

VS-12: A Novel Large-pore Vanadium Silicate with ZSM-12 Structure

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A new large-pore vanadium silicate with ZSM-12 structure has been synthesized; ESR and NMR data indicate that the vanadium is located in the zeolite framework.

Transition-metal modified zeolites, particularly those containing titanium and vanadium cations, were found to have excellent catalytic properties in the partial oxidation of a variety of organic substrates by diluted H_2O_2 .^{1,2} Several reports have dealt with the synthesis, characterization and catalytic properties of vanadium-containing zeolites.¹ A large number of techniques including FTIR, ESR, XRD and ^{51}V solid-state NMR provided strong evidence that the vanadium is located in the zeolite framework probably as a defect site.^{1b} So far five vanadium silicates have been reported in the literature. Three of these were medium-pore zeolites with ZSM-5,^{1a,b} ZSM-11^{1c} and ZSM-48^{1d} structures. The fourth was a large-pore zeolite of NCL-1^{1e} structure. The last vanadium silicate had MCM-41 structure with a unidimensional mesoporous system of 25 Å diameter.³

Because of the severe restrictions to diffusion of large molecules in the pores of medium-pore zeolites, particularly in liquid-phase media, a strong need for developing transition-metal modified large-pore zeolites has evolved. We report here preliminary results on the synthesis and characterization of a new large-pore vanadium silicate with ZSM-12 structure. ZSM-12 has a unidimensional channel system with twelve-membered ring openings.

Two V-ZSM-12 samples (VS-12/1 and VS-12/2) with different Si:V molar ratios and their silica polymorph were synthesized hydrothermally. The molar gel composition used was $\text{SiO}_2 \cdot x\text{VO}_2 \cdot 0.08\text{Na}_2\text{O} \cdot 0.06\text{PI}_2 \cdot 44\text{H}_2\text{O}$, where PI_2 refers to the organic template, 4,4'-trimethylenebis(dimethylpiperidinium) iodide. In a typical synthesis, fumed silica (4.5 g, Sigma, USA) was dissolved in a NaOH solution (0.48 g NaOH in 35 g H_2O) under stirring for 1 h, after which an aqueous solution of $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ (0.31 g, Aldrich) in water (10 ml) was added. After 1 h stirring, organic template (2.26 g) was added followed by the remaining water. The completely homogeneous mixture was then stirred for another 2 h. The resulting synthesis gel was loaded into a Teflon lined autoclave which was tumbled at 25 rpm in an oven at 423 K for 10 days.

After crystallization, the product was filtered, washed with excess deionised water, dried at 373 K and calcined in air at 823 K for 10 h. During calcination, the furnace temperature was raised at a rate of 2°C min^{-1} . All solids were white before and after calcination. Sample VS-12/1 was treated with a 1 mol dm^{-3} ammonium acetate solution at room temperature for 18 h to remove any possible non-framework vanadium species. X-ray powder diffraction profiles of all calcined samples resembled closely the standard pattern of ZSM-12.⁴ The XRD peaks were sharp indicating that all samples have an excellent crystallinity.

Table 1 indicates that the vanadium content in the final solids is much lower than in the gel. This behaviour was also observed in all other vanadium silicates reported in the literature.¹ However, in VS-12 the retention of vanadium in the solid is low compared to other vanadium silicates. This could be due to different crystallization conditions and to the nature of the template.

Results of nitrogen sorption at liquid-nitrogen temperature are shown in Table 1. The shape of the adsorption isotherms indicated that all samples were typically microporous materials. The micropore volumes of all samples were close to the theoretical volume of $0.116 \text{ cm}^3 \text{ g}^{-1}$ calculated on the basis of geometrical considerations.⁴ BET surface areas for all samples were also in full agreement with reported data.⁵

A typical ESR spectrum of as-synthesized VS-12 is shown in Fig. 1. It consists of an anisotropic signal with eight equally spaced hyperfine splittings indicating the presence of paramagnetic, atomically dispersed and immobile V^{4+} ions.¹ The

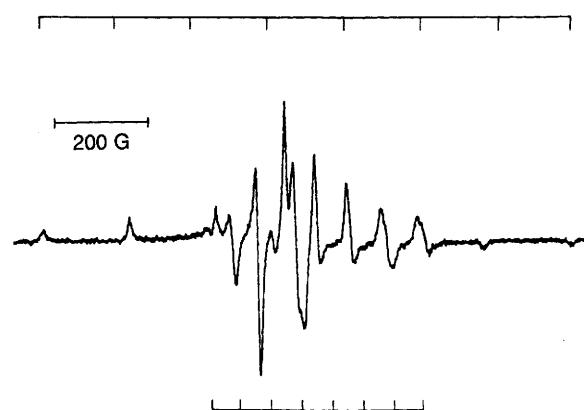


Fig. 1 ESR spectrum of as-synthesized VS-12/1. Spectrum recorded at room temperature with a microwave frequency of 9.1 GHz.

Table 1 Physicochemical properties of silica and vanadium ZSM-12 samples

Sample	Si:V in gel	Si:V in product	BET surface area / $\text{m}^2 \text{ g}^{-1}$	Micropore volume / $\text{cm}^3 \text{ g}^{-1}$
Si-ZSM-12	—	—	201	0.118
VS-12/1	100	322	198	0.113
VS-12/2	50	158	205	0.118

Table 2 Oxidation of phenol over VS-12 samples

Sample	Conversion (mole %)	H_2O_2 selectivity (%)	Product distribution (%)	
			Catechol	Hydroquinone
VS-12/2	10.6	31.9	66.5	33.5
VS-12/1	18.3	56.8	62.8	37.2
VS-12/1 ^a	16.9	52.3	66.7	33.3
$\text{V}_2\text{O}_5/\text{Si-ZSM-12}^b$	3.7	11.4	65.0	35.0

^a Treated with 1 mol dm^{-3} ammonium acetate for 18 h at 298 K. ^b Vanadium impregnated silica polymorph of ZSM-12. This sample had the same vanadium content as VS-12/1, and was prepared by impregnation of Si-ZSM-12 with a solution of V_2O_5 in ammonia, followed by drying and air calcination at 823 K.

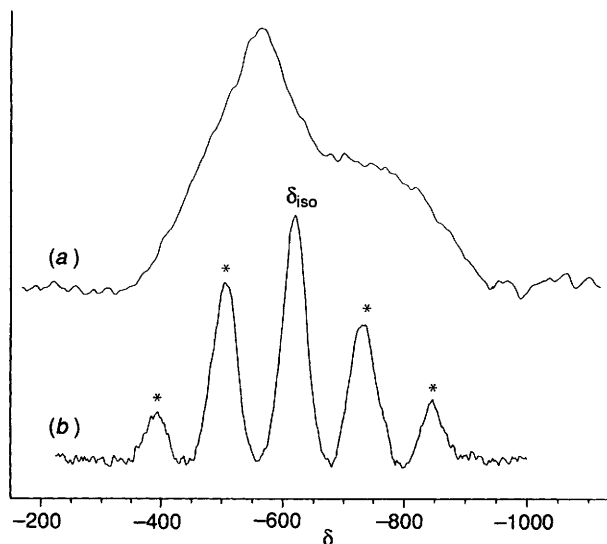


Fig. 2 ^{51}V NMR spectra of calcined VS-12/2 sample at (a) static and (b) MAS (7.2 kHz)

intensity of the ESR signal increased with the vanadium content. The absence of any superimposed broad singlet is an indication that no clusters of extra framework vanadium species were present.^{1a} The g values and hyperfine splitting constants ($g_{\parallel} = 1.935$; $g_{\perp} = 1.991$; $A_{\parallel} = 184$ G and $A_{\perp} = 68$ G) are characteristic of vanadyl VO^{2+} species. Upon calcination of the samples at 823 K, the ESR signal disappeared indicating a complete oxidation of the V^{4+} to the V^{5+} state.

The ^{51}V NMR spectra of calcined VS-12/2 recorded at static and at 8.9 kHz magic-angle spinning are shown in Fig. 2. The VS-12/1 sample had essentially similar but weaker NMR spectra. Absolute intensities of the spectra correlate with the total content of vanadium. The MAS NMR spectra show that the central line remains quite narrow indicating that all vanadium species are in identical or in very similar environments. Parameters of the NMR spectra were as follows: isotropic chemical shift (obtained from experiments with MAS) $\delta_{\text{iso}} = -625$, anisotropy $\Delta\delta = -245$ ppm and asymmetry parameter $\eta = 0.4$. Such values for anisotropy and for isotropic chemical shift are characteristic of isolated vanadium atoms with tetrahedral oxygen coordination.^{1,6} A relatively small value of the asymmetry parameter indicates that the tetrahedra are only slightly distorted and the symmetry of vanadium–oxygen tetrahedra is close to axial.⁶ A detailed characterization of our VS-12 samples by ESR and NMR will be reported in a forthcoming paper.⁷ However, it is of importance that the NMR spectra of the present catalysts are different from previously reported spectra of vanadium modified ZSM-48^{1d} and MCM-41.³ Fig. 2 shows a distinct anisotropy. The spinning side-bands in the MAS NMR spectra of ^{51}V in VS-2 reported by Prasad Rao *et al.*^{1c} indicate the presence of some anisotropy, but no wideline spectrum was available for confirmation. On the contrary, spectra of ^{51}V in V-ZSM-48⁸ and V-MCM-41³ have no anisotropy. Notice that based on the wide-line spectrum of V-ZSM-48 an anisotropy of -105 ppm has been calculated,^{1d} but no MAS NMR spectrum was available to confirm the occurrence of anisotropy. In addition, contrary to vanadium species anchored on oxides,^{9,10} NMR spectra of our VS-12 samples were not sensitive to hydration even after equilibration of the samples in water vapour saturated atmosphere. This indicates the strong stabilization effect of the zeolite. Finally, no signal around $\delta = -300$ which would correspond to δ_{\perp} of V_2O_5 was observed.

Table 2 shows the catalytic activities of both VS-12 samples along with ammonium acetate treated VS-12/1 and a V_2O_5 impregnated Si-ZSM-12. All samples except V_2O_5 impregnated Si-ZSM-12 had good catalytic activities and reasonably high H_2O_2 yields. It is inferred that non-framework vanadium species catalyse the unselective decomposition of H_2O_2 . The VS-12/2 sample with the highest vanadium content was less active compared to VS-12/1 and exhibited a lower H_2O_2 yield. This is maybe due to the presence of some non-framework vanadium species, the amount of which must be below the detection limit of NMR. Ammonium acetate leaching of VS-12/1 had almost no effect on the catalytic properties indicating the absence of extra framework vanadium species in the original sample.

Likewise, it was found that VS-12 is catalytically active in the hydroxylation of bulky molecules such as 1-naphthol with H_2O_2 . The reactions conditions were as follows: 0.1 g catalyst; 1 g naphthol; H_2O_2 : naphthol ratio (molar) = 0.3:1, solvent (acetonitrile) = 10 ml; $T = 353$ K; reaction time = 10 h. The main products were naphthoquinones. VS-12/1 gave 7.6% conversion with a 43.5% H_2O_2 yield, while the vanadium oxide impregnated sample gave only 1.5% conversion and 9.0% H_2O_2 yield.

In conclusion, a novel large-pore vanadium silicate with ZSM-12 structure has been synthesized. ESR and NMR spectroscopies indicated the presence of isolated, well dispersed vanadium ions strongly stabilized within the zeolite lattice. VS-12 silicate showed good catalytic activities in the hydroxylation of both small and bulky organic molecules with diluted H_2O_2 . The hydroxylation efficiency of VS-12 was attributed to the presence of framework vanadium cations.

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