Some observations on the synthesis and characterisation of pillared layered materials of varied pillar density

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A practical approach to the synthesis from a given layered host of pillared derivatives of varied, and controlled, pillar density is described. An analytical technique allowing measurement of the pillar density is outlined and it is shown that, if the stoichiometric composition of the host is known, the measurements permit elucidation of the charge on the ionic pillar precursor. Once established for fixed conditions of synthesis this would allow calculation of pillar density from a knowledge of the cation exchange capacity of the original host.

Keywords: Pillared layered materials; synthesis; characterisation; pillar density

Interest in layered inorganic materials has increased dramatically in the past two decades. Initially, this stemmed from observations regarding the catalytic potential of ion-exchanged clays [1] but, progressively, a wide range of alternative applications has been recognised. Most layered species have a considerable ability to intercalate liquids and gases and to expand the inter-sheet distance to accommodate these. The process, known as swelling, is necessary to provide for intercalation but, at temperatures above about 350°C, collapse occurs progressively eventually becoming irreversible. A remedy for this was first described by Vaughan, Lussier and Magee [2] who introduced the concept of pillaring. In this, an ionic pillar precursor is exchanged into the interlamellar space and then fixed by calcination to provide an open, rigid, three-dimensional structure. This innovation led to a substantial international interest in pillared structures [3]; in the EC, for instance, a Concerted European Action has been initiated. The potential of these pillared materials is immense and so their synthesis and characterisation is a matter of importance. Little is yet known, however, of the relevance of pillar density, the issue addressed here.

When a layered species is pillared by the initial introduction into the interlamellar space of an ionic pillar precursor it is clear that the number of precursor ions, and thus of eventual pillar "molecules", is limited by the cation exchange capacity (CEC) of the host and the charge on the ionic precursor. For a given host–precursor pair there is thus a maximum attainable pillar density, the maximum natural density (MND). For ion-exchangeable clay materials it is readily possible by controlled calcination to reduce the effective CEC to desired levels as a result of migration of the interlamellar anions into the TOT sheet. This generally involves loss of H^+ which can, as required, subsequently be drawn back into the interlamellar region by heating in strong base, e.g. NH_3 or cyclohexylamine. Thus, from any single clay sample, we can prepare a series of samples of CEC ranging from that of the raw material down to virtually zero. Correspondingly, we are then, in principle, able to create pillared versions of a given host of pillar density ranging down from the MND to zero. These can then be proton regenerated by base treatment as described, an essential procedure if the pillared material is needed for use in any proton catalysed process since, following the high temperature calcination involved in producing, e.g. alumina pillars in montmorillonite ($\approx 500°C +$), the CEC of the pillared material is so low (< 10 m.equiv/100 g) that it is (protonically) catalytically inactive.

The foregoing outlines a practicable approach to the production of closely related pillared samples varying in pillar density which would then allow study of the effect of varied pillar density on the physical and chemical properties of the material. The remaining question is, however, following synthesis, do we experimentally ascertain the achieved pillar density? We have described previously [4] how, for an alumina pillared clay for example, provided the charge deficit of the clay sheets is known, the difference in Si/Al ratio between the pillared and unpillared clays allows calculation of the number of pillars per unit weight of unpillared host, and inter alia, of the effective charge on the ionic pillar precursor. However, the accuracy required in the analytical determination of the required elemental ratio is very considerable and experience establishes that the determination of Al, and even more so of Si, in clay samples is difficult to achieve with high accuracy.

In contrast, the determination by wet chemical methods followed by AAS or FES analysis, of the metals such as Li, Mg or Fe, commonly found in isomorphous replacement, is capable of being conducted with considerable accuracy as repeatability tests conducted in this laboratory have shown. Since the pillaring process leads to no loss of these elements, as pillars are introduced the molecular mass of the material increases and so the mass per unit weight of pillared host of, for example, Mg is proportionately reduced. Knowing this value, the Mg content, and formula weight of the original clay and that of the alumina pillar, the number of pillars per unit formula weight of the original host clay can be calculated. Thus, pillar density can be established and, further, knowing the CEC (charge deficit) of the relevant (original or charge reduced) host clay, the charge on the pillar precursor ion can be calculated. This will be constant from clay to clay if the basic proposal regarding synthesis is correct and so, such measurements provide a test of the proposition.

As an example let us consider a montmorillonite of formula $Si_8Al_{3.5}Mg_{0.5}O_{20}$-$(OH)_4$ which has been proton exchanged. The (dry) formula weight is about 730 and so the magnesium content is 69.4 mg ion/100 g. If we assume that the alumina pillar precursor ion has a charge of 3+ we expect to introduce 0.5/3 (0.167) mol of alumina pillars (molecular mass $\approx$ 650) per formula weight of the clay, i.e. the formula weight of the pillared clay rises to 839 and the magnesium content reduces to 60.4 mg ion/100 g clay. The accuracy of Mg analysis by AAS is entirely adequate for the task as indicated.

Such isomorphous metal dilution (IMD) should have wide application in clay systems since the other commonly substituted metals, Fe, Ni, Li, for example, can be determined as readily as is Mg. In the wider context, there should be opportunities for its application in the study of pillaring of other layered materials. We recognise that, in circumstances where the pillar contains a readily determinable element(s) not present in the host, its (their) determination alone provides the necessary information if the formula weight of the pillar is known. In numerous cases of pillars other than alumina, of current interest, this information is not known with certainty, nor is the effective precursor ion charge. However, combining IMD with pillar element analysis can resolve this problem. The extent of dilution of an isomorphously replaced metal, as described, provides a value of the formula weight of the pillared material and, hence, the mass of pillars per formula weight of host. Knowing then the corresponding mass of the pillar element(s) from the independent analysis, and the general chemistry of the precursor, a pillar formula may be evaluated. Once this is done calculation of the effective pillar precursor ion charge follows.

The foregoing proposals thus seem to offer a viable technical approach to the elucidation of basic information about pillar precursors, the pillaring process and the eventual pillars themselves.

References

[1] J.M. Adams, J.A. Ballantine, S.H. Graham, R.J. Laub, J.H. Purnell, P.I. Reed, W.Y.M. Shamam and J.M. Thomas, J. Catal. 58 (1979) 238.

[2] D.E.W. Vaughan, R.J. Lussier and J.S. Magee, US Patent 4,176,090 (1979).

[3] I.V. Mitchell, ed., *Pillared layered structures: Current trends and applications* (Elsevier, Amsterdam, 1990).

[4] J.H. Purnell, in: *Pillared layered structures: Current trends and applications*, ed. I.V. Mitchell (Elsevier, Amsterdam, 1990) p. 107.