

# Hydrothermal synthesis and characterization of the vanadium-containing zeolite beta

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Vanadium-containing zeolite beta (V-Beta) with molar atomic composition of V/Al/Si = 0.013/1/23 was synthesized by direct hydrothermal method. The synthesized V-Beta exhibits a unique structure that was characterized by ICP-mass, XRD, TEM, STEM/EDS, i.r., u.v.-vis,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS n.m.r., and EPR spectroscopies. The structure of V-Beta is isomorphous with H-form zeolite beta (H-Beta) of the same Si/Al ratio and is like H-Beta in cubic shape, but the average size is significantly larger. The incorporated vanadium also shows remarkable effect on  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS n.m.r. spectra that seems to increase the framework Si/Al ratio and the T-O-T angle of the zeolite Beta. A typical EPR spectrum of vanadyl ions ( $\text{VO}^{2+}$ ) was clearly presented by the synthesized V-Beta after calcination, and an additional superhyperfine structure due to interaction with  $^{27}\text{Al}$  appeared after dehydration. The spectroscopic results indicate that isolated V(IV) ions are atomically dispersed at cation or vacant acid sites near Al. The infrared spectrum of pyridine adsorption shows an enhanced Lewis acidity for the vanadium-containing zeolite beta. © Elsevier Science Inc. 1977

**Keywords:** Vanadium; zeolite Beta; hydrothermal synthesis; MAS n.m.r., EPR

## INTRODUCTION

Vanadium-containing zeolites have attracted attention because of their acidic and redox properties, and their interesting catalytic properties.<sup>1-3</sup> Several studies have been reported on the preparation, structure characterization, and spectroscopic studies of the V-containing zeolites,<sup>1-6</sup> as well as the interaction of vanadium compounds or complexes with zeolites.<sup>7-11</sup> Most reports have been on the zeolite ZSM-5 system.<sup>6-10</sup> In the present paper we report the unique structure of the dispersed vanadium-containing zeolite beta synthesized by direct hydrothermal method. The particular interest in the zeolite Beta system is due to its large pores, a wide range of Si/Al ratios, and the potentially catalytic properties.<sup>12-17</sup>

## EXPERIMENTAL

### Synthesis of vanadium-containing zeolite beta

Vanadium-containing zeolite beta (V-Beta) was synthesized hydrothermally in a stainless steel autoclave by modifying the Cambior's method.<sup>18</sup> Tetraethyl ammonium hydroxide (TEAOH, 40%, Alfa), amorphous silica (Aerosil 200, Degussa), aluminum nitrate

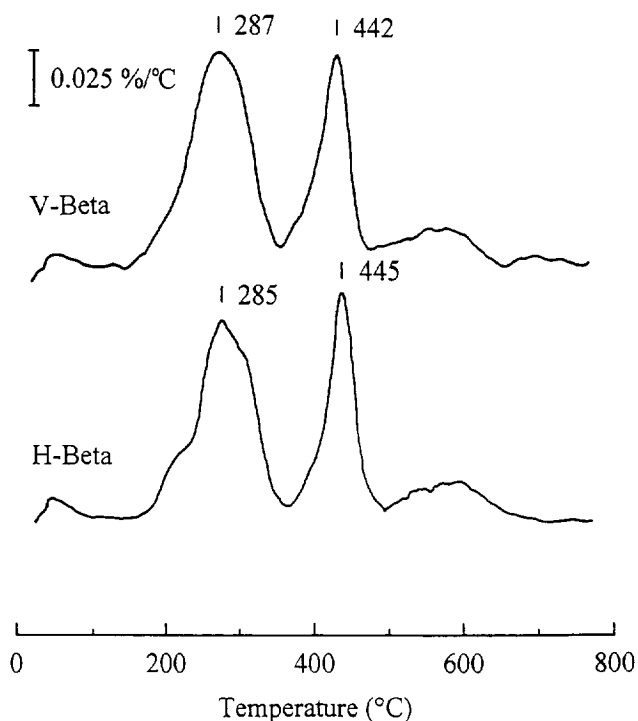
(Merck), and vanadium oxide (Merck) were used as reagents. The gel is prepared according to the following molar chemical composition:  $1/2 \text{V}_2\text{O}_5 : \text{Al}(\text{NO}_3)_3 : 30 \text{SiO}_2 : 220 \text{H}_2\text{O}_2 : 780 \text{H}_2\text{O} : 15 \text{TEAOH}$ . The procedures are as follows: vanadium oxide was oxidized by hydrogen peroxide first, then it was slowly added to an aqueous solution of TEAOH, silica, and finally aluminum nitrate. The mixture was stirred in a water-bath at 80°C for 30 min before transfer to an autoclave, which was then heated in an oven at 140°C for 20 days. After cooling the autoclave, the sample was centrifuged at 10,000 rpm, and the solid part was calcined at 550°C for 15 h. The  $\text{TEA}^+$  cations were then removed from the zeolite pores. Such a zeolite synthesized after calcination is denoted as "the synthesized V-Beta" or "V-Beta" zeolite. In order to make a comparison, H-form beta zeolite (H-Beta) with the same Si/Al ratio was prepared in the mean time.

### Characterization of catalysts

The synthesized zeolites were analyzed by inductively coupled plasma-mass spectrometry (ICP-Mass) and well characterized by X-ray powder diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), infrared (i.r.), diffuse reflectance u.v.-vis, solid-state nuclear magnetic resonance (MAS n.m.r.), and electron paramagnetic resonance (EPR) spectroscopies.

Thermal analyses of the as-synthesized TEA-beta zeo-

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**Figure 1** DTG profiles of as-synthesized template-containing V-Beta and H-Beta zeolite samples in flowing oxygen at a programmed temperature rate of 10°C/min.

lites were carried out in an oxygen flow and taken with a Du Pont TGA 951 thermogravimetric analyzer. The ICP-mass analysis of the synthesized zeolites was performed on a Perkin Elmer Sciex Elan 5000 spectrometer. Surface areas were determined following the BET method for nitrogen adsorption at 77 K, the data being collected with a Micromeritics AccuSorb-2100E surface area analyzer. The XRD measurements were performed on a Rigaku D/Max-III diffractometer with nickel-filtered  $\text{CuK}\alpha$  radiation. STEM/EDS and SEM/EDS were carried out on Joel JSM-2000FX and Hitachi S-800 SEM system, respectively. Diffuse reflectance u.v.-vis spectra were taken on an Hitachi U-3410 spectrometer with 60  $\phi$  integrating sphere accessory. Infrared spectra were obtained with a Bomem DA-8 FT i.r. spectrometer. The acidity of the zeolite was investigated by *in situ* FT i.r. spectroscopic studies of pyridine adsorption. The i.r.-cell used in the present study is the same as described previously.<sup>19</sup> The solid-state  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS n.m.r. spectra were acquired on Bruker MSL-200 and MSL-500 spectrometers with commercial magic angle spinning (MAS) probes. The EPR spectrum was recorded at 77 K using a Bruker X-band ESP-300E EPR spectrometer.

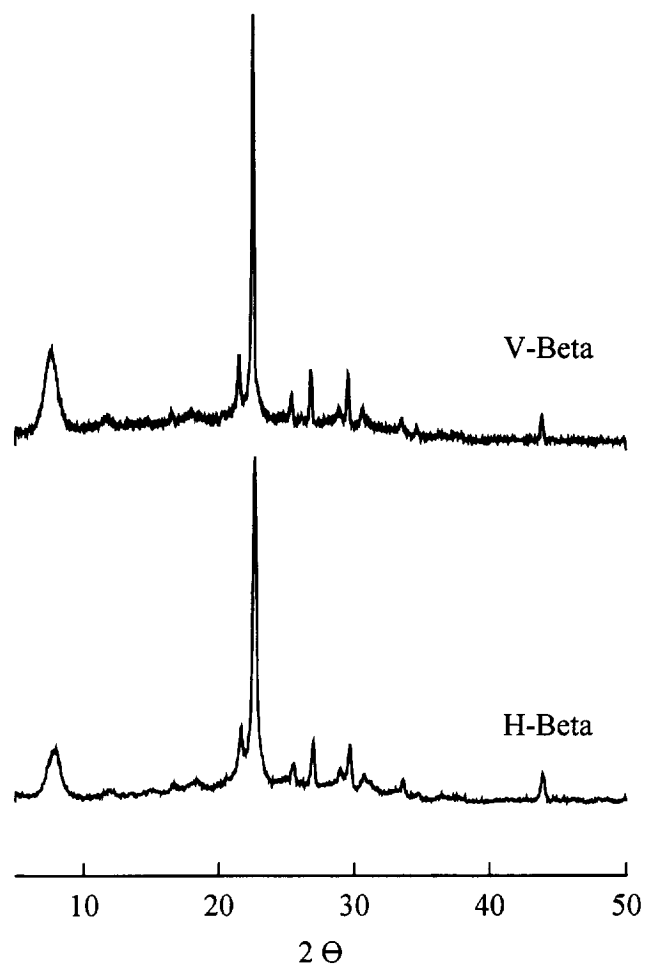
## RESULTS AND DISCUSSION

We have successfully synthesized the well-dispersed vanadium-containing zeolite beta (V-Beta) by direct hydrothermal method. The thermogravimetric analysis (t.g.a.) of as-synthesized TEA-beta zeolite samples was taken in the oxygen stream with a flow rate of 25  $\text{cm}^3/\text{min}$  and the programmed temperature rate of 10°C/

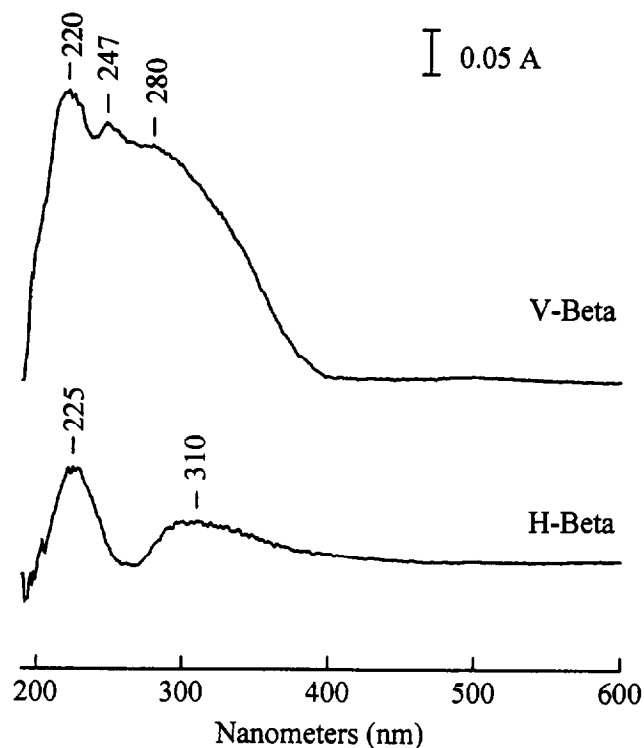
min. The results were shown in Figure 1, in which the first derivative of the thermogravimetric analysis (DTG) pattern was presented. According to the literature,<sup>15</sup> the peak before 220°C is due to the desorption of water. The large peak centered at ~285°C is ascribed to the decomposition of TEOH; the peak centered at ~445°C is due to the decomposition of  $\text{TEA}^+$  ions. The peak beyond 500°C is corresponding to the oxidative decomposition of organic materials. It can be seen that the desorption of templates from V-Beta is similar to the H-Beta zeolite. Accordingly, the calcination of the as-synthesized template-containing zeolites were performed in oxygen flow at 550°C for 15 h.

Figure 2 shows the powder X-ray diffraction (XRD) patterns of synthesized V-Beta and H-Beta samples. The XRD spectrum shows no visible change in peak position after calcination of the as-synthesized TEA-Beta zeolites, but slightly decrease in crystallinity. The crystalline structures are all in the Beta-form zeolites.<sup>13</sup> The SEM micrographs of both samples exhibit almost the same morphologies of cubic shapes, but the average particle sizes of V-Beta (~0.6  $\mu\text{m}$ ) are larger than H-Beta (~0.4  $\mu\text{m}$ ). STEM/EDS shows a well-dispersed vanadium in V-Beta zeolite. The BET surface areas are around 520  $\text{m}^2/\text{g}$  without significant difference.

The atomic ratios of the synthesized zeolites obtained



**Figure 2** Powder X-ray diffraction patterns of the synthesized V-Beta and H-Beta zeolites.



**Figure 3** The diffuse reflectance u.v.-vis spectra of V-Beta and H-Beta zeolites.

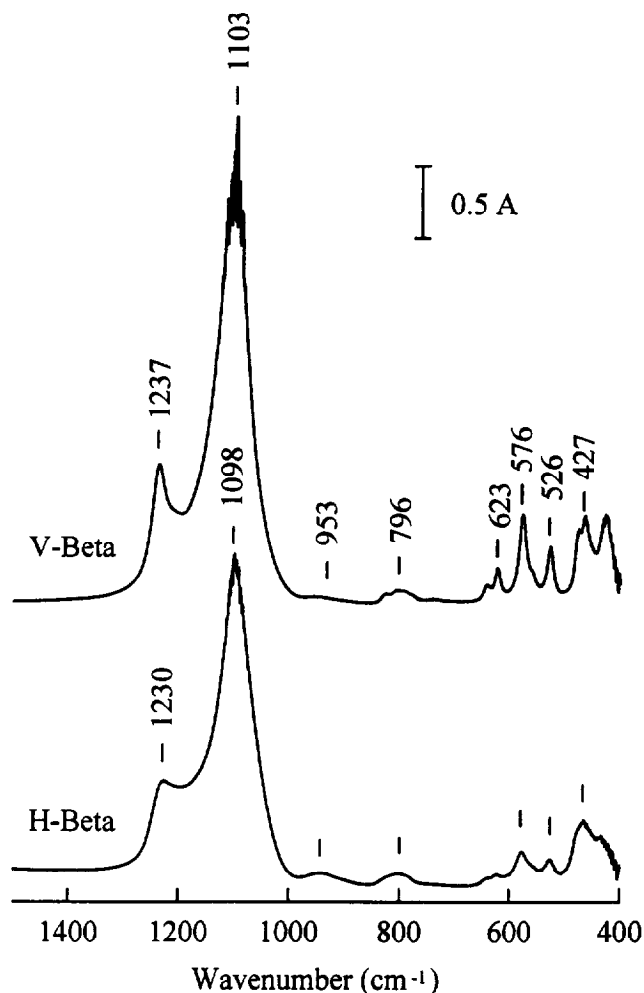
by ICP-mass, SEM/EDS, and solid-state MAS n.m.r. are shown in Table 1. In all cases, the Si/Al atomic ratios are less than 30 except the n.m.r. results of the V-Beta zeolite. The discrepancy will be discussed later. It is noticeable from the ICP data that only 1.3% vanadium was incorporated into Beta zeolite by the present hydrothermal synthesis. The vanadium content is too low to be detected by SEM/EDS. However, the STEM/EDS has shown the uniform dispersion of vanadium in a cubic shaped zeolite Beta.

Figure 3 shows the diffuse reflectance u.v.-vis spectra of both synthesized V-Beta and H-Beta zeolites. Figure 4 exhibits the corresponding infrared spectra. The infrared spectrum of V-Beta shows clearly the characteristic spectrum of H-Beta zeolite.<sup>15</sup> However, by comparing of the u.v.-vis spectra of both zeolites, the effect of the incorporated vanadium on the spectra of zeolite beta is significant. The u.v.-vis spectrum of V-Beta clearly displays a high-intensity band below 400 nm raised from O-V charge-transfer.<sup>4</sup> Because the absorption band between 550 and 800 nm is hardly observed, the presence of V<sup>4+</sup> ions in tetrahedral coordination is doubtful.<sup>4,5</sup> The i.r. peak that appeared at 960 cm<sup>-1</sup> has been used for identifying the framework-incorporated ion,<sup>4</sup> however, the peak intensity is fairly weak in the V-Beta zeolite. An enhanced i.r. spectrum resolution and likely slight blue shifts of i.r. asymmetric stretching bands of the V-Beta as compared to H-Beta are noticeable. All these spectroscopic results tend to indicate that the vanadium ions are immobilized and dispersed in the cation sites.

The acidic properties of the synthesized zeolites were measured by *in situ* FT i.r. spectroscopic studies of pyr-

idine adsorption. The results are given as shown in Figure 5. The pyridine adsorption was carried out under 1 torr vapor of pyridine at 150°C for an hour, the i.r. spectra were taken after outgassing at room temperature for 10 min. It is obvious that both V-Beta and H-Beta possess strong Lewis acidity (1,445 cm<sup>-1</sup>) and very weak Brønsted acidity (1,547 cm<sup>-1</sup>). Apparently, when incorporating vanadium to zeolite beta, Lewis acidity is enhanced and Brønsted acidity is weakened slightly. There appears a strong hydrogen-bonded pyridine (1,440 cm<sup>-1</sup>) on V-Beta as well.

Figure 6 shows the <sup>29</sup>Si and <sup>27</sup>Al MAS n.m.r. spectra of the synthesized zeolites. The <sup>29</sup>Si MAS n.m.r. spectrum of V-Beta exhibits a steep up-slope peak at -110.7 ppm and a well-resolved shoulder-peak at -114.4 ppm. These two peaks can be assigned as the nonequivalent Si atoms, with no Al in the second coordination sphere (Si surrounded by 4 Si), occupying different structural sites in the zeolite. By using the Loewenstein's formula, the framework Si/Al ratios of 235 and 144 were obtained based on the <sup>29</sup>Si MAS n.m.r. spectra taken from 200 and 500 MHz n.m.r., respectively. As compared to the Si/Al ratio of about 23 for the synthesized V-Beta measured from ICP-mass measurement, the high Si/Al ratio (>100) estimated from Loewenstein's rule looks unrealistic. The <sup>29</sup>Si MAS n.m.r. spectral shape of V-Beta



**Figure 4** The infrared spectra of V-Beta and H-Beta zeolites.

**Table 1** The atomic ratio of H-Beta and V-Beta zeolites obtained by various methods

	ICP-AES			EDS			<sup>29</sup> Si n.m.r.	
	V	Al	Si	V	Al	Si	Si/Al <sup>a</sup>	Si/Al <sup>b</sup>
H-Beta	—	1	23.0	—	1	19.6	24.5	29.0
V-Beta	0.013	1	22.7	0	1	21.6	[235]	[144]

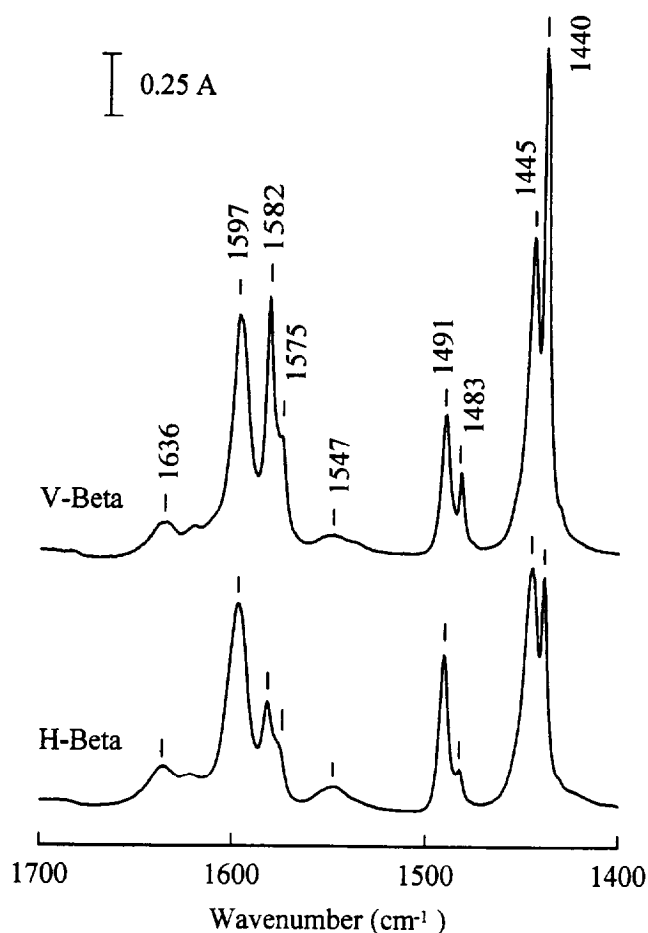
<sup>a</sup> 200 MHz.<sup>b</sup> 500-MHz n.m.r. (using Loewenstein rule).

is quite similar to the dealuminated zeolite beta with Si/Al ratio > 100 in a tetragonal structure,<sup>20</sup> but the shoulder-peak appeared at -116 ppm in the latter. The highly siliceous zeolite beta seems to show the peaks near -116 ppm;<sup>21</sup> that is not the case for the V-Beta. Moreover, the phenomenon that the <sup>29</sup>Si n.m.r. peaks of V-Beta appear more negative in chemical shifts as compared to H-Beta might be considered to be due to the larger T-O-T angle in V-Beta.<sup>22,23</sup> The increase in T-O-T angle has also been reported to correspond to a decrease in Brønsted acidity of zeolites.<sup>24</sup> It is in good agreement with the former i.r. results. In the <sup>27</sup>Al n.m.r. spectrum, it shows two poorly resolved tetrahedral Al peaks at 54.2 and 56.5 ppm and a small extraframework Al peak at 0.1 ppm. Although the extraframework Al peak of V-Beta exhibits a broad shoulder, dealumina-

tion due to the incorporation of vanadium should not be serious. Concerning the enhanced intensity ratio of 54.2 to 56.5 ppm peak for V-Beta sample, it is also a consequence of the zeolite with either the higher Si/Al ratio<sup>20</sup> or the larger T-O-T angle.<sup>25</sup> All the results will likely show that the T-O-T angle in V-Beta is larger than that in H-Beta. Moreover, the higher resolution in the <sup>29</sup>Si n.m.r. spectrum of V-Beta might indicate less structure defect, as suggested by Pérez-Pariente et al.<sup>20</sup> We expect that in the direct hydrothermal synthesized V-Beta there exist certain sites for preferential occupation by V and Al in the zeolite beta structure.

The EPR results of V-Beta are unique as well. *Figure 7* shows the EPR spectra of the synthesized V-Beta before and after dehydration, recording at 77 K. The well-resolved anisotropic spectrum shows two sets of 8-fold hyperfine splitting with signals at  $g_{\parallel} = 1.936$ ,  $A_{\parallel} = 201$  G and  $g_{\perp} = 1.987$ ,  $A_{\perp} = 84$  G, the typical spectrum of isolated vanadyl cations ( $\text{VO}^{2+}$ , V(IV),  $3d^1$ ,  $^{51}\text{V}$ ,  $I = 7/2$ ). The spectrum is similar to those of  $\text{VO}^{2+}$  cations embedded in X and Y zeolites and was assigned in a square pyramidal coordination, with  $|B_2\rangle$  as the ground state.<sup>11</sup> No significant difference was observed when recording at 298 and 77 K, indicating that the isolated vanadyl ions are immobilized in the zeolite, and V(IV) ions are not in a  $T_d$  symmetry position.<sup>4</sup>

When V-Beta was dehydrated at room temperature or at higher temperature, the EPR spectrum retained the original two sets of 8-fold hyperfine splitting without significant changes in the  $g$ -values and the hyperfine constants. However, there appeared an additional superhyperfine structure (shfs) with  $A = 4$  G. The higher the recording temperature, the better the resolution of the shfs lines. Expansions of part of the spectrum and its second derivative spectrum are shown in *Figure 7* as well. The superhyperfine interaction was apparently masked by the water molecules. The spectrum is similar to the vanadium in H-ZSM-5 as reported by Kucherov and Slinkin,<sup>9</sup> except the smaller shfs splitting. The shfs structure was assigned to be due to the electronic interaction between vanadyl cation and nearby lattice  $\text{Al}^{3+}$  ions. Because the bridged -OH acid sites in zeolites usually act as powerful traps for migrating ions, the vanadyl ions in Beta zeolite might be thus localized as isolated cationic species. Stabilization of such isolated paramagnetic ions in the cationic position of the zeolite might be accompanied by an electronic interaction between the ion and the nearest lattice  $\text{Al}^{3+}$  ion. This interaction then led to the formation of additional superhyperfine structure in EPR spectra caused by the partial location of unpaired electron den-

**Figure 5** *In situ* FT i.r. spectra of pyridine adsorption on V-Beta and H-Beta zeolites.

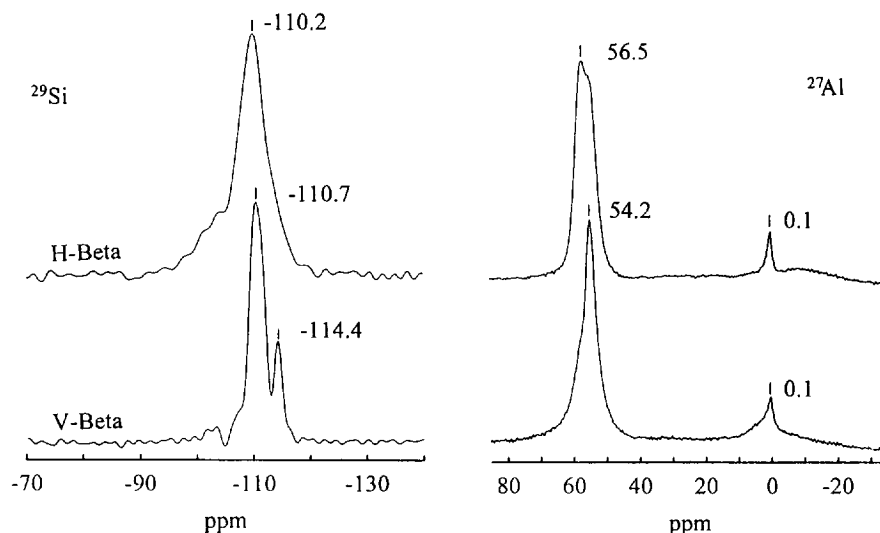


Figure 6 The  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS n.m.r. spectra of V-Beta and H-Beta zeolites.

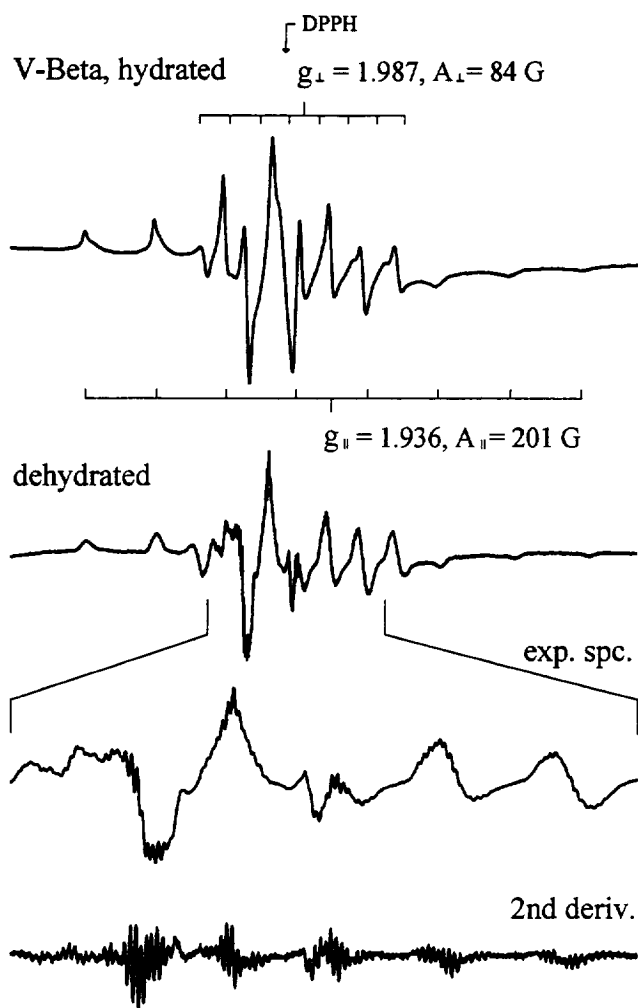


Figure 7 The EPR spectra of the synthesized V-Beta zeolites before and after dehydration, taken at 77 K.

sity on  $^{27}\text{Al}$  ( $I = 5/2$ ) as proposed by Kucherov and Slinkin.<sup>9</sup>

## CONCLUSIONS

A unique structure of vanadium-containing zeolite beta, with molar atomic composition of  $\text{V} : \text{Al} : \text{Si} = 0.013 : 1 : 23$  was synthesized by the direct hydrothermal method. The spectroscopic studies indicate that such a unique structure of V-Beta contains the isolated V(IV) atomically dispersed at the cation or vacant acid sites near Al. The effect of vanadium on the framework Si/Al ratio and the T-O-T angles, as well as the acidity of zeolite beta, is remarkable. The unique characteristics of V-Beta zeolites are worth further study. We believe that the results are important and helpful in the catalytic processes occurring in these systems.

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