The First Silica-pillared Layered Niobate

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$NH_2(CH_2)_3Si(OC_2H_5)_3$ has been exchanged into layered niobate KNb_3O_8 to form an intercalate with an interlayer distance of 26.8 Å, calcination of this intercalate in O_2 at 600 °C gives rise to the first porous silica-pillared layered niobate with a Brunauer-Emmett-Teller (BET) surface area of 165 $m^2\ g^{-1}$.

Smectite clays and layered four-valent metal phosphates can be pillared by inorganic oligomers such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ to produce expanded porous materials with high specific area.[1-3] A number of titanates, titanoniobates and niobates based on octahedral framework structures can also incorporate amines to form intercalated derivatives.[4,5] These new materials have received much attention because of their potential use in separations, sorption, conduction, mineralogy and catalysis. However, since intercalated organic compounds are inherently thermally unstable,

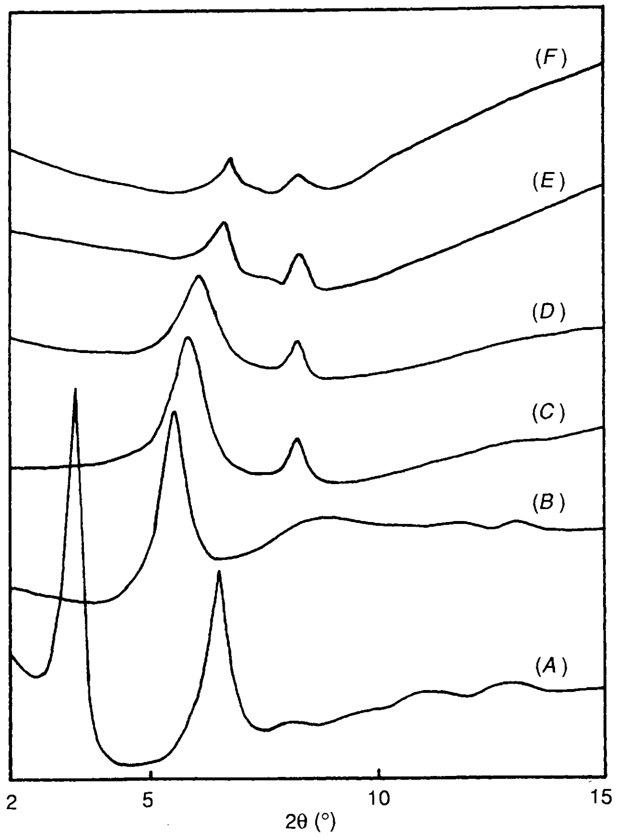

Fig. 1 Cu-Kα XRD patterns of $NH_2(CH_2)_3Si(OC_2H_5)_3$ intercalated niobate: (*A*) dried in air at 50 °C. Calcined in O_2 at (*B*) 400 °C for 4 h; (*C*) 450 °C, 16.5 h, (*D*) 500 °C, 5 h, (*E*) 550 °C, 4 h and (*F*) 600 °C, 5 h.

the usefulness of these materials as catalysts is severely limited. The acid–base properties of Nb_2O_5 have been studied recently. Hydrated Nb_2O_5 is making an impact in its application as an unusual solid acid catalyst.[6] However, niobic acid has weaker acidity and a relatively lower surface area at high temperatures. In order to increase the surface area and acidity of niobic acid calcined at high temperatures, the approach in our work is to prop open the layered niobate KNb_3O_8 with thermally stable inorganic pillars. Here, we report that $NH_2(CH_2)_3Si(OC_2H_5)_3$ can be intercalated into layered niobate, giving rise to the first porous silica-pillared layered niobate with a high specific surface area after calcination.

KNb_3O_8 was obtained by a solid-state reaction of a stiochiometric mixture of Nb_2O_5 and KNO_3 powder, and exchanged with 7 mol dm^{-3} HNO_3 to give HNb_3O_8. The resultant HNb_3O_8 has an interlayer distance of 10.5 Å, HNb_3O_8 powder was added, under stirring, to a 10 wt% aqueous solution of $NH_2(CH_2)_3Si(OC_2H_5)_3$ (Si : Nb = 13 : 3). The mixture was refluxed for 72 h, followed by centrifuging and washing with distilled water. According to ^{29}Si MAS NMR, the organosilicon compound undergoes polymerization through the OH groups (formed *via* hydrolysis) between the molecules. The intercalate dried in air at 50 °C has an interlayer distance of 26.8 Å (Fig. 1). The increase of the interlayer spacing by as much as 16.3 Å upon treatment clearly shows that intercalation has indeed taken place and the *d* spacing of the uncalcined material corresponds to a bilayer of aminosilane. Differential thermal analysis demonstrates that the interlayer organic ammonium ions begin to decompose at 277 °C. Therefore, after calcinating this intercalate at 400 °C in O_2, a silica-pillared material is obtained. This material has an interlayer distance of 15.8 Å ($2\theta = 5.6°$). Further calcination at higher temperatures leads to the gradual decrease of the interlayer distance from 15.8 to 13 Å ($2\theta = 6.8°$). X-Ray diffraction (XRD) analysis also indicates that this silica-pillared material has a thermal stability in excess of 600 °C and the structure of layers remains intact after calcination.

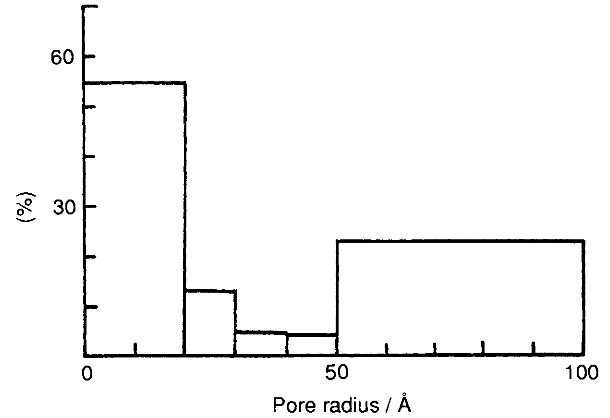

Fig. 2 Pore-size distribution of $NH_2(CH_2)_3Si(OC_2H_5)_3$ intercalated niobate calcined in O_2 at 600 °C for 5 h

KNb_3O_8 itself is a non-porous solid with a rather low specific surface area [2.5 $m^2\,g^{-1}$; BET(N_2)] and high ion-exchange capacity. In contrast, silica-pillared material (600 °C, O_2, 5 h) possesses quite high specific surface area [165 $m^2\,g^{-1}$; BET(N_2)]. Pore-size distribution analysis indicates that this material has both micropores and mesopores (Fig. 2).

Formation of thermally unstable $NH_2(CH_2)_3Si(OC_2H_5)_3$ intercalate precursor provides a promising route to prepare thermally stable, porous, silica-pillared layered metal oxides with a high specific surface area. Moreover, Ti- and Al-containing organic amines can also be used to prepare TiO_2 and Al_2O_3 pillared materials. Further research work is underway in our laboratory.

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