

Pillared clay: a new breed of catalyst

As finite supplies of crude oil begin to dwindle, refineries will find they no longer have ready access to easily refinable light crudes. Instead they will have to use heavier types that are more difficult to process.

To meet this expected change in circumstance, refineries will treat their crude more severely — more cracking and treating will be necessary to convert large, highly branched, or polycyclic hydrocarbon molecules into the smaller, lighter molecules required for petrol.

Catalytic cracking is more difficult with heavier hydrocarbons because the catalysts most commonly used are based on a group of minerals called zeolites, best suited to processing relatively simple, straight-chain molecules.

Dr Linda Bruce, Dr Terry Turney, and colleagues at the CSIRO Division of Materials Science and Technology, together with a research group at the Chemical Engineering Department of Monash University, led by Professor Joe Mathews, are investigating a different class of catalysts — pillared clays — that may prove suited to larger, moderately branched molecules.

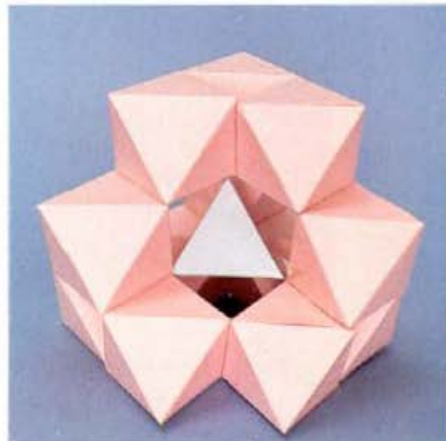
Pillared clays are made by processing common clays to give them the right pore size. As well as showing promise in 'cracking' and processes involving reaction with hydrogen, they have potential refinery applications in polymerisation — the reverse process to cracking — in which small molecules are built up to larger ones. They could also be useful in other refinery processes such as isomerisation, alkylation, and catalytic de-waxing.

Zeolites are aluminosilicates, consisting of a three-dimensional lattice of aluminium, silicon, and oxygen (see *Ecos* 23). Regular pores occur in the lattice like holes in a honeycomb, and

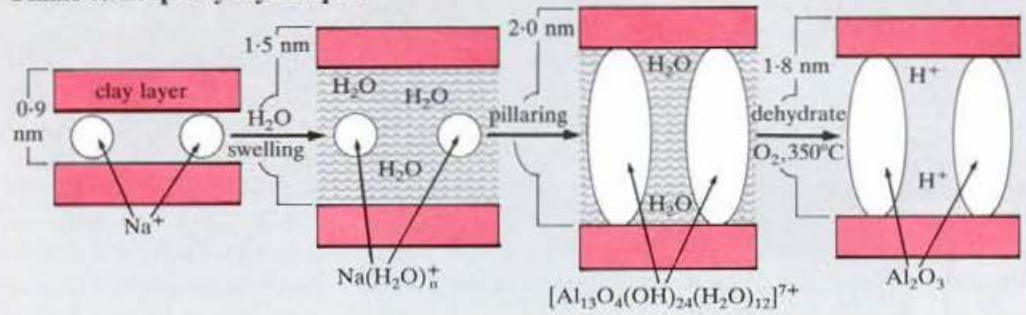
their size and shape vary depending on the type of zeolite (more than 100 are known).

However, the pore size is always less than 0.8 nm, preventing bulky molecules from gaining access to the

A model of a large ion that can prop open clay layers. It is $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, and at the centre of each back-to-back pyramid is an aluminium atom.



Pillars to keep clay layers apart



reactive sites contained within these pores. This means that heavier fractions can only be broken down by the relatively few active sites on the outside surface of these zeolite catalysts.

Pillared clays, first recognised by chemists more than two decades ago, also have well-defined pores, but they can provide, in theory, a huge range of pore sizes — anything up to three times larger than zeolites. An added attraction is that it should be possible to tailor the pore size and shape to fit specific requirements.

However, zeolites achieved commercial success before much progress had been made in controlling the properties of pillared clays. Only recently have chemists renewed their interest in these substances, partly because they saw, during last decade's fuel crisis, that greater flexibility in catalyst performance was needed for processing diverse natural and synthetic

The clay layers are prised apart and a large ion — a 'pillar' — is used to prop them open.

feedstocks — whether they be light or heavy crude, natural gas, methanol, ethanol, shale oil, or coal liquids.

Instead of the porous, but rigid, three-dimensional atomic lattice of zeolites, clays contain negatively charged layers, extending in two dimensions only. These layers loosely stack one on top of another like a pack of cards. The pack is only held together by relatively weak electrostatic forces; these arise from positively charged ions, sandwiched between the layers, that are needed to balance the charge.

(Talc has a similar structure, but in this case the layers are uncharged — so the intermolecular bonds between the layers are very weak and the material readily falls apart into a powder. At the other extreme, mica, with highly charged layers, forms thin extensive sheets.)

The formation of pillared

clays depends upon two properties of the natural clay. Firstly, the interlayer spacing increases when the clay is wet — that is, it swells. Secondly, swollen clay can exchange the naturally occurring interlayer ions, usually sodium or calcium, for much larger polymeric cations.

If the swollen, ion-exchanged clay is now heated, the water is driven off and bulky ions (or their decomposition products) form a network of pillars. The pillars in this pillared clay prevent it shrinking back to the original interlayer spacing.

Scientists can readily determine the height of the pillar by X-ray diffraction, and they can alter the size of the aperture between the pillars by varying the number, charge, size, and shape of the pillars.

Australia has extensive deposits of swelling clays — just ask those people in Melbourne and Adelaide whose houses are built upon the stuff. Australian industry could possibly make economical catalysts through working such deposits.

The CSIRO group, which is experimenting with a number of different cation pillars, has regularly achieved pore sizes of 0.9 nm, and has made some pillared clays with a gap twice that. The ultimate aim is to devise ways to consistently achieve desired pore sizes and pillar densities.

At present, the ion most often used as a prop is a polymeric oxoaluminium cation, partially hydrolysed,

that is found in aluminium chlorhydrol — the active ingredient in cans of anti-perspirant. It is a large ion — $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$.

The research workers compare their newly prepared catalysts with commercial zeolites in experiments that involve passing a mixture of heated hydrocarbons over small samples of the catalyst in a reaction tube. They analyse the product stream by gas chromatography; the main property they measure is the catalyst's selectivity for particular sizes and shapes of molecules.

One problem encountered is that pillared clays — like other catalysts — tend to coke up with use and require regeneration. The more active the catalyst is, the faster it cokes up.

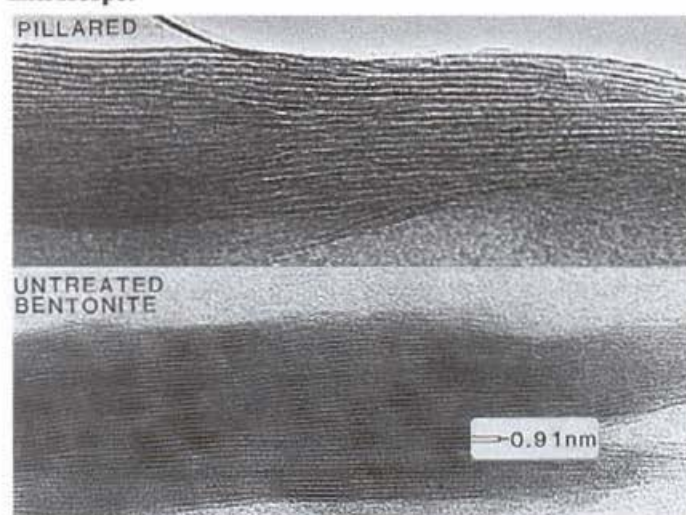
The answer, they find, is to carry out ion-exchange on the clay after pillaring. If the exchange is done in a particular fashion (which is proprietary at the moment), then coking is largely prevented.

To regenerate their catalyst they heat it in a stream of oxygen. Using this method, they have successfully regenerated one sample 14 times. The usual catalyst-regeneration method — heating with steam and then air — won't work because the combination of heat and water decomposes the clay.

Another of the group's interests is in incorporating an active Fischer-Tropsch (F-T) catalyst — like cobalt or iron — into a pillared clay. Normal F-T synthesis creates chains of hydrocarbons from carbon monoxide and hydrogen. Control of the chain length is particularly difficult, so that very short and very long chains appear — yet these are not particularly useful for liquid fuel production.

Theoretically, a maximum of only 27% of the hydrocarbon can be produced as distillate (hydrocarbon

Clay before and after pillaring, as seen through the electron microscope.



chains with 10–20 carbon atoms) by F-T synthesis using current catalysts. If a pillared clay with a pore size of 1.5–2.0 nm could be produced, F-T synthesis of transport fuels, particularly distillate, could be made very much more efficient by selectively increasing yields.

In 1985, a plant to turn methanol (derived from natural gas) into gasoline began operating in New Zealand. It uses a zeolite catalyst and does not produce distillate or heavier fractions. But if pillared clays live up to their promise, they may provide a route from natural gas to such fuels, which are essential for aviation and industrial use, as well as enhancing the versatility, cost, and efficiency of refinery processing of crude natural oils.

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Pillared clays as catalysts for cracking of C₈ hydrocarbons. L.A. Bruce, T.W. Turney, P.T.T. Ho, and J.F. Mathews. *Proceedings, Chemeca 86 conference, Adelaide, August 1986.*