Synthesis and Characterization of a Large Pore Vanadium-containing Molecular Sieve, V-NCL-1

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Vanadium-containing large pore molecular sieves (Si/V ratios above 150) have been synthesized; changes in unit cell volume, IR data and catalytic activity in the oxidation of *m*-xylene and naphthalene indicate that vanadium is incorporated in framework positions.

The activity and selectivity of vanadium-containing catalysts in oxidation reactions depend on the local structural environment around vanadium.[1] Vanadium-incorporated molecular sieves are a new class of catalysts with interesting properties in a number of oxidation reactions of hydrocarbons.[2–4] So far, only three vanadium-containing molecular sieves are known and well characterized.[5–10] Two are metallosilicates and belong to the medium-pore pentasil family (V-MFI[5–8] and V-MEL,[9] respectively). The third (VAPO-5) is a metallophosphate.[10] The vanadium silicate molecular sieves are catalytically active in the hydroxylation of phenol, oxyfunctionalization of n-alkanes, cycloalkanes and toluene with aqueous H_2O_2[9,11,12] as well as the oxidative dehydrogenation of C_3 and C_4 hydrocarbons.[4,8] Recently, we have synthesized and characterized a new large pore zeolite designated as NCL-1 with an Si/Al ratio of $\geqslant 20$ and its Al-free silica polymorph.[13] The adsorption and catalytic properties of NCL-1 are characteristic of zeolites with pore openings constituted by 12-membered tetrahedra. The effective pore diameter of NCL-1 (from adsorption and diffusivity measurements) is close to that of mordenite (*ca.* 0.7 nm).[13] We report here our preliminary results on the synthesis and characterization of V-NCL-1, the first vanadium-containing large pore molecular sieve. V-NCL-1 is also active in the oxidation of a number of bulky hydrocarbon molecules.

The hydrothermal synthesis of vanadium silicate was carried out using gels of the following molar compositions:

$$SiO_2 : xVO_2 : 0.075\ Na_2O : 0.05\ RBr_2 : 52\ H_2O$$

where $x = 0.0051$, 0.0104 and 0.0208 and RBr_2 is the organic template.

In a typical synthesis, fumed silica (Sigma, USA, S-5005) was dissolved in NaOH solution with stirring for 1 h, after which an aqueous solution of vanadyl sulfate was added. This mixture was stirred for 1 h and then the organic template, hexamethylenebis(triethylammonium bromide) was added. The homogeneous reaction mixture was stirred for 2 h,

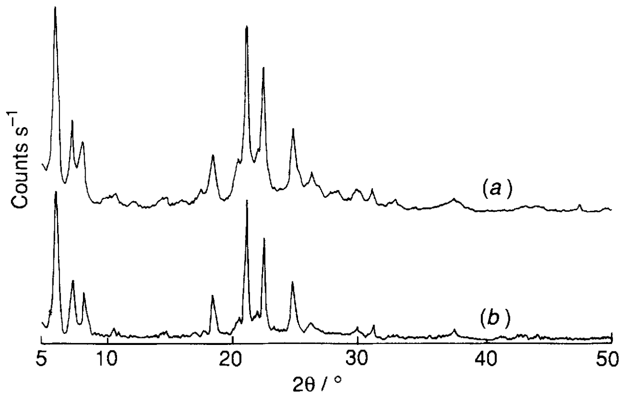

Fig. 1 X-Ray powder diffraction profiles of (*a*) silica polymorph of NCL-1 and (*b*) V-NCL-1B sample. Data collected on a Rigaku Max III VC instrument using Ni-filtered Cu-Kα radiation.

charged into a stainless steel autoclave and heated at 443 K for 15 days with rotation at 60 rpm. After crystallization, the product was filtered, washed with deionised water, dried at 383 K and calcined at 723 K. The product yield was between 90 and 95 wt%. Three such V-NCL-1 samples with Si/V input ratios of 48, 96 and 175 (samples A, B and C) were prepared and characterized by X-ray powder diffraction (XRD), and IR and ESR spectral techniques.

The XRD profiles of the three V-NCL-1 samples match well with that of the V-free silica polymorph NCL-1 (Fig. 1). The XRD patterns are novel, the principal lines being at d = 1.435, 1.195, 1.098, 0.418, 0.396 and 0.356 nm, respectively.[13] NCL-1 and the corresponding vanadium analogues have a novel (as yet not fully known) structure. No peaks other than those ascribable to the silica polymorph NCL-1 structure are observed in V-NCL-1 samples. Table 1 shows the physicochemical properties of V-NCL-1 samples and the silica polymorph of NCL-1. If vanadium is located within the framework, the unit cell should increase, as observed in the case of V-MEL.[9] The orthorhombic unit cell volumes of the samples show, indeed, an increase with increasing vanadium content (Table 1). The N_2 adsorption isotherms of V-NCL-1 samples are characteristic of microporous materials. The amount of N_2 adsorbed at 77 K and at $p/p_0 = 0.01$ are given in Table 1. Their surface areas were around 350 m^2 g^{-1}.

Table 1 Properties of V-NCL-1 samples

Sample	Si/V in gel	Si/V in product	N_2 adsorbed, v/ml g^{-1}	Unit cell volume, U/Å^3
V-NCL-1A	48	150	—	2927
V-NCL-1B	96	250	71.4	2904
V-NCL-1C	175	400	70.0	2879
NCL-1 silica polymorph	—	—	77.9	2867

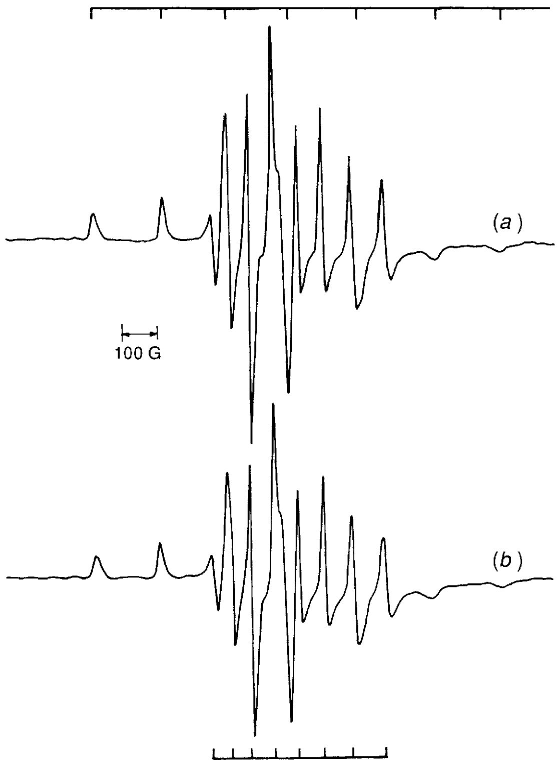

Fig. 2 ESR spectra of as-synthesized V-NCL-1A (a) and V-NCL-1B (b) samples. Spectra recorded at room temperature on a Bruker ER 200D spectrometer.

The probable framework location of V in the NCL-1 structure is suggested from the observation of an IR band at around 960 cm^{-1} for V-NCL-1 samples. Vanadium-free samples of NCL-1 as well as those wherein vanadium was deposited on the silica polymorph of NCL-1 do not exhibit this band. Similar observations made in the case of titanium silicates (TS-1, TS-2 and Ti-ZSM-48)[14] and vanadium silicates (V-MFI and V-MEL)[6,9] have been attributed to Si–O–Ti (or V) vibrations, when Ti (or V) would probably be in the framework positions.

The ESR spectra of the as-synthesized V-NCL-1 samples (Fig. 2) exhibit anisotropic and eight equally spaced hyperfine splittings indicating the presence of paramagnetic, atomically dispersed and immobile V^{4+} ions. The g tensors and the A parameters calculated from the spectra ($g_{\parallel} = 1.929$; $g_{\perp} = 1.973$; $A_{\parallel} = 197$ G; $A_{\perp} = 72$ G; 1 G = 10^{-4} T) identify the vanadium as most probably being in the framework positions of the NCL-1 structure.[7,9,15] The relative intensities of the ESR signals [curves (a) and (b) of samples V-NCL-1A and V-NCL-1B, respectively] are also roughly proportional to their vanadium concentrations.

The catalytic activity of V-NCL-1 samples in the oxidation of m-xylene by H_2O_2 is illustrated in Table 2. The product distribution shows that side-chain oxidation is preferred to aromatic ring hydroxylation. 3-Methylbenzyl alcohol and its secondary oxidation product, 3-methylbenzaldehyde, are the predominant products (66.4%). 2,6-, 2,4- and 3,5-dimethylphenols in total constitute only about 15.5% in the product. The oxyfunctionalization of side-chain carbon atoms appears to be a characteristic feature of vanadium silicates, as observed in the case of toluene oxidation in the presence of V-MEL catalysts.[12] Titanium-containing molecular sieves, on the other hand, oxidise the aromatic carbon atom giving rise to phenols only.[16] The pure silica polymorph, NCL-1, is inactive under the same conditions. Even the silica polymorph of NCL-1 impregnated with vanadium (equal in quantity to that in V-NCL-1A) exhibits only negligible activity (Table 2). Larger molecules like naphthalene are also found to be oxidised (by V-NCL-1B, *ca.* 10.0 wt.% conversion) to naphthols, naphthoquinones and phthalic anhydride (with selectivities of 50, 20 and 30 wt%, respectively) under similar conditions.

Table 2 Oxidation of m-xylene[a]

Sample	m-Xylene conversion, wt.%	Product distribution, wt.%					
		3-Methylbenzyl alcohol	3-methylbenz-aldehyde	2,6-DMP[b]	2,4-DMP	3,5-DMP	Others[c]
V-NCL-1(B)	9.2	34.3	32.1	6.4	6.9	2.2	18.1
V-impregnated silica polymorph of NCL-1	0.5	nd[d]	60.0	nd	nd	nd	40.0

[a] Conditions: catalyst, 0.1 g; reactant, 1 g; solvent, acetonitrile, 10 g; reactant/H_2O_2 = 2.3 mol/mol; T, 353 K; reaction time = 24 h. [b] DMP = Dimethylphenol. [c] Others = heavier, high boiling products. [d] nd: not detected.

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