

## Microporous niobium phosphates and catalytic properties prepared by a supramolecular templating mechanism

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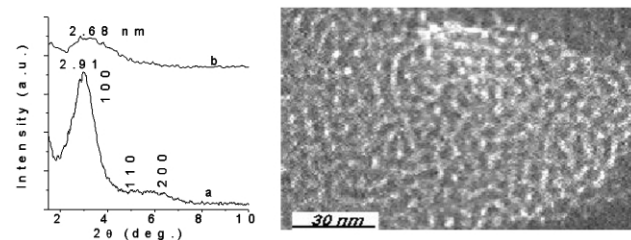
**Microporous hexagonal niobium phosphate synthesized using neutral surfactants of molecular length, C<sub>6</sub> to C<sub>10</sub> hydrocarbons, by a supramolecular templating mechanism (S<sup>0</sup>I<sup>0</sup>) possesses strong hydrophilic character, which leads to high selectivity for catechol formation (95.3%) in the presence of protic solvent (MeOH) in the hydroxylation of phenol using aqueous H<sub>2</sub>O<sub>2</sub>.**

Porous inorganic materials synthesized with high surface areas and narrow pore size distributions are highly useful as active and/or selective catalytic materials.<sup>1</sup> Organic templates, as discrete entities around which the framework crystallizes, have been used to construct microporous zeolitic frameworks of sizes ranging from small pore (0.4 nm) to extra large pore (1.2 nm, VPI-5),<sup>2</sup> but our understanding of their function in the process remains rather limited and incongruent.<sup>3</sup> In contrast, a more generalized approach for the formation of mesoporous structures with a supramolecular templating mechanism has been developed after the discovery of MCM-41 silicates by Mobil scientists in 1992.<sup>4</sup> Such a mechanism has been used for the synthesis of materials less than mesopore in size (<2 nm) such as super-microporous tin<sup>5</sup> and niobium<sup>6</sup> phosphates using long chain alkyl (C<sub>16</sub>) groups, and microporous transition metal (niobium) oxide using a short chain alkylamine (C<sub>6</sub>) as a surfactant.<sup>7,8</sup> Recently, we have reported the synthesis of super-microporous distorted hexagonal niobium phosphate with high anion exchange capacity (6.3 mmol g<sup>-1</sup>) and its catalytic activity using hexadecyl amine as a surfactant (S<sup>0</sup>I<sup>0</sup>).<sup>6</sup> Super-microporous materials are those porous materials whose pore size is bigger than that of extra-large-pore zeolitic materials and smaller than that of mesoporous materials. The dimensions range from 1.4 to 2.0 nm.<sup>6,9,10</sup> However, the synthesis of microporous metal phosphates has not yet been reported. Therefore, the synthesis of microporous metal phosphates with tailored pore size should be useful in shape- and size-selective molecular sieving applications. Herein we describe, for the first time, the synthesis of a microporous metal (Nb) phosphate using short chain alkylamines (C<sub>6</sub> and C<sub>10</sub>) as surfactants, which has interesting catalytic activity in the hydroxylation of phenol.

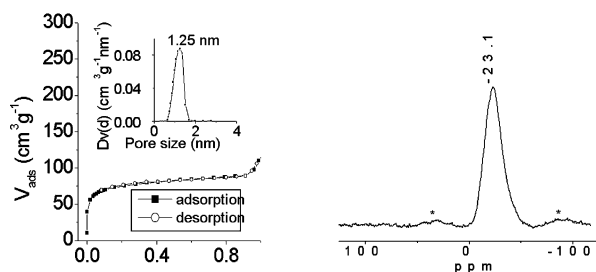
We mixed the metal source and phosphoric acid prior to addition of surfactant, otherwise no reproducible phosphorus/metal ratio in the final solids could be obtained.<sup>6,11</sup> In a typical synthesis, 3.46 g of H<sub>3</sub>PO<sub>4</sub> (30 mmol, 85% aq., Wako Chem.) was added to 4.09 g of NbCl<sub>5</sub> (15 mmol, Aldrich) in 70 g of H<sub>2</sub>O under stirring for 10 min. Aqueous ammonia was added until the pH stabilized around 4.90. The precipitate was filtered and washed with distilled water several times to remove excess chloride ions. H<sub>2</sub>O (20 g) and 2.36 g of decylamine (15 mmol) were added to the precipitate in a plastic beaker and stirred for 30 min. Finally, the required amount of H<sub>3</sub>PO<sub>4</sub> (1.15 g, 10 mmol) was added, with the pH maintained at 3.88 under stirring for 30 min. The gel was heated in a Teflon lined stainless steel autoclave at 75 °C under autogenous pressure for 1 day. The final product was filtered, washed with distilled water, dried at

100 °C and calcined at 450 °C for 6 h. Elemental analyses of the samples were carried out using ICP (Shimadzu ICPV-1017). The samples were characterized using XRD (Cu-K $\alpha$  radiation,  $\lambda$  = 0.15406 nm, Shimadzu XRD-6000), TEM (Hitachi H-9000NA, 300 kV), and N<sub>2</sub> sorption at -196 °C using a Bellsorp 28 instrument. The sorption measurement was carried out gravimetrically in an electrobalance (Chan, USA) at 25 °C with a fixed  $p/p_0$  ratio of 0.4 each of triisopropylbenzene and water as adsorbents after equilibration for 3 h. <sup>31</sup>P spectra were recorded on a Bruker DSX500 machine at 202.42 MHz with a spinning rate of 8 kHz, pulse time (P1) of 3.0  $\mu$ s and a repetition time (D1) of 30 s. Chemical shift are reported relative to 85 wt% H<sub>3</sub>PO<sub>4</sub>. The catalytic activity of the niobium phosphate sample was tested in the hydroxylation of phenol, batchwise in a round bottomed flask in the presence of aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%) as oxidant using different solvents. The products were analyzed using GC (GC-17A, Shimadzu) using a capillary column and confirmed by standard product and GC-MS.

The XRD patterns and TEM image of niobium phosphate are shown in Fig. 1. The XRD spectrum of the as-synthesized sample shows one sharp reflection at low angle and two broad reflections at higher angles; assuming a hexagonal structure like MCM-41, these reflection can be indexed as (100), (110) and (200), respectively. The calcined sample shows a single reflection which can be indexed as (100) indicating the local disorder in the structure.<sup>12</sup> The interplanar spacings,  $d_{100}$ , of the as-synthesized and calcined samples are 2.91 and 2.68 nm, respectively. The TEM image of niobium phosphate confirms its disordered hexagonal structure due to disordered packing of cylindrical pores<sup>12,13</sup> or wormholes, as reported by Pinnavaia *et al.*<sup>14</sup> for the synthesis of Ti-HMS using hexadecylamine as surfactant (Fig. 1; right). Note that the pore size of the sample is within the micropore range. In Fig. 2, N<sub>2</sub> adsorption-desorption isotherms and the solid-state <sup>31</sup>P NMR spectrum of calcined microporous niobium phosphate are shown. The microporosity of niobium phosphate is further illustrated by the type I N<sub>2</sub> adsorption-desorption isotherms. The pore size of the sample calculated using the MP method is 1.25 nm (Fig. 2; left, inset), which is slightly bigger than that of one-dimensional microporous VPI-5 (pore diameter = 1.21 nm).<sup>2</sup> This was confirmed when a comparison of the adsorption capacities of niobium



**Fig. 1** XRD profiles (left) of as-synthesized (a) and calcined (b), and TEM image (right) of calcined niobium phosphate.



**Fig. 2** N<sub>2</sub> adsorption–desorption isotherms (inset: pore size distribution curve from MP method) (left) and <sup>31</sup>P MAS NMR of calcined microporous niobium phosphate (right) (\* spinning bands).

phosphate (0.122 cm<sup>3</sup> g<sup>-1</sup>) and VPI-5 (0.117 cm<sup>3</sup> g<sup>-1</sup>)<sup>2</sup> for triisopropylbenzene (diameter = 0.85 nm) was carried out, suggesting the pore size of niobium phosphate is probably slightly bigger than that of VPI-5 (Table 1). The H<sub>2</sub>O adsorption capacities of niobium phosphate and VPI-5 are 0.42 and 0.35 cm<sup>3</sup> g<sup>-1</sup>, respectively, which might also be due to interparticle adsorption. The higher hydrophilicity of microporous niobium phosphate is due to the larger metal size. The BET specific surface area of niobium phosphate is 283 m<sup>2</sup> g<sup>-1</sup>, which is smaller than that of a sample prepared using hexadecylamine (C<sub>16</sub>) as surfactant (482 m<sup>2</sup> g<sup>-1</sup>).<sup>6</sup> The <sup>31</sup>P MAS NMR spectrum of calcined niobium phosphate gives a resonance at -23.1 ppm with respect to H<sub>3</sub>PO<sub>4</sub> (85% aq.), confirming the tetrahedral coordination of phosphorus (Fig. 2; right). As the connectivity increases, an upfield shift is observed from -5.3 to -10.6 ppm for H<sub>2</sub>PO<sub>4</sub>, to -18.1 ppm for HPO<sub>4</sub> and finally to -19 to -32.5 ppm for PO<sub>4</sub>.<sup>15,16</sup> Niobium ions (Nb<sup>5+</sup>) in niobium phosphate are tetra- or penta-coordinated and not hexa-coordinated.<sup>6</sup> The P/Nb molar ratio in the niobium phosphate is 1.13. Nb(v) oxidation state is present in microporous niobium phosphate, which is most stable under our hydrothermal reaction conditions (acidic medium). Nb<sup>5+</sup> ions are in tetrahedral coordination state; in such a case, the P/Nb molar ratio is expected to be 1. In addition, the double positive charge is due to framework Nb<sup>5+</sup> and P<sup>5+</sup> ions balanced by the extraframework excess of phosphorus (HPO<sub>4</sub><sup>2-</sup>) and Cl<sup>-</sup> anions. The composition of the microporous niobium phosphate is [Nb<sub>1.0</sub>(PO<sub>4</sub>)<sub>1.0</sub>](H-PO<sub>4</sub>)<sub>0.13</sub>Cl<sub>0.74</sub>. Effects of pH of the gel, temperature and alkyl chain length of the surfactant on mesophase formation are given in Table 1. A mesophase was obtained for decylamine as surfactant in the gel pH range 3 to 6.5 and temperature 65 to 120 °C, whereas above 130 °C a lamellar phase was produced. However, when n-hexylamine was used as surfactant in a narrow gel pH range 3.6 to 4.2 and temperature 65 to 80 °C, the resulting materials were mesophases. TG analysis of niobium phosphate shows that the weight loss between 150 and 450 °C due to removal of surfactant and condensation of hydroxy groups is 36.3%, which is 27.7% less than that of a sample prepared using hexadecylamine (C<sub>16</sub>) as surfactant (50.2%).

The catalytic activity of niobium phosphate in the hydroxylation of phenol is presented in Table 2. The phenol conversion (mol% phenol consumed) and H<sub>2</sub>O<sub>2</sub> efficiency (mol% H<sub>2</sub>O<sub>2</sub> consumed) are 13.1 and 40.2%, respectively, in acetonitrile and

**Table 1** Effect of pH, surfactant and temperature on mesophase formation<sup>a</sup>

pH	Surfactant	Temperature/°C	Phase
3–6.5	Decylamine	65–120	m.p.
3–6.5	Decylamine	> 130	l.p.
3.6–4.2	Hexylamine	65–80	m.p.
3–6.5	Hexylamine	> 90	l.p.

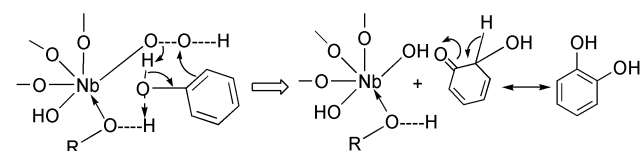
<sup>a</sup> m.p. = mesophase, l.p. = lamellar phase.

**Table 2** Catalytic activity in the oxidation of phenol<sup>a</sup>

Solvent	Conversion (mol%)	H <sub>2</sub> O <sub>2</sub> efficiency (mol%)	Product distribution (mol%)			
			CAT	HQ	PBQ	CAT/HQ
CH <sub>3</sub> CN	13.1	40.2	62.6	35.0	2.4	1.79
MeOH	15.3	46.0	95.3	4.5	0.2	21.18

<sup>a</sup> Reaction conditions: catalyst = 0.10 g, phenol = 1 g, solvent = 5 g, temp. = 80 °C, phenol/H<sub>2</sub>O<sub>2</sub> = 3 (molar ratio), reaction time = 15 h, conversion = mol% of phenol consumed during the reaction, H<sub>2</sub>O<sub>2</sub> efficiency = mol% of H<sub>2</sub>O<sub>2</sub> consumed in the formation of catechol (CAT), hydroquinone (HQ) and *para*-benzoquinone (PBQ).

15.3 and 46%, respectively, in methanol. However, the catechol selectivities in aprotic (acetonitrile) and protic solvents (methanol) are quite different: 62.6 and 95.3%, respectively. The catechol to hydroquinone ratios in acetonitrile and methanol are 1.79 and 21.18%, respectively. This unusual high catechol selectivity in protic solvent may be probably due to the formation of hydrogen bonds between the OH group of phenol and the solvent (MeOH) in a transition state, thereby inducing the *ortho* position of phenol to form catechol (Fig. 3), since the strong hydrophilic character of niobium phosphate (H<sub>2</sub>O adsorption = 42 wt%) has the tendency to coordinate with protic solvents and expand their coordination.



**Fig. 3** Mechanism for the formation of catechol in protic solvent (MeOH) (R = CH<sub>3</sub> or H) over microporous niobium phosphate.

In conclusion, a microporous transition metal (niobium) phosphate has been synthesized by a supramolecular templating mechanism for the first time, which exhibits an unusual high selectivity for catechol formation (95.3%) in protic solvents (MeOH) in the hydroxylation of phenol.

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