Synthesis of a new solid acid: silica pillared lanthanum niobate with a supergallery

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Stepwise intercalations of *n*-decylamine and oligosiloxanes followed by calcination at 823 K in air results in a thermostable supergallery layered lanthanum niobate; the new material shows an interlayer free spacing of 17.4 Å along with a high Brunauer–Emmett–Teller surface area of 251 m² g⁻¹; the acidity of the new pillared material is markedly enhanced with respect to the original lanthanum niobate.

As an approach to obtain thermally stable porous materials, various inorganic oxo-cations have been intercalated into layered solids such as smectite clays and phosphates.[1,2] Calcination of these cation-intercalated materials formed inorganic pillared solids with different characteristics.[3] Metal oxides based on octahedral framework structures but possessing lamellar structures showed unusual properties in applications for separations, sorption and conduction[4] as well as photocatalysis.[5] However, the non-swelling nature of these layered metal oxides prevents the facile ion exchange of large oxo-cations so that only a few papers concerning pillared metal oxides have been published so far.[6] Among these lamellar oxides, lanthanum niobate (lanthanum niobium oxide, $HLaNb_2O_7$) whose layers are only built of corner-sharing octahedra to form thick perovskite slabs is found to show stronger Brønsted acidity than $HTiNbO_5$ and similar layered oxides.[7] Its photocatalytic activity is also notable.[5] Unfortunately, it loses almost all of its acidity upon heat treatment at 773 K due to the removal of interlayer water.[8]

In most of the reported lamellar solids pillared by inorganic pillars such as aluminium Keggin ions and tetrameric zirconium cations, the gallery heights are comparable to the van der Waals thickness of the host layers.[3,9] Pillared materials in which the gallery height is substantially larger than (twice or more) the thickness of the host layer have scarcely been obtained by pillaring with inorganic pillars to date.[10,11] Silica also is one of the most commonly used pillars. The lateral spacing of silica pillared materials may easily be varied based upon the preparation conditions.[11–13] The use of organosiloxanes as the source of silica enables facile intercalation of the pillar precursor and pore formation upon calcination of the organic groups.[11,12]

On the basis of progress concerning the pillared layered oxides materials made in the laboratory,[6,15,16] we report here the first synthesis of a new type of solid acid material: a silica pillared lanthanum niobate with a supergallery. The new material showed a supergallery of 17.4 Å accompanied by a Brunauer–Emmett–Teller (BET) surface area as high as 251 m² g⁻¹. Additionally, the acidity of the new pillared material was markedly enhanced with respect to the original lanthanum niobate and hence its activity might be expected to be comparable to that of strong solid acid hydrated niobium oxide, $Nb_2O_5 \cdot nH_2O$ for the dehydration of Pr^{i}OH.

The starting material, $KLaNb_2O_7$, was prepared by a solid-state reaction of a mixture of K_2CO_3, La_2O_3 and Nb_2O_5 in molar ratios of 1.25 : 1.0 : 2.0 at 1373 K overnight. The proton exchange reaction was carried out at 333 K in a solution of HNO_3 (6 mol dm⁻³) for 3 d (solution changed daily). *n*-Hexylamine was intercalated by stirring lanthanum niobate powder with a *n*-hexylamine solution (50% v/v, EtOH) at 333 K for 36 h. After the separation of *n*-hexylamine-intercalated $HLaNb_2O_7$ by centrifugation, the solid (2 g, dried at 333 K) was treated with *n*-decylamine (100 cm³, 50% v/v, EtOH) at 348 K for 2 weeks. Oligosiloxane-intercalated $HLaNb_2O_7$ was prepared by refluxing the *n*-decylammonium-intercalated lanthanum niobate with an aqueous solution of $H_2NC_3H_6Si(OEt)_3$ (20% v/v, 200 cm³) for 4 days with stirring. The solid was then separated by centrifugation followed by drying at 363 K. The calcination of the above solid in air at 823 K resulted in the novel silica-pillared material with a supergallery.

The obtained $HLaNb_2O_7$ showed an X-ray diffraction (XRD) pattern [Fig. 1(*a*)] coincident with that reported in the literature.[7] The intercalation of *n*-hexylamine gave rise to a material with an expanded interlayer distance of *ca.* 26 Å shown by the (001) reflection at $2\theta = 3.4°$ where the peak positions other than (00*l*) reflections remain unchanged. Further substitution by *n*-decylammonium led to a layered material with (001) reflection at $2\theta = 2.45°$, which indicates the formation of an even larger basal spacing of *ca.* 36 Å. The interlayer gallery height occupied by *n*-decylammonium ions is *ca.* 28.4 Å by subtraction of the host layer thickness of 7.6 Å.[7] The oligosiloxane cation-intercalated $HLaNb_2O_7$ showed a (001) reflection at an even lower 2θ value of 1.9°, corresponding to an interlayer distance of *ca.* 46 Å. After calcination at 823 K, the inorganic silica pillared material showed an interlayer distance of *ca.* 25.0 Å as suggested by the (001) reflection at $2\theta = 3.5°$ [Fig. 1(*b*)]. This indicates a 'supergallery' of *ca.* 17.4 Å which is substantially larger than the host layer thickness. A significant increase in gallery height is achieved compared to that of non-pillared $HLaNb_2O_7$ where the basal spacing is only *ca.* 10.8 Å. The layered structure of the new supergallery pillared material is thermally very stable and its structure was retained upon heat treatment at 973 K with only a slightly decreased interlayer distance of *ca.* 24.2 Å as shown by its (001) reflection at $2\theta = 3.6°$.

The porosity of $HLaNb_2O_7$ is greatly increased by pillaring with silica. The BET surface area of the new pillared material reaches 251 m² g⁻¹ most of which arises from micropores (micropore area = 197 m² g⁻¹). The original $HLaNb_2O_7$ is
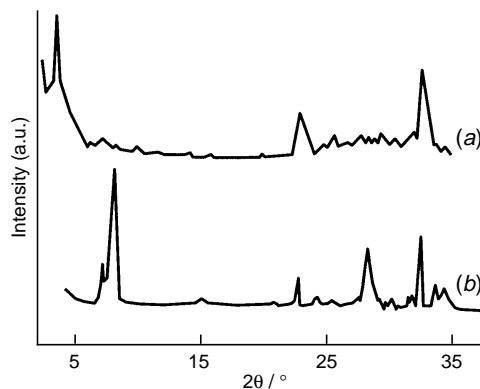
Fig. 1 X-Ray diffraction (XRD) patterns of (*a*) $HLaNb_2O_7$ (dried at 333 K) and (*b*) silica-pillared $HLaNb_2O_7$

actually a non-porous solid with a surface area of only *ca.* 5 $m^2 g^{-1}$. Considering the fact that the gallery height resulting from pillaring reaches 17.4 Å, a new type of nanoporous material[9] is thought to be formed by pillaring with silica. The new material shows an adsorption–desorption isotherm with a hysteresis loop (Fig. 2) upon N_2 adsorption at 77 K. The obtained hysteresis loop may be classified as type H4 or H3 (by IUPAC classification) suggesting the existence of narrow slit-like pores associated with aggregates of plate-like particles where the type I character of the adsorption isotherm indicates the microporosity predominated in the new material.[18] It is also in good agreement with the micropore area measurement.

The possibility of using this material for acid catalysed reactions was investigated by the probe reaction of Pr^iOH decomposition at 573 K which showed complete conversion of the reactant to dehydration products, illustrating the strong acidic property of the new material. In comparison, non-pillared $HLaNb_2O_7$ pretreated at 573 K showed only 32% conversion under the same reaction conditions. A significant enhancement of acidity is achieved by pillaring the lanthanum niobium oxide with silica. The new pillared material showed catalytic activities as high as that of the strong solid acid niobic acid under the same conditions.

To conclude, silica pillared $HLaNb_2O_7$ is a thermostable porous layered solid acid material containing a supergallery. The new material is expected to show shape selective effects for catalytic reactions in which larger molecules can be used. The high thermal stability of the n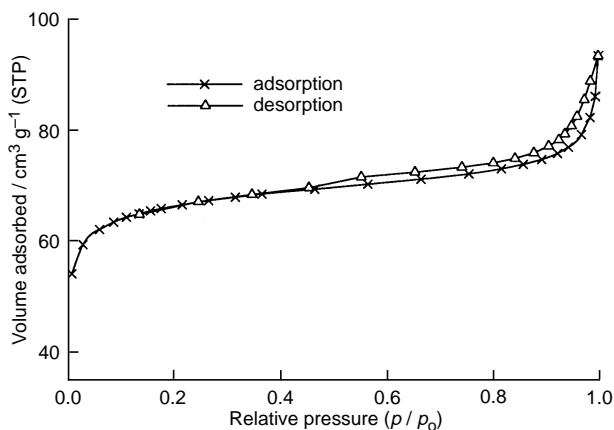ew pillared material also enables its application at some critical conditions either as an acid catalyst or as a catalyst support. Further systematic characterization of this new material and investigations on its shape selectivity in catalysis as well as other fields are actively being undertaken.

Footnote

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Fig. 2 Adsorption–desorption isotherm of N_2 at 77 K on silica-pillared $HLaNb_2O_7$