Catalysis Letters 31 (1995) 91–102

Incorporation of vanadium into the mordenite structure by direct hydrothermal crystallization and secondary synthesis

Geon-Joong Kim [a,1], Dong-Su Cho [a], Kwang-Ho Kim [b], Wan-Suk Ko [b],
Jong-Ho Kim [c] and Hiroshi Shoji [d]

[a] *Department of Chemical Engineering, Inha University, Inchon 402-751, Korea*
[b] *Department of Industrial Chemistry, Inha Technical College, Inchon 402-752, Korea*
[c] *Department of Materials Science, Faculty of Engineering, Tottori University, Tottori 680, Japan*
[d] *Maruzen Petrochemical Co. Ltd., Ichihara, Chiba 290, Japan*

Received 19 July 1994; accepted 23 August 1994

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 vanadium into the mordenite framework was demonstrated by XRD, FTIR, UV-Vis techniques and tested with catalytic oxidation reactions. These vanadium-containing zeolites have selective catalytic properties in the various oxidation reactions as compared with vanadia-impregnated catalysts.

Keywords: vanadium-containing mordenite; hydrothermal synthesis; dealumination; secondary synthesis framework incorporation; benzene hydroxylation; hexane, ethanol, benzene oxidation

1. Introduction

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 MEL structure, was reported recently [3–6]. The activities of these catalysts depend substantially on the oxidation state and redox properties of the catalysts [7]. The direct hydrothermal synthesis is known as the unique method to obtain vanadium-containing zeolites such as vanadium silicate with MFI or MEL structure. However, Sulikowski and Klinowski [8] have shown that boron and aluminum can be isomorphously substituted for silicon in

---

[1] To whom correspondence should be addressed.

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. Some evidence for the incorporation of elements such as B, V and Ti into zeolitic frameworks after the completion of hydrothermal synthesis has been reported. Kraushaar and Van Hooff [9] have proposed a new preparation method of titanium silicalite from ZSM-5 by dealumination and subsequent treatment with $TiCl_4$. This titanium silicalite exhibited the same catalytic properties as hydrothermally synthesized TS-1 of high purity in the hydroxylation of phenol. This modified method has been applied to obtain the large pore zeolite analog of mordenite [10]. Ferrini and Kouwenhoven [11] have also reported on the secondary synthesis of Ti-modified ZSM-5, zeolite beta and Y by reaction with $TiCl_4$ or H-zeolites with Ti-tetraisopropylate. Even though successful and consistent crystallization of a VS-1 analog of ZSM-5 has been relatively well estab-

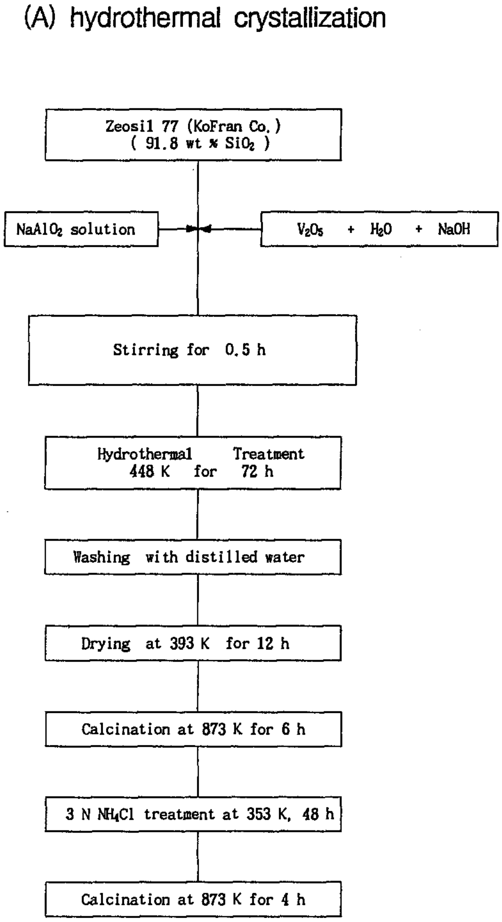
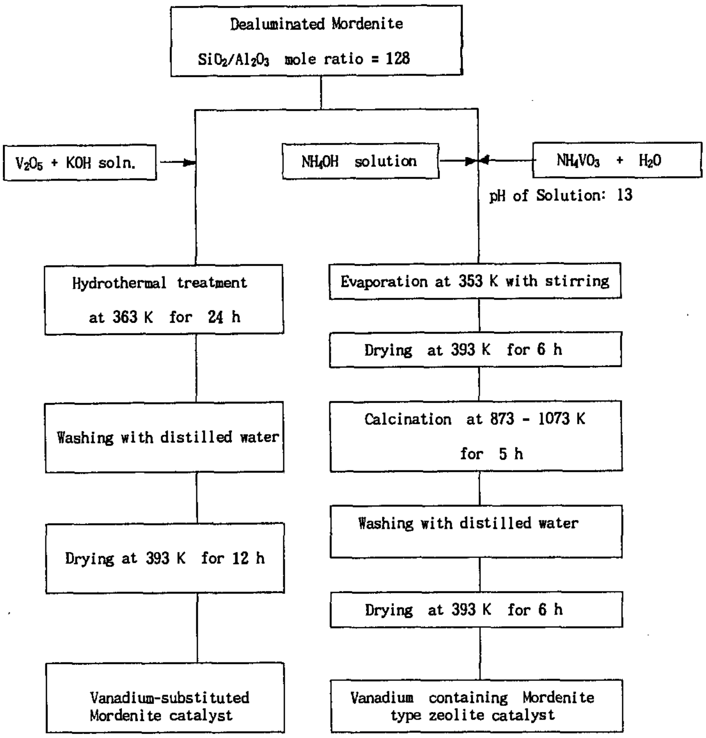

(A) hydrothermal crystallization

Fig. 1. Schematic diagrams for the preparation of vanadium-containing mordenite by hydrothermal synthesis and by modified methods.



(B) Secondary synthesis (C) Impregnation/Calcination method

Fig. 1. (Continued.)

lished, until recently the attempt to introduce vanadium into the mordenite structure is very limited. In this work, we prepared V-Al-mordenite by direct hydrothermal synthesis, and then demonstrated that the vanadium-incorporated zeolite with mordenite type structure could be obtained by secondary hydrothermal synthesis in the strong base solution or by impregnation/calcination treatment after dealumination. The incorporation of vanadium into the mordenite framework was demonstrated by XRD, UV–Vis, FTIR techniques, and tested with catalytic oxidation reactions.

2. Experimental

The vanadium-incorporated zeolites with mordenite type structure could be obtained by direct hydrothermal synthesis or by modified treatments after dealuminating the zeolite. In fig. 1, the methods of synthesis are shown schematically. Firstly, vanadium-containing mordenite was synthesized hydro-thermally from the substrate composition of $4Na_2O{\cdot}Al_2O_3{\cdot}30SiO_2{\cdot}(0.3\text{–}1)\ V_2O_5{\cdot}520H_2O$. A fine amorphous silica powder (Zeosil 77 from KoFran Co. 91.8% SiO_2–8.2%

H_2O), sodium aluminate (Junsei), V_2O_5 powder (Aldrich) and sodium hydroxide (Junsei) were used for V-Al-mordenite synthesis. The hydrothermal synthesis reaction was carried out in a 250 ml stainless steel autoclave at 448 K, without agitation, for 3 days. The obtained samples were washed, filtered and dried at 393 K for 12 h. The as-synthesized Na-type zeolite was ion exchanged with a 1 N NH_4Cl solution and calcined subsequently at 823 K to obtain H-type zeolite for using as a catalyst in the reaction of benzene or *n*-hexane with H_2O_2. But as-synthesized zeolites were used mainly as catalysts in ethanol and benzene oxidation with oxygen.

Secondly, the substitution of vanadium into the dealuminated mordenite could be achieved by secondary synthesis using V_2O_5 + KOH solution at 363 K. The parent zeolite was a dealuminated mordenite (Si/Al = 64). The method of secondary synthesis has been described by Sulikowski and Klinowski [8], and the complete experimental procedure is shown in fig. 1B. Thirdly, the impregnation/calcination method was also used to obtain the vanadium-containing zeolites. Dealuminated samples were added to the desired amount of NH_4VO_3 solution. The final pH of the suspension (pH = 13) was adjusted with an ammonia solution. The suspended solution was then heated to dryness and the obtained solid was further dried at 393 K for 6 h, and calcined in air at 873–1073 K for 5 h. The samples were washed subsequently with distilled water, as small amounts of vanadium oxide could be present in the pore system after this impregnation treatment (V_2O_5 solubility in cold water = 0.8 g/100 cm^3). Conventional spectroscopic techniques were used for the characterization of vanadium-modified mordenites. The structure of zeolite was demonstrated using X-ray diffractometer (Philips, PW-1700) and FT-IR spectroscope (BIO RAD, FTS-40). UV–Vis diffuse reflectance spectroscopy was performed on a double beam spectrometer using $BaSO_4$ as a standard. The hydroxylation of benzene and the oxidation of *n*-hexane with 35% hydrogen peroxide were carried out in a batch reactor at 333 K. The catalytic activities of the vanadium-substituted mordenites for the oxidation of methanol, ethanol and benzene were measured in a continuous fixed-bed reactor operating at atmospheric pressure. The products were analysed by a GC-mass spectrometer (VG Trio 2000, OV-101 capillary column).

3. Results and discussion

A typical XRD pattern of vanadium-containing mordenite is shown in fig. 2. The hydrothermally synthesized vanadium-containing mordenite has essentially the same XRD pattern and the framework structure as the typical Al-mordenite. Especially, the result of X-ray diffraction analysis showed that the unit cell parameters increased after introducing vanadium by the treatment shown in fig. 1B. 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 sub-

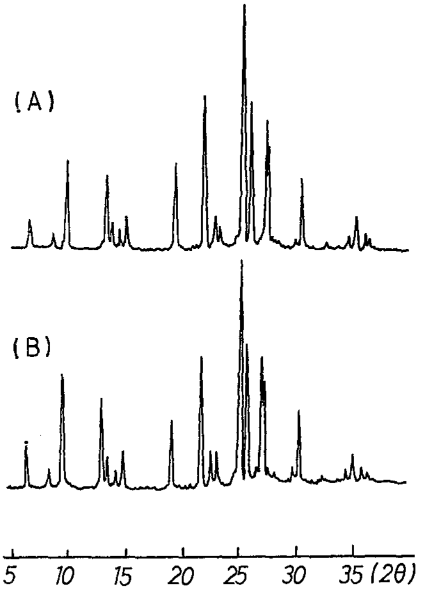


Fig. 2. X-ray diffractograms of hydrothermally synthesized Al-mordenite (A) and V-Al-mordenite (B).

sequent reaction in V_2O_5 + KOH solution, indicating that the substitution of the larger V atoms could cause a slight expansion in the unit cell parameters. This result is in agreement with the reported characteristics of titanium-mordenite obtained by the reaction of dealuminated mordenite with $TiCl_4$ vapor [10]. 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, no change in the unit cell parameters was found as compared to those of Al-mordenite due to the coexistence of aluminum with vanadium. All the samples recovered after direct hydrothermal crystallization or secondary hydrothermal treatment were completely white, while V-mordenite prepared via impregnation and calcination treatment had a bright orange color. Thus vanadium(V) oxides were suspected to exist within the mordenite pores after impregnation and calcination of the relatively vanadium rich samples at high vanadium loading.

Fig. 3 shows the morphologies of Al-mordenite and V-Al-mordenite crystals obtained by hydrothermal synthesis. Al-mordenite showed agglomerated discus-shaped crystals. V-Al-mordenite was formed mainly as agglomerated thin plate-shaped crystals.

Fig. 4 shows the IR spectra of vanadium-containing zeolites. The absorption band near 800 cm^{-1} shifted toward the lower frequency region after incorporation of vanadium as compared with the absorption bands of dealuminated H-type zeolites. As shown in this figure, the IR spectra of vanadium-incorporated mordenite

A B

Fig. 3. SEM photographs of hydrothermally synthesized Al-mordenite (A) and V-Al-mordenite (B).

also exhibited an absorption band at 960 cm^{-1}, which was not found in vanadia powder and dealuminated H-type zeolites. This characteristic absorption band is attributed to the =Ti=O group or an asymmetric stretching mode of tetrahedral Si–O–Ti linkages in the zeolite framework. A characteristic absorption band at about 970 cm^{-1} has been observed in all the framework IR spectra of titanium-containing silicates [12]. The band around 940–980 cm^{-1} is associated with the monolayer vanadium species and this absorption is assigned to the =V=O group [13,14]. It is expected that the substitution of V for Si in the zeolite framework results in an absorption band shift to a lower frequency region owing to the longer V–O bond distance as compared with the Si–O bond. In addition, vanadium-containing mordenites have a weak band at 650 cm^{-1}, which can be assigned to the symmetric Si–O–V stretching band. This peak has also been observed on ferrisilicate and vanadosilicate with MFI structure [15].

The UV–Vis diffuse reflectance spectra of the obtained samples are shown in fig. 5. It is known that the electron charge transfer energy is strongly influenced by the number of ligands on the central ion and it has been reported that as the number of ligands on vanadium increases from 6 to 4, the absorption band shifts to shorter wavelength. UV–Vis spectra of the vanadium-containing zeolites show an 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

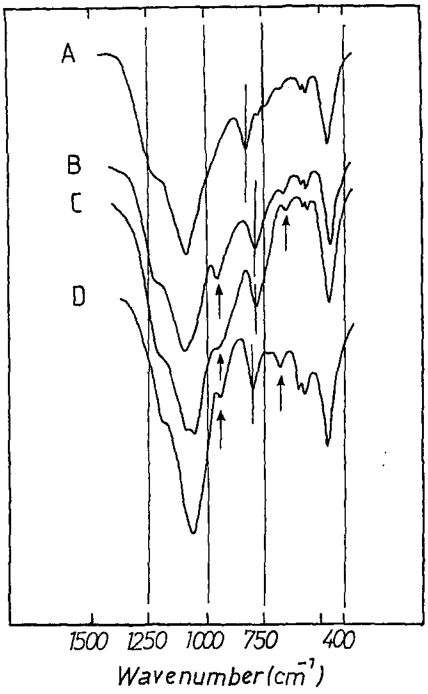


Fig. 4. FT-IR spectra of (A) dealuminated mordenite (SiO_2/Al_2O_3 = 128), (B) vanadium-containing mordenite obtained by the impregnation–calcination method, (C) hydrothermally synthesized V-Al-mordenite, and (D) secondary synthesized V-mordenite.

particles possibly located inside the pore system. This result is in good agreement with that of UV–Vis spectra obtained for titanium-containing zeolites (TS-1) [12]. From the charge transfer transitions observed at the wavelength of 240 nm it is assumed that these high energy transitions are due to highly dispersed or isolated vanadium atoms, as interpreted in the case of TS-1. Even though, it is known that the tetrahedrally coordinated V^{5+} shows absorption bands below 350 nm [5], the UV–Vis spectra in fig. 5 do not support the incorporation on the presence of vanadium(V) in the tetrahedral framework positions.

ESR spectra for both as-synthesized and calcined samples have been recorded at room temperature and the obtained spectra are shown in fig. 6. Both as-synthesized and calcined zeolites have very similar ESR spectra except for the difference in intensity. 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 be detected only at 77 K or lower temperature [4,16]. This ESR result also showed the hyperfine splitting, indicating monodispersion and immobility of the vanadium(IV) species. These vanadium species in the zeolites underwent redox cycles by the repeated oxidation–reduction treatment. It is believed that some form of vanadium bonding to the zeolite frame-

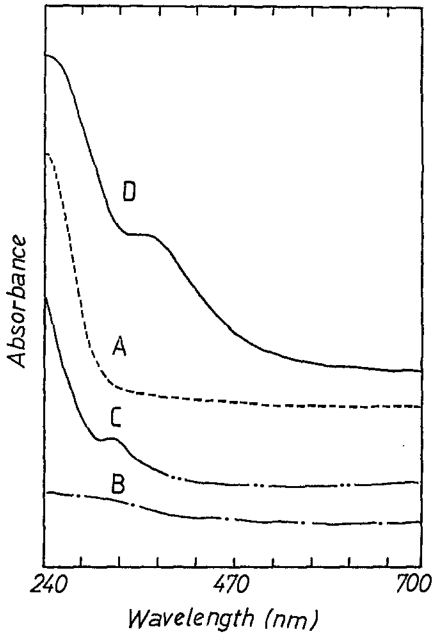


Fig. 5. Diffuse reflectance UV–Vis spectra of (A) hydrothermally synthesized V-Al-mordenite, (B) dealuminated mordenite (SiO_2/Al_2O_3 = 128), (C) secondary synthesized V-mordenite and (D) vanadium-containing mordenite obtained by the impregnation/calcination method.

work probably occurs at defect sites [4]. The calcined vanadium-containing mordenite has a very small spin concentration as compared with that of as-synthesized zeolite, which showed that calcination resulted in a change of oxidation state from V^{4+} to V^{5+}.

In order to obtain information on the catalytic behaviour of the vanadium-containing mordenite, the catalytic activities of samples were examined in the oxidation reaction of benzene or *n*-hexane with H_2O_2 and the obtained results are compared in table 1. As shown in this table, H-type zeolites showed no catalytic activity at all in *n*-hexane oxidation, suggesting that vanadium atoms associated with the zeolite framework structure are responsible for the observed catalytic activity. When Na^+ or K^+ was included in the zeolite, this catalyst showed no catalytic activity in the oxidation of benzene or *n*-hexane with H_2O_2.

V_2O_5 powder itself decomposed H_2O_2 very fast to H_2O and O_2 and it dissolved in the H_2O_2 solution. But the vanadium species present in the zeolite were stable in the aqueous solution and in this case the homogeneous action of vanadium could be ruled out. When the vanadium was loaded over Na-type mordenite or SiO_2, a part of the vanadium deposited was soluble in the aqueous solution of hydrogen peroxide. In the catalysts prepared by the method as shown in fig. 1, most of the vanadium species remained bound to the zeolite. This difference can be rationalized considering the specific reaction that can occur between vanadium and free

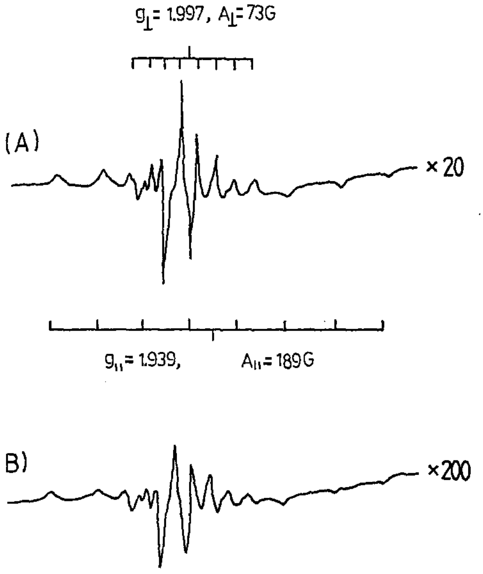


Fig. 6. ESR spectra of hydrothermally synthesized V- Al-mordenite (A) and secondary synthesized V-mordenite (B).

Table 1
The catalytic properties of vanadium-containing zeolites in oxidation of benzene and *n*-hexane with H_2O_2 [a]

Catalyst	Reactants	Yield of products [b] (%)
H-mordenite	*n*-hexane + H_2O_2	no reaction
	benzene + H_2O_2	phenol 1.1
HS-V-Mor	*n*-hexane + H_2O_2	2-ol 1.1, 3-ol 0.8, 2-one 1.7, 3-one 1.6, trace of 1-ol
	benzene + H_2O_2	phenol 5.1, benzoquinone 0.5
SS-V-Mor	*n*-hexane + H_2O_2	2-ol 2.4, 3-ol 1.5, 2-one 2.6, 3-one 2.5, trace of 1-ol, 1-al
	benzene + H_2O_2	phenol 5.3, benzoquinone 1.6
Imp-V-Mor	*n*-hexane + H_2O_2	2-ol 0.8, 3-ol 0.7, 2-one 2.1, 3-one 1.9, trace of 1-ol, 1-al
	benzene + H_2O_2	phenol 6.1, benzoquinone 1.8

[a] A proton type zeolite was used in the reaction. HS-V-Mor: hydrothermally synthesized V-Al-mordenite (Si/V = 31, Si/Al = 8); SS-V-Mor: secondary synthesized V-mordenite (Si/V = 14); Imp-V-Mor: impregnation/calcination treated V-mordenite (3 wt% V loading). Reaction condition: hydrocarbon/H_2O_2 = 5, temperature = 333 K, acetonitrile solvent (70 v/v%).

[b] Basis on hydrocarbons.

OH groups of dealuminated H-mordenite at the defect sites. The comparison between the different preparations suggests that the incorporation of vanadium into the zeolite structure leads to the formation of the strongly-bonded species, thermally stable and insoluble in an acidic (or basic) medium as compared to the vanadia supported over SiO_2 or Na-mordenite. Furthermore, table 2 shows the catalytic properties of vanadium-containing mordenites in the oxidation of methanol, ethanol and benzene with oxygen. When the as-synthesized zeolites were used as catalysts in these oxidation reactions, HS-V-Mor and SS-V-Mor in table 2 exhibited no acidic properties but oxidizing activity. H-type zeolites which contained

Table 2
Yield of products obtained over vanadium containing zeolites in various oxidation reactions[a]

Catalyst	Reactants	Yield of products[b] (%)
HZSM-5[c] (Si/Al = 21)	methanol + O_2	DME 97, CO + CO_2 2
H-mordenite[c]	methanol + O_2	DME 93.1, CO + CO_2 6.7
HS-V-MFI[c]	methanol + O_2	DME 40.5, CO 27.0, CO_2 21.6 HCHO 2.7, hydroxy aldehyde 8.1
	ethanol + O_2	DEE 25.2, ethoxy acetic acid 26.5, hydroxy acetaldehyde 12.1, CH_3CHO 13.3, CH_3COOH 12.7, CO 4.7, CO_2 5.2
HS-V-Mor	ethanol + O_2	HCHO 11.6, CH_3CHO 19.1, trace of acetone, CH_3COOH 18.6, CO 17.5, CO_2 13.9
SS-V-Mor	ethanol + O_2	HCHO 14.2, CH_3CHO 23.5, acetone 3.3, CH_3COOH 19.1, CO 13.2, CO_2 15.4
	benzene + O_2	2-ethyl-1-hexanol 38.4, CO + CO_2 7.1 maleic acid 50.6, phenylester benzoic acid 2.8
Imp-V-Mor	methanol + O_2	DME 6.4, HCHO 4.9, CO 43.3 CO_2 38.7
	ethanol + O_2	HCHO 8.6, CH_3CHO 35.2, DEE 0.7, methoxy acetaldehyde 3.4, CH_3COOH 24.1, CO 14.2, CO_2 13.8
	benzene + O_2	2-ethyl-1-hexanol 45.3, CO + CO_2 7.1, maleic acid 42.7, HCHO + CH_3COOH 2.0
V_2O_5/SiO_2	methanol + O_2	CO 57.8, CO_2 41.2
	ethanol + O_2	CH_3CHO 13.8, CH_3COOH 27.1, CO 26.4, CO_2 38.5
	benzene + O_2	2-propenoic acid 3.3, propanedioic acid 7.8 malic acid 76.4, CH_3COOH 0.8, CO + CO_2 10.2

[a] The catalysts except (c) are as-synthesized form. DME = dimethylether; DEE = diethylether; HS-V-MFI: hydrothermally synthesized vanadium-containing MFI. Reaction condition: O_2/hydrocarbon mole ratio = 10, temperature = 623 K, WHSV = 7.3 h^{-1}.

[b] Basis on hydrocarbons.

[c] Proton type zeolite obtained by ion exchange.

no vanadium, such as H-mordenite and H-ZSM-5, showed only acidic properties in the oxidation of methanol with oxygen, producing dimethylether with a trace of CO and CO_2. Over the zeolite catalyst obtained by the impregnation–calcination method, dimethylether was also formed in methanol oxidation, indicating the presence of Brønsted acid sites. When the obtained zeolites were ion exchanged with a NH_4Cl solution and used as a catalyst in the oxidation reaction of methanol and ethanol, they showed both of acidic property and oxidizing activity. The vanadium-containing MFI catalyst was also synthesized hydrothermally in the absence of aluminum and then it was converted into the acidic form to compare the catalytic properties with vanadium-substituted mordenites. In the ethanol oxidation, acetaldehyde, hydroxy acetaldehyde and ethoxy acetic acid were obtained and, moreover, diethyl ether was also formed on this zeolite, indicating the presence of Brønsted acid sites due to the incorporation of V into the zeolite structure as proposed by Rigutto and Van Bekkum [4]. Then formaldehyde, CO and CO_2 without dimethyl ether were produced over the vanadium-substituted zeolite catalysts of Na or K type in the methanol oxidation. This result indicates that the vanadium-containing zeolite contains exchangeable protons, which participate in the reaction catalysed by Brønsted acids. Especially acetone and acetaldehyde were found, in the oxidation of ethanol, on vanadium-containing mordenite which was obtained by secondary synthesis in V_2O_5 + KOH solution and by hydrothermal crystallization. The supported vanadia catalysts (V_2O_5 over SiO_2) behaved completely differently from the vanadium-substituted mordenite. Maleic acid and 2-ethyl-1-hexanol were obtained mainly over vanadium-containing mordenite in the oxidation of benzene with oxygen at 633 K, while malic acid and 2-propenoic acid with propanedioic acid were formed over V_2O_5 supported catalyst. The vanadium-containing zeolites obtained by secondary synthesis have exhibited the similar catalytic properties as hydrothermally synthesized zeolites. The combined analyses results provided an evidence for the substitution of vanadium into the zeolite framework structure after modified treatment as well as direct hydrothermal synthesis. It is noteworthy that vanadium-substituted zeolites show the selective catalytic properties in the oxidation reactions as compared to the vanadia-impregnated catalysts. It is clearly reasonable to expect that the introduction of vanadium atoms, by means of modified treatments such as secondary synthesis after dealuminating the zeolites, 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.

References

[1] F. Cavani, F. Trifirò, P. Jiru, K. Habersberger and Z. Tvaruzkova, Zeolites 8 (1988) 12.
[2] A. Miyamoto, Y. Iwamoto, H. Matsuda and T. Inui, Stud. Surf. Sci. Catal. 49B (1989) 1233.

[3] E.M. Flanigen, B.M. Lok, R.L. Patton and S.T. Wilson, Eur. Patent 0158976 (1985).
[4] M.S. Rigutto and H. van Bekkum, Appl. Catal. 68 (1991) L1.
[5] S.H. Jhung, Y.S. Uh and H.Z. Chon, Appl. Catal. 62 (1990) 61.
[6] P.R.H.P. Rao, A.V. Ramaswamy and P. Ratnasamy, J. Catal. 137 (1992) 225.
[7] M.S. Wainwright and N.R. Foster, Catal. Rev. Sci. Eng. 19 (1979) 211.
[8] B. Salikowski and J. Klinowski, in: *Zeolite Synthesis*, eds. M.L. Occelli and H.E. Robson (Am. Chem. Soc., Washington, 1989) p. 393.
[9] B. Kraushaar and J.H.C. van Hooff, Catal. Lett. 22 (1988) 81.
[10] G.J. Kim, B.R. Cho and J.H. Kim, Catal. Lett. 22 (1993) 259.
[11] C. Ferrini and H.W. Kouwenhoven, in: *New Developments in Selective Oxidation*, eds. G. Centi and F. Trifirò (Elsevier, Amsterdam, 1990) p. 53.
[12] D.R.C. Huybrechts, P.L. Buskens and P.A. Jacobs, J. Mol. Catal. 71 (1992) 129.
[13] R.Y. Saleh, I.E. Wachs, S.S. Chan and C.C. Chersich, J. Catal. 98 (1986) 102.
[14] A.J. van Hengstum, J.G. van Ommen, H. Bosh and P.J. Gellings, Appl. Catal. 8 (1983) 369.
[15] S.B. Hong, C.G. Kim, Y.S. Uh, Y.K. Park and S.I. Woo, Korean J. Chem. Eng. 9 (1992) 16.
[16] G. Martini, M.F. Ottaviani and G.L. Seravelli, J. Phys. Chem. 79 (1975) 1716.