

## Synthesis and Application of Nanolayered and Nanoporous Materials

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Nanoscale materials are currently an attractive research subject because their properties are in contrast to their macroscopic counterparts. An inert material, such as bulk platinum metal for example, is known to exhibit a catalytic properties when its size is reduced into nanoscale. A stable material can become flammable or combustible, such as aluminum, and isolator material can become a conductor. Many attractive quantum phenomena also arise from reducing a material size into nanoscale dimensions. This review article discusses the concept, synthesis, and characterization of organic and inorganic nanolayered and nanoporous materials; and their application to catalysis and adsorption processes. Past achievements and future perspectives in the field of nanomaterial researches will be discussed as well. Furthermore, in the era of green chemistry, nanomaterials with all their derivatives are also required to have sustainable characteristics, such as biodegradable and renewable; which emphasizes that the development of nanomaterials in the framework of green chemistry should always be a priority. Through the synthesis of novel and functional nanomaterials using natural and local-based materials around us that are environmentally friendly and relatively easy to be obtained, our goal toward the inheritance of a greener world for the future generations is not an impossible dream.

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### 1 Introduction

At present, there is still no agreement on the definition of nanomaterial among the experts. However, the terminology of nanomaterial itself is commonly associated with the materials whose dimension lies within 1 - 100 nm and typically has different characteristics with their bulk counterpart. The construction of nano-

material requires nanotechnology approaches. Nanotechnology is defined as the synthesis and application of ideas from science and engineering to the understanding and tool production of new materials in nanoscale. Nanomaterials have been investigated for more than two decades in multidisciplinary and interdisciplinary

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throughout nanotechnology approaches<sup>1-6</sup>. Chemistry, particularly the discipline of materials chemistry, as a branch of science that deals with the material synthesis also has contributed significantly to the recent advances of nanomaterial, especially in the fine control and delivery of unique nanomaterial characteristics.

Most of the nanomaterial researches today are focused on the structure design. Several nanomaterial structures, particularly based on the weak bonds and organic systems (nanosupramolecular materials), are designed through the nanotechnology of crystal engineering. With the crystal engineering, various types of porous and layered materials with nanoscale dimensions have been successfully synthesized. Their characteristics have been identified, and they have been applied in industry, medicine, pharmacy, and agriculture<sup>1,7</sup>. The weak bonds and their complementarity, molecular recognition, self-assembly, pre-organization, and self-replication play an important role. As a result, nanomaterial research tends to be interdisciplinary activities that require mastery of research procedures of chemistry, physics, biology, mathematics and adequate engineering.

This review discusses nanolayered and nanoporous materials that are widely used as adsorbents, catalysts, antibacterials and other applications. Nanolayered material is a layered structure nanomaterial, such as clay and graphite, while nanoporous material is a nanomaterial that has nanoscale pores, such as zeolite and pillared clay. Table 1 shows the classification of nanoporous materials based on their pore dimensions.

## 2 Layered and porous nanomaterial with inorganic materials base

As the name suggests, this type of nanomaterial is built from inorganic components. A widely studied group of layered nanomaterials includes clay, hydrotalcite, layered titanium(IV) phosphate and vanadium pentoxide gel, while from the group of porous nanomaterials are zeolites, pillared clay and silica. These materials have been actively studied in the Material Cluster, Department of Chemistry, FMIPA, Universitas Gadjah Mada. Some nanomaterials that become the focus of research are clay, hydrotalcite, zeolite, silica and pillared clay, which will be the subjects of the following discussions. The structures of zeolite, clay and hydrotalcite are depicted in Figure 1.

Clay, including nanoclay, is an aluminosilicate compound layer architected with interlayers cations that are generally interchangeable. Bentonite is a trade term for a type of clay that contains montmorillonite (smectite) more than 85%. This type of clay is found in almost all the areas of Indonesia with a high deposit. The remaining fragment is generally a mixture of mineral quartz or cristobalite, feldspar, calcite, gypsum, kaolinite, plagioclase, Illite, etc. Structurally, montmorillonite has three-layer structures with octahedral alumina layers as a central, stacked between two tetrahedral silica layers. The composition of montmorillonite from bentonite varies depending on the

**Table 1** Different types of pore in a material<sup>8</sup>

Pore size	Classification	Examples
< 2 nm	Microporous	Zeolite-based materials, pillared clays
2 – 50 nm	Mesoporous	MCM-41, MCM-48, MCM-50, SBA-15, SBA-16
> 50 nm	Macroporous	Ceramic-based materials, porous gels, porous glasses



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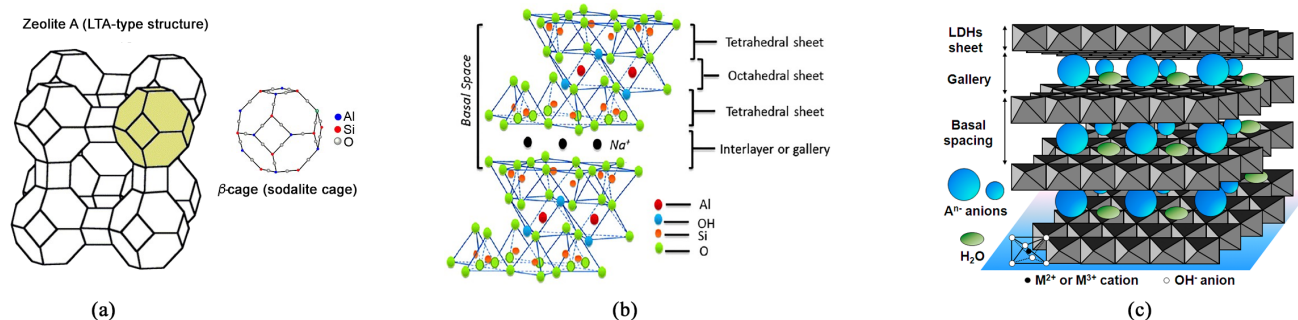
process of its formation in nature, and the origin of the bentonite was. General characteristics of bentonite are white colored base with a slight brownish or reddish or greenish, depending on the amount and type of the mineral fragments, has a very soft physical characteristic, mild, friable, taste like soap, easy to absorb water and do the ion exchange. Based on the cations composition in the inter-layers of bentonite that affect the deployment properties, bentonite is classified into two major categories, namely Sodium-bentonite (swelling bentonite) and Calcium-bentonite (non-swelling bentonite). Sodium-bentonite, often referred as a Wyoming bentonite, contains Na ions that are relatively higher than the Ca and Mg ions. This bentonite has an expanded characteristic when exposed to water, so that its suspension viscosity increases. On the other side, Calcium-bentonite contains Ca and Mg ions that are relatively higher than Na ions. When the bentonite is dispersed into water, it absorbs less water and settles quickly. Montmorillonite has a combination of ion exchange characteristic, intercalation and the ability to expand. The capacity for ion exchange is the basis of intercalation characteristic and its deployment capabilities. Based on the minerals ability to interact with various cations and neutral molecules, then almost all the intercalation process may occur. The most important characteristic of montmorillonite for adsorbent and catalyst is the ability to expand, which is influenced by the agent developer characteristic, the cation exchanger, the layer charge and layer charge location. Montmorillonite can adsorb polar organic compounds or cations between its layers. Adsorption of organic compounds form the organic-inorganic materials from the montmorillonite. The basal spacing of this material depends on the size and the density of organic molecules<sup>9,10</sup>.

As well as clay, zeolite is a mineral that has a high abundance and widely spread in Indonesia. More than 200 years ago, this mineral was found by Cronstedt in rocks that were used as a

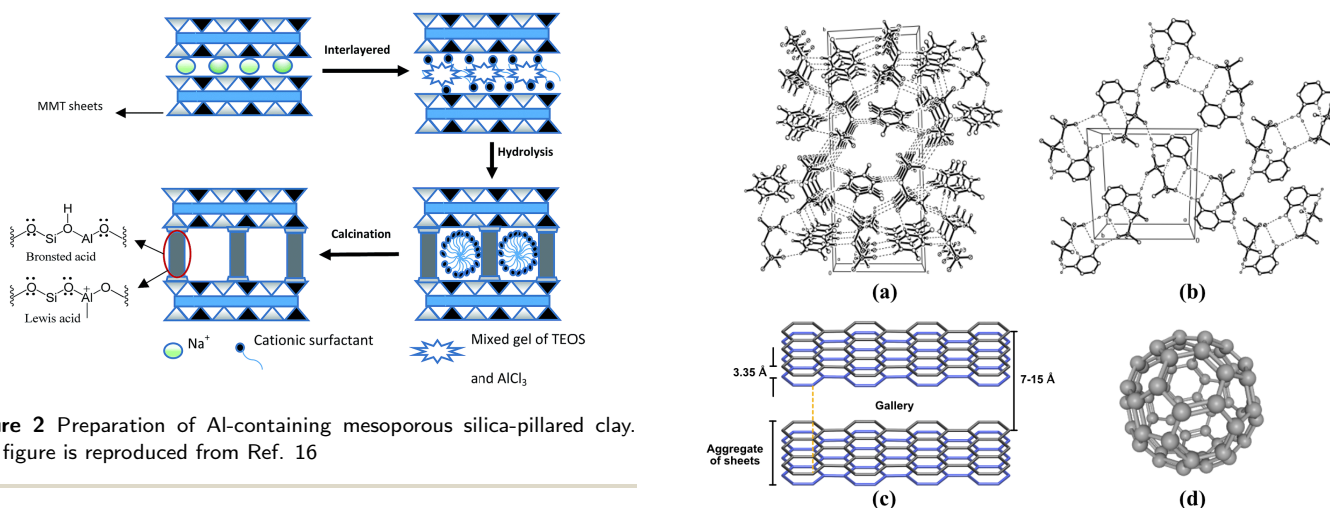
building material. This new species is a porous crystalline aluminosilicate which later was named zeolite, or stone that can boil. Mordenite is a member of the zeolites group that spread in nature with high abundance. Mordenite is in the zeolite micropore group (nanoporous) whose crystal structure is orthorhombic with canals or open channels. These canals or channels allow water and large-sized ions to move in and out of those channels. The size of the channels is diverse so that mordenite can function as molecular filters and adsorbents. In addition to mordenite, clinoptilolite is a member of zeolite group that is also encountered in nature. Clinoptilolite is a monoclinic crystal with a hardness level of 3.5 to 4 and has a high thermal resistance<sup>11,12</sup>.

Pillared clay is a porous material modified from clay. Chemically pillared clay is defined as the derivative of smectite where the cations are exchanged with bulk-sized cations, and those cations play a role as a pillar micelles, as shown in Figure 2. Several kinds of cations have been used as a pillaring agent, includes alkylammonium, bicyclic amine and some cation complexes. Pillared clay offers a route in the preparation of a new class of molecular sieving materials. Pore size formed through the variation of pillars can reach 2 nm, which exceeded the pore size of zeolites known today. In addition to the pore size, pillared clay has a specific surface area, total pore volume and thermal stability that are comparable to those of zeolite. Thermal stability of pillared clays spans to the temperatures of 500 °C. Unlike zeolite, pillared clay has a wider pore size distribution with relatively less homogeneous forms due to the semi-crystalline nature of pillared clay itself<sup>13,14</sup>.

Silica is a porous material whose main components are silicium and oxygen. Silica gel is a popular example of a silica material. It was invented and patented by Walter A. Patrick from Johns Hopkins University, Baltimore, Maryland in 1919. Silica gel has a chemical formula of  $\text{SiO}_2$ , a material that is similar to the sand component. The differences between silica gel and sand is that silica gel has a non-crystalline structure and highly porous, while sand has almost non-porous crystalline structure. Silica gel is an amorphous adsorbent with a stable chemical characteristic, specific surface area, high mechanical strength, and a non-uniform pore structure<sup>17</sup>. Other characteristics of silica gel are odourless, tasteless, non-toxic, inert, neutral and has a high sorption capac-



**Figure 1** The structure of (a) zeolite, (b) clay, and (c) hydrotalcite. The figures are reproduced from Refs. 2 and 15.

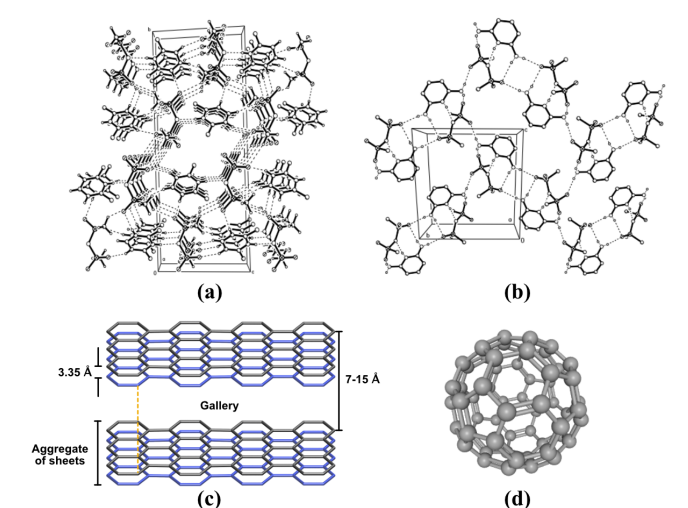


**Figure 2** Preparation of Al-containing mesoporous silica-pillared clay. The figure is reproduced from Ref. 16

ity to the water, thus it is used to reduce air humidity. Silica gel has been used in World War I as an adsorbent material in a gas mask. Silica compounds belong to the nanoporous material due to the average dimensions of pores below 100 nm<sup>14</sup>.

### 3 Layered and porous nanomaterials with organic material base

The formation of layered and porous materials with organic materials base through molecular recognition methods has been long reported. However, it started to become popular only from about two-decade recently after Lehn developed the concept of molecular recognition<sup>7</sup>. The molecular recognition is often interpreted as a chemical binding with a specific molecule. More broadly, molecular recognition is defined as the energy and information involved in the binding and selection of substrate by a given receptor molecule<sup>7</sup>. In molecular recognition, weak chemical bonds or secondary bonds, such as hydrogen bonding, van der Waals interactions, dipole interactions and synthon as a supramolecular fragment resulting from complementarity weak bonds play a very crucial role. Through the weak chemical bonds that are complementary and synthon, many varieties of layered nanomaterials and porous structures can be designed with a reasonably high accuracy (Figure 3). Among those weak chemical bonds, hydrogen bonds are the strongest and reliable in the design of layered and porous nanomaterials; thus, it became the most widely utilized bond in the nanomaterial structure design. Hydrogen bond is an attractive interaction between a proton donor with a proton ac-



**Figure 3** (a, b) Porous and layered Structure network formed from hydrogen bonds network<sup>10</sup>, while (c) graphite and (d) fullerene are formed by covalent bonds between carbon.

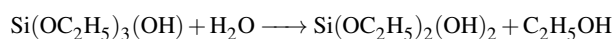
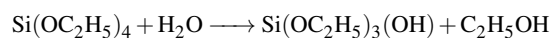
ceptor. Common proton donor groups are C-H, N-H, O-H, S-H, P-H, F-H, Cl-H, Br-H and I-H, whereas from the proton acceptor group are N, O, P, S, F, Cl, Br and I<sup>7</sup>.

In the principle of porous and layered nano supramolecule engineering, the selection of shapes and sizes of molecules complementary pairs and the presence of two or more subunits of the hydrogen bond will determine the final architecture and characteristics of the nanomaterial. Some examples of layered and porous nano supramolecule are formed from a network of complicated hydrogen bonding, such as dimesylamide imidazolium, 1-adamantylammonium-dimesylamide, 2,6-diamino-4-pyridil-1,3,5-triazine-1-ium dimesylamide, and 2,4,6-Tri-amino-1,3,5-triazinium-dimesylamide. These compounds are known to have a layered structure and 2,6-dimethylpyridinium-dimesylamide, 2,6-diamino-4-oxo-3,4-dihydro-pyrimidine-1-ium-dimesylamide, acet-amidinium-2-thioxo-2,3-dihydro-pyrimidine-2-um dimesylamide are identified to have a porous structure with average dimensions below 100 nm<sup>18</sup>. However, whether a nano supramolecule will ultimately be interwoven with porous or layered structure is unpredictable. Nevertheless, crystal engineering technique can predict with reasonable accuracy at the level of its asymmetric unit.

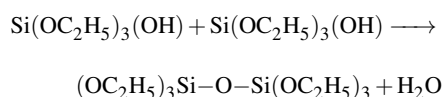
Other nanomaterials that are neither organic nor inorganic compound based, simply because they are constructed from elements, are graphite and fullerene (Figure 3). Graphite is an allotrope of carbon and classified as layered nanomaterials because it is composed of layers formed by hexagonal rings of carbon with interlayer separation distance of  $\sim 0.35$  nm<sup>19</sup>. Exfoliating a layer of graphite gives a two-dimensional material named graphene with exceptional properties<sup>20</sup>. Fullerene is also classified into a carbon allotrope that is conceptually a graphene sheet rolled up into a ball with pore sizes below 100 nm<sup>21</sup>.

## 4 Synthesis and characterization of nanomaterials

The sol-gel method, intercalation and inclusion are the preparation methods that are often used in the synthesis of layered and porous nanomaterials. This method is also used for the preparation of the derivatives of porous and layered nanomaterial, such as nanocomposite. The sol-gel method is a solid preparation method with a low-temperature technique that involves transitioning from a system with microscopic particles dispersed in a liquid (sol) into macroscopic materials (gel) containing a liquid. When the liquid evaporates, hard material such as glass remains. Sol-gel is an amorphous material and does not have a uniform pore dimension. Sol-gel synthesis is generally through the stages of hydrolysis and condensation. For example, nanosilica making process with sol-gel techniques can be written in two stages: alkoxide hydrolysis,

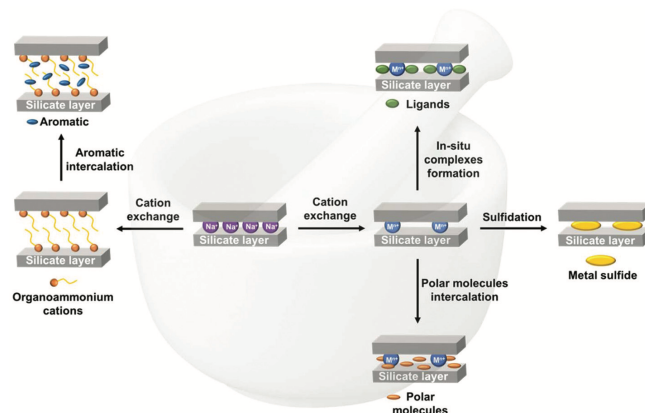


Followed by a condensation phase precursor into oxide networks,

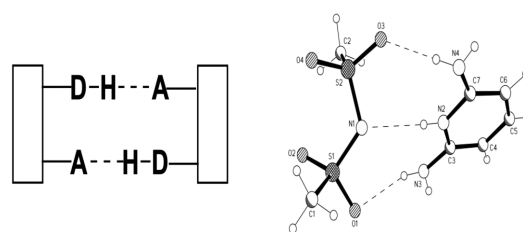


Parameters that must be considered in the sol-gel synthesis is pH. Changes in pH will lead to changes in networking and space group of nanomaterial<sup>19</sup>.

Intercalation is the reversible insertion of guest species into layered material while maintaining the features of the host<sup>13</sup>. Inclusion is the terminology for the insertion of guest species into porous materials. Intercalation belongs to the low-temperature reactions or *Chimie Douce* where the topotactic reactant is retained in the product. Ion exchange reactions are also included in the *Chimie Douce* group<sup>19</sup>. Intercalation technique, ion exchange, or inclusion are preferred because they are relatively easy and have fairly high reproducibility. Pillared clays are synthesized through the ion exchange and intercalation techniques various oxides such as Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> into the area between layers or gallery clay, so that pores with particular dimensions are formed. The basic phenomenon used in preparing pillared clay is cation interlamellar exchange with bulk cationic species that serves as a "prop" to keep the structure open (Figure 4).



**Figure 4** Schematic illustration of the process of intercalation of chemical species into the clay gallery. The figure is reproduced from Ref. 22.

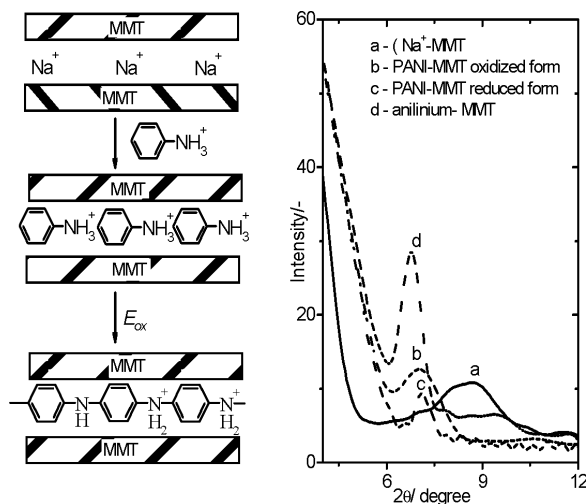


**Figure 5** Cocrystallisation (D: donor proton, H: protons, A: proton acceptor) between dimesylamine and 2,6-diaminopyridine. The figure is reproduced from Ref. 18.

Through hydrolysis and dehydration, the bulk cations are gradually converted into stable oxides that act as a buffer in between layers of clay. Pore size, specific surface area, thermal stability, pore radius, and total pore volume are determined from the size of the pillars, the space between them in the clay galleries, and the type of bulk cations that are used. The pillared clays characteristic can be identified through the analysis of X-ray diffractometry, electron microscopy, porosimetry method, and thermal analysis. The determination of dimensions and pore distribution is based on the study of adsorption-desorption isotherm of nitrogen at 77 K. The surface morphology can be analyzed by the method of electron microscopy. The pillars dimensions and galleries are determined by the method of X-ray diffractometry and the physical or chemical properties of the substance as it is heated was characterized by thermal analysis method (DTA and/or TGA)<sup>10,23</sup>.

Cocrystallisation between a species and its complement is the most popular technique in crystal engineering for the synthesis of porous and layered nano supramolecules with organic materials base. Coccrystallisation is the crystallization of two or more chemical species in a particular solvent simultaneously. Coccrystallisation product is a single crystal. The best single crystal was taken through a careful selection and then analyzed using single-crystal X-ray analysis techniques. From the study of single-crystal X-ray, the crystal can be brought to the final architecture (Figure 5).

*In situ* polymerization is one of the technique to prepare nanocomposite layered material (Figure 6). Polymerization tech-



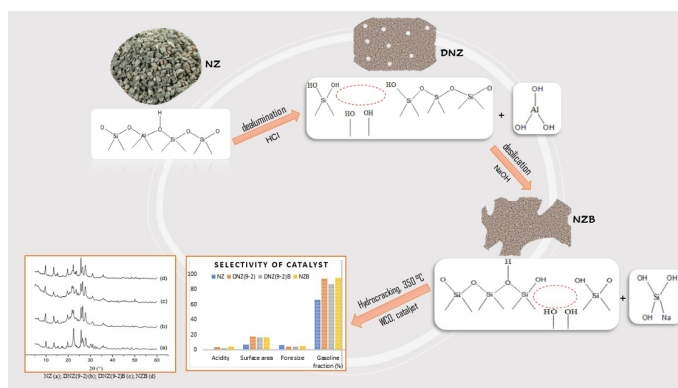
**Figure 6** Schematic illustration process of the layered nanomaterial electropolymerization *in situ*. The figure is reproduced from Ref. 24.

nique is usually preceded by an ion exchange between the monomer with exchangeable cations, or by monomers intercalation directly into the inter-layers or pores of the matrix followed by *in situ* polymerization. This polymerization method causes changes in the nature of the nanocomposite product dramatically, such as changes in conductivity and the matrix polarity. The success of the polymerization can be identified by using the technique of X-ray diffractometry analysis, IR-spectrophotometry and thermal analysis.

## 5 Nanomaterial as multifunctional materials: research achievements

Layered nanomaterial with nanostructures such as clay, graphite and hydrotalcite through nanotechnologies such as self-assembly and other preparation methods can be converted into functional materials with superior characteristics. Among them are nanocomposites with high mechanical, chemical and physical-properties, such as organoaluminium intercalated smectites and clay-polymer nanocomposite. The former can be used to absorb contaminants in organic species, which is difficult to dissolve in water, and the latter can be used as interior vehicle components. In industry, the zeolites are used as catalysts in the processing of petroleum, in the conversion of hydrocarbons into the chemicals with higher economic value (petrochemicals), and in the C1 technology (Figure 7). The characteristics of clay nanomaterial in binding and adsorb drugs and biomolecules also have brought attention to its potential as a drug delivery agent<sup>5</sup>. Montmorillonite, for example, has been studied for drug delivery to human's eye<sup>25</sup> and colon<sup>26</sup>. Nanoporous pillared clay, another derivative of natural clay obtained through pillarization method<sup>27</sup>, has been reported to be useful in water treatment<sup>28-30</sup> and greenhouse gas adsorption<sup>31</sup>.

Zeolite can be formed into a membrane gas separator with less dimension and applied in agriculture, livestock, and fisheries as an adsorbent and nutrient regulator. Pillared clay is porous nanocomposite is useful as a material of wastewater processing,



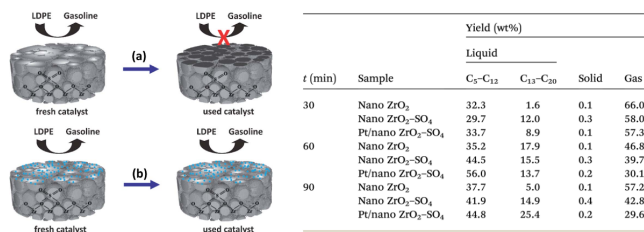
**Figure 7** Application of natural zeolite as hydrocracking catalyst. The figure is reproduced from Ref. 32

antibacterial matrix, cracking catalysts and photocatalysts. Silica with its exotic pores can be used as adsorbents and molecular sieves, or it can be formed into a nanocomposite that has potential as an adsorbent of heavy metal cations through the insertion of ligands. Pt/nano  $ZrO_2-SO_4$  was useful for converting LDPE plastics into biogasoline<sup>33</sup>.

The security of clean water, as well as clean air, is one of the colossal issue that remain as a goal for many research works<sup>4,6,34</sup>. With more than 95% of earth water is comprised of salty water, many nanomaterials have been developed for the purpose of removing salt content from saline water<sup>3,35-38</sup>, mainly through reverse osmosis (RO) mechanism. The nanoporous graphene membrane was reported to provide a greater permeability over the conventional RO membranes with 100% rejection rate to salt ions while allowing water passage at  $10 - 100 \text{ L cm}^{-2} \text{ day}^{-1} \text{ MPa}^{-1}$ <sup>39</sup>. By choosing an appropriate support, the mechanical integrity of nanoporous graphene can be maintained under pressure of ten times more than typical pressures for seawater RO<sup>40</sup>. It is interesting to note that decorating the layered graphene pores with hydrophilic group was reported to double the water permeation<sup>41</sup>. This shows the possibility to expand the nanoporous material capability in water desalination through the chemistry of functional groups<sup>36</sup>. Graphene oxide (GO), a chemical derivative of graphene, also found its potential as a water desalination membrane due to its convenient synthesis route in industrial scale<sup>42-44</sup>. The nanopores of GO allows water to pass exclusively, while it is impermeable to other chemical species including helium<sup>45</sup>. Other than graphene, composite membranes based on zeolite also have been applied for water desalination<sup>46-49</sup>. Molecular dynamics simulation study suggested that zeolite with pore size comparable to the first hydrated shell diameter of chloride can be expected to improve salt rejection rate<sup>47</sup>.

## 6 Future perspective of porous and layered nanomaterials

We laid out some facts about the unique nature of nanomaterials and multifunctional materials based on inorganic and organic base. Our research priorities lie in the material product of self-assembly between organic or inorganic species with an inorganic matrix. Through careful selection of guest and host species and



**Figure 8** (Left) A proposed illustration for the catalytic stability difference between (a) nano ZrO<sub>2</sub>-SO<sub>4</sub> and (b) Pt/nano ZrO<sub>2</sub>-SO<sub>4</sub>, and (right) products distributions from the hydrocracking of waste LDPE at various catalyst-to-feed proportions ( $T = 250^{\circ}\text{C}$ ,  $t = 60\text{ min}$ ). The figure is reproduced from Ref. 33

also by controlling the interaction of guest and host species, the derivative characteristics can be altered significantly to fit various purposes. With a motivated and inspired by the success of designing porous and layered nanomaterial and the guest species insertion into the gallery or pores, the synthesis of various types of novel intercalation and inclusion nanomaterials with a specific function can be expected.

In terms of layered nanomaterial research, the success of converting layered solids into nanopore solids with new microstructural and adsorptive properties has been followed up and developed continuously, however, high-precision control of the orientation and distribution of guest species within the interlayer will continue to be studied in the future. The study of interface dynamics, in particular the dynamics of molecular fluids and polymers in confined spaces, such as between layers or pores of nanomaterials has increased theoretical and experimental attention, because the results of this study have broad scientific and engineering implications. The study of interface dynamics is also relatively difficult to do due to the unified nature of the phases of the immersed guest species and the nanomaterial interface, which means that until now only a few analytical apparatus have been able to reveal these dynamics with high precision. Considering the limitations of existing analytical tools, an approach from the realm of computational chemistry through modeling and simulation would be of great help and be an alternative solution to these problems<sup>1,9,39,41,47,49,50</sup>.

In today's era of green chemistry, layered and porous nanomaterials and all their derivatives are also required to have green characteristics (biodegradable and renewable). Therefore researches that are oriented towards the engineering of smarteco nanomaterials should always be the priority of researchers. Through the use of synthetic raw materials as well as raw materials based on local genius materials that are environmentally friendly and relatively easy to obtain around us, hopefully our common dream about inheriting a greener world to our children and grandchildren will soon become a reality.

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