

# Synthesis and Characterization of Large Surface Hexagonal Polyoxometalate Platelets

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The polyoxometalates, or POMs (clusters comprising at least two metal and many oxygen atoms), have recently gained significant interest, owing to their versatile architecture and especially catalytic activities. Due to their high catalytic activity but low surface area, there is always a demand for making high-surface-area POMs, particularly high-surface-area Keggin. Our present work demonstrates the 'gluing' of the anionic phosphomolybdate Keggin on gibbsite nanoplatelets with a residual positive charge to form large-surface-area composites. The resulting composite reported here has been characterized using TEM imaging, EDX/TEM (elemental) analysis, FTIR spectroscopy, potentiometric titrations, electrophoretic mobility determination, and XRD. The composite reported here could be useful in catalysis.

## Introduction

The polyoxometalates, or POMs (clusters comprising at least two metal and many oxygen atoms), have recently gained significant interest, owing to their versatile architecture, facile synthesis, magnetic, material properties, and especially catalytic activities.<sup>1</sup> One of the first structurally characterized POM, the phosphomolybdate Keggin<sup>2</sup> has been extensively studied mainly because of its attractive catalytic properties, for instance, oxidation of aldehydes, CO, oxidative dehydrogenation, etc., and has been extensively reviewed.<sup>3</sup> Owing to their high catalytic activity, but low surface area (usually around 1–10 m<sup>2</sup> g<sup>-1</sup>) there has always been a demand for making high-surface-area POMs, and especially high-surface-area Keggin. To achieve that goal, Keggin have been placed between pillared clays or layered double hydroxides and on molecular sieves MCM-41, on silica, polyaniline and polypyrrole films,<sup>4</sup> and even very recently on silica nanoparticles.<sup>5</sup> They have further been placed on a highly oriented pyrolytic graphite surface by the so-called technique of 'solvent casting' and investigated by STM/STS.<sup>6</sup> In the molecular paradigm, the search for high-surface-area POMs has been accomplished by the use of pentagonal building blocks from a 'virtual library', using 'soft chemistry'.<sup>7</sup> Clusters like the {Mo<sub>132</sub>}, {Mo<sub>154</sub>}, and {Mo<sub>368</sub>} have been synthesized this way. Additionally, in the molecular regime, the technique of 'stitching' smaller POMs to form large clusters by other metal ions has been adopted<sup>8</sup> and continues to be explored.<sup>9</sup> These clusters have

in turn been superstructured to form supramolecular 'blackberry'-type species.<sup>10</sup> However, the demand for large-surface-area POMs continues. The incentive to synthesize 'supported POMs' with a large surface area that could act as a 'bridge' between surface type catalysts and 'pseudoliquid phase' of bulk type catalysts is still high,<sup>4</sup> but the question is how to obtain such high-surface-area POMs in a controlled way in an aqueous solution, given the fact that the surface area of molecular POMs are small and they tend to decompose<sup>1a</sup> or superstructure<sup>10</sup> in solution.

In our laboratory, high-surface-area platelike gibbsite nanoparticles (85 m<sup>2</sup> g<sup>-1</sup>) have been developed and their synthesis optimized.<sup>11</sup> Hexagonal gibbsite-templated silica-coated nanoparticles and fluorescent platelets have also been prepared.<sup>12,13</sup> Hence, keeping in view the demand of very high-surface-area POMs and the high surface area of the gibbsites, it becomes obvious that our present work which combines high-surface-area gibbsite with that of POMs could augment the ongoing search for large mesoscopic POMs. Conceptually, this work shares the principle of heterogenization of POMs as catalysts and pursues the line of research published recently.<sup>5</sup> The present letter demonstrates the 'gluing' of one of the first characterized POM, the so-called anionic phosphomolybdate Keggin<sup>2</sup> on gibbsite nanoplatelets with a residual positive charge to form large surface area hexagonal POM platelets. (Figure 1) The idea of using gibbsite (as a template) was further seconded by the involvement of cationic Al<sub>13</sub>-type Keggin in the crystallization of gibbsite due to obvious stereo-electronic reasons.<sup>14</sup> The Keggin–gibbsite composite reported here has been characterized using TEM imaging, EDX/TEM (elemental) analysis, FTIR spectroscopy, potentiometric titrations, electrophoretic mobility determination, and XRD. The composite reported here could have implications in catalysis.

## Materials and Methods

**Synthesis.** To a colloidal dispersion of 10 mL of gibbsite platelet (12 g/L) prepared according to ref 11, 25 mg (14.4 μmol) of

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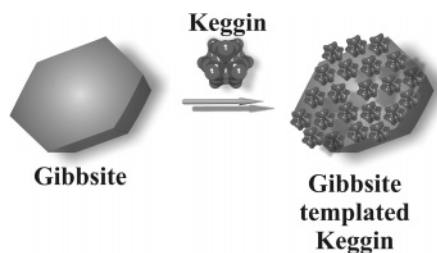
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**Figure 1.** Schematic model of a gibbsite nanocrystal (left) used as a colloidal template for forming hexagonal mesoscopic phosphomolybdate Keggin superstructure (right). The phosphomolybdate Keggin units are shown in a space filling model. The picture is schematic and does not imply any structural information of the interface.

ammonium phosphomolybdate was added. The resulting dispersion was diluted to 15 mL and was vortexed for 5 min. The pH of the dispersion was 5.5. The turbid dispersion with flecks of yellow precipitate (undissolved Keggin) was left overnight, and the next day the dispersion was centrifuged at 1200 rpm for 5 min. The faintly turbid yellowish supernatant containing the composite was separated. The composite was characterized using TEM imaging, EDX/TEM (elemental) analysis, AFM, FTIR spectroscopy, potentiometric titrations, electrophoretic mobility determination, and XRD experiments.

**Transmission Electron Microscopy and EDX/TEM.** The characterization of the Keggin–gibbsite composite was primarily done by the use of a Tecnai 10 (FEI Company) transmission electron microscope operated at an accelerating voltage of 100 kV. At least 1000 particles were imaged, and nearly all of them revealed corrugations on edges and surfaces. Further confirmation was carried out by EDX/TEM using a Tecnai 20 EDX/TEM detector, operated at an accelerating voltage of 200 kV, which also confirmed the presence of P, Mo, and also Al. The TEM micrographs have been processed using TIA software (Tecnai imaging and analysis software).

**FTIR Spectroscopy.** A part of the dispersion containing the Keggin–gibbsite composite was dried, and the FTIR spectrum was recorded on a Perkin-Elmer FTIR 2000 as a KBr pellet. The major FTIR bands observed are listed (in  $\text{cm}^{-1}$ ): 1064 ( $\nu_{\text{as}}$ ,  $\text{PO}_4$ ), 1021, 963 ( $\nu$ ,  $\text{MoO}_4$ ), 864, 785, 666.

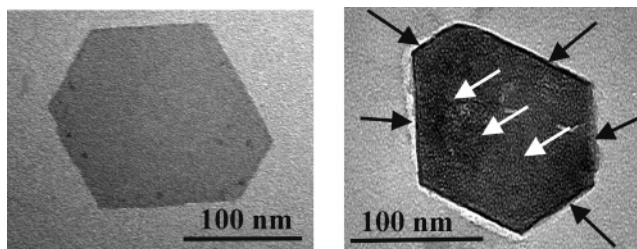
**Electrophoretic Mobility.** The electrophoretic mobilities were measured using dilute samples of gibbsite and Keggin–gibbsite composite by Coulter DELSA 440 SX in water at a pH ca. 5.5 and a temperature of 298 K. The electrophoretic mobilities of the composite and gibbsite were found to be +3 and  $+5.6 \mu\text{m cm s}^{-1} \text{V}^{-1}$ , respectively.

**Potentiometric Titration.** The potentiometric titrations were carried out using 15 mL of 2.4 g/L of Keggin–gibbsite composite with freshly prepared 0.001 M NaOH solution. For the complete titration, 9 mL of the NaOH solution was required. The pH of the dispersions for the purpose was measured with a Schott–Geräte pH meter.

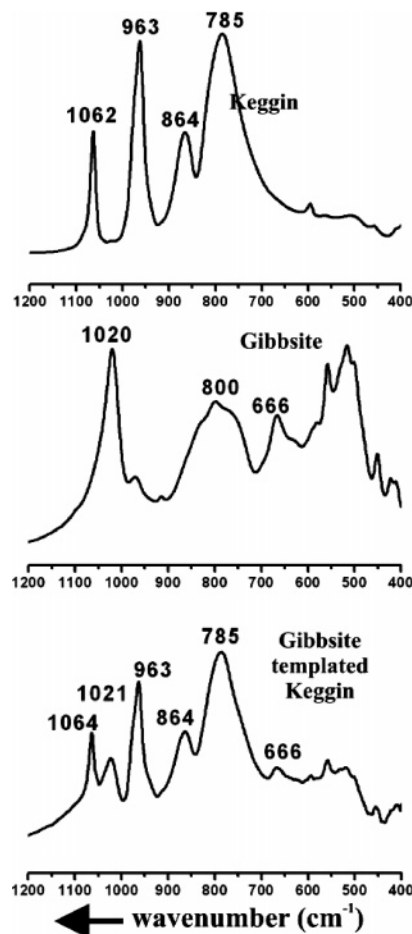
**X-ray Diffraction Experiments.** XRD measurements were carried out on a D8 theta–theta system from Bruker AXS in Bragg–Brentano geometry, automatic divergency slit (6 mm for gibbsite + keggin and gibbsite; 20 mm for keggin),  $2.5^\circ$  Soller slits,  $\text{Co K}_{\alpha 1,2}$  radiation ( $\lambda = 1.79026 \text{ \AA}$ ).

## Results and Discussion

The TEM image of the composite (Figure 2) revealed clear corrugations and darkened edges, as compared to the sharp and smooth edge of a smooth gibbsite nanocrystal, and a ‘mottled’ surface rather than the smooth surface of a templating gibbsite, implying its ‘coverage’ by the negatively charged phosphomolybdates. The corrugations on the edges and surfaces of Keggin–gibbsite composite are highlighted in the TEM image by arrows in Figure 2. The EDX analyses on the corrugated surface of individual particles revealed a ratio of P/Mo of 1:12, implying



**Figure 2.** TEM image of gibbsite nanocrystals (used as templates here) (left) and that of a single nanocrystal of Keggin–gibbsite composite (right) with darkened or corrugated edges and spotted surfaces shown by arrows, clearly implying gluing of phosphomolybdate Keggin on the edges and surface of composite Keggin–gibbsite composite nanocrystal (right).

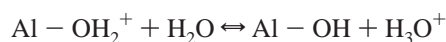


**Figure 3.** Comparative FTIR spectra of Keggin, gibbsite, and the gibbsite-templated Keggin.

the elemental intactness of the Keggin on the interface. However, to pin down the structural integrity of the Keggin, a spectroscopic signature of Keggin’s integrity was required. FTIR spectroscopy provided us with the answer. A part of the phosphomolybdate-stabilized, separated supernatant rich in Keggin–gibbsite composite was dried and analyzed by FTIR spectroscopy. The FTIR spectra revealed a superposition of the gibbsite and Keggin’s fingerprints (Figure 3), confirming the successful templation of the Keggin by the gibbsite by proving the elemental and molecular integrity of the Keggin on the surface of the gibbsite. (Note: after a few days, probably due to the hydrolytic decomposition of the Keggin, the elemental ratios change and formation of lacunary Keggin on the surface is observed, though the spectral patterns do not change. Likewise also note an enhanced thermal stability of the composite might be expected.)

Having shown the integrity of the molecular Keggin (from elemental analyses by EDX/TEM and FTIR spectroscopy), we wanted to have some information of the interface structure. However, it was not possible for us to obtain information on the interface from XRD or from AFM. From XRD, we were only able to see additional broad bands in the diffractogram which might be due to two-dimensional liquid-like disposition of the Keggin. They were, however, not informative enough to provide us with information on the structure of the interface. For AFM, the dimensions of the Keggin were too small to be resolved clearly. No regular lattice of the Keggin on the surface of the gibbsite was observed. To 'guess' how the Keggin 'sit' on the gibbsite surface, we undertook potentiometric titrations of the stable composite.

The gibbsite nanocrystal is positively charged at the pH (5.5) of our reaction. This is so because the pH (5.5) of the reaction is much lower than the isoelectric point of gibbsite (pH  $\approx$  10.1),<sup>15</sup> and hence, according to the following equilibrium, the nanocrystal surface is positively charged.



This surface charge of the nanocrystal can be estimated as surface charge density ( $\sigma$ ) by potentiometric titration.

When  $n_{\text{OH}}$  is the molal number of NaOH (determined by potentiometric titration) required to reach the isoelectric point (i.e., pH  $\approx$  10, see later),  $S$ , the specific surface area,  $F$ , the Faraday constant, and  $m_{\text{gibb}}$ , the mass of the gibbsite present, then the surface charge density is given as<sup>15</sup>

$$\sigma = n_{\text{OH}}F/m_{\text{gibb}}S$$

For gibbsite, we estimated the surface charge density to be 0.8 C m<sup>-2</sup>, which in turn corresponds to 5 protonated groups per nm<sup>2</sup> and conforms to the value published in the literature,<sup>15</sup> whereas for Keggin–gibbsite composite, a surface charge density of 0.3 C m<sup>-2</sup> for the composite was obtained, i.e., 2 protonated groups per nm<sup>2</sup>. Hence, it logically follows from the above observation that between the gibbsite template and the composite there is a difference of 3 positive charges per nm<sup>2</sup>. In other words, on average, the charge density of Keggin–gibbsite composite is reduced by 3 unit charges per nm<sup>2</sup> as compared to the bare gibbsite. Interestingly, the charge of the phosphomolybdate Keggin is 3-. Hence, we infer that in the composite there is *one* Keggin anion per nm<sup>2</sup> and propose the following geometric argument for a likely structure of the interface of the Keggin–gibbsite composite. (Note, the electrophoretic mobility measurements did *not* show a charge inversion, but the electrophoretic mobility of the composite was reduced to +3.0  $\mu\text{m cm s}^{-1} \text{V}^{-1}$  in the composite from +5.6  $\mu\text{m cm s}^{-1} \text{V}^{-1}$  of gibbsite. The electrophoretic mobilities indicate that both gibbsite and the composite are positively charge-stabilized and are consistent with the results of our potentiometric titrations.)

We know from potentiometric titration that in the composite there is 1 Keggin anion per nm<sup>2</sup>. A plausible packing arrangement (or model) to fit this experimental observation would be a monolayer of hexagonal close-packed Keggin with a center-to-center distance of ca. 1.2 nm (corresponding to the van der Waals diameter of the {PMo<sub>12</sub>O<sub>40</sub>}<sup>3-</sup>). With this model, the length of a side of the equilateral triangle formed by 3 Keggin at closest separation turns out to be  $\sim$ 1.2 nm, and hence, the area of the corresponding closest-packed Keggin triangle  $\approx$ 1.2<sup>2</sup>( $\sqrt{3}/4$ ) nm<sup>2</sup>,

i.e., 0.6 nm<sup>2</sup>, but this triangle has an occupancy factor of 0.5. Hence, the number of Keggin units per nm<sup>2</sup> according to this packing model turns out to be around 1.6/2, i.e., 0.8. Note: this number is in close agreement with the experimentally found *one* Keggin per nm<sup>2</sup>. Hence, a reasonably close-packed 'liquid-like' disposition of the Keggin on the surface of the gibbsite might be proposed, though a detailed structure of the interface could not be obtained.

We further propose to refer to this technique of using a colloidal particle as a template for forming large surface area POMs as colloidal casting. The requirements for successful colloidal casting might be summarized as follows. (1) Complementarities of charge between the colloidal templates and the POM to be templated (as mentioned above, here it is between the positively charged gibbsite platelets and anionic Keggin). (It is also to be noted that there is a significant difference in the matter of the chemistry of the edges and faces of the gibbsite nanocrystal, and hence, nonuniformity in distribution of the Keggin might take place as well.), (2) a common solvent for both the components for effective templation (here water), and (3) formation of a stable colloidal dispersion.

## Conclusion

In this letter, we demonstrate that it is possible to 'glue' smaller POMs like the Keggin on the surface of gibbsite platelets to form large surface hexagonal POM platelets. (Note: the phosphomolybdate Keggin are unstable in dilute aqueous dispersion and the surface area of the molecular Keggin is order of magnitude smaller as compared to the composite reported here.) Additionally, it is still a challenge to predict and control cluster size and morphology of POMs in the mesoscopic regime (in the range of 100–900 nm). The reasons are difficulty to maneuver the interplay of chemistry of multiple metal centers, pH, and redox state of the complete system. Hence, in this regime, techniques like that of 'colloidal casting' as reported in this letter and in the literature can be crucial, since it bypasses the complex chemical crossroad and resorts to the use of preformed colloidal entities as templates/scaffolds for an engineered design of a mesoscopic POM architecture. The technique is evidently supramolecular (in the sense that it involves supramolecular electrostatic and induced dipole interactions way 'beyond the chemistry of molecules'), and it also provides a platform to 'glue' molecules to form mesoscopic supramolecular architecture. As a second step, a simple condensation reaction between the POMs can be thought of. The possibility of using such high-surface-area composites as reported here can potentially pave the path for the ongoing search of high-surface-area POMs for catalytic applications.

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**Note added in proof.** As our work was undergoing peer review prior to publication, a somewhat related work has been published by Tarlani, A., Abedini, M., Nemati, A., Khabaz, M., and Amini, M. in *J. Colloid Interface Sci.* **2006**, *303*, 32–38.

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