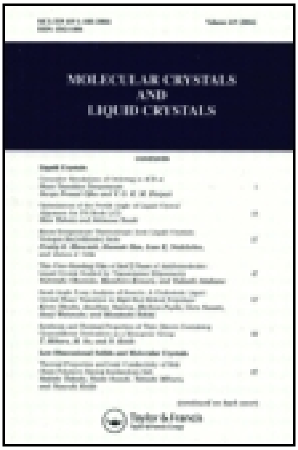

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Tantalum Pillared Montmorillonite: A New Family of Bidimensional Microporous Catalysts

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TANTALUM PILLARED MONTMORILLONITE: A NEW FAMILY OF BIDIMENSIONAL MICROPOROUS CATALYSTS.

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Abstract Careful control of (i) the hydrolysis of $Ta(C_2H_5)_5$ in ethanolic solution and (ii) of the pillaring process allows the synthesis of a stable tantalum pillared montmorillonite (Ta PILC).This solid presents a basal spacing of 26 Å after calcination at 500°C. The surface area and the microporosity were evaluated by N_2 adsorption isotherms and through the α_S-plot method.

INTRODUCTION

The pillared clays (PILC) are solid acid materials synthesised by interlayering expandable clays with polyoxocations as pillars. These oxide intercalated clays can be used as bidimensional microporous catalysts. The choice of different pillar precursors produces a large variety of pillared clays with different properties. These solid properties depend also on synthesis conditions : ageing temperature, ageing time, solution pH, concentration of pillaring precursor, existence of molecular additives in the solution.

The intercalation of several inorganic pillars have already been studied: Al , Zr, Si, Fe, Ti, Ni, Ga,Ta and Cr (4, 5, 6).

Only one reference exists where tantalum is used as a pillar precursor. The obtained solid exhibits a surface area of 70 m^2/g and a basal spacing of 19.1 Å at 350 °C. This pillared clay collapses at 400 °C (7).

In the present paper the first results concerning montmorillonite intercalation with tantalum ethoxide are presented as well as a comparative study of structural and textural properties of tantalum pillared clays resulting from the use of different concentrations of pillaring precursor, and the influence of addition of acetic acid during the preparation.

EXPERIMENTAL

Synthesis

The clay used in this work is a sodium montmorillonite: Kumine-Pure F commercialized by Kumine Industry Co. Ltd.. The tantalum pillaring solution is formed by dissolving tantalum ethoxide $Ta(C_2H_5)_5$ in an acidified ethanolic solution.

In the pillaring process 50 ml of a Na^+-montmorillonite suspension, 10 g clay/l of water, is added slowly, dropwise, stirring continuously, to 200 ml of the tantalum alkoxide alcoholic solution. The final suspension is vigorously stirred at room temperature for three hours. The samples are centrifuged and washed with distilled water five times until the conductivity of the residual water remains constant. The samples are finally dried at 100°C.

The meq Ta/g clay in the pillaring suspension, and the presence of CH_3COOH in the prepared samples are listed in table 1.

TABLE I. Prepared samples

Sample	meq Ta/g clay	meq HCl/g clay	acetic acid ml/g clay
Ea3	2.31	1.5	5.0
Ea4	3.08	1.5	5.0
Ea5	3.86	1.5	5.0
Ea6	4.63	1.5	5.0
Ea7	5.40	1.5	5.0
Ea31	2.31	1.5	---
Ea32	3.08	1.5	---
Ea33	3.86	1.5	---
Ea34	4.63	1.5	---

Characterization

In preparation for XRD analysis, a few drops of the sample suspension were deposited on a glass plate and dried at room temperature. The interlayer distance, in Å, can be directly obtained from X-ray diffraction measurement by subtraction from the first order reflection, d(001), the thickness of the silicate layer (9.6 Å). The XRD spectra were recorded, between 1.5 and 20 2Θ at 100, 200, 300, 400, 500 and 600°C with a Siemens D5000 apparatus. In this way, the pillared/non pillared montmorillonite ratio, as well as the evolution of the pillar size, can be analysed as a function of temperature.

The study of the texture was carried out by nitrogen adsorption using a Micromeritics A.S.A.P. 2000 apparatus . The values of specific surface were calculated by the BET equation. The α_S-plot method (8,9) was used to determine the developed external surface area and microporous volume.

RESULTS

Pillared clays synthesized with acetic acid at different meq Ta/g clay ratios were dried at room temperature and subjected to X-ray analysis at different temperatures. These results are presented in figure 1.

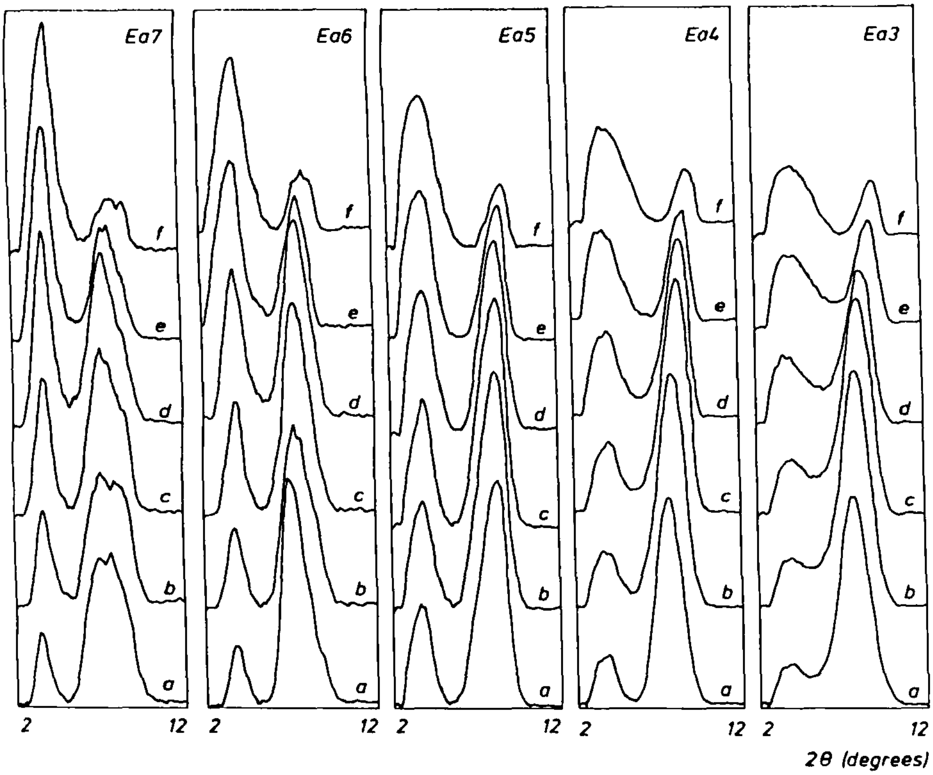

FIGURE 1 : XRD spectra . Calcination temperature: (a) 100°C; (b) 200°C; (c) 300°C; (d) 400°C; (e) 500°C ; (f) 600°C

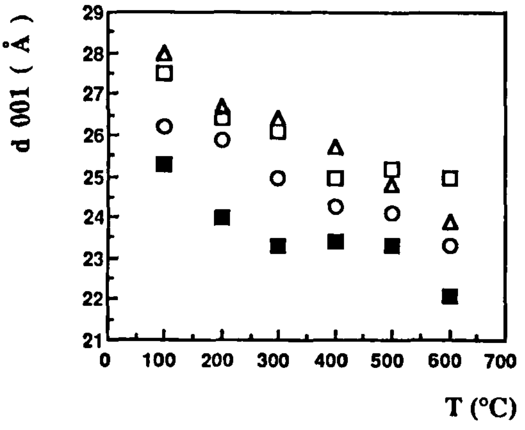

FIGURE 2: Evolution of basal spacing with calcination temperature.

□ : Ea5 ○ : Ea6 ; ▲ : Ea7 ■ : Ea34 .

Figure 1 presents the first order reflection, d(001), for: (i) pillared clay,Ta-PILC, at lower diffraction angles and (ii) non pillared clay, indicating that not all the initial montmorillonite has been interlayered.

The thermal stability of these samples was studied by comparing the basal spacing developed by the tantalum pillared clays at different temperatures. Figure 2 presents the relationship between the pillar clay size and the calcination temperature.The interlayer distances were accurate within the limit of +/- 1Å and depended on the peak width.

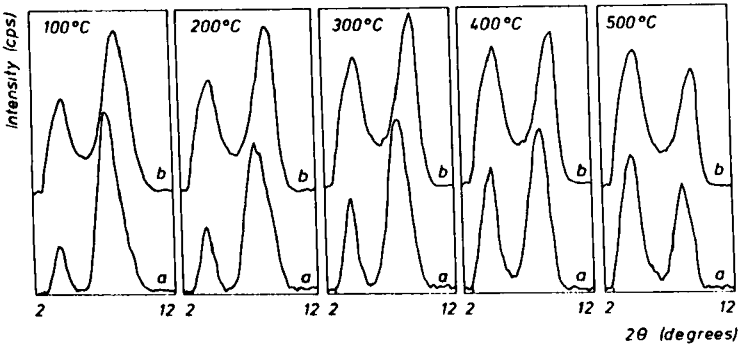

FIGURE 3 : XRD spectra (a) Ea6; (b) Ea34 at different calcination temperatures.

Table 2 presents all the textural data for samples prepared with and without acetic acid.

TABLE 2: Textural data of prepared samples calcined at 500°C.

Sample	Stotal (BET) (m^2g^{-1})	Vtotal (BET) (cm^3g^{-1})	S total (αs) (m^2g^{-1})	S ext .(αs) (m^2g^{-1})	Vmicr. (αs) (cm^3g^{-1})
Ea3	162	0.178	169	76	0.045
Ea4	148	0.136	146	59	0.047
Ea5	126	0.130	126	57	0.037
Ea6	163	0.114	163	100	0.036
Ea7	193	0.113	197	103	0.049
Ea31	117	0.111	126	63	0.027
Ea32	104	0.099	118	58	0.024
Ea33	106	0.087	109	63	0.021
Ea34	98	0.085	103	58	0.020

DISCUSSION

For samples prepared with acetic acid the increase of the tantalum concentration in the clay pillaring solution improves the development of the pillared clay structure. As shown (fig.1), a narrower peak width and a greater intensity are obtained for samples with higher initial tantalum concentrations, i.e. Ea7. A minimal meqTa/g clay is required in order to have a well defined pillared clay diffraction peak. Lower quantities of meqTa/g clay than those used in the preparation of Ea3 do not show a diffraction peak for the pillared fraction. The obtained basal spacings are greater than almost all pillared clays synthesized to date (4, 5, 6), a maximum of 25.2 Å at 600°C was observed for the Ea5 sample. Heating to 600°C does not result in the collapse of the pillared clay structure, the stacking order of the clay sheets is maintained. This is good evidence of the thermal stability of the clays. The increase in the calcination temperature induces a better resolution of the diffraction line attributed to the pillared clay. Therefore, the heat treatment produces a narrower distribution of the tantalum oxide pillar size.

As with the samples prepared with acetic acid the clays prepared without acetic acid exhibits similar pillaring properties with increase in meq Ta/g clay and they also have a good thermal stability up to 600°C. See figure 2.

The ratio pillared/unpillared clay, for the same tantalum precursor concentration, is larger when the pillared clay is synthesized without acetic acid. For samples dried at 100°C the difference observed is at a maximum but decreases with thermal treatment.

All the nitrogen adsorption isotherms for the obtained solids are of type IV and their adsorption -desorption curves exhibit a hysteresis loop, of type B, at higher relative pressures (10). Both, the adsorption isotherm type as well as hysteresis loop shape are in accordance with the textural characteristics expected for pillared clays (10). The total surface area calculated by the BET equation is in good agreement with values obtained using the α_S-plot method for all samples tested.

As already discussed, for a identical meq Ta/ g clay ratio, a higher quantity of initial clay is pillared in the absence of acetic acid, resulting in a simultaneous decrease in microporous volume and total surface. Otherwise, the external surface area developed by the two groups of samples are quite similar.Therefore, the decrease in the surface area and microporous volume with increase in pillar density must be as a result of pore blocking.

Theoretically acetic acid can influence the Ta-PILC synthesis in two ways. Either by modifying the clay suspension properties or acting on the tantalum pillar precursor hydrolysis condensation step. First, during pillaring the tridimensional structure in the edges of the montmorillonite layers is broken and the aluminium is not bonded. In aqueous suspensions, therefore, Al-OH groups can be formed. When the montmorillonite suspension is at low pH values, these edges are positively charged. In this case the negatively loaded montmorillonite layer can interact with the positively loaded edges. In this way a " card-house" structure would be favoured and flocculation could take place (11). This would decrease the stacked order of the clay sheet and thus increase the mesoporosity. The acetic acid can modify the properties of the clay suspension by bonding to these edges and the interaction between edges and layers is inhibited, thus preserving the layered structure. Secondly, acetic acid could form a new molecularly modified metal alkoxide precursor. There is very little reported in the literature concerning the modification of the tantalum ethoxide reaction. However, P. P. Phulé (12) presents preliminary results regarding the reaction between tantalum ethoxide and acetic acid. The conclusions were that when the acetic acid reacts with tantalum ethoxide at room temperature a stable tantalum alkoxo acylate is formed. The hydrolysis-condensation step of the molecularly modified tantalum ethoxide produces a tantalum pillar precursor of a different nature to that which forms when the synthesis is carried out without acetic acid. The exclusion of acetic acid in the pillaring suspension does not result in a higher external surface area or a decrease in the stacking order of the pillared clay product. The acetic acid does not seem to influence the clay behaviour of the suspension, in our synthesis and analysis conditions.

On the other hand, the increase of the ratio of pillared/unpillared clay as well as the decrease of the interlayer distances for samples synthesized without acetic acid, seems to confirm the formation of a molecularly modified tantalum ethoxide. This results in the production of a tantalum pillar precursor with different characteristics than those obtained with acetic acid. This is translated in the different properties and behaviour of the final pillared clay.

CONCLUSION

A new family of pillared clays have been synthesized. These Ta-PILC have very interesting properties, i.e. high basal spacing and high thermal stability, i.e., 25.2 Å at 600°C.

The influence of acetic acid in the pillaring suspension seems to be associated with interactions with tantalum alkoxide, changing its hydrolysis-condensation behaviour rather than influencing the clay suspension properties.

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