# The Synthesis of Pillared Vanadium Oxide

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A double ion exchange method permits pillaring of the layered vanadium pentoxide xerogel with $Al_{13}$ oxyhydroxide polymers and a single ion exchange permits pillaring it with $Mo_6$ and $Nb_6$ polynuclear cations.

Pillaring is the process which is commonly referred to when a layered solid is permanently expanded by intercalating a strongly bound bulky molecule or ion, in such a way as to yield a material with microporous galleries. Pillaring has been extensively applied to swelling layered silicates (smectite clays), using organic molecules, inorganic polymeric ions, or even oxide colloids.[1—3] For instance, ion-exchanging the negatively charged montmorillonite host lattice with $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ or $M_6Cl_8(OH)_n(H_2O)_m^{(4-n)+}$ (M = Mo or Nb) cations yields gallery heights of the order of 0.9 nm.[3]

Although smectite clays are a unique family of layered solids with a permanent negative charge, several other layered materials, such as chalcogenides,[4] perovskite-related oxides,[5] and phosphates,[6] are potentially capable of being pillared by cation exchange. We report here the first successful pillaring of vanadium pentoxide xerogel, $V_2O_5 \cdot nH_2O$ ($n$ <5), with the same ions as above (referred to as $Al_{13}$, $Mo_6$, and $Nb_6$).[7] The layered structure of vanadium oxide gel stems from the parallel arrangement of elementary fibres, 2.7 nm wide, into corrugated ribbons.[8,9] It can be prepared by pouring molten $V_2O_5$ into cold water or by polycondensation of decavanadic acid, which is itself obtained by passing sodium metavanadate, $NaVO_3$ (0.3 M) over an acidic resin (20—50 mesh).[10] Ionization of decavanadic acid gives the gel particles a negative charge of the order of 0.2 $e^-$/vanadium, compensated by $H_3O^+$ ions.[10,11] In addition to this acidic character, the gel has a weak mixed valence $V^V$–$V^{IV}$ character.[12]

As shown by Aldebert *et al.*,[13] drying the gel at room temperature leads to a composition close to $V_2O_5 \cdot 1.7\ H_2O$. The 001 diffraction lines indicate a stacking periodicity, $d_{001}$, of 1.15 nm. At 500 K, the water content drops to 0.1 $H_2O$ per $V_2O_5$ unit and $d_{001}$ drops to 0.88 nm, which corresponds to a collapsed interlayer space. The difference between the two values (0.27 nm) corresponds to a monolayer of water molecules. The nitrogen Brunauer–Emmett–Teller (BET) surface area of a dried vanadium pentoxide xerogel powder is low, of the order of 3 $m^2/g$, and its micro- or meso-porosity is negligible (this work).

Our first attempts to pillar the gel by direct ion exchange with $Al_{13}$ polymer solutions, classically prepared by slowly adding 0.2 M NaOH to an aluminium nitrate solution ($10^{-2}$ to $10^{-1}$ M), at 40 °C,[14] led to non-reproducible results, which were dependent on the age of the gel. Since the best results were obtained with aged gels, which are likely to undergo hydrolysis due to the action of the interlayer acidity of $H_3O^+$, we thought that the presence of vanadyl ions, $VO^{2+}$, as counterions in the aged gels could have caused the improvement. Indeed, $VO^{2+}$ (aq) exchanged gels are characterized by a larger (~0.54 nm) interlayer spacing than $H_3O^+$ gels (~0.27 nm),[15] and this might have facilitated the interlayer diffusion of the large and highly charged $Al_{13}$ ions.

In order to check and to control the process, several batches of fresh $H_3O^+$ gel (0.5% dry matter) were first cation-exchanged with a number of inorganic ions, including $VO^{2+}$, $Li^+$, $Na^+$, $K^+$, $Ag^+$, $Cs^+$, $Rb^+$, $NH_4^+$, $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $La^{3+}$, $Al^{3+}$, and $Fe^{3+}$, by mixing the gel with solutions of the appropriate salt ($10^{-2}$ M salt/g $V_2O_5$). After washing and air-drying, these pre-exchanged precipitates were redispersed in water and mixed with the hydrolysed Al solution (OH/Al = 2; 17 mM Al/g $V_2O_5$) in order to perform, if possible, a second cation

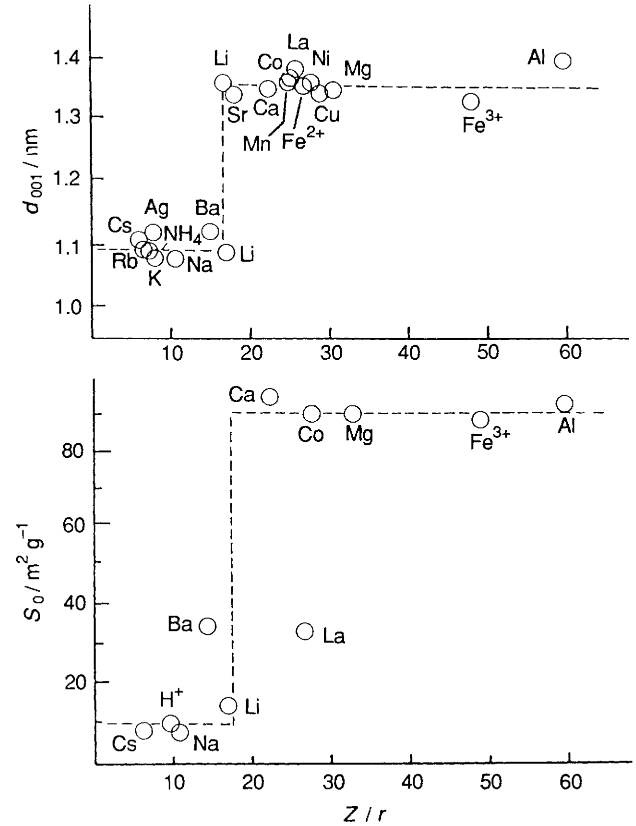

**Figure 1.** (A) $d_{001}$ distance (room temperature; air-dried) of $V_2O_5$ gels exchanged with a number of cations, as a function of the polarizing power (charge/radius, $e^-$/nm) of the cations. (B) Nitrogen BET surface area of some of the foregoing, after pillaring with aluminium hydroxide solution.

exchange with the $Al_{13}$ polymer. After a contact time of a few hours, the solids were washed, dialysed, and freeze-dried.

Remarkably, the pre-exchanged gels as well as the final materials can be classified into two classes [Figure 1(a) and (b)]. The first class includes the gels pre-exchanged with cations having a charge/radius ratio, $Z/r$, smaller than 16.7 $e^-$/nm. In the pre-exchanged state, these gels are characterized by a $d_{001}$ distance close to 1.15 nm under air-dried conditions (room temperature and a relative water vapour pressure in the ambient atmosphere of *ca.* 0.75). This corresponds to a monolayer of water between the $V_2O_5$ ribbons. After the second ion exchange with the aluminium solution, their $d_{001}$ distance increases to ~1.5 nm and their nitrogen BET surface area, $S_0$, is between 10 and 30 m$^2$/g. Although this is a significant improvement with respect to the original gel, it does not correspond to what one expects for layers propped apart with the $Al_{13}$ ion.

On the other hand, the second class includes the gels pre-exchanged with $VO^{2+}$ (aq) or with cations having a $Z/r$ ratio larger than 16.7 $e^-$/nm. In the pre-exchanged state they have a $d_{001}$ distance close to 1.36 nm, which corresponds to a bilayer of water molecules. In the final Al-exchanged state, they have a $d_{001}$ distance of the order of 1.8 nm and a nitrogen BET surface area, $S_0$, larger than 80 m$^2$/g. Interestingly, the largest $d_{001}$ and $S_0$ values were always obtained with the $VO^{2+}$ pre-exchanged gels.

The second class can be considered as $Al_{13}$-pillared $V_2O_5$ xerogels. Their microporous void volume is of the order of 0.3 ml/g. Their interlayer distance at room temperature (0.94 nm) is close to that of $Al_{13}$-pillared smectite clays and corresponds to the diameter of the $Al_{13}$ cation. $^{27}$Al NMR spectra of the supernatant solutions showed that the $Al_{13}$ polymer was indeed preferentially adsorbed (the polymer is easily identified by its central tetraco-ordinated Al). However, the thermal stability of $Al_{13}$-pillared $V_2O_5$ seems to be lower than that of $Al_{13}$-pillared smectite clays. Indeed, at 530 K, the $d_{001}$ distance drops to 1.46 nm but this modifies neither the pore volume nor the surface area (which suggests that the gallery height is never large enough to allow for a bilayer of nitrogen molecules).

$V_2O_5$ xerogel can also be pillared by simple ion exchange with the $Mo_6$ and $Nb_6$ chloride clusters, by mixing an aqueous gel of vanadium oxide, containing 1% of dry matter, with 200 ml of a 1.6 M ethanolic solution of the cluster ions. The mixture is vigorously shaken for 15 min, slowly evaporated at 55 °C for 24 h and washed by dialysis for 48 h. The $d_{001}$ distance of the pillared gels dried at room temperature is close to 1.43 nm and their nitrogen surface area is of the order of 15 m$^2$/g.

Although these features are less interesting than with the $Al_{13}$ gels, the stacking order of the $Mo_6$ and $Nb_6$ gels is better than that of the $Al_{13}$ gels. Six 00*l* diffraction orders could be observed in the former case, whereas only two could be observed in the latter case. This, as well as the lower surface area and microporosity of the $Mo_6$ and $Nb_6$ gels with respect to the $Al_{13}$ gel, can be assigned to the much lower cationic charge of the $M_6$ hydroxyhalide clusters and, concomitantly, to the larger number of $M_6$ polycations necessary to saturate the negative charge of the $V_2O_5$ layers. Thus, $Mo_6$- and $Nb_6$ -$V_2O_5$ have to be considered as well ordered but encumbered layered structures, whereas $Al_{13}$-$V_2O_5$ is a less well ordered but much more open pillared structure.

M. K. is grateful to the Conseil Régional de la Région Centre for a scholarship. This work was supported by Rhône Poulenc Recherches.

*Received, 21st February 1990; Com. 0/00801J*

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