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THERMOGRAVIMETRIC ANALYSIS FOR ACIDITY DETERMINATION IN PILLARED CLAYS

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Abstract

Thermogravimetric analysis of pyridine adsorption was applied to study the acidity at different temperatures of clays pillared with Al pillars and mixed Al–Ga pillars, in relation to the starting montmorillonite. These results were compared with those obtained by means of a pulse-chromatographic technique. The pillaring process produces a large number of acid centers in the samples. Al–Ga–PILC has a higher acidity than Al–PILC.

Keywords: pillared clays, surface acidity measurements, TG analysis

Introduction

Pillared clays are smectite clay minerals that have been modified through the introduction of large inorganic polyoxycations into their interlayer regions. The resultant materials, after calcination, contain oxide pillars capable of preventing the collapse of the interlayer spaces. This generates a microporous structure, a high specific surface area and the presence of acid centers both on the surface of the layers and on their pillars, which makes these materials suitable for use as adsorbents and catalysts [1–4].

To prevent the clay from sintering, the thermal resistance of the pillars must be increased. One well-tested way of achieving this is to use mixed pillars. We applied Ga^{3+} as a stabilizing cation in pillars of Al polyoxycations. The thermal and hydrothermal stabilities of this material are higher than those of products pillared only with Al; at the same time, the new material has similar acid properties [5].

In general, in pillared clays, the acidity associated with Lewis centers present in the pillars predominates over that of the Brönsted centers, which arises mainly

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from the structural hydroxyl groups in the layers. It is therefore important to evaluate the nature, number and strength of the acid centers of materials to be used as catalysts [2, 6].

In the present work, we used the thermogravimetric analysis of pyridine adsorption to study the acidity at different temperatures of the starting material and pillared clays: one with only Al pillars and the other with mixed Al–Ga pillars. The results were compared with those obtained with a pulse-chromatographic technique.

Experimental

Starting material

The starting material for the preparation of the catalysts was a montmorillonite from Wyoming (Wy-Mont). The sample had a surface area of 33 $m^2 g^{-1}$ and a pore volume of 0.048 $cm^3 g^{-1}$ at P/P_o=0.98.

Synthesis

Preparation of the pillaring agent

An aluminium hydroxy oligomeric solution was prepared according to a previously reported method [7] to obtain an OH/Al ratio of 2.0. The method of preparation of the pillaring agent with Al and Ga was the same as that described by González *et al.* [5]. Appropriate volumes of NaOH were added gradually to stirred $AlCl_3 \cdot 6H_2O + GaCl_3$ solutions with an Al/Ga ratio of 12/1 in order to obtain an OH/(Al+Ga) ratio of 2.0. The solutions obtained in this way were aged at 333 K for 2 h before being used in the pillaring process.

Pillaring process

The solutions of pillaring agent were added during vigorous stirring to a clay slurry of 2.5 g/100 ml. The final proportion in the two cases was 20 mequiv of (Al+Ga)/g of clay, with a solid/liquid ratio of 0.5%. The reaction mixture was stirred continuously for 24 h at room temperature. It was then washed by means of dialysis with distilled water, using 1 l of water/g of clay. Dialysis was continued, with the water being renewed every 24 h until the Cl^- concentration had decreased to a point where the conductivity of the washed water was <30μS. Finally, the samples were freeze-dried.

Equipment and methods

Thermal analysis

This was performed in a Setaram TG-DSC 111 aparatus (France). The sample was first pretreated at 673 K for 2 h. Adsorption of pyridine was then carried out

at room temperature until the sample was saturated, followed by temperature-programmed desorption (TPD) up to 873 K in order to determine the number and strength of the acid centers.

Gas chromatography

This was carried out with a Perkin-Elmer Autosystem gas chromatograph. The surface acidity was measured by means of the gas-phase adsorption of pyridine, using a pulse-chromatographic technique [8]. The amount of pyridine adsorbed (μmol g^{-1} sample) was determined at different temperatures in the range 573–673 K. Pulses of 2 μl of an 1 M solution of pyridine in cyclohexane were injected into a N_2 flow of 20 ml min^{-1} until the sample was satureted.

All the samples weighed 10 mg and were previously calcined at 673 K for 2 h. The samples were re-heated in the reactor at 773 K for 30 min, and the temperature was then adjusted to the temperature for pyridine adsorption.

Determination of textural parameters

Specific surface areas were obtained by adsorption of N_2 at 77 K in a Micromeritics ASAP 2000 instrument, applying the BET equation to the initial points of the isotherm [9]. The total volume, V_p, was estimated to be the liquid volume of N_2 adsorbed at a relative pressure of 0.98. The *t*-plot method [10] was used to determine the total micropore volume.

Results and discussion

The textural evolution of the montmorillonite due to the pillaring process was analysed by adsorption-desorption isotherms established at liquid nitrogen temperature. The samples were outgassed at 413 K for 16 h under vacuum (10^{-3} mm Hg).

The specific area increased from 33 m^2 g^{-1} for the initial sample to 283 and 304 m^2 g^{-1} for Al–PILC and Al–Ga–PILC, respectively. When the samples were

Table 1 Surface area and volume of micropores of samples pretreated at different temperatures

Sample	S_{BET}/m^2 g^{-1}	V_p (0.98)/cm^3 g^{-1}	$V\mu_p$/cm^3 g^{-1}
		Temperature: 298 K	
Wy-Mont	33	0.048	–
Al–PILC	283	0.163	0.099
Al–Ga–PILC	304	0.234	0.109
		Temperature: 673 K	
Al–PILC	248	0.168	0.093
Al–Ga–PILC	320	0.209	0.117

pretreated at 673 K for 2 h, the specific areas were 248 and 320 $m^2 g^{-1}$ for Al–PILC and Al–Ga–PILC, respectively. These changes in S_{BET} are due to the water loss from the materials, caused by the temperature increase. In the Al–PILC sample, the surface area decreased because there was a loss of porosity in the material, whereas for the Al–Ga–PILC sample, the porous structure was maintained and the mass loss resulted in an increase in the surface area per g of sample (Table 1).

The specific surface area of the starting montmorillonite is due to mesopores (20–200 Å). The increase for the pillared samples is essentially related to the creation of micropores by the pillaring process (Table 1).

Figure 1 shows the pyridine adsorption until saturation in terms of time at 303 K for the starting sample and the two pillared samples. The Figure also de-

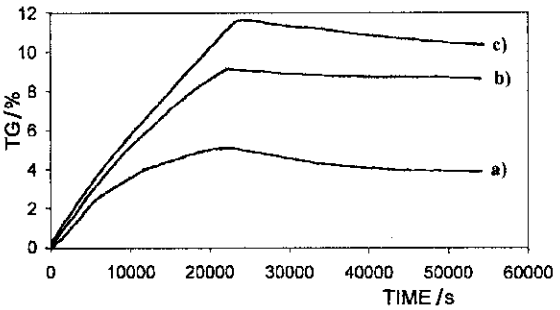

Fig. 1 Pyridine adsorption in terms of time for (a) the starting material, (b) the Al–PILC sample and (c) the Al–Ga–PILC sample

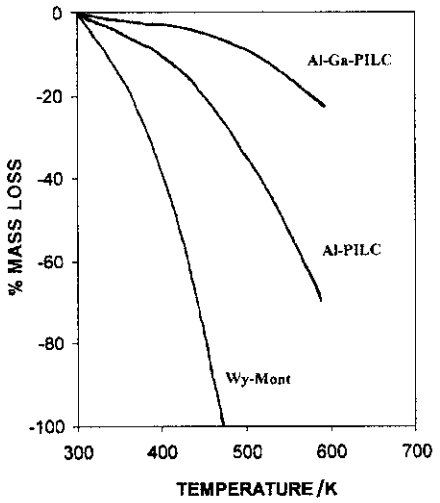

Fig. 2 Percentage mass loss of the adsorbed pyridine *vs.* temperature for the three samples

picts the desorption of physisorbed pyridine for 10 h under a flow of N_2. The smaller quantity of pyridine adsorbed for the starting material indicates the creation of acid centers by the pillaring process. The difference between the extents of pyridine adsorption for the pillared samples reflects the higher number of acid centers in Al–Ga–PILC.

Table 2 Pyridine adsorption (μmol Py/g sample) obtained by TG and GC techniques for the pillared samples

Temperature/ K	Al–PILC		Al–Ga–PILC	
	TG	GC	TG	GC
573	269	241	295	260
623	149	145	218	218
673	45	96	128	136

Figure 2 presents the percentage mass loss of the adsorbed pyridine *vs.* temperature for the three samples. It can be seen that 1) the starting sample lost most of the acid centers at low temperatures, and 2) over the whole temperature range tested, this percentage is always higher for Al–PILC than for Al–Ga–PILC. The mass loss from these samples correlates with the higher thermal stability of Al–Ga–PILC as previously reported [11].

Table 2 gives the pyridine adsorption data obtained by the TG and GC techniques for the pillared samples. The quantity of pyridine adsorbed/g of sample is always higher for Al–Ga–PILC than for AL–PILC over the whole temperature range tested. This indicates that there are more acid sites in Al–Ga–PILC than in Al–PILC. A decrease in acidity was observed for both samples when the temperature was increased.

Conclusions

The results indicate that the total pyridine adsorbed on the pillared samples is greater than that for the starting material, due to the pillaring process. Moreover, Al–Ga–PILC contains a higher number of acid centers than Al–PILC. This is true for the whole temperature range tested, which indicates the higher thermal stability of Al–Ga–PILC. A decrease in the acidity is observed for all samples when the temperature is increased.

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