Room-temperature Synthesis of a Highly Active Vanadium-containing Mesoporous Molecular Sieve, V-HMS

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A thermally stable vanadium-containing mesoporous molecular sieve, V-HMS is synthesized at room temperature; V-HMS catalysts exhibit excellent catalytic activity in the oxidation of phenol and 2,6-di-*tert*-butylphenol using either hydrogen peroxide or *tert*-butyl hydroperoxide as the oxidant.

Since the breakthrough discovery of titanium silicalites with their remarkable performance as catalysts for the selective oxidation of organic substrates in the presence of diluted hydrogen peroxide,[1] researchers have focused their attention on the design of new catalytic sites through the incorporation of other transition-metal cations in the framework of zeolites[2] and on the development of similar but more accessible redox sites in framework positions of large-pore zeolites and mesoporous molecular sieves.[3,4a]

Among the various methods for the synthesis of crystalline mesoporous silica-based materials,[5] Tanev *et al.* developed a method using long-chain primary alkylamines instead of ionic surfactants.[4] So far, these materials, referred to as hexagonal mesoporous silicates (HMS), have been prepared as pure and Ti-modified silicates.[4a] We recently extended this preparation method to lamellar $AlPO_4$s.[6] The objective of this communication is twofold, (*i*) to report on the synthesis and characterization of vanadium-modified HMS materials and (*ii*) to discuss the important problem of leaching of active ingredients from solid catalysts during reactions in liquid media.

V-HMS samples were prepared using a procedure similar to that of Ti-HMS. A typical synthesis is as follows. Solution A was prepared by adding ethanol (21 g) and isopropyl alcohol (4.2 g) to tetraethyl orthosilicate (15 g, Aldrich). To this solution was added the required amount of vanadyl sulfate ($VOSO_4 \cdot 5H_2O$, Aldrich). The resulting solution was stirred for 30 min. Solution B was prepared by adding water (46 g) and 1.4 ml of 1 mol dm^{-3} HCl to dodecylamine (3.5 g, DDA, Aldrich) and stirring for *ca.* 5 min. Solutions A and B were mixed and gently stirred at room temperature (298 K) for 18 h. The molar gel composition of the final reaction mixture was $SiO_2 : x\ VO_2 : 0.27\ DDA : 0.02\ HCl : 6.5\ EtOH : 1.0\ Pr^iOH : 37\ H_2O$, where x was between 0.0025 and 0.05. Pure silica HMS was prepared using the same procedure except that no vanadyl sulfate and no isopropyl alcohol were added. The products were filtered, washed thoroughly with deionized water, dried at 353 K and calcined at 773 K for 6 h in dry air. A sample referred to as V_2O_5-SiO_2(I) was prepared using the same procedure adopted for V-HMS except that no surfactant was added. V_2O_5-SiO_2(II) xerogel was prepared using a sol–gel procedure as reported in the literature.[7] After calcination at 773 K for 6 h in dry air, these mixed oxides were amorphous.

V-HMS samples were characterised using the following techniques: atomic absorption (Perkin Elmer 2380), X-ray diffraction (D5000, Siemens diffractometer with Cu-Kα radiation; $\lambda = 1.5406$ Å), transmission electron microscopy (Philips CM20), N_2 adsorption–desorption (Coulter, Omnisorp 100), UV–VIS spectroscopy (Perkin Elmer) and solid-state NMR (Bruker AMX-300 spectrometer at a frequency of 78.9 MHz). Static ^{51}V NMR spectra were obtained using a θ–τ–θ spin-echo sequence with a delay $\tau = 40$ μs. Only the central $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition was observed. Magic angle spinning NMR spectra were acquired with one pulse sequence and $\pi/4$ solid pulse. The speed of rotation was in the range 10–12 kHz. Chemical shifts were determined using $VOCl_3$ as external reference.

Table 1 Properties of V-HMS samples

Sample no.	Sample	Si/V ratio Gel	Si/V ratio Product	d_{100} spacing/Å	S_{BET}/m^2 g^{-1}
1	Si-HMS	∞	∞	40.1	1087
2	V-HMS	400	405	40.9	1080
3	V-HMS	200	232	40.2	1185
4	V-HMS	100	124	40.8	1097
5	V-HMS	50	60	44.6	1080
6	V_2O_5-SiO_2(I)	100	100	—	—
7	V_2O_5-SiO_2(II)	100	100	—	245

XRD d_{100} spacings, surface areas and the vanadium concentration before and after the synthesis for all samples are reported in Table 1. Chemical analysis data show that there is excellent retention of vanadium during the formation of V-HMS materials. Consistent with literature data, the XRD pattern of HMS samples showed only one low-angle diffraction peak. The absence of higher Bragg reflections in HMS materials was attributed to small scattering domain size effect.[4] Contrary to previous data on Si-HMS and Ti-HMS,[4] our V-HMS samples exhibited a hysteresis-free N_2 adsorption–desorption isotherm, with a sharp step, characteristic of capillary condensation in uniform mesopores. All samples had very high BET surface areas of more than 1000 m^2 g^{-1} (Table 1). Application of the Horvath–Kawazoe model shows that the mean pore size is *ca.* 29 Å with a relatively narrow distribution. TEM data revealed that the particles of HMS materials have a different morphology from MCM-41 particles. They were spherical (0.2–0.3 μm in diameter) instead of hexagonal, and their pore structure was much less ordered than in MCM-41 materials.[8]

Diffuse reflectance spectra of V-HMS samples exhibited two main absorption bands at 379 and 265 nm. These bands are very close to those observed in V-silicalite-1 at 384 and 265 nm.[9] We concur that the charge transfer (CT) band at 379 nm is

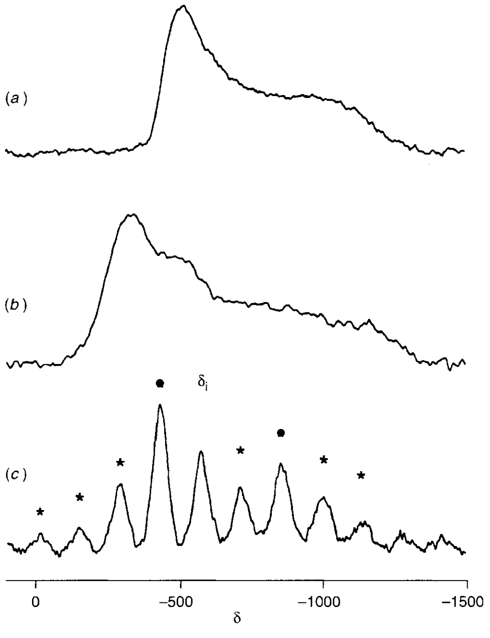

Fig. 1 ^{51}V NMR spectra of V-HMS (sample 5); (*a*) dehydrated V-HMS, static, (*b*) hydrated V-HMS, MAS, $\nu_{rot} = 11.2$ kHz and (*c*) hydrated V-HMS, static

Table 2 Oxidation of 2,6-di-*tert*-butylphenol and phenol

Substrate	Sample no.[a]	Conv. (%)	H_2O_2 Eff. (%)[b]	Product selectivity (%)[c]		
				Quinone	CAT	HQ
2,6-DTBP[d]	4	70	64	92	—	—
2,6-DTBP	4[e]	95	95[f]	100	—	—
2,6-DTBP	6[g]	24	22	92	—	—
2,6-DTBP	6	3	3	100	—	—
2,6-DTBP	7	2	2	100	—	—
2,6-DTBP	No catalyst	2	2	100	—	—
2,6-DTBP	Ti-HMS[h]	26	7	54	—	—
2,6-DTBP	Ti-HMS[i]	15	48	93	—	—
Phenol[j]	4[k]	13.4	69	—	58	42
Phenol	4[l]	11.7	59	—	57	43

[a] All the catalysts were used in the calcined form unless otherwise stated. [b] H_2O_2 efficiency = (mol H_2O_2 utilized for the formation of quinone/mol H_2O_2 added) × 100. [c] CAT = catechol, HQ = hydroquinone. [d] Catalyst (0.1 g), 2,6-di-*tert*-butylphenol (1.03 g), hydrogen peroxide (30 mass %) (1.7 g), acetone (7.8 g), 335 K, reaction time 2 h. [e] *tert*-butylhydroperoxide was used as the oxidant. [f] TBHP efficiency. [g] As-synthesized catalyst. [h] Ref. 12 (Si:Ti = 100). [i] Ref. 8 (Si:Ti = 100). [j] Catalyst (0.5 g), phenol (5.0 g) hydrogen peroxide (30 mass %) (2.0 g) solvent (15 g) 353 K, reaction time 15 h. [k] Solvent: water. [l] Catalyst was re- generated and reused.

attributable to V^{5+} with a short V=O double bond and three longer V–O bonds. The 265 nm CT transition is consistent with a V^{5+} species in a tetrahedral environment.[9]

The ^{51}V NMR spectra of dehydrated and hydrated V-HMS samples are shown in Fig. 1. The isotropic chemical shift was δ −708 and −580 and the anisotropy was −475 and −640 ppm for the dehydrated and hydrated sample, respectively. These parameters are very close to those previously reported for hydrated and dehydrated V_2O_5-SiO_2.[10] Based on this, we conclude that the structure of vanadium sites must be similar. It was shown that vanadium in dehydrated V_2O_5-SiO_2 is present on the silica surface as a three-legged species $(SiO)_3V{=}O$, which can coordinate water to form six-coordinate vanadium species. This assignment is also consistent with the UV–VIS data. The facile change in coordination state upon exposure of V-HMS to water vapour suggests that all V in $(SiO)_3V{=}O$ is easily accessible. Most likely the vanadium resides on the surface of the channels in a relatively exposed position.

Data concerning the catalytic activity in the oxidation of phenol and 2,6-di-*tert*-butylphenol (2,6-DTBP) are reported in Table 2. Similar to other vanadium-containing molecular sieves, V-HMS exhibited very good activity in the hydroxylation of phenol to catechol and hydroquinone. They also catalysed the hydroxylation of di-*tert*-butylphenol into 2,6-di-*tert*-butyl-1,4-benzoquinone with exceptionally high conversion, selectivity and H_2O_2 utilization efficiency. For comparison, the results reported in the oxidation of 2,6-DTBP over Ti-HMS with similar titanium content were included in Table 2. It is seen that V-HMS is by far the superior catalyst for this oxidation reaction as compared to its titanium analogue. When the as-synthesized form V-HMS was used as a catalyst, very low activity was observed, indicating the importance of the accessibility of the pore walls to reactants. V-HMS samples with different vanadium contents have almost similar catalytic activity. Table 2 also shows that as-synthesized V_2O_5-SiO_2 xerogel gives considerable conversion of 2,6-DTBP. However, after calcination of even a fresh catalyst no activity was found, most probably because of V_2O_5 sintering.

Data obtained in liquid phase in the presence of fresh solid catalysts may be misleading. Indeed, it is crucial to ascertain that no leaching of active ingredients occurs and no homogeneous catalysis is taking place. To evaluate this problem we first used a method employed by Neumann and Levin-Elad.[11] V-HMS catalyst was treated with 30 mass% H_2O_2 at 353 K for 2 h in the presence of one of four solvents, water, ethanol, acetone or acetonitrile, without any substrate. After separation of the catalyst, the filtrate was used in the oxidation of 2,6-DTBP. The organic substrate and H_2O_2 were added to each filtrate and no catalytic activity was detected in any of the solvents. Note that under the same conditions, vanadyl sulfate dissolved in water gave excellent conversion.

It is still premature to conclude that no vanadium leaching takes place. Indeed, after hydroxylation of 2,6-DTBP and filtration of the spent catalyst, addition of reactants to the filtrate gave more products, while the catalyst after drying or calcination had no activity. This indicates that leaching is not necessarily due to the solvent, it can be induced by the substrate.

In contrast, during the hydroxylation of phenol in water, no leaching took place. In addition, after calcination in air, the spent V-HMS displayed similar catalytic activity as a fresh V-HMS catalyst (Table 2), whereas, calcination of either fresh or spent xerogel V_2O_5-SiO_2 led to catalytically inactive materials.

We wish to thank Dr I. L. Moudrakovski for the NMR spectra. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). J. S. R. thanks NSERC for a Canada International Fellowship.

Received, 5th July 1995; Com. 5/04360C

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