Synthesis and Catalytic Properties of Crystalline, Microporous Vanadium Silicates with MEL Structure

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A thermally stable, vanadium-containing silicate with the MEL structure has been prepared by hydrothermal crystallization. XRD and framework IR spectra of samples with three different Si/V ratios suggest the presence of V ions in framework positions wherein the concentration of SiOH groups is likely to be high. ESR spectra of the as-synthesized and reduced samples indicate that vanadium (in the tetravalent state) is in an atomically dispersed state, but not in T_d symmetry positions. Only V^{5+} ions were present on calcination, and the V^{4+} to V^{5+} transition was found to be reversible. The calcined samples contain exchangeable protons. These vanadium silicates are mildly acidic and are catalytically active in both acid-catalyzed (isomerisation of *m*-xylene) as well as oxidation (phenol to hydroquinone and catechol) reactions. A plausible environment of vanadium at defect sites in the MEL lattice is suggested. © 1992 Academic Press, Inc.

INTRODUCTION

Isomorphous substitution of Al^{3+} by other trivalent ions (like Fe^{3+}, Ga^{3+}, and B^{3+}) has been one of the significant achievements in the area of zeolite synthesis during the last decade. Metallosilicate analogs of zeolites containing transition metal ions with variable valency in the framework and which can catalyze oxidation reactions in a shape-selective manner will be an useful addition to the growing list of such materials. Several reports have appeared recently on the synthesis of vanadium-containing zeolites and their interesting catalytic properties (*1–3*). The location and state of vanadium in these zeolites are, however, still ambiguous. Recently, Rigutto and Van Bekkum (*4*) and Fejes *et al.* (*5*) have reported the synthesis and characterization of vanadium-containing silicalite-1 with MFI structure by hydrothermal crystallization. In the reduced catalyst, vanadium was present as V(IV) ions, while the pentavalent state predominated in the oxidized form. It was postulated that vanadium ions are located at defect sites. Earlier, Korantowski *et al.* (*6*) had also reported the synthesis of

vanadium silicates with MFI structure. In a recent report, Centi *et al.* (*7*) have identified more than three different vanadium species in a vanadium-MFI sample following extensive characterization of their samples, which contained extractable and occluded vanadium in the pore structure. We now report for the first time the synthesis, characterization, and catalytic properties of a novel, crystalline and microporous vanadium silicate, VS-2, with MEL structure. Our experimental results show that in carefully prepared samples only one type of vanadium species is present, which in all probability forms part of the lattice and is not extractable.

EXPERIMENTAL

VS-2 was synthesized as follows: 18 g of tetrabutyl ammonium hydroxide, TBAOH (Aldrich, 40%) was added slowly at 298 K to a mixture of 45.5 g of tetraethylorthosilicate (Aldrich, 98%) and 15 g of isopropanol. To the resultant mixture, an aqueous solution of 1.2 g of vanadyl sulfate trihydrate ($VOSO_4 \cdot 3H_2O$) (Aldrich) in 10 g of distilled water was added very slowly under vigorous stirring. The mixture was then stirred at

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313–323 K for about 30 min before adding to it 9 g of TBAOH in 50 g of distilled water. This final clear liquid reaction mixture was then stirred at 323 K for 6 h before transferring it into a SS autoclave. The crystallization of VS-2 was carried out under static conditions at 443 K for 4 days. After crystallization was completed, the white solid material was recovered by filtration, washed thoroughly with deionized water, and dried at 398 K for 6 h in air. The organic materials were removed by calcining the solid at 763 K in a flow of air. A total of three VS-2 samples with different Si/V ratios (160, 80, and 40, respectively) were synthesized by the above procedure. The influence of various synthesis parameters on the crystallization process is described elsewhere (8). The samples were analyzed by wet chemical methods and atomic absorption spectroscopy (Hitachi). The Si/Al ratio was found be >2000 in all the samples. The calcined samples (white in color) were characterized by XRD (Rigaku, D-Max/III-VC model), IR spectroscopy (FT-IR, Perkin–Elmer), and adsorption techniques (Omnisorb 100 CX analyser and Cahn Electrobalance). For ESR measurements, a Brucker ER 200 D spectrometer was used.

For use in catalytic reactions, the calcined VS-2 samples were treated with 1 N ammonium acetate solution and then calcined at 753 K in air for 8 h. Particles between 10 and 20 mesh size were used for catalytic reactions. The isomerisation of m-xylene over VS-2 was carried out in a downflow integral reactor and the products were analysed by on-line GC (Shimadzu, bentone column). The oxidation of phenol to dihydroxybenzenes using H_2O_2 (30% aqueous solution) was carried out in a batch reactor (9). The products were analysed by gas chromatography (HP 5880, 50-m cross-linked silicone gum capillary column).

RESULTS AND DISCUSSION

X-ray Diffraction

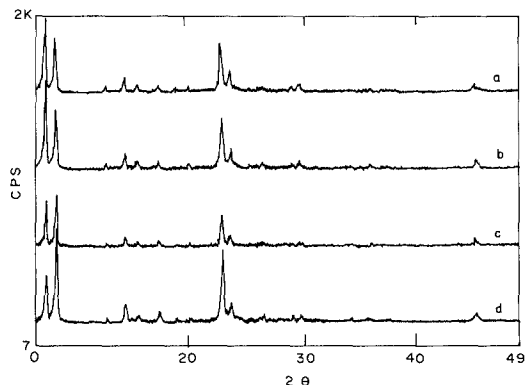The X-ray diffraction patterns of VS-2 were similar to that of silicalite-2 (10) (Fig.

FIG. 1. X-ray diffraction patterns of calcined samples of silicalite-2 (a) and vanadium silicates with Si/V ratios of 160, 80, and 40 (b–d), respectively.

1). The structure belonged to the tetragonal space group I4m2 [119]. The unit cell parameters increased uniformly and regularly with the vanadium content in the sample (Figs. 2A–C, curve 1), suggesting the incorporation of vanadium in the framework of the MEL structure. On steaming the samples at 873 K for 2 h in a flow of 100% H_2O, all the vanadium-silicates exhibited a reduction in the unit cell parameters to values typical of silicalite-2 (curve 2, in Figs. 2A–C), evidently due to the removal of vanadium from the framework to nonframework positions. Silicalite-2 itself did not show any decrease in the unit cell parameters after similar steam treatment. The results of the steaming experiments, thus, suggest that in the original as-synthesized VS-2 samples the vanadium ions are in the framework structure.

IR Spectroscopy

Additional support for the location of vanadium is suggested by the observation of an absorption band at around 967 cm^{-1} in the framework IR spectra of VS-2 samples (Fig. 3). Bands in this region are characteristic of metal–oxygen stretching vibrations. Titanium silicates (both TS-1 and TS-2) containing titanium in lattice positions also exhibit this band around 960 cm^{-1} due to Si–O–Ti linkages (11, 12). This band is ab-
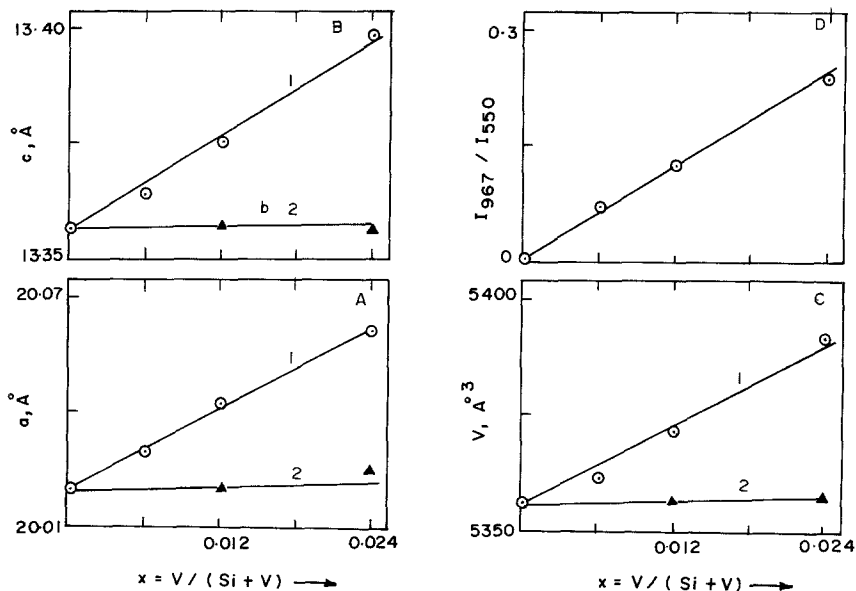
FIG. 2. Unit cell parameters a (A), c (B), unit cell volume V (C), and the ratio of IR intensities at 967 cm^{-1} to that at 550 cm^{-1} (D) vs mole fraction of vanadium in various VS-2 samples; Curves (1) refer to samples calcined in air at 753 K and curves (2) to those obtained by steaming the calcined samples at 873 K for 1 h in 100% steam.

sent in the IR spectra of pure silicalite-2 as well as in samples of silicalite-2 impregnated with oxides of vanadium (or titanium (11, 12)). The intensity of this IR band increased linearly with the vanadium content in VS-2. The ratio of the 967 to 550 cm^{-1} band also increases with unit cell parameters (Fig. 2D). The band at 550 cm^{-1} is characteristic of the MEL framework structure. IR spectroscopic results, thus, lend additional support to the presence of vanadium in framework positions.

The IR spectra in the 4000–1500 cm^{-1} range of the three vanadium samples evacuated at 773 K were recorded in a Nicolet model 60 SX spectrometer. The intensity of the absorption band at 3742 cm^{-1} due to silanol –OH groups and the broad OH absorption band at 3550 cm^{-1} due to H-bonded silanol groups were found to increase linearly with the vanadium content. Detailed IR spectral results which include adsorption of different weakly basic probe molecules on the samples will be reported in a subse-

quent publication. The preliminary IR results, however, point to increasing Si–OH nests with increasing vanadium, probably stabilizing the V^{4+} ions in the as-synthesized samples and V^{5+} in the calcined form.

Adsorption Measurements

The low pressure ($p/p_0 = 0.001$) N$_2$ adsorption isotherm at liquid N$_2$ temperature is typical of molecular sieves. In the sample VS-2 (Si/V = 40), the BET area was 501 m^2/g. The t-area calculated was only 19 m^2/g. Thus the content of the amorphous phase in the sample is very low. The sorption data (6.1, 13.6, and 8.4 wt% for H$_2$O, n-hexane, and cyclohexane, respectively, at 300 K and $p/p_0 = 0.5$) indicate the absence of any occluded material within the zeolite pores. The corresponding values for silicalite-2 were 2.1, 12.4, and 6.5 wt%, respectively.

Ion Exchange

The vanadium ions could not be exchanged for other cations (like NH$_4^+$) in ion
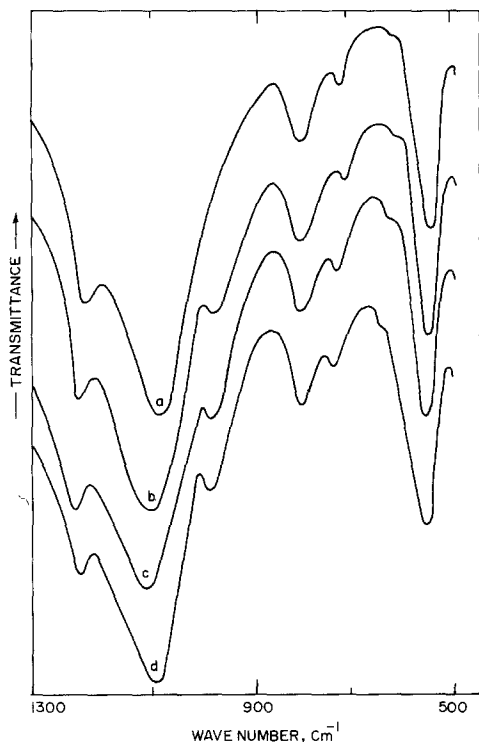
FIG. 3. Framework IR spectra of VS-2 samples (legend as in Fig. 1).

bly oxidized to the V^{5+} (d^0) state on calcination. On reducing the calcined samples in H_2, the typical spectrum of V^{4+} reappeared (curve c), indicating the reversibility of the V^{4+}–V^{5+} transition. This is further confirmed by the observation of V^{4+} ESR signals for the sample after the catalytic reaction (curve d). Table 1 compares the g-values and hyperfine coupling constants (A) observed in VS-2 with those observed in other but similar matrices. In the closely related silicalite-1 system, Rigutto and Van Bekkum (4) concluded that when hydrated in the reduced (IV) state, vanadium is five-coordinated (square pyramidal), probably at defect sites. The different ESR signal response with the magnetic field for samples with VO^{2+} in ion-exchanged positions and V^{4+} in framework positions of ZSM-5 has recently been discussed by Fejes et al. (5). The observed g-values in our samples are consistent with the argument that the V^{4+}

exchange experiments. Calcined VS-2 samples exhibited cation exchange capacity indicating the presence of exchangeable protons on their surface. Na-exchange indicated values of Na/V around 0.5–0.7.

ESR Spectroscopy

The ESR spectra of the VS-2 samples (in the as-synthesized form) are shown in Fig. 4 (curve a). They are characteristic of atomically dispersed and immobile V^{4+} ions and consist of eight nearly equally spaced lines arising from the hyperfine interactions of the d electrons on the V^{4+} ion with the $I = 7/2$ spin of the 100% abundant ^{51}V nucleus. Identical spectra were obtained at 298 and 77 K, indicating that the V^{4+} ions are not in T_d symmetry positions. On calcination of the samples in air at 753 K, the samples did not exhibit any ESR spectra either at 298 or at 77 K (curve b). The V^{4+} ions are, proba-
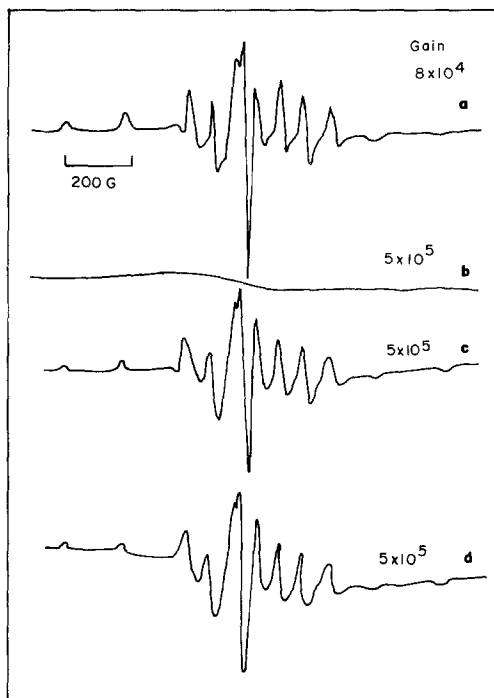

FIG. 4. ESR spectra of as-synthesized vanadium silicate-2 (a), calcined (b), calcined and then reduced in H_2 at 723 K (c), and after use as catalyst (d).

TABLE 1

Principal Values of g and A for V^{4+} in Some Host Matrices

Sample	Temp. (K)	$g_\parallel$	$g_\perp$	$A_\parallel{}^a$	$A_\perp{}^a$	Ref.
1. VS-2						
As-synthesized	298	1.932	1.981	185	72	This study
	77	1.935	1.981	185	70	
Calcined in air	298		No ESR signals			
	77					
Reduced in H_2	298	1.933	1.972	185	71	
	77	1.929	1.975	185	69	
2. VS-1						
As-synthesized	298	1.935	1.994	183	69	(4)
Reduced in benzene	298	1.935	1.996	179	65	
3. VO^{2+} (ex) – ZSM-5		1.963	2.007	190.8	75.4	(5)
V^{4+} (f)-ZSM-5 (as)		1.949	1.990	185.8	72.5	
4. VAPO-5	300	1.932	1.983	198	78	(13)
	77	1.932	1.983	198	78	
5. V-ThGeO$_4$						
(V^{4+} in T_d)	77	1.831	1.980	166	32	(14)
6. Garnet (V^{4+} in T_d)						
(Ga$_2$NaMg$_2$V$_3$O$_{12}$)	4.7	1.855	1.98	152	30	(15)

^{a} Units $\times 10^{-4}$ cm^{-1}.

ions are in the framework positions in addition to being well dispersed and immobile. In the case of the VAPO-5 system, Montes et al. (13) proposed that vanadium in the as-synthesized VAPO-5 is V^{4+} in a vanadyl-like environment and that upon calcination in O_2 at 773 K most of the vanadyl species were converted to V^{5+} in framework positions. This transition was found to be reversible on reduction.

Optical Absorption

The optical absorption spectra of the VS-2 samples are presented in Fig. 5. The bands below 400 nm arise from O–V charge transfer and do not throw light on the coordination state of vanadium. No significant absorption was observed in the 400–800 nm region (consistent with the white color of the material). The absence of any absorption above 550 nm shows that no V^{4+} ions in tetrahedral coordination are present (16).

Catalytic Activity

A. Oxidation of phenol with H_2O_2. These vanadium silicate samples are catalytically active in hydroxylation of phenol to hydroquinone and catechol. VS-2 (Si/V = 40) oxidized phenol to a mixture of hydroquinone and catechol (41.1 and 58.1%). (Reaction conditions: 100 mg catalyst; phenol/H_2O_2 mole ratio = 3; duration = 10 h; temperature = 353 K; solvent = water.) The selectivity to dihydroxy benzenes on the basis of H_2O_2 was 62%. Silicalite-2 and vanadium-impregnated silicalite-2 (containing the
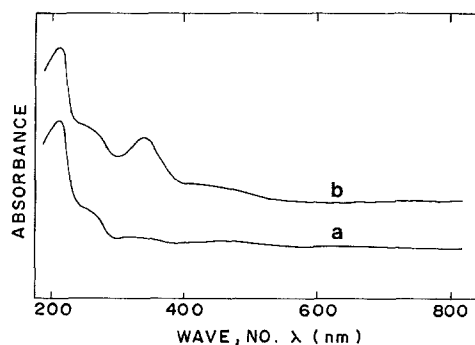

FIG. 5. Diffuse reflectance UV–VIS spectra of vanadium silicates: (a) Si/V = 160; (b) Si/V = 40.

same amount of V as in VS-2) samples were completely inactive for this reaction. It is likely that, as in the case of the titanium silicates, only those V ions which are in framework positions catalyse this oxidation reaction. However, the product distributions and the influence of different solvents on the activity and selectivity are found to be different on the vanadium silicates requiring more detailed studies (17).

B. Isomerisation of m-xylene. Both oxidised and reduced forms of VS-2 possessed similar activities in a typical Brønsted acid catalyzed reaction like the isomerization of *m*-xylene. At 623 K, WHSV of 0.87 h^{-1}, N$_2$/xylene mole ratio of 4 and atmospheric pressure, the conversion of *m*-xylene was 8.8 wt% on a catalyst with an Si/V ratio of 40. The products were mainly *para-* and *ortho-*xylenes (47.0 and 50.7%, respectively). Smaller quantities of benzene (0.3) and toluene (1.4) were also formed. Significantly, trimethylbenzenes were not present. For comparison, it may be mentioned that ZSM-11 with an Si/Al ratio of 40 was active at temperatures even lower than 473 K. At 523 K, almost equilibrium conversions were observed on the aluminum sample. While this difference is due, obviously, to different strength of the acid sites in the two samples, the shape-selective behavior is similar and typical of medium pore zeolites (18) and indicates that the acid sites in VS-2 (associated with V) are located within the 10-ring pore system and not on the external surface of the zeolite. The catalytic activity declined in a period of 5–6 h. However, when the reaction was carried out using H$_2$ (instead of N$_2$) as the carrier gas, stable activity (at least for 5–6 h) was observed. Active sites are, hence, present or generated in VS-2 samples during catalytic reactions.

Our results bearing on the structural identity of vanadium in VS-2 samples may be summarized as follows:

1. There is a linear and progressive increase in the unit cell parameters (from X-ray diffraction) of the MEL lattice with increasing vanadium content. On hydrothermal treatment the unit cell parameters decrease to values characteristic of the vanadium-free silicalite-2, presumably due to the exit of vanadium from MEL framework positions.

2. The intensity of the IR absorption band at around 967 cm^{-1} (due probably to Si–O–V linkages) also increases linearly with the vanadium content and crystalline unit cell volume of the vanadium silicate material. The number of defect sites associated with IR band at 3550 cm^{-1} also increases with the vanadium content in the sample.

3. Adsorption experiments indicate that the pore volume is free of occluded oxides of vanadium.

4. Vanadium ions are not exchanged by other cations in ion-exchange experiments. The material, however, contains exchangeable protons, which participate in a typical Brønsted acid catalysed reaction like the isomerization of *m*-xylene.

5. ESR experiments indicate that in the as-synthesized samples, the vanadium occurs as atomically dispersed V^{4+} ions in a nontetrahedral symmetric location. On calcining in air, the spectra disappear indicating the oxidation of V^{4+} to V^{5+} species. Reduction in H$_2$ restored the original spectra. The vanadium ions are, hence, accessible to gas molecules and the V^{4+}–V^{5+} transition is reversible. The complete oxidation of V^{4+} ions to V^{5+} indicates the absence of any clustered vanadium (6).

6. The absence of absorption bands in the 400–800 nm range in the optical absorption spectra indicate the absence of vanadyl groups or V^{4+} ions in T_d symmetry in the calcined VS-2 samples.

A possible structure and environment for the vanadium in VS-2 consistent with our results and those of others (4, 7, 13) (for other systems like V-silicalite-1 and VAPO-5) may be envisaged as shown in Fig. 6. The proton of the OH group attached to vanadium can be exchanged for Na$^+$ ions (as indeed observed).
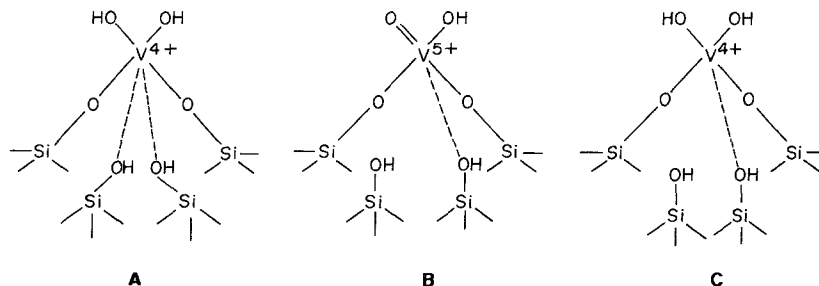
FIG. 6. Environment of vanadium in VS-2 in the as-synthesized (A), calcined (B), and reduced (C) forms, respectively.

The vanadium ions are probably coordinated at defect sites wherein the concentration of SiOH groups is likely to be high. This tentative model is consistent with several of the above observations. During the preparation of pure silicalite, only some silanol groups are present on the external surface due to defects or crystal faults. It is quite possible that specific defects are created by the presence of vanadium during hydrothermal synthesis and that these are associated with the stabilization of vanadium in the silicalite structure. The linear increase in the IR intensity of the silanol groups with the vanadium content of the samples support this hypothesis.

ACKNOWLEDGMENTS

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