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PILLARED CLAYS AND PILLARED LAYERED SOLIDS

(Technical Report)

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Pillared clays and pillared layered solids (Technical Report)

Abstract: Pillaring is a commonly used procedure to transform a layered crystalline inorganic compound into a material with microporosity and mesoporosity. First, the terms layered compound, pillaring, pillaring agent and interlayer region are defined, followed by the terms pillared layered solid or pillared compound. In the second part, the standard characterization methods and procedures and a systematic classification scheme are proposed.

HISTORY

Barrer and MacLeod [1] first introduced the concept of transforming a lamellar solid into a porous structure by inserting laterally spaced molecular props between the layers of a smectite clay mineral. The terms 'pillared' and 'pillaring' originate from the work of Brindley & Semples [2] and Vaughan & Lussier [3] in the 1970s on smectite-type clay minerals. They found that thermally stable, robust inorganic moieties could be intercalated between the individual clay platelets of the stack or aggregate of clay lamellae. The mechanism was proposed to be an ion exchange reaction, followed by solvent removal. The latter is typically a calcination process with preservation of the clay mineral structure and of a pillar structure. The resulting materials have an increased interlamellar distance, an increased pore volume, especially in the micropore range, and are accessible by molecules in a specific size range, i.e. they have molecular sieving properties.

Nowadays, the range of materials that can be pillared has expanded beyond smectite-type clay minerals. Pillaring agents include inorganic and organic compounds. A consistent system of nomenclature can be set up in order to avoid confusion and make comparison of data between different laboratories possible.

DEFINITIONS

Layered compound

A layered compound is a crystalline material wherein the atoms in the layers are cross-linked by chemical bonds, while the atoms of adjacent layers interact by physical forces. A single layer is called a *lamella*, *slab*, or *sheet* [4]. A layered compound has a well-defined X-ray diffraction (XRD) pattern, which demonstrates its lamellar structure.

Intercalation

Intercalation is the insertion of a guest species in the interlayer region of a layered solid with preservation of the layered structure [4]. The material obtained is called an *intercalation compound*. Intercalation is proven by the XRD pattern, which must unambiguously show an increase in the spacing between adjacent layers, i.e. an increase in the basal spacing.

Comment: There is no restriction on the nature of the intercalating agent or on the mechanism of intercalation.

Pillaring

Pillaring is the process by which a layered compound is transformed into a thermally stable micro- and/or mesoporous material with retention of the layer structure. The material obtained is a *pillared compound* or a *pillared layered solid*. A pillared derivative is distinguished from an ordinary intercalate by virtue of intracrystalline porosity made possible by the lateral separation of the intercalated guest.

Comment: Thermal stability and porosity distinguish a pillared compound from an intercalation

compound. The latter can be, but must not be, thermally stable. They also may have, but must not have, porosity. Thus, expansion of the layer stacking direction only (basal spacing) by the intercalation agent is insufficient evidence for pillaring.

Pillaring agent

A pillaring agent is any compound, which can be intercalated between adjacent layers of a layered compound, which maintains the spacing between adjacent layers upon removal of the solvent, and which induces an experimentally observable pore structure between the layers.

Interlayer region

The interlayer region is the space between adjacent layers of a layered compound.

Comment: The term 'gallery' is synonymous with 'interlayer'.

Pillared layered solids or pillared compounds

A pillared layered solid or pillared compound has the following characteristics: (i) the layers are propped apart vertically and do not collapse upon removal of the solvent; (ii) the minimum increase in basal spacing is the diameter of the N_2 molecule, commonly used to measure surface areas and pore volumes: 0.315–0.353 nm; (iii) the pillaring agent has molecular dimensions and is laterally spaced in the interlamellar space on a molecular length scale; (iv) the interlamellar space is porous and at least accessible to molecules as large as N_2; there is no upper limit to the size of the pores.

Comment: There is no restriction on the type of layered compound, the type of pillaring agent or the mechanism of pillaring.

The minimum criteria for a material to be called pillared are: chemical and thermal stability and molecular distribution of pillars, but no order of the pillars is required in the interlayer region. The lamellae of the layered compound must be ordered so as to give an XRD pattern which allows the determination of the d_{001} spacing. The final criterion is accessibility of the interlayer region by molecules at least as large as N_2.

The way to obtain pillared compounds is intercalation followed by any treatment which provides the requirements given above.

There is no restriction on the pillar–host interaction: electrostatic, van der Waals, chemical bond. The structure and therefore crystallinity of the layered compound must be retained upon pillaring.

CHARACTERIZATION CHART OF PILLARED LAYERED SOLIDS

In general terms, pillared compounds must be characterized according to the 'Recommendations for the characterization of porous solids' [5]. More specifically, the minimum characterization procedures are:

- basal spacing: powder XRD pattern after removal of the solvent, e.g. heating at 120 °C in air or N_2 (Ar, He) for the removal of water. The XRD pattern must show clearly the d_{001} line, but a rational series of d_{001} lines is not required.
- porosity and surface area: the same pretreatment as for the determination of the basal spacing is recommended for the determination of porosity and surface area; N_2 adsorption–desorption isotherms are necessary, which are analysed via *t*- and α-plots.

Any pillared compound should be accompanied by the following data: an empirical formula or unit cell formula that provides the pillar-to-layered host composition; an XRD basal spacing, compared with that of the precursor layered compound; a surface area of the pillared compound compared with that of the precursor layered compound, both conditioned in exactly the same way prior to the measurement; micropore volume from *t*- and α-plots; surface area outside micropores. Care must be taken to ensure that the observed porosity is the result of pillaring and not simply a consequence of interparticle texture.

RECOMMENDED NOMENCLATURE OF PILLARED COMPOUNDS

The name of the pillared compound consists of the adjective 'pillared', followed by the name of the pillar and by the name of the layered host.

Type of host compound

The correct name of the host is used, according to the inorganic chemistry nomenclature rules, published by the International Union of Pure and Applied Chemistry (IUPAC) [6].

Comments: A 'clay' *per se* cannot be pillared, because the term 'clay' refers to a rock or an ore containing one or more clay minerals as components. It is the clay minerals in the clay that are pillared. We use the correct name of the clay mineral, e.g. saponite, hectorite, montmorillonite. The terms 'anionic clays' and 'cationic clays' are shorthand terms for 'anionic clay minerals' and 'cationic clay minerals'. What is sometimes given the name 'anionic clay' in the literature is more accurately a layered double hydroxide (LDH). So, we prefer 'pillared LDH' but not 'pillared anionic clay'.

The pillaring agent

If the chemical formula of the pillaring agent is known, it is preferable to use it. In many cases, particularly for inorganic oligomers, the precise formula is not known. Then the pillaring agent is given its general name, e.g. polyhydroxyaluminum, which in its dehydrated form is polyoxoaluminum.

Examples:

- pillared polyhydroxyaluminum montmorillonite;
- pillared polyoxoaluminum saponite.

Short cut names provide only the cation in the pillar, followed by 'pillared' and the name of the host layered compound, e.g. Cr-pillared montmorillonite; A1,Ti-pillared hectorite.

HIERARCHY OF MATERIALS

Layered compounds → intercalation compounds → pillared compounds.

REMARKS

1 Regularly ordered microporous materials, prepared by direct synthesis, are zeolites or molecular sieves. They cannot be called intercalation compounds or pillared compounds, because nothing has been intercalated.

2 If a guest molecule is intercalated during synthesis of the layered compound, an intercalated compound is obtained. If, after removal of the solvent, the material fullfils the thermal stability and porosity criteria of a pillared compound, it is called a pillared compound.

3 If, by adsorption of a compound, an amorphous material acquires an XRD pattern of a layered compound, it is called an intercalation compound. If, after removal of the solvent, the stability and porosity criteria for a pillared compound are fullfilled, it is a pillared compound.

4 Several other names have been circulating in the literature.

- Expanded layered structures (ELS) are obtained by the intercalation of organic molecules or coordination compounds. They are intercalation compounds. When heat stable and having porosity after removal of the solvent, they are pillared compounds.
- Molecularly engineered layered structures (MELS) are obtained by chemical bonding (grafting) of organic groups to the layered host. If they are obtained by direct synthesis, such as M(IV) phosphonates, the material may be porous. In this case, the material should be referred to as a molecular sieve. If the organic moiety is grafted on the surface atoms in the interlayer region of a preformed lamellar host, an intercalation compound is obtained which, when thermally stable and having porosity after removal of the solvent, may be a pillared derivative.

- Colloidal nanocomposites (CNC) have been termed 'amorphous pillared' compounds. Because of their amorphous character, it is incorrect to call these pillared compounds. They are simply colloids.

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