

Studies on Crystalline Microporous Vanadium Silicates

II. FTIR, NMR, and ESR Spectroscopy and Catalytic Oxidation of Alkylaromatics over VS-2

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Three crystalline, microporous, vanadium silicates, VS-2 (Si/V = 79, 122, and 161, respectively) with MEL structure have been synthesized. The spectroscopic (IR, NMR, and ESR) features and catalytic properties (in the oxidation of toluene and xylenes by H_2O_2) have been elucidated. IR spectra of the adsorbed ammonia and pyridine reveal the presence of both weak Brønsted and Lewis acid sites. There is a direct correlation between the concentration of hydrogen-bonded hydroxyl groups and the amount of vanadium incorporated in the material. In carefully prepared samples of VS-2, the ^{51}V MAS-NMR studies reveal the presence of only a single vanadium species with a chemical shift parameter (-573 ppm) and a signal linewidth (50 ppm) similar to those observed in monomeric orthovanadates having tetrahedrally coordinated vanadium ions. Clusters of vanadium as well as V_2O_5 -like phases are absent. A linear increase in the intensity of the ESR peaks with both the vanadium content and unit cell volume of the MEL phase suggests that the V^{4+} ions are associated, in a manner yet undefined, with the MEL lattice. VS-2 oxidizes toluene to a mixture of cresols, benzyl alcohol, and benzaldehyde. The difference in the rates of oxidation of xylene isomers confirms that most of the V ions are located inside the channel system of MEL. © 1993 Academic Press, Inc.

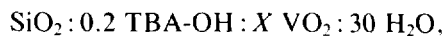
INTRODUCTION

Vanadium silicate molecular sieves with isomorphously substituted vanadium in framework positions of the MFI lattice have recently been claimed (1-5). In part I of this series, we had reported (6) the preparation of thermally stable, vanadium-containing silicalite-2 samples by hydrothermal crystallization. The plausible environment of V in the as-synthesized, calcined, and reduced states was described. These materials are catalytically active in both acid-catalyzed and oxidation reactions. In the present paper, we report further on the characterization of these vanadium silicates, VS-2 with MEL topology (as revealed by XRD), by IR, ESR, and ^{51}V -NMR spectroscopic techniques and on their catalytic activity in the oxidation of alkyl aromatics using aqueous H_2O_2 .

EXPERIMENTAL

Synthesis

The hydrothermal crystallization of vanadium silicates with MEL structure (VS-2) was carried out using the molar compositions



where $X = 0.03-0.01$ and TBA-OH = tetrabutyl ammoniumhydroxide.

The syntheses were carried out in the absence of any Na^+ ions and with negligible amount of Al (Si/Al > 2000). Tetraethylorthosilicate (TEOS, Aldrich) was used as the silica source and vanadyl sulfate trihydrate ($VO_2SO_4 \cdot 3H_2O$, Aldrich) as the vanadium source. Other details of the synthesis and characterization (by XRD, IR and ESR) of the vanadium silicates with different Si/V ratios were presented in our earlier

TABLE I
Physicochemical Properties of Vanadium Silicates

Catalyst	Si/V gel (input)	Si/V sample (output)	Si/V sample ^a	Na/V ^b	Surface area (m ² /g)	Unit cell volume ^c	ESR signal intensity ^d
VS-2	40	78	79	0.56	550	5373	33
VS-2	60	116	122	0.51	506	5368	24
VS-2	80	161	161	0.53	554	5363	14
S-2	∞	—	—	—	548	5354	—

^a After treating the calcined sample with 0.5 M ammonium acetate solution at 300 K.

^b After treating the calcined sample with 0.05 M NaCl solution at 300 K.

^c From powder XRD patterns (Rigaku, model Max IIIID/VC, Cu-K α) using PDP-11 software (Dept. of Chemical Sciences, University of Trieste, Italy); values are accurate to $\pm 1 \text{ \AA}^3$.

^d Integrated intensity (arbitrary units) of ESR signals due to V⁴⁺ ions in the as-synthesized samples.

report (6). The kinetics of crystallization and the influence of various preparation parameters on the synthesis of vanadium silicates have been described elsewhere (7). Samples with Si/V (output) ratios of 79, 122, and 161 after treatment with 0.5 M ammonium acetate solution at room temperature have been chosen for detailed studies. A sample of silicalite-2 (S-2) prepared using a similar hydrothermal procedure but excluding vanadium was utilized to bring forth the distinctive spectroscopic and catalytic features induced by the presence of vanadium in the MEL structure. Some of the physicochemical properties of the samples are given in Table I.

Characterization

The *in situ* FTIR spectra of vanadium silicates were recorded in the 4000–1500 cm⁻¹ range, using self-supported wafers, which were outgassed *in vacuo* at increasing temperatures upto 723 K. The spectra were recorded in a Nicolet 60 SXB FT-IR spectrometer. The absence of any changes in the XRD pattern and the framework IR spectrum monitored show that the MEL structure did not collapse during thermal treatments (at least upto 723 K). A Bruker ER-200 D spectrometer was used to record the ESR spectra of the samples at room temperature. ⁵¹V MAS NMR measurements were recorded in a Bruker MSL 400

FT-NMR spectrometer operated at 293 K and at 105 MHz. The spectral width was 2.5 MHz and 200 ms repetition time was used. The spectra were obtained from accumulation of 20,000 to 30,000 transitions. VOCl₃ was used as the reference sample to measure the chemical shift.

Catalysis

The oxidation of alkylaromatic compounds was carried out in a batch glass reactor. In a typical reaction, 100 mg of the catalyst was dispersed in a solution containing 1 g of the reactant and 10 g of solvent (acetonitrile). The mixture was heated to 353 K under vigorous stirring and H₂O₂ (26 wt%, aqueous solution, reactant/H₂O₂ = 3 mol) was then slowly added. After completion of the reaction, the products were separated from the catalyst and analyzed by GC (HP 5880) using a capillary (cross-linked methyl silicone gum) column and flame ionization detector. The products were identified by GCMS (QP-2000A, Shimadzu) using standard compounds as reference samples.

RESULTS AND DISCUSSION

FTIR Spectroscopy

Figure 1 illustrates the IR spectra of the calcined samples in the hydroxyl stretching region (4000–2800 cm⁻¹) after outgassing in vacuum at 673 K. A sharp band at 3728

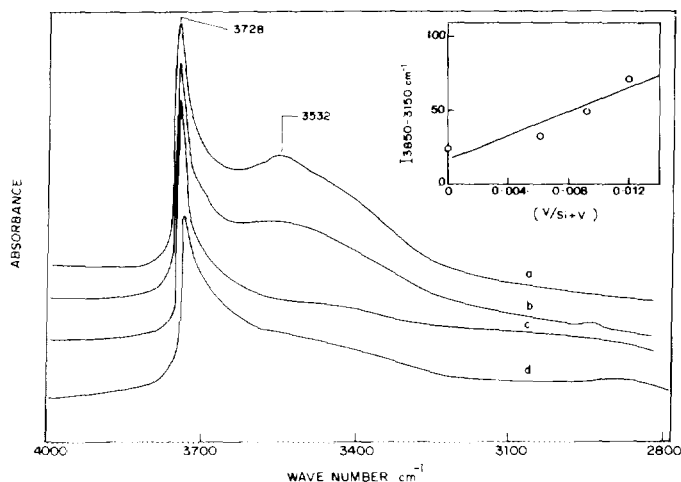


FIG. 1. FTIR spectra of vanadium silicates. Curves a to c refer to samples with Si/V ratios of 79, 122, and 161, respectively and curve d for silicalite-2 sample. Inset: correlation between integrated intensity of IR absorbance in the range 3850–3150 cm^{-1} and vanadium content. The samples were evacuated at 673 K and cooled to 323 K before recording the spectra.

cm^{-1} and a broad band at 3532 cm^{-1} can be seen. The former is due to terminal silanol groups and the latter is assigned to H-bonded hydroxyl groups (8). The sharp peak due to isolated silanols, probably located on the external surface, is present in pure silicalite-2 also (Fig. 1, curve d). The broad band at 3532 cm^{-1} is found in all vanadium silicate samples, their intensity increasing with the vanadium content. Centi *et al.* (4) have in addition reported a band at 3682 cm^{-1} , attributed to less thermally stable -OH groups. This band is also present but as a shoulder in our samples (Fig. 1). The band ascribable to V-OH vibration, however, is not clearly distinguished due probably to the broad nature of the 3532 cm^{-1} band and the low vanadium content in the samples. It was earlier suggested that the vanadium ions are probably at surface defect sites where the Si-OH concentration is likely to be high (2, 4, 6). That the formation of such sites could be enhanced by the presence of vanadium during the hydrothermal synthesis is indicated by the linear increase in the total integrated intensity of the absorption in the region 3850 to 3150 cm^{-1} with the vanadium content in the

three samples (inset in Fig. 1). Irrespective of the differences in the preparation of vanadium silicates, this correlation supports the model proposed by us for V-MEL (6) and by Rigutto and Van Bekkum (2) and Centi *et al.* (4) for V-MFI samples for the possible environment of vanadium in the pentasil structure.

In order to study the surface acidity of the above samples, adsorption of ammonia was performed on a vanadium silicate (Si/V = 79) sample. The spectra on desorption of ammonia from the calcined sample at various temperatures are shown in Fig. 2. Two bands at 1680 and 1450 cm^{-1} due to ammonium ions (δ_s and δ_{as} of NH_4^+ , respectively) indicate the presence of Brønsted acid sites (9–11). The intensity of these bands decreased drastically on evacuation even at 373 K, indicating the presence of only weak Brønsted acid sites. At 373 K when most of the bands due to Brønsted acidic sites have disappeared, a distinct band at 1620 cm^{-1} is seen clearly. This band is due to ammonia coordinatively bonded to Lewis acid sites (9). Brønsted acid sites were not observed in pure silicalite. These observations are in broad agreement with

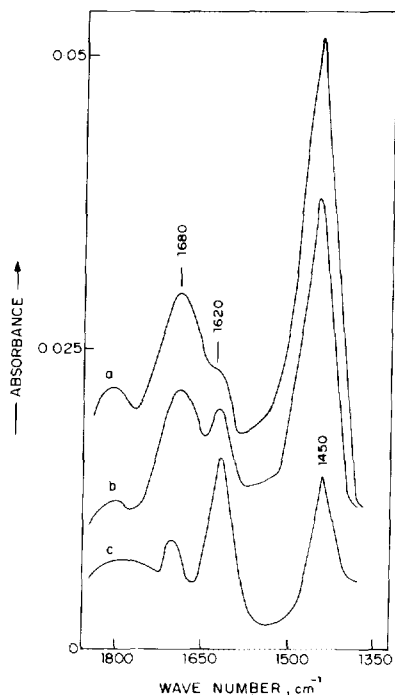


FIG. 2. FTIR spectra of VS-2 ($\text{Si/V} = 79$) sample after adsorption of ammonia at 303 K and evacuation at 303, 323 and 373 K (curves a, b, and c, respectively).

the recent report of Centi *et al.* (4) on vanadium silicate ($\text{Si/V} = 262$) with MFI structure. However, the presence of a distinct band at 1620 cm^{-1} band after evacuation at 373 K due, probably, to the presence of Lewis acid sites, had not been observed earlier.

The spectra of the adsorbed pyridine after evacuation at 323 K for the three vanadium silicates and pure silicalite-2 are presented in Fig. 3 (curves a to d, respectively). Figure 4 illustrates the spectra of adsorbed pyridine on vanadium silicate ($\text{Si/V} = 79$) after evacuation at 323, 373, and 423 K (curves a, b, and c), respectively. A weak band at 1581 cm^{-1} observed in the spectra supports the presence of H-bonded pyridine (9, 12). The position of these bands and their temperature dependence indicate the presence of weak Lewis acid sites both on silicalite-2 and V-silicate

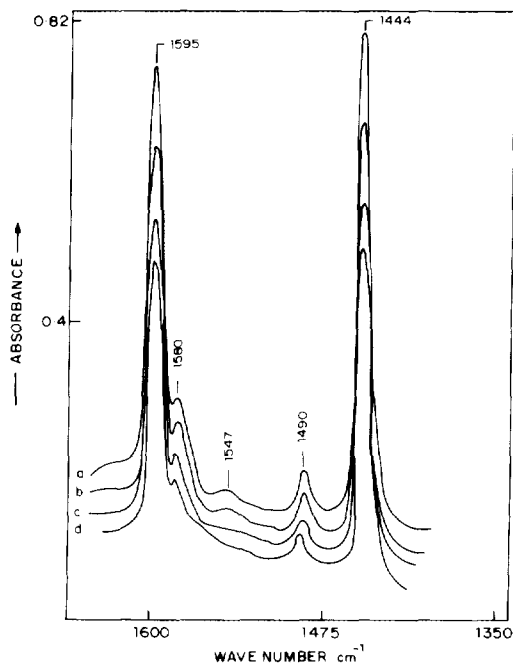


FIG. 3. FTIR spectra adsorption of pyridine at 303 K and evacuation at 323 K, curves a to d refer to samples with $\text{Si/V} = 79, 122,$ and 161 and silicalite-2, respectively.

samples. In addition, a weak band at 1547 cm^{-1} due to Brønsted acid sites is seen in the vanadium silicate samples. The 1547-cm^{-1} band is absent in pure silicalite-2. The intensity of this band increases with the vanadium content. The pyridinium ions on vanadium silicates are unstable on evacuation at 423 K (Fig. 4). Hence only weak Brønsted acid sites are present in the vanadium silicates. They are (Table 1) probably related to V-OH species. This is in agreement with the sodium ion-exchange behavior of the samples reported earlier (Table 1) (2, 4, 6).

^{51}V MAS-NMR Spectroscopy

The ^{51}V -NMR spectrum of a vanadium silicate sample ($\text{Si/V} = 79$) is shown in Fig. 5a. The spectrum is quite complex due to simultaneous line-broadening effects arising from second order quadrupolar and

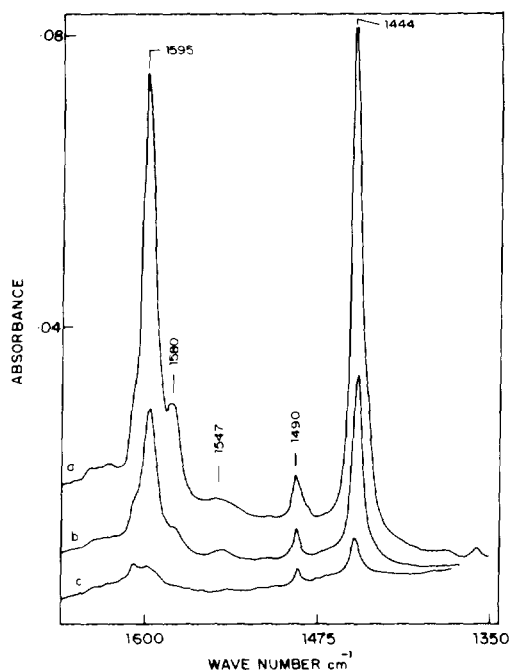


FIG. 4. FTIR spectra of VS-2 ($\text{Si/V} = 79$) after adsorption of pyridine at 303 K and evacuation at 323, 373, and 423 K (curves a to c, respectively).

chemical shift anisotropy interactions. The spectrum shows a main signal at -573 ppm (relative to VOCl_3). The observed line width at half-height (approximately 50 ppm) is much narrower than that reported (around 250 ppm) for other supported vanadium oxide catalysts (13–16). The ^{51}V -NMR spectrum of a vanadium silicate prepared using VCl_3 as the source of vanadium (instead of VOSO_4) is shown in Fig. 5b. The main signal is around -513 ppm, with a linewidth of about 60 ppm. Monomeric orthovanadates such as Na_3VO_4 and $\text{Mg}_3(\text{VO}_4)_2$ contain isolated tetrahedrally coordinated vanadium ions in a nearly symmetrical environment and show characteristic ^{51}V NMR spectrum of narrow symmetrical lines centered around -550 ppm (17, 18). The wide line ^{51}V NMR spectrum of V_2O_5 , which has a square pyramidal geometry around V is, on the other hand, dominated by a central line around -300 ppm (14, 17). The absence of an absorption band

around -300 ppm shows that no V_2O_5 -like phase is present in our samples.

Rigutto and Van Bekkum (2) have reported a main signal at -500 ppm for their samples (with MFI structure) prepared using vanadyl sulfate. For vanadium silicates (MFI) prepared using VCl_3 as the vanadium source, Centi *et al.* (4), on the other hand, reported a symmetrical spectrum with a line centered at -480 ppm and interpreted the lineshape due to the presence of V^{5+} sites in a nearly symmetrical tetrahedral environment. The considerable shift in the line position from that normally observed for orthovanadates (520–590 ppm) was attributed by them to the presence of a slightly shorter V–O bond length. For a ZSM-5 ($\text{Si/Al} = 30$) sample treated with VCl_3 at 600°C for 48 h, Fejes *et al.* observed the ^{51}V NMR signal at -512 ppm (19). In the same study, vanadium silicate prepared using $\text{VO}(\text{COO})_2$ in the synthesis mixture exhibited two signals at -567 ppm (10%) and -575 ppm (90%), respectively. They concluded that at least two different V^{5+} species both in the framework positions of MFI are present in their samples. These

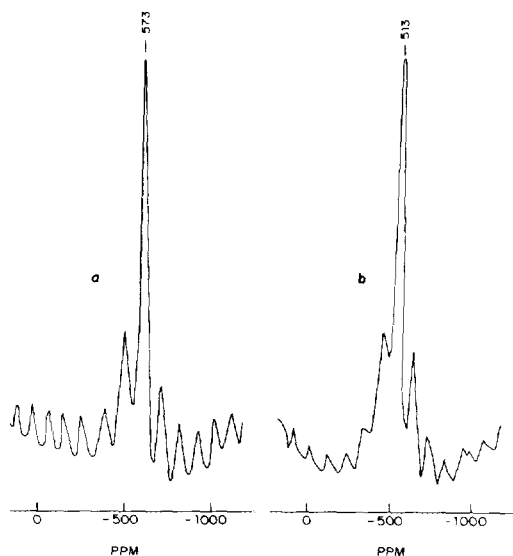


FIG. 5. ^{51}V MAS-NMR spectra of VS-2 sample prepared using VOSO_4 ($\text{Si/V} = 79$, spectrum a) and VCl_3 ($\text{Si/V} = 68$, spectrum b) as the source of vanadium.

results clearly show the difference in the environment of the vanadium in samples synthesized using different vanadium sources and synthesis procedures. The single signal for ^{51}V observed in our studies (Fig. 5) indicates that vanadium ions are located in a single structural environment. The value of the chemical shift (-573 ppm) and linewidth (50 ppm) in the sample prepared using vanadyl sulfate as the raw material suggests that the vanadium ions in these samples are probably in distorted tetrahedral symmetry. More detailed studies using samples prepared under well defined conditions are needed for a definitive assignment of NMR signals of ^{51}V in vanadium silicates.

ESR Spectroscopy

The ESR spectra of the as-synthesized samples (in hydrated form) have been recorded at room temperature in the presence of atmospheric air. The spectra are characteristic of atomically dispersed and immobile V^{4+} ions (Fig. 6 for a sample with $\text{Si}/\text{V} = 79$). The anisotropic 8-line hyperfine splitting caused by the ^{51}V nucleus is well

resolved in all the cases, without the presence of any superimposed broad singlet confirming the absence of vanadium clusters. Both the ESR signal intensity of as-synthesized samples and the unit cell volume (from XRD) of the calcined samples increase with increasing vanadium content (Fig. 6, inset). For the calculation of unit cell parameters, a PDP-11 software program (Dept. of Chemical Sciences, University of Trieste, Italy) was used. The unit cell volumes are accurate to $\pm 1 \text{ \AA}^3$ after repeated scans and measurements of duplicate samples. While these results may suggest that V^{4+} ions are probably incorporated at framework positions, this conclusion is not definitive since our earlier ESR results (6) had indicated that V^{4+} ions are not in T_d symmetry positions. Perhaps, a situation wherein vanadium is "grafted" to the internal Si-OH groups, instead of being in substitutional positions, would also explain our results including the observed lattice expansion with V content, provided there is still a crystallographic order. The presence of such groups in our samples has been mentioned earlier (IR data, Fig. 1).

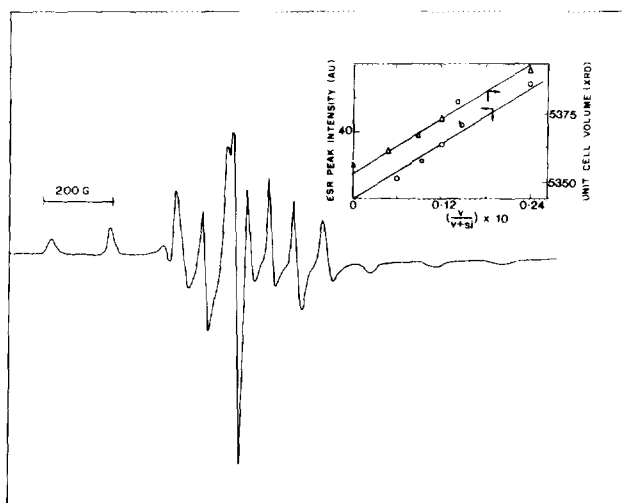


FIG. 6. ESR spectra of as-synthesized VS-2 ($\text{Si}/\text{V} = 79$) sample recorded at 298 K. Inset: correlation between ESR peak intensity (AU), unit cell volume (XRD) and vanadium content in various VS-2 samples.

Oxidation of Alkyl Aromatics

Vanadium silicates are active in both hydroxylation of the aromatic nucleus and oxidation of the alkyl substituent on the aromatic ring in presence of aqueous H_2O_2 at 353 to 373 K. In our earlier studies on the hydroxylation of phenol to dihydroxy benzenes, their activity was found to be comparable to that of titanium silicates (20). Interestingly, in the oxidation of alkanes we had observed the oxyfunctionalization of primary carbon atoms as well, by vanadium silicates, yielding primary alcohols and aldehydes in addition to secondary alcohols and ketones (21). Here, we illustrate the oxidation activity of the vanadium silicates for alkyl aromatics. The oxidation of toluene over the three vanadium silicate samples is illustrated in Table 2. For comparison, the activities of V-free silicalite-2 and titanium silicate (TS-2) are also included in Table 2. The products of oxidation of toluene on vanadium silicates are mainly benzyl alcohol, benzaldehyde (formed by secondary oxidation of benzyl alcohol), and *o*- and *p*-cresols. The conversion increases with vanadium content in the samples. The formation of significant quantities of benzyl alcohol and benzaldehyde is in contrast to the observation with titanium silicates wherein

the products are mainly *o*- and *p*-cresols. On a titanium silicate sample (TS-2 with Si/Ti = 82), for example, except cresols, no benzyl alcohol and/or benzaldehyde were detected in the products (Table 2). Under these conditions, silicalite-2 is completely inactive. It may also be mentioned that silicalite-2 impregnated with vanadium (through $VOSO_4$ solution) of concentration similar to VS-2 (Si/V = 79) showed negligible activity in the above oxidation reactions. The possibility that vanadium ions, leached into solution from the solid in the presence of aqueous H_2O_2 , may be responsible for the observed catalytic activity was also considered. One gram of VS-2 was taken in 100 ml of acetonitrile and 4.7 g of H_2O_2 (26 wt% aqueous solution) and stirred for 5 h at 353 K. The catalyst was then separated by filtration, washed, and dried. Both the solution and the catalyst were analyzed for V content. The XRF and AAS analyses show that the Si/V ratio of the catalyst after treatment was 84 compared to the initial Si/V ratio of 79. The loss corresponded to 3.7 wt% in one case and 5.7% in a duplicate experiment. Hence, the contribution of the dissolved vanadium ions to the rates of oxidation is considered negligible. This conclusion is also supported by further information given below.

TABLE 2
Oxidation of Toluene over Vanadium Silicate Molecular Sieves^a

Catalyst	Si/V ratio	Conversion (wt%)	H_2O_2 ^b selectivity	Product distribution (wt%)				
				Benzyl alcohol	Benzaldehyde	<i>o</i> -Cresol	<i>p</i> -Cresol	Others ^c
VS-2	79	11.7	49.5	7.7	52.2	19.7	17.1	3.7
VS-2	122	8.2	32.4	17.0	38.0	24.4	14.2	6.4
VS-2	161	6.9	23.4	17.7	28.6	26.6	17.7	9.4
S-2	∞	0	0	—	—	—	—	—
TS-2	82	13.2	38	nd	nd	36	59	5

nd: Not detected.

^a Reaction conditions: catalyst (g) = 0.1; toluene (g) = 1; temperature (K) = 353; toluene/ H_2O_2 (mole ratio) = 3; solvent = acetonitrile (10 ml); reaction duration = 12 h.

^b H_2O_2 utilized in the formation of benzyl alcohol, benzaldehyde, and cresols.

^c Mainly polyhydroxy compounds.

Vanadium silicates are also active in the oxidation of xylenes and trimethyl benzenes. Both ring hydroxylation and side-chain oxidation occur. The relative rates of conversions were toluene (3.6) > *p*-xylene (2.4) > *m*-xylene (1) = *o*-xylene (1) = 1,3,5-trimethylbenzene (1). This trend parallels the diffusivity of these molecules in the MEL molecular sieves (22). For example, the ratio of the diffusion coefficients (at 373 K) of *p*-xylene or benzene to *o*-xylene in silicalite is about 9.3 (see Table 1 in Ref. 22). For catalysts with uniformly distributed active sites and assuming diffusion-controlled first order reactions (i.e., effectiveness factor less than 0.5), one has (23)

$$\frac{\text{rate}(1)}{\text{rate}(2)} \propto \left(\frac{D(1)}{D(2)} \right)^{1/2}$$

Hence,

$$\frac{\text{rate (toluene or } p\text{-xylene)}}{\text{rate (} o\text{-xylene)}} \approx \left(\frac{9.3}{1} \right)^{1/2} = 3.1,$$

which compares reasonably well with the observed relative rates of conversion mentioned earlier (2.4 to 3.6). In addition to confirming that the vanadium active sites are indeed located inside the zeolite channels, these results also indicate that the contribution of the vanadium ions dissolved in the aqueous H₂O₂ solution to the observed rates of conversion is not significant.

SUMMARY AND CONCLUSIONS

In VS-2 samples prepared carefully using VOSO₄ as source of vanadium:

(1) There is a correlation between the vanadium content and the concentration of H-bonded hydroxyl groups (Fig. 1). It is possible that (a) the presence of V ions during the hydrothermal synthesis enhances the concentration of such hydroxyl groups and that (b) the hydroxyl groups once formed bind the vanadium ions in a coordinative manner to generate VS-2. This observation supports the model for vanadium silicate proposed earlier (6).

(2) There are weak Brønsted and Lewis acid sites on VS-2 as may be seen from the spectra of adsorbed ammonia and pyridine at various temperatures (Figs. 2–4). They originate from the modification induced by vanadium in the silicalite structure.

(3) The ⁵¹V-NMR spectra of VS-2 reveal that the nature of the vanadium species depends strongly on the source of vanadium utilized during the synthesis procedure. Samples prepared from VOSO₄ contain only one vanadium species with a chemical shift parameter (–573 ppm) and signal line-width (50 ppm) similar to those observed in monomeric orthovanadates and contain isolated vanadium ions in distorted tetrahedral coordination. Clusters of vanadium as well as V₂O₅-like phases are absent.

(4) A linear increase in the integrated intensities of ESR signals and the unit cell volume of the samples with vanadium content suggest that the atomically dispersed vanadium ions observed by ESR spectroscopy are located within the MEL structure.

(5) In the oxidation of toluene with H₂O₂, VS-2 is active both in ring hydroxylation (to *ortho*- and *para*-cresols) and in side-chain oxidation (to benzyl alcohol and benzaldehyde). In this respect they differ from titanium-containing molecular sieves. The latter are active in the ring hydroxylation of the aromatic nucleus only. The shape selectivity observed in the oxidation of xylene isomers confirms that most of the V ions are located inside the channel system of MEL.

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REFERENCES

1. Kornatowski, J., Sychev, M., Goncharuk, V., and Baur, W. H., *Stud. Surf. Sci. Catal.*, **65**, 581 (1991).
2. Rigutto, M. S., and Van Bekkum, H., *Appl. Catal.*, **68**, L1 (1991).
3. Fejes, P., Marsi, I., Kiricsi, I., Halasz, J., Hannus, I., Rockenbauer, A., Tasi, Gy., Korecz, L., and

- Schobel, Gy., *Stud. Surf. Sci. Catal.* **69**, 173 (1991).
4. Centi, G., Perathoner, S., Trifiro, F., Aboukais, A., Aissi, C. F., and Guelton, M., *J. Phys. Chem.* **96**, 2617 (1992).
 5. Bellussi, G., Maddinelli, G., Carati, A., Gervasini, A., Millini, R., *9th International Zeolite Conference*, Montreal, Canada, 1992, Abstract A8.
 6. Hari Prasad Rao, P. R., Ramaswamy, A. V., and Ratnasamy, P., *J. Catal.* **137**, 225 (1992).
 7. Hari Prasad Rao, P. R., Ramaswamy, A. V., Kumar, R., and Ratnasamy, P., *Zeolites*, in press.
 8. Woolery, G. L., Alemany, L. B., Dessau, R. M., and Chester, A. M., *Zeolites* **6**, 14 (1986).
 9. Kung, M. C., and Kung, H. H., *Catal. Rev.-Sci. Eng.* **27**, 425 (1985).
 10. Tsyganenko, A. A. Pozdnyakov, D. V., and Filimonov, V. N., *J. Mol. Struct.* **29**, 299 (1975).
 11. Jobson, E., Baiker, A., and Wokaum, A., *J. Chem. Soc. Faraday Trans.* **86**, 1131 (1990).
 12. Knozinger, H., *Adv. Catal.* **25**, 184 (1976).
 13. Le Costoumer, L. R., Taouk, B., Le Meur, M., Payen, E., Guelton, M., and Grimblot, J., *J. Phys. Chem.* **92**, 1230 (1988).
 14. Taouk, B., Guelton, M., Grimblot, J., and Bonnelle, J. P., *J. Phys. Chem.* **92**, 6700 (1988).
 15. Echert, H., and Wachs, I. E., *J. Phys. Chem.* **93**, 6796 (1989).
 16. Sobalik, Z., Markvart, M., Stopka, P., Lapina, O. B., and Mastikhin, V. M., *J. Mol. Catal.* **71**, 69 (1992).
 17. Centi, G., Lena, V., Trifiro, F., Ghossoub, D., Aissi, C. F., Guelton, M., and Bonnelle, J. P., *J. Chem. Soc. Faraday Trans.* **86**, 2775 (1990).
 18. Lapina, O. B., Simakov, A. V., Mastikhin, V. M., Veniaminov, S. A., and Shibin, A. A., *J. Mol. Catal.* **50**, 55 (1989).
 19. Fejes, P., and Nagy, J. B., submitted for publication.
 20. Hari Prasad Rao, P. R., and Ramaswamy, A. V., *Appl. Catal. A: General* **93**, 123 (1993).
 21. Hari Prasad Rao, P. R., and Ramaswamy, A. V., *J. Chem. Soc. Chem. Commun.*, 1245 (1992).
 22. Ruthven, D. M., Eic, M., and Richard, E., *Zeolites* **11**, 647 (1991).
 23. Satterfield, C. N., and Shrewood, T. K., "Role of Diffusion in Catalysis," p. 66. Addison-Wesley, Reading, MA, 1963.