Role of templating agents on the growth morphology of $AlPO_4$

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Large numbers of techniques are known to yield advanced materials, particularly ceramics, and currently the templating techniques, where the templating agents are used to control the nucleation of inorganic clusters from the aqueous or nonaqueous solution are gaining importance [1, 2]. Preorganized architectures consisting of functionalized surfaces act as templates for the nucleation and growth of inorganic materials [3]. The templates are frequently used to promote the formation of the desired structure during synthesis of inorganic materials and it is understood that the templating agents, normally organic nitrogen-containing bases, may serve as structure directing agents, as buffers or as void fillers [4]. The templating is a well-known step for the nucleation and growth of inorganic compounds in the biomineralization process, where the inorganic–organic interaction leads to preorganization, nucleation, and growth of biomaterials [5]. Several groups have investigated the preparation of aluminum phosphate using a templating agent in a nonaqueous medium [6–8]. In the last few years, the research on the molecular sieves particularly, Al-phosphate, has increased due to its importance as catalyst carrier for the oxidation of linear alkanes using molecular oxygen [9] and its possible use in nano-laser tubes [10]. In this letter, the effect of templating agents on the synthesis of microporous $AlPO_4$ is discussed.

We used aluminum-isopropoxide to prepare boehmite sol, which was reacted with orthophosphoric acid to yield $AlPO_4$ in ethylene glycol medium. Al-isopropoxide with purity >99.96% was prepared by reacting aluminum metal with isopropyl alcohol followed by vacuum distillation. In the present investigation, 100 g of Al-isopropoxide were hydrolyzed in 1000 cm^3 distilled water. Subsequently, 50 cm^3 of the Al-sol was dissolved in 100 cm^3 ethylene glycol and reacted with H_3PO_4 acid at 373 K for 3 h to yield $AlPO_4$ by the following reaction.

$$Al{-}O{-}OH + H_3PO_4 \rightarrow AlPO_4 + 2H_2O \quad (1)$$

After the completion of the reaction, the water of the sol was evaporated to yield a transparent sol of Al-phosphate in ethylene glycol medium. The aluminum phosphate was known to be insoluble in water but made a clear sol-like solution in the ethylene glycol medium. Various templating agents (2 cm^3) and growth inhibitor (alkyl ammonium bromide) (500 mg) were added to the sol, which was then aged for 24 h. The several templating agents used in the present investigation were tributyl amine, decayl amine, and dodecyl amine and the alkyl-ammonium bromide was ethyl-ammonium bromide. It was observed that precipitation of Al-phosphate took place during aging, which were subsequently filtered and washed thoroughly with water and alcohol. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques were used to characterize the precipitates. Coatings of aluminum phosphate sol on the cleaned glass substrates were also made by the dip coating technique before aging of the sol. The coated glass was also aged for 24 h at room temperature and subsequently heated at 993 K for 30 min and characterized by XRD and SEM.

The scanning electron microscopic investigations clearly showed significant changes in the morphologies of the synthesized $AlPO_4$ powders with change of templating agents. The tributyl amine was found to grow in the crystobolite morphology of the $AlPO_4$ (Fig. 1), whereas, the decayl amine and dodecyl amines resulted in the plate-like verscite and metaverscite ($AlPO_4$, $2H_2O$) morphologies, respectively (Figs 2 and 3). The metaverscite phases also revealed the presence of tubular shapes having micropores (Fig. 4). Since all the experiments were carried out identically, the morphological changes could be assigned only to the role of templating agents. These morphological variations are also in agreement with the fact that the organic amines can act as real structure-directing agents [4, 11] and as space fillers [4, 12]. Here, templating agents, amines have controlled the nucleation of organic clusters during precipitation and growth from solution. In this templating technique, the preorganized architecture consisting of functionalized surfaces of amines act as a template for inorganic nucleation. The formation of faceted crystals during tributyl amine templating was due to the inability of the small molecular amines to form self-assembled aggregates [5]. Though templating techniques are being investigated over the last one decade, the details regarding process of templating are not yet clearly understood and therefore also not been attempted in the present investigation. The scanning electron microscopic investigation revealed the presence of micropores in the powder synthesized using dodecyl amine as templating agent, which was also been confirmed from the TEM study of the said powders (Fig. 5). The pores were found to be less than 10 nm in size. Coating on glass substrate showed the retention of morphology after aging and therefore, it could be used as a microporous membrane.

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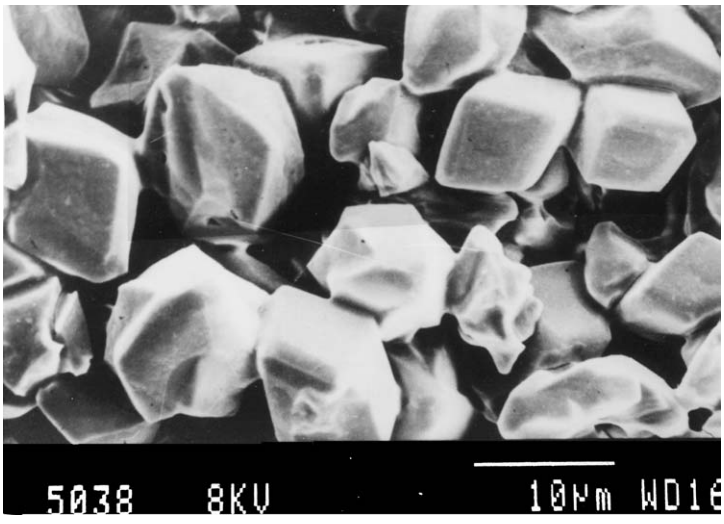

Figure 1 SEM image of the crystobolite polymorph of $AlPO_4$ particles prepared by templating with tributyl amine.

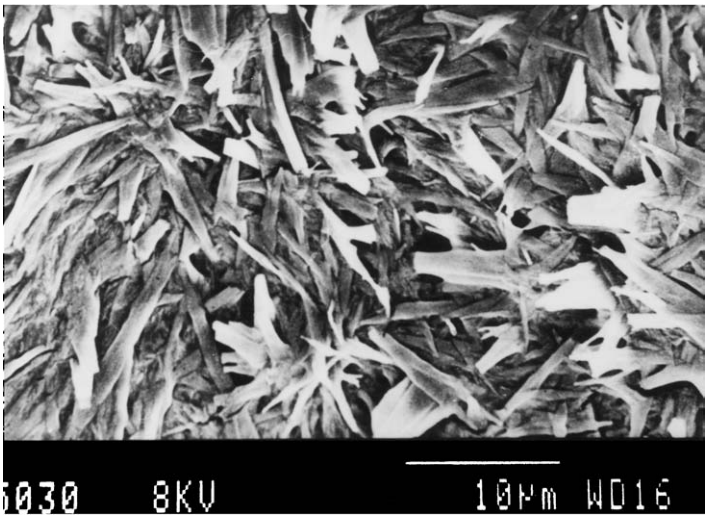

Figure 2 SEM image of the varscite polymorph of $AlPO_4$ particles prepared by templating with dacyl amine.

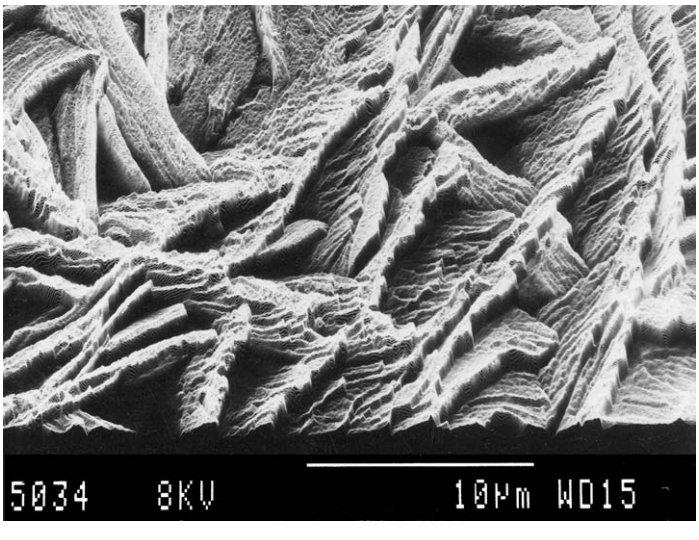

Figure 3 SEM image of the metavarscite polymorph of $AlPO_4$ particles prepared by templating with dodecyl amine.

In essence, we conclude that microporous $AlPO_4$ powder prepared by a templating mediated solution process and the effect of templating agents on the growth behavior of Al-phosphate particulates was studied. The growth morphology of the Al-phosphate powder was found to depend upon the templating agents and transmission electron microscopy studied indicated the presence of nano-sized pores (<10 nm) within the particles.

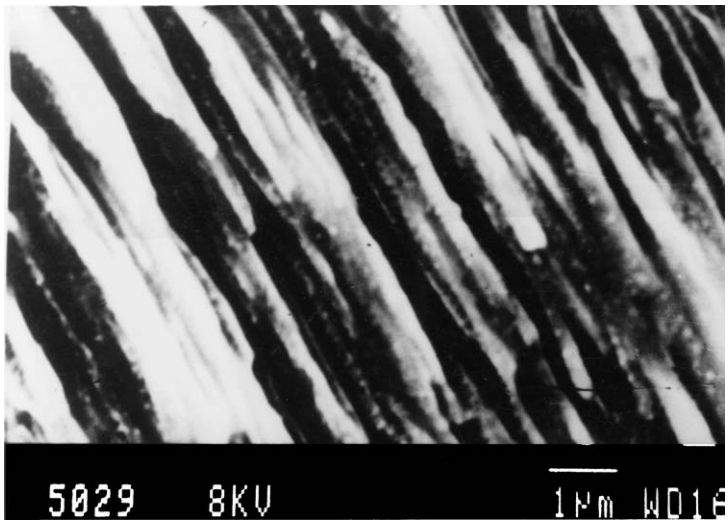

Figure 4 High magnification SEM image of the needle shaped $AlPO_4$ particles prepared by templating with dodecyl amine showing the prorous structures.

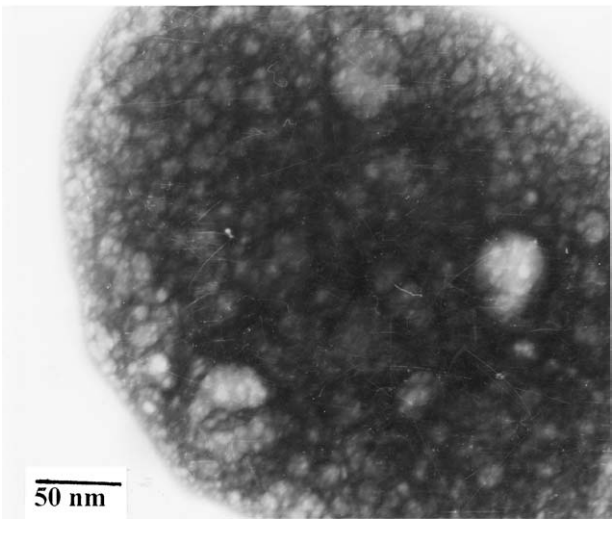

Figure 5 TEM image of the $AlPO_4$ particles prepared by templating with dodecyl amine showing the presence of nano-sized prorous structures.

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