

# A Novel Vanadium Pillared Montmorillonite Catalyst for Molecular Recognition of Benzyl Alcohols

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An unusual molecular recognition of primary and *para*-substituted benzyl alcohols discriminating between the secondary and *ortho*-substituted ones by a novel, covalently cross-linked vanadium pillared montmorillonite synthesized for the first time is described.

Zeolites,<sup>1-7</sup> and layered<sup>8</sup> and pillared clays,<sup>9,10</sup> which are known for their interesting behaviour for selective adsorption, have been the target of attention in shape-selective catalysis. Pd-Fe systems in zeolite supercages display high substrate selectivity in the competitive oxidation of *n*-octane and cyclohexane mixtures.<sup>3</sup> Vanadyl alkylphosphonates, a new family of layered compounds, recognised primary benzyl alcohols selectively in complexation discriminating against branched alcohols.<sup>8</sup>

Clays attain high thermal stability and rigid structures required for molecular sieving by pillaring with polycationic complexes of Al, Zr, Cr, Ti *etc.* in the interlayers *via* the process of cation exchange.<sup>9,10</sup> We report here for the first time the design and synthesis of a novel vanadium pillared clay (V-PILC) by covalently cross-linking the interlayers of montmorillonite with vanadia and its unusual recognition of primary and *para*-substituted benzyl alcohols discriminating against the secondary and *ortho*-substituted ones. The striking discrimination of secondary benzylic alcohol in catalytic oxidation is the first example in this area of catalysis.

It is known that the reaction of diphenyldichlorosilane with NaVO<sub>3</sub> or V<sub>2</sub>O<sub>5</sub> afforded a polymeric vanadium species.<sup>11</sup> V-PILC was synthesised by refluxing chloromontmorillonite (5g, a grey-white powder obtained from the reaction of H-montmorillonite with SOCl<sub>2</sub>)<sup>12</sup> with NH<sub>4</sub>VO<sub>3</sub> (0.4 g) in dry acetone (80 ml) for 12 h followed by thorough washing with 2% KOH to remove excess of NH<sub>4</sub>VO<sub>3</sub>. Finally, it was washed with deionised water immediately after the base washing to remove traces of base and was dried in an oven below 70 °C overnight. The V-PILC obtained had a well defined and reproducible XRD pattern with *d*(001) spacing of 15.4 Å giving an interlayer spacing of 5.8 Å and was found to be thermally stable up to 480 °C according to thermogravimetric analysis. From the Brunauer-Emmett-Teller (BET) method, the surface area is calculated as 128.66 m<sup>2</sup> g<sup>-1</sup> with a pore volume of 0.214 cm<sup>3</sup> g<sup>-1</sup>. Plasma analysis for metal showed a loading of 0.2 mmol g<sup>-1</sup> of vanadium. The FTIR spectrum of V-PILC showed characteristic sharp bands in the range

1040–980 and at 820 cm<sup>-1</sup> due to the V=O and V–O–V stretching vibrations respectively. Bands in the range 600–400 cm<sup>-1</sup> have been assigned to the V–O–V rocking vibrations<sup>13,14</sup> and absorption in the 930–910 cm<sup>-1</sup> region indicates the presence of the V–O–Si fragment.<sup>11</sup> Thus, the pillared species may be V<sub>2</sub>O<sub>5</sub> or a polymer with two or more vanadium atoms per pillar as schematically represented in Figure 1. However, the exact number of metal atoms in each pillar could not be found at present. These results are in good agreement with the ESR spectrum of V-PILC, which shows a singlet with *g*<sub>eff</sub> = 1.97 assigned to the partially reduced V<sup>4+</sup> species resembling the pure V<sub>2</sub>O<sub>5</sub> spectrum.<sup>15</sup> The singlet observed in the ESR spectrum indicates that the vanadium species is not dispersed on the surface, but pillared between the interlayers of the clay, maybe as a polymer with microscopically dispersed V<sup>4+</sup> species.<sup>6,17</sup> Further, the ESR spectrum of an oriented thin film is not affected by the angular variation between the film plane and the magnetic field as in a similar experiment conducted by Kijima *et al.*<sup>18</sup> This angular invariance indicates that the plane of the vanadium coordination sphere is perpendicular to the silicate layers of the montmorillonite.

The general method for oxidation reactions is as follows. Substrate (5 mmol), H<sub>2</sub>O<sub>2</sub> (2.5 ml, 30% w/w), and the catalyst, V-PILC (500 mg, 0.1 mmol of vanadium) were added sequentially to a flask containing dry dioxane (15 ml); the reaction mixture was refluxed for 6 h or for 48 h for those substrates which are inert towards oxidation (see later). The catalyst was then filtered off and the reaction mixture purified by column chromatography (using silica gel as adsorbent to isolate pure products). All the products were characterised by comparison of their IR, NMR and mass spectra with those of authentic samples.

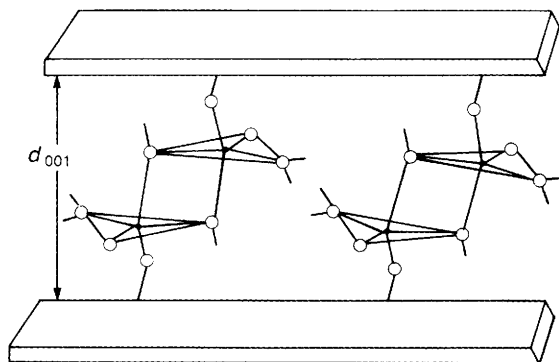


Figure 1. Vanadia pillaring in the interlayers of montmorillonite; ●: Vanadium; ○: Oxygen.

Table 1. Shape-selective oxidation of benzyl alcohols ArCH<sub>2</sub>OH.

Ar	Yield (%) <sup>a</sup> of products		Conversion (%)
	ArCO <sub>2</sub> H	ArCO <sub>2</sub> CH <sub>2</sub> Ar	
Ph	62	34	96
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	86	11	97
<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	3	—	3 <sup>b</sup>
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	86	12	98
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	29	48	77
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	82	—	82
<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	—	—	0 <sup>b</sup>
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	91	8	99
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	2	—	2 <sup>b</sup>
<i>m</i> -MeOC <sub>6</sub> H <sub>4</sub>	5	—	5 <sup>b</sup>
<i>o,p</i> -Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	—	—	0 <sup>b</sup>

<sup>a</sup> Isolated yields (based on consumption of the substrate). Products were characterised by IR, NMR, and mass spectrometry. Reactions were carried out for 6 h unless otherwise noted. <sup>b</sup> Reaction for 48 h. PhCHMeOH was not oxidised after 48 h.

Benzyl alcohols and *para*-substituted benzyl alcohols are readily oxidised by V-PILC to afford acids and esters (Table 1). The significant amount of ester formation is induced by the acidic sites of montmorillonite. *ortho*-Substituted benzyl alcohols, except *ortho*-chlorobenzyl alcohol, are not oxidised and are recovered as such; negligible yields are obtained even after prolonged reaction times. However, *ortho*-chlorobenzyl alcohol, whose kinetic diameter is relatively small, was 75% oxidised. The secondary alcohol 1-phenylethanol was recovered unchanged after 48 h under identical conditions. All the alcohols in Table 1 were oxidised in the presence of V<sub>2</sub>O<sub>5</sub> within 4–5 h with no discrimination under the same conditions in a homogeneous environment.

Proper alignment for the complexation of *ortho*-substituted benzyl alcohols and the secondary benzyl alcohol, as described above, with vanadium may not be possible owing to the space restriction imposed on the interlayers, thus leading to their inertness to oxidation.

In conclusion, the use of the covalently pillared clay, even in the liquid-phase reactions, leads to molecular recognition of primary and *para*-substituted alcohols. No reaction was observed for secondary and *ortho*-substituted alcohols under the same conditions. This makes available a potential alternative to the zeolites and other pillared clays synthesised by cationic exchange.

We thank Dr A. V. Rama Rao for his interest, Dr K. V. R. Chary for useful discussions, and CSIR, India, for financial assistance to V. L. K. V.

Received, 12th March 1990; Com. 0/01092H

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