Synthesis and Characterization of Tantalum Pillared Montmorillonite

Garbine Guiu and Paul Grange*

Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 2/17, 1348 Louvain-la-Neuve, Belgium

The preparation of tantalum pillared montmorillonite, resulting in a basal spacing of 26 Å at 500 °C, is described; dehydration of butan-1-ol results in a 100% selectivity to butene with no detectable formation of butylaldehyde or dibutyl ether.

Pillared clays (PILC) are a new class of microporous solid acid materials prepared by intercalating a metal oxide precursor between the layers of an expandable clay mineral. After calcination, a bidimensional zeolite-like structure is obtained. The size of the micropores are generally larger than those in the zeolite cage. The dimension of the microporous structure as well as the acid-base properties of the PILC depend on the nature of the chosen pillar precursor and on the pillaring conditions.

The most promising PILC for catalytic applications have been obtained by intercalation of polynuclear oxycations of Al and Zr. Nevertheless, several other precursors have been studied *e.g.* Si, Ti, Ga. Several reviews have been published on this subject.[1,2] The enlargement of the PILC family with new pillar precursors promises to be a very interesting advancement in catalysis but is severely limited by the difficult control of the solution chemistry of the metal ion used as the pillar precursor.[3]

The acid-base properties of tantalum oxide have been studied very recently, particularly the hydrated tantalum oxide. Much interest is shown in Ta_2O_5, due to its unusual properties as a solid acid catalyst.[4,5]

Only one attempt of clay intercalation with tantalum has been reported. The obtained solid exhibits a surface area of 70 m^2 g^{-1} and a basal spacing of 19.1 Å, after calcination at 350°C. This pillared clay collapses at 400 °C.[6]

Here we describe the synthesis of a stable, large pore, tantalum pillared montmorillonite (Ta–PILC) and present the preliminary studies of its acidic and catalytic properties.

The clay used is a sodium montmorillonite: Kumine-Pure F commercialised by Kumine Industry Co. Ltd. The tantalum pillaring solution is prepared by careful control of the hydrolysis of a tantalum alkoxide precursor, $Ta(OC_2H_5)_5$, in an ethanolic acidic solution. In the pillaring process, 50 ml of a Na^+-montmorillonite suspension, (10 g clay l^{-1} of water) is added dropwise, stirring continuously, to 200 ml of the tantalum pillar precursor solution. The final suspension, containing 4.63 meq Ta g^{-1} clay, was allowed to stand for three hours stirring vigorously at room temperature. The suspension was then centrifuged and washed with distilled water until the conductivity of the residual water remained constant.

The XRD spectra recorded with a Siemens D5000 apparatus at different calcination temperatures, illustrated in Fig. 1, allows the evaluation of the pillared/nonpillared montmorillonite ratio, as well as the evolution of the pillar size as a function of temperature.

The XRD spectra presents two peaks for the first order diffraction, one for pillared clay at lower diffraction angles, and another at higher diffraction angles due to non pillared clay, indicating that not all the initial montmorillonite had been interlayed. From this XRD analysis it was concluded that the Ta–PILC possesses a high thermal stability, the pillared structure was preserved even after calcination at 600 °C, and the basal spacing, 26 Å at 500 °C, is one of the greater values described in the literature.

The study of the texture was carried out by nitrogen adsorption using a Micrometrics A.S.A.P. 2000 apparatus. The nitrogen adsorption values were treated by the BET equation and the α-s plot method.[7] The BET surface area of the Ta–PILC sample at 500 °C was 180 m^2 g^{-1} and the α-s plot method confirmed that most of the developed surface area was due to microporosity. These results showed that, in spite of the extremely large size of the pillars, the high tantalum oxide content of the PILC reduced the microporous volume of the solid compared with that of Zr- and Al-PILC.[8,9]

The acidic properties were studied by TPD of NH_3. This consisted of adsorbing NH_3 (g) at 120 °C, on the Ta–PILC calcined at 500 °C. The chemisorbed NH_3 was then desorbed between 120 and 500 °C and measured using a thermal conductivity detector and the Kjeldahl titration method. The

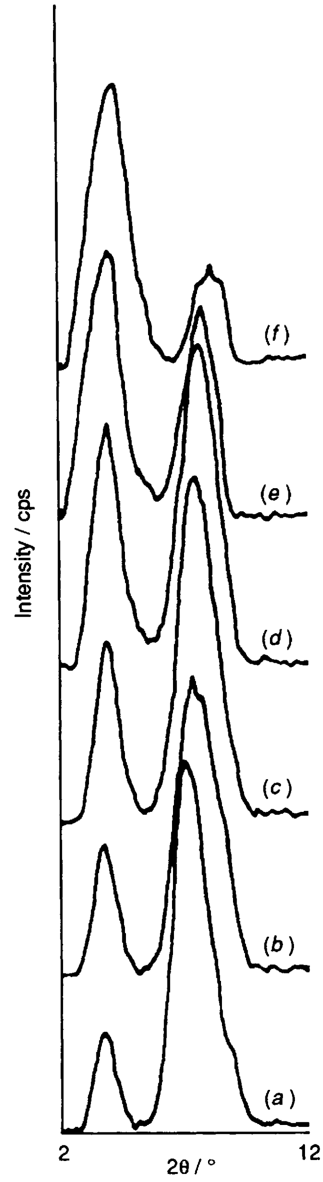

Fig. 1 XRD spectra recorded at several calcination temperatures: (*a*) 120, (*b*) 200, (*c*) 300, (*d*) 400, (*e*) 500 and (*f*) 600 °C

Table 1 Activity and selectivity of butan-1-ol dehydration over Ta–PILC calcined at 500 °C.

T/°C	Conversion (%)	Yield/µmol min^{-1} 1B	*cis*-2B	*trans*-2B	*Cis*-2B/*Trans* 2B
250	15.0	5.6	7.4	6.6	1.2
275	26.6	10.6	13.1	11.1	1.2
300	41.1	17.1	20.4	16.4	1.1

number of acidic centres on the catalyst surface obtained by this method was 600 meq g^{-1}. The acidity of this Ta–PILC is comparable to Al and Zr–PILC.[8,9]

Dehydration of butan-1-ol was used as a test reaction to characterise the catalytic properties of the pillared clay. The reaction was carried out in a continuous fixed bed glass reactor (4 mm, i.d.) at 1 atm. A sample of 60 mg (100–200 µm fraction) was used. A reactant mixture of helium saturated with butan-1-ol was then passed at a given reaction temperature (250–300 °C) through the catalytic bed (LHSV = 9.8 h^{-1}).

Using these reaction conditions, the conversions for Ta–PILC, (Table 1), are similar to those described for AL–PILC[10] and greater than those reported for Ti–PILC.[11] But the great advantage in the case of the tantalum pillared clays, with respect to all the catalysts (PILC or otherwise) described for the butan-1-ol dehydration, is the selectivity: 100% butene formation with no butyraldehyde or dibutylether detected.

Dehydration of butan-1-ol is frequently employed as a model reaction since it is possible to associate the reaction products with the nature of active centres on the catalyst surface.[12] The absence of butyraldehyde or dibutylether in the product stream[13] and the *cis*/*trans* but-2-ene ratio obtained from the but-1-ene isomerization reaction[14] indicates acid centres as the only catalytic sites present. From the isomerisation reaction it can be concluded that under the reaction conditons used a large proportion of the catalytic centres are of the type Brönsted.[14]

From the XRD and textural characterisation it is shown that for the first a thermally stable, large port Ta–PILC has been synthesised. The NH_3 TPD measurements indicate that its acidity is comparable to the Zr, Al, or Ti pillared clays, which are the most studies at the moment due to their potential industrial applications. The results from the catalytic test are very promising, because in addition to this PILC activity, the nature of the Ta–PILC active centres results in a 100% selectivity to the butenes.

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