assigned to a composite of the nonequivalent sites. For ZSM-5, the intense ^{29}Si -NMR peak around -113 ppm is attributed to Si bonded to 0 Al, Si(0 Al), and the signal at -106 ppm is assigned to Si(3Si, 1Al) or Si(3Si, 0H) structural units in the dealuminated samples of ZSM-5. As shown in Fig. 5, there is a slight shift of all signals to less negative field after V incorporation. In addition, the relative intensities of Si (n T) signals in V containing zeolites are different from those in the dealuminated zeolites or Silicalite-1. This is due to the increase of the number of V atoms in the coordination of every Si and clearly shows that vanadium may be inserted into the vacant T-atom positions in the lattice by secondary treatment. The ^{29}Si MAS NMR signal near -106 ppm due to silanol groups decreased and the spectra exhibited an additional peak at about -116 ppm as a result of secondary treatment. Aluminum leaching of zeolite can provide highly siliceous products with vacant T-atom positions in the lattice which are available for the insertion of vanadium atoms, as concluded by above-mentioned authors [12]. However, in agreement with literature data [12], the increase in the peak intensity for Si(1~4 T-atom) signal strongly supports the incorporation of V into the zeolite framework.

3.5. UV-Vis diffuse spectroscopy

The UV-Vis diffuse reflectance spectra

of the obtained samples are shown in Fig. 6. UV-Vis spectra of the vanadium-containing zeolites show the characteristic absorption at wavelength near 240 nm with an additional weak band near 340 nm. A second shoulder peak at 340 nm may be ascribed to extraframework vanadia particles possibly located inside pore system. The absence of any absorption

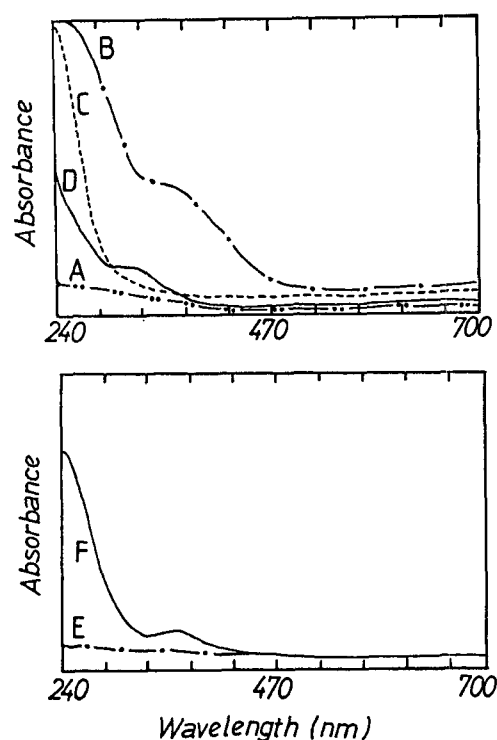


Fig. 6. Diffuse reflectance UV-Vis spectra of vanadium-containing zeolites. (A) dealuminated Mordenite (Si/Al=64) (B) V-Mordenite by impregnation-calcination method (C) hydrothermally crystallized V-Mordenite (D) V-Mordenite obtained by secondary synthesis (E) dealuminated ZSM-5 (F) hydrothermally crystallized V-ZSM-5 zeolite (Si/V=62).

above 550 nm shows that no V^{4+} ions in tetrahedral coordination are present [4]. This result is in good agreement with that of UV-Vis spectra obtained for titanium-containing zeolites [13]. The charge transfer transitions observed at the wavelength of 240 nm is assumed that these high energy transitions are due to highly dispersed or isolated vanadium atoms, as interpreted in the case of titanium containing zeolites.

3.6. ESR spectroscopy

ESR spectra for both as-synthesized and calcined sample have been recorded at room temperature and the spectra are shown in Fig. 7. The observed g -values and hyperfine coupling constants on the ESR spectra of vanadium-containing zeolites are typical of $V(IV)$ complexes with square pyramidal coordination. Tetrahedral species are known to have much smaller coupling constants and the peaks can only be detected at 77 K or lower temperature. ESR results also showed the hyperfine splitting, indicating monodispersity and immobility of the vanadium(IV) species [3]. These vanadium species in zeolites underwent redox cycles by the repeated oxidation-reduction treatment.

3.7. Internal silanol groups

The hydroxyl vibration FT-IR spectra of zeolite samples are shown in Fig. 9. Na type Al-ZSM-5 and as-synthesized V-

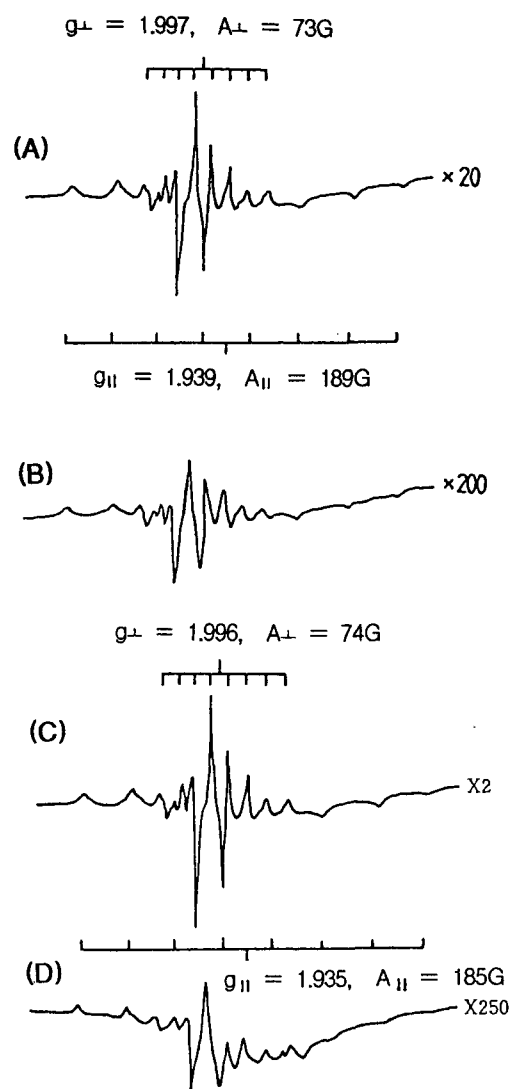


Fig. 7. ESR spectra of vanadium-containing zeolites. (A) hydrothermally crystallized V-Al-Mordenite (B) secondary synthesized V-Al-Mordenite (C) hydrothermally crystallized V-ZSM-5 zeolite (as-synthesized) (D) V-ZSM-5 zeolite calcined in air at 973 K.

ZSM-5 showed only one peak at 3700 cm^{-1} . Two major $\nu(\text{OH})$ bands at near 3730 and 3500 cm^{-1} are observed for VS-1

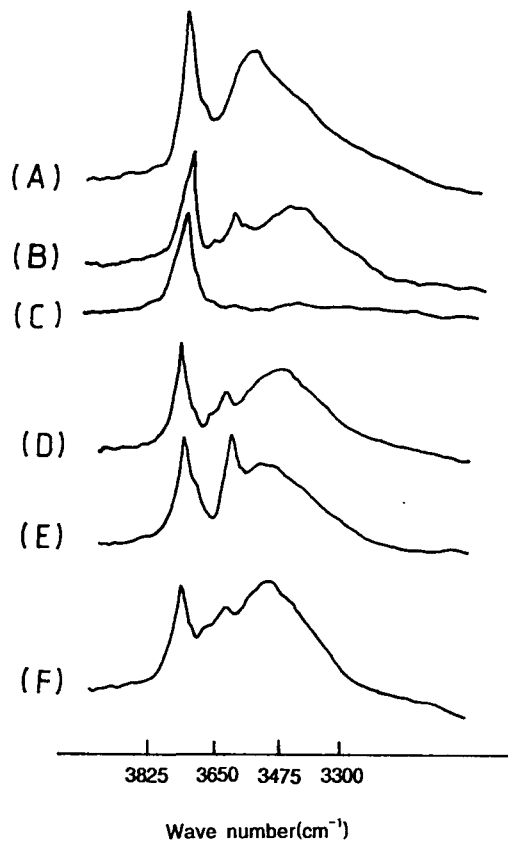


Fig. 8. FT-IR spectra of vanadium-containing zeolites. (A) H^+ type V-ZSM-5 zeolite (no Al, Si/V=62) (B) H^+ type Al-ZSM-5 zeolite (Si/Al=16) (C) Na^+ type Al-ZSM-5 (D) H^+ type V-Al-Mordenite (E) dealuminated H^+ type Mordenite (Si/Al=64) (F) H^+ type V-Mordenite obtained by secondary synthesis.

after NH_4Cl solution and calcination treatment. It is difficult to detect a significant peak at 3610 cm^{-1} over this zeolite. For dealuminated Mordenite, hydrothermally crystallized H-type V-Al-Mordenite and secondarily synthesized V-Mordenite, three bands are present at 3730 , 3610 and 3500 cm^{-1} . These bands in the spectra of vana-

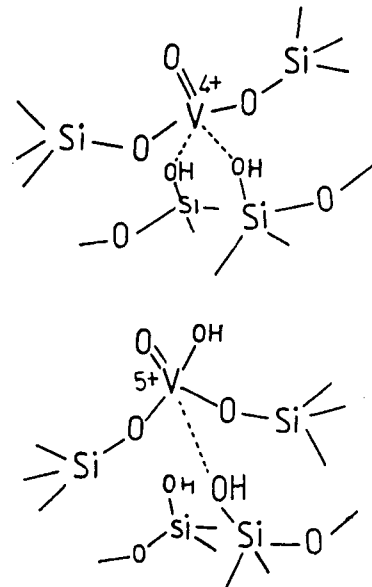


Fig. 9. Possible structure of Vanadium in the zeolite crystal framework.

dium containing zeolites are ascribed to the presence of three type of silanol groups. The 3700 cm^{-1} band is ascribed to terminal SiOH species which are required to terminate the finite crystallite lattice and 3610 cm^{-1} band is due to the Al associated Bronsted acid sites [14]. The broad band around 3500 cm^{-1} is associated with internal SiOH groups which are greatly affected by zeolite and subjected to a high degree of hydrogen bonding. The band at 3610 cm^{-1} in the spectra of V-Mordenites is indicative of the presence of acid sites. However these zeolites have Al atoms as expected and Bronsted acidity is found in the IR spectrum after adsorption of pyridine. Rigutto and Bekkum [3] proposed the possible structure of the vanadium species in zeolite and reported that the weakly acidic pro-

ton of the vanadium(V)-bound hydroxyl group could account for the cation exchange capacity of samples. Rao et al.[9] have reported that vanadium containing silicate with the MEL structure contains exchangeable protons and these vanadium silicates are mildly acidic and are catalytically active in both acid-catalysed as well as oxidation. Since the monodispersion and immobility of vanadium species requires strong bonding to the framework, a possible structure for the vanadium containing zeolites consistent with all the experimental evidence of this result and those of others [3,15] may be present as shown in Fig. 9.

4. Conclusions

It was possible to synthesize the vanadium substituted zeolites of Mordenite and ZSM-5 structure by direct hydrothermal crystallization and by secondary hydrothermal treatment in the strong bases after dealumination. The incorporation of V into the zeolite framework has been demonstrated by instrumental analysis and the observed results support that the vanadium species is probably connected to the framework. It is clearly reasonable to expect that the incorporation of vanadium species into the zeolite crystal structure, by means of modified treatments such as secondary synthesis, may also be applied to the large pore zeolites as well as direct hydrothermal crystallization. Acid leaching

of zeolites can provide highly siliceous products with vacant T-atom positions in the lattice which are available for the insertion of vanadium.

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