

Sulphide Pillared Interlayer Clays

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Stable two dimensional zeolitic-type materials containing Fe sulphide pillars have been prepared by ion exchanging a smectite clay with polyhydroxy cations of Fe, followed by a sulphiding treatment at elevated temperatures.

The cations trapped between the layers of a naturally occurring smectite clay can be exchanged with large inorganic hydroxycations to produce a material which after calcination contains oxide pillars. These pillared interlayer clays (PILC) may be synthesised with interlayer spacings from 0.4 to about 1.5 nm and with large (>2.0 nm) lateral spacings between the pillars. Consequently, the cavities in PILC are much larger than the channels or cages in a typical zeolite.

There has been a surge of interest in PILC recently¹⁻³ because of the possibility that they could be used as cracking catalysts for the treatment of very heavy crude oil fractions. Only alumina or zirconia pillared clays have been studied in any detail as catalysts although the preparation of Fe oxide⁴ and Cr oxide⁵ PILC have been reported. All the PILC described in the literature contain oxide pillars.

We have now obtained results which demonstrate for the first time that oxide pillars can be converted into sulphide pillars while still retaining the overall PILC structure. Such

materials are of interest as catalysts because many sulphides are known to be active as hydrogenation or hydrotreating catalysts. Combination of the acidic properties of a PILC with

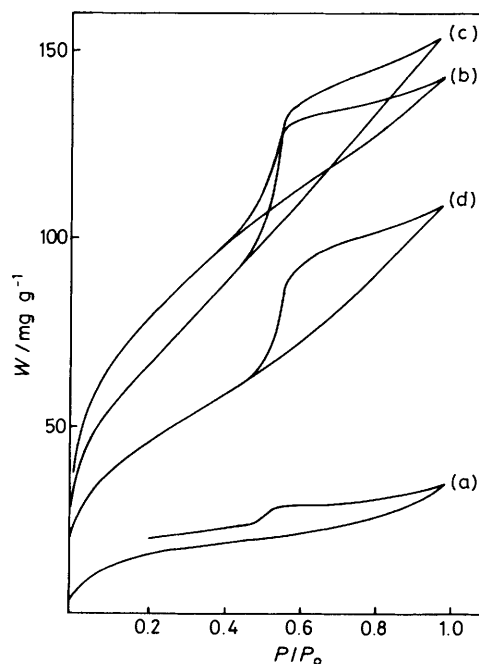


Figure 1. Nitrogen adsorption isotherms at 77 K for (a) the original clay; (b) the Fe-pillared clay after drying at 373 K; (c) the Fe-pillared clay after calcining at 773 K; (d) the sulphided pillared clay. W is the weight of nitrogen adsorbed by the samples, P/P_0 is the relative partial pressure of nitrogen.

Table 1. Surface areas (S) and pore volumes (V) of various samples.

Sample	S_{BET}^a	S_{meso}^b	V_{micro}^c	V_{meso}^d	V_{total}^e
Clay	58	15	0.015	0.026	0.041
Fe-PILC ^f	216	72	0.071	0.104	0.041
Fe-PILC ^g	192	105	0.056	0.131	0.187
Fe-PILC ^h	128	78	0.041	0.091	0.132

^a BET surface area, units $\text{m}^2 \text{g}^{-1}$. ^b Surface area of mesopores, units $\text{m}^2 \text{g}^{-1}$. ^c Micropore volume, units $\text{cm}^3 \text{g}^{-1}$. ^d Mesopore volume, units $\text{cm}^3 \text{g}^{-1}$. ^e Total pore volume, units $\text{cm}^3 \text{g}^{-1}$. ^f Pillared clay after drying. ^g Pillared clay after calcination. ^h Pillared clay after sulphiding.

the hydrogenation activity of a sulphide pillar creates a unique catalytic microenvironment.

The sulphide pillared interlayer clays (SPILC) were prepared following Tzou⁶ by using a Na-exchanged montmorillonite. The Fe-PILC were sulphided in a 10% H₂S-H₂ mixture at 673 K.

At each stage in the preparation the physical structure of the samples was investigated by analysis of the N₂ adsorption isotherms measured at 77 K. X-Ray diffraction (x.r.d.) analysis was used in an attempt to determine the expansion of the interlayer spacing due to pillaring. The x.r.d. results showed that after introduction of the Fe the regular basal spacing of the clay was destroyed. No distinct lines corresponding to larger interlayer spacings were observed. This indicates either that the pillaring has produced a range of interlayer spacings or that during pillaring the clay has become delaminated and that during drying delaminated aggregates are preserved.²

Figure 1 shows the N₂ adsorption isotherms for the various samples and Table 1 gives details of the calculated Brunauer-Emmett-Teller (BET) areas, the micropore volumes, and the mesopore volumes, all of which were obtained using standard procedures.⁷

The original clay has a relatively low surface area and a small mesopore volume. The hysteresis in the N₂ isotherm is indicative of very fine micropores.⁸ After drying, the Fe-PILC has a large surface area and a much larger micropore and mesopore volume than the original clay. Calcination of the Fe-PILC, which converts the pillars into Fe oxide, results in a decrease in surface area, an increase in mesoporosity, and a decrease in microporosity. Although sulphiding causes a further decrease in surface area and porosity the basic structure of the PILC is retained and the surface area is still twice that of the original clay. This sulphide-pillared clay

structure is stable during prolonged catalyst testing at elevated temperatures and pressures.

In conclusion, it has been demonstrated that stable Fe sulphide-pillared clays can be prepared. In work to be presented elsewhere it will be demonstrated that these materials are active catalysts for a range of hydrotreating reactions.

We are grateful to the S.E.R.C. for financial support of this research.

Received, 17th September 1986; Com. 1335

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