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Reactive nanocomposites based on pillared clays†

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This work concerns the preparation of novel nanocomposite materials deriving from pillared clays, which have been functionalised by treatment with either vanadium pentoxide or *p*-toluenesulfonic acid, with the aim to obtain porous materials with oxidant or strong acid character, respectively. The synthesis involves the use of montmorillonites and saponites, as starting 2:1 charged phyllosilicates to give the alumina pillared clays employed as host matrices for reagent inclusion. Characterisation of the resulting materials was provided by chemical and thermal analyses, XRD, SEM–EDX, FTIR and XPS spectroscopies, specific surface area and porosity measurements, and electrochemical impedance technique. The reactivities of the nanocomposite materials have been tested with positive results in the oxidation of alcohols to carbonyl compounds, in particular in the oxidation of benzyl alcohol to benzaldehyde, and also in the syntheses of methyl *tert*-butyl ether (MTBE) and bisphenol A. Good correlation between the proton conductivity obtained from electrochemical impedance and the acid catalytic activity of nanocomposites containing *p*-toluenesulfonic acid has been found.

Introduction

Pillared clays (PILCs) are microporous materials derived from layered silicates which are expanded along the *c** crystallographic direction by the insertion of metal oxides (*e.g.* alumina) acting as 'pillars'. Such oxides are formed by thermal decomposition of oxy-hydroxide species that are initially introduced in cationic form by ion-exchange with homoionic samples of synthetic or natural silicates usually belonging to the smectite clays group: montmorillonite, saponite, beidellite, *etc.* The permanent separation gives interlayer regions which can be considered as galleries, making these materials like zeolites with a two-dimensional framework organisation (Fig. 1). Much work has been devoted in the last years to the study of these materials: see for instance the general overviews in ref. 1. Among this class of solids, the most widely studied are the PILCs containing pillars of alumina, which have been traditionally regarded either as acid catalysts and/or as potential selective adsorbents (molecular sieves). The insertion of active pillars with pre-determined chemical functions, such as oxidant character, has also been a challenge in order to obtain microporous materials useful for tailor-made applications. In this way, transition metal (Fe, Cr, Ti, Cu, *etc.*) oxides have been introduced as pillars between the silicate layers giving porous materials with different catalytic activities and stabilities.[1g,2]

We have developed an alternative strategy consisting of the modification of well characterised alumina pillared clays (Al-PILCs) derived from 2:1 charged phyllosilicates belonging to the smectite group. Such silicates include dioctahedral aluminium clays, such as montmorillonite ($[Si_8]^{IV}[Al_{4-x}Mg_x]^{VI}O_{20}(OH)_4(M_{x/n})^{n+}\cdot yH_2O$ ideal formula), where the layer charge originates from octahedral substitution of Al^{III} by Mg^{II}, and trioctahedral magnesium clays, such as saponites ($[Si_{8-x}Al_x]^{IV}[Mg_6]^{VI}O_{20}(OH)_4(M_{x/n})^{n+}\cdot yH_2O$ ideal formula), where the layer charge originates from tetrahedral substitution of Si^{IV} by Al^{III}. Thus, as we report in this work, the functionalisation of the alumina pillars located in the interlayer region by treatment either with vanadium pentoxide or with an arylsulfonic compound gives Al-PILC derivatives with marked oxidant or acid character, respectively (Fig. 1).

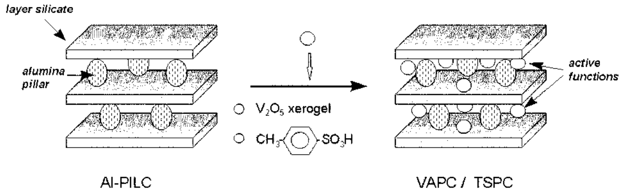

Fig. 1 Schematic representation of the preparation of reactive nanocomposites derived from Al-PILCs functionalised by vanadium pentoxide or *p*-toluenesulfonic acid incorporation giving VAPCs or TSPCs, respectively.

Vanadium pentoxide is generally considered as one of the most energetic oxidants,[3] requiring a strong acid medium, which is given by the presence of either sulfuric or perchloric acid.[4] Such experimental conditions result in oxidative reactivity which is often too high to control, so selective processes take place.[5] Although vanadium pentoxide, alone or associated with silica or other metal oxides, is intensively used in industrial catalytic oxidations (*e.g.* $SO_2 \rightarrow SO_3$ in sulfuric acid production), V_2O_5 is seldom used as an oxidant for organic synthesis purposes, unlike potassium dichromate.[6] For this reason, we have attempted to develop suitable oxidant systems based on supported V_2O_5 because of its ease of handling and its potentially controlled reactivity. In this way, we have used Al-PILCs as starting materials, V_2O_5 being homogeneously dispersed into the pore texture. In addition, it is expected that the reactivity can be also improved by the topological control of such a nanostructured environment. It is necessary to take into account that there are still two other main factors that must also be controlled in order to obtain solid state materials acting with effective oxidant character: (i) the accessibility of the reagents, either in aqueous or in organic media, to the V_2O_5 centres and (ii) the acid–base behaviour of the V_2O_5 environment. On the other hand, an additional role of such reagents may be expected, based on the control of the water content which appears to be critical in avoiding or favouring the further oxidation of carbonyl intermediates towards carboxylic acids [see for instance the use of chromium trioxide in pyridine (Sarett's reagent) to stop alcohol oxidation in the corresponding carbonyl compound[7]]. Based on the above

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concepts, we have successfully developed a new class of oxidant reagent, namely vanadium pentoxide doped aluminium oxide pillared clays (VAPCs), which possess unusual oxidative behaviour as well as a particular selectivity in certain organic reactions, compared with conventional V_2O_5 operating under the same experimental conditions. As a model reaction the oxidation of benzyl alcohol to benzaldehyde using VAPC materials was chosen. This reaction is also of interest because it constitutes one of the industrial routes for benzaldehyde preparation.[8]

On the other hand, arylsulfonic compounds derived from silica and silicates are functional materials showing strong Brønsted acidity useful for applications either as a stationary phase in chromatography or as catalysts for fine chemicals.[9–12] Compounds of this type have been obtained by grafting of phenyl groups onto inorganic solid surfaces *e.g.* treating silica and sepiolite natural silicate with organophenylsilanes. Further sulfonation of the aromatic rings gives arylsulfonic materials that can be compared to polystyrene sulfonic resins (*e.g.* commercial Amberlyst) exhibiting high cation exchange capacity and efficient acid catalytic activity. However, higher thermal stability, specific surface area and porosity than Amberlyst are characteristics of the arylsulfonic compounds derived from silica substrates.

In order to improve the acidity in PILCs we attempted the incorporation of a strong acid, *p*-toluenesulfonic acid $CH_3–C_6H_4–SO_3H$, with the aim to prepare new microporous nanocomposites with active and well dispersed sulfonic groups, *i.e.* to obtain modified PILCs, providing materials (TSPCs) which are useful as organic reagents that are otherwise difficult to handle. So, nanocomposite materials with strong acid character together with controlled topology can be efficiently prepared from PILCs. This new class of solids can be used as supported reagents or as heterogeneous catalysts. In addition, they exhibit interesting properties owing to their proton conductivity that could be potentially profitable for electrochemical device applications (fuel cells, H-sensors, *etc.*).

Experimental

Starting clays and pillared clays

Clays used to prepare the Al-PILCs were SWy-1 Wyoming montmorillonite supplied by the Source Clay Repository of the Clay Mineral Society, University of Missouri, Columbia, USA, and two saponites from Vicálvaro and Yunclillos, provided by TOLSA S.A., Madrid, Spain.[13] The Fulcat F22B acid activated montmorillonite from Laporte, which was used to obtain the pillared clay produced in large scale (Al-FULCAT 2C) by Papayannakos *et al.* (Greece), was also used.[14]

Clay samples were purified by water washing, recovering the <2 µm fraction, after treatment with a 1 M sodium chloride solution. This treatment provides Na^+-homoionic samples which were washed and dialysed with distilled water until free from chloride ions ($AgNO_3$ test).

Al-PILCs were prepared as described by Jacobs *et al.*[15] and Plee *et al.*,[16] *i.e.* mixing $Al(NO_3)_3·9H_2O$ and NaOH solutions until achieving a $OH/Al=2.4$ molar ratio. These solutions were added to 2% clay suspensions (Na^+-homoionic samples) and the mixture was continuously stirred for 2 h at room temperature. The resulting gel was dialysed until elimination of NO_3^- ions. Finally, the solid was centrifuged, air-dried at 60 °C (24 h) and calcined at 450 °C (6 h).

VAPCs

VAPCs were prepared by impregnation of Al-PILCs derived either from Wyoming montmorillonite or from saponites (Vicálvaro and Yunclillos samples) with an aqueous dispersion of vanadium pentoxide gel. The V_2O_5 gels were prepared by a sol–gel method as described elsewhere.[17] The general procedure for VAPC preparation consisted of the addition of V_2O_5 gel dispersed in water (10% w/w) to an aqueous suspension of either pre-pillared clays (*i.e.*, PILCs before calcination) or pillared clays (already calcined at 450 °C) using adequate amounts to produce a final V_2O_5–clay composition of either 10% or 30% (w/w) in vanadium pentoxide. The mixture was stirred and allowed to stand until the colour of the liquid phase disappeared. After filtration, the solid was air dried and, in some cases, was then thermally treated at 400 °C for several hours.

TSPCs

The synthesis of the TSPC materials was carried out by incorporation of *p*-toluenesulfonic acid into Al-PILCs previously obtained from Na-montmorillonite (Wyoming) or from acid-activated montmorillonite (Al-FULCAT 2C). The PILCs were impregnated with a solution of *p*-toluenesulfonic acid in methanol or acetone (2.5 mmol of acid per g of PILC) operating at room temperature. The mixture was continuously stirred for 10 min at room temperature. The solvent was then removed by using a rotatory evaporator and the product (residual solid) was dried at 50 °C for several hours and stored in vial flasks for less than 15 days before use.

Characterisation

The resulting VAPC and TSPC nanocomposite materials were characterised by different techniques: specific surface area (N_2 adsorption, BET) in a Coulter Omnisorp 100 model, XRD (Philips PW 1710 instrument with a Cu anode and Ni filter), IR spectroscopy (Nicolet 205XC FTIR spectrophotometer), SEM–EDX (Zeiss DSM 960), TG and DTA (Perkin Elmer TGA 7). XPS spectra (Fisons ESCALAB 200R with Al-Kα X-ray excitation source, $h\nu=1486.6$ eV, and hemispherical electron analyser; binding energy accuracy ±0.2 eV) were obtained without any specific cleaning treatment at the Departamento de Química Inorgánica, Universidad de Málaga, Spain. For the electrochemical impedance study, powders of TSPC materials were pressed (3 tonnes cm^{-2}) into pellets of 260–300 µm thickness and 13 mm diameter. The pellets were Au sputtered and subsequently sandwiched between two identical platinum electrodes in a conductivity cell. The impedance measurements were made in the frequency range 0.1 MHz–100 mHz with a Solartron 1255 Frequency Response Analyser coupled to a Princeton Applied Research PAR 273A potentiostat/galvanostat, and applying a 100 mV amplitude signal.

Reactivity tests

The general procedure to test the oxidant character of VAPCs required the use of an adequate amount of VAPC containing 0.3 mmol of V_2O_5 added to a solution of 0.15 mmol of benzyl alcohol in 1–5 ml of an organic solvent. The mixture was kept at a selected temperature for 24 h. Then the reaction mixture was cooled, filtered and thoroughly washed with methylene dichloride. The solution was diluted and ready for analysis of products using a HP 5890 Series II gas chromatograph with HP 5971 Series Mass Selective Detector (GC-MS technique) using a HP1 crosslinked methylsilicone 12 m column.

The general procedure followed to study the synthesis of bisphenol A consisted of a series of batch processes using Teflon vessels (autogenic reactors) in which acetone, phenol and the TSPC were mixed and heated in the 80–110 °C temperature range for different periods of time. The products were extracted with dichloromethane and then analysed by GC-MS.

The MTBE synthesis tests were performed at the Unité de

Catalyse et Chimie des Matériaux, Université Catholique de Louvain, Belgium.

Table 1 Variation of the specific surface area in saponite Al-pillared clay samples after V $_2O_5$ impregnation

Al-PILC sample/ V_2O_5 content	Specific surface area/m^2 g^{-1} before V_2O_5 impregnation	after V_2O_5 impregnation
Vicálvaro saponite/30% V_2O_5	223	169
Yunclillos saponite/10% V_2O_5	360	254

Results and discussion

VAPC nanocomposites

Vanadium pentoxide doped aluminium pillared clays (VAPCs) are obtained by treatment of either Al-PILC or their precursor ('pre-PILC', Al-oxyhydroxy cations intercalated into the clay minerals, *i.e.* non-calcined Al-PILCs) in an aqueous dispersion with V_2O_5 gel. Adsorption by the silicates is clearly inferred from the change of colour in a mixture of V_2O_5 gel with an aqueous suspension of either PILC or pre-PILC, from red–brown to a colourless supernatant. As indicated in the Experimental section, some of the PILCs loaded with the V_2O_5 xerogel were thermally treated at 400 °C for several hours.

The partial filling by the V_2O_5 of the intracrystalline PILC cavities is indicated by the decrease of the specific surface area of the resulting solids compared to the pristine material. Thus, for instance, the surface area of Al-PILC derived from Vicálvaro saponite changes from 223 to 169 m^2 g^{-1} when 30% of V_2O_5 is incorporated and from 360 to 254 m^2 g^{-1} for Al-PILC derived from Yunclillos saponite containing in this case 10% V_2O_5 (Table 1).

The V_2O_5 loading is practically quantitative as revealed by the EDX analyses of samples prepared under different experimental conditions as indicated in Table 2. Such analyses combined with the SEM imaging technique indicate: (i) the homogeneous distribution of vanadium in the resulting solid, and (ii) the typical texture of porous clay materials (Fig. 2). Occasionally, small crystals attributed to orthorhombic V_2O_5 deposited on the modified PILC can be observed in VAPCs containing 30% V_2O_5 that were thermally treated in the optional further calcination step. XRD patterns of such phases support this observation. From the EDX analyses it may be inferred that the main compositions of pre-pillared and pillared clays are found to be Al_2O_3 and SiO_2 (around 43% and 52%, respectively; samples 1 and 2 in Table 2). These samples also contain small amounts of Fe and Mg (1–3.5% MgO and Fe_2O_3, respectively) and other elements in minor quantities. Concerning the vanadium content, it appears that after treatment of both pre-pillared and pillared clays with vanadium pentoxide gels, V_2O_5 has been quantitatively loaded without significant changes in the compositions of the other elements contained in the low loaded (10%) samples (samples 3 and 5 in Table 2). The XPS spectra agree with these results showing also that the V(2p) signal of VAPCs (*i.e.* 516.9 eV in Al-PILCs containing 10% V_2O_5) appears at similar binding energies to the V_2O_5 xerogel (517.4 eV). A decrease in the Al_2O_3 content is observed by EDX after calcination at 400 °C for several hours of the 10% loaded samples (samples 4 and 6 in Table 2) and in samples with higher V_2O_5 content (samples 7, 8a and 9 in Table 2). After using of VAPCs in oxidation reactions of alcohols little apparent change in their elemental composition is observed (compare for instance samples 8a and 8b in Table 2).

Table 2 Composition (%) deduced from the EDX analyses of some VAPC samples obtained from Al-montmorillonite PILCs

Sample[a]	Al_2O_3	SiO_2	V_2O_5	MgO	Fe_2O_3
1	43.1	51.9	—	1.5	3.5
2	43.4	51.7	—	1.6	3.2
3	37.9	45.9	12.0	1.4	2.7
4	31.2	55.4	10.3	1.8	1.4
5	38.3	47.0	10.9	1.4	2.4
6	30.7	54.4	11.5	1.8	1.7
7	22.3	45.2	29.2	1.6	1.8
8a	23.0	45.8	28.0	1.4	1.8
8b	22.7	45.7	28.3	1.5	1.7
9	31.9	38.9	26.5	1.1	1.7

[a] 1. pre-PILC; 2. PILC; 3. 10% of V_2O_5–pre-PILC before calcination; 4. 10% of V_2O_5–pre-PILC after calcination; 5. 10% of V_2O_5–PILC before calcination; 6. 10% of V_2O_5–PILC after calcination; 7. 30% of V_2O_5–pre-PILC without calcination; 8a and 9. 30% of V_2O_5–PILC without calcination; 8b. 30% of V_2O_5–PILC without calcination after use in oxidation reactions.

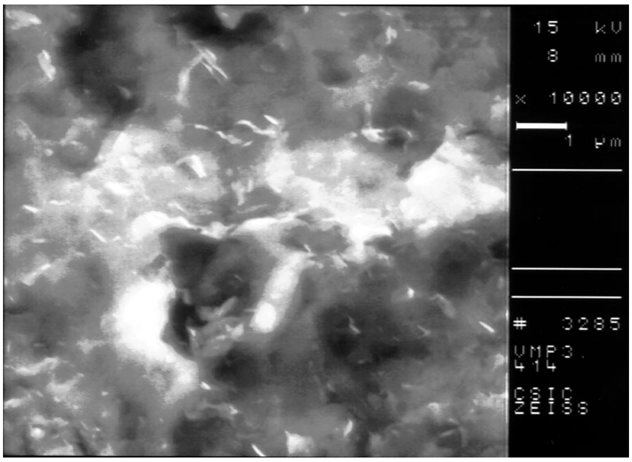


Fig. 2 SEM image of a VAPC derived from Wyoming montmorillonite Al-PILC containing about 30% V_2O_5.

The XRD patterns of starting AL-PILCs showing d_L basal spacing values of about 18 Å (see for instance Fig. 3B), indicate that the interlayer distance after V_2O_5 impregnation is maintained (Fig. 3C). In certain cases significant changes of the d_L values are observed. Some Al-PILCs loaded with V_2O_5 without further calcination show d_{001} peaks at 15.5 Å for 30% V_2O_5 content (see for instance Fig. 3D). Such changes are also observed in samples prepared by V_2O_5 impregnation of pre-PILCs showing, in these cases, interlayer distances around 16 Å before calcination. This behaviour could be related to

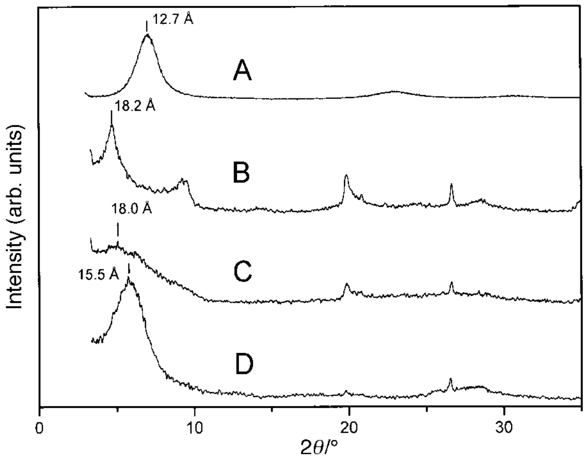
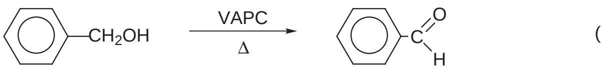


Fig. 3 XRD patterns of: A, V_2O_5 xerogel; B, Al-PILC from Wyoming montmorillonite; C, VAPC derived from PILC B, containing 10% V_2O_5 after calcination at 400 °C; D, VAPC derived from PILC B containing 30% V_2O_5 without further calcination.

the alteration of the pillar nature, even including changes in the pillar composition, *i.e.*, with the formation of interlayer clusters of complex nature. In this way the development of polynuclear species of vanadium oxide may be assumed, by condensation between hydroxyls of the intercalated Al-polyoxyhydroxy pillar species and the OH groups of the V_2O_5 gel at the pillar interphase. So, the formation of domains of aluminium vanadate species onto the alumina pillar surfaces can be postulated. Some changes detected in the Al XPS signals may be tentatively related to this hypothesis. The Al signal at 74 eV in Al-PILCs is observed as a broad band, close to signals observed in zeolites. Larger bands appear in VAPCs with a shift to higher binding energies as the V_2O_5 content increases, rising to about 75 eV for VAPCs containing 30% V_2O_5. Nevertheless, as the V(2p) XPS signals remain almost unaltered compared with the same signal in V_2O_5 xerogels, it could be inferred that most of the vanadium in VAPCs is present as vanadium pentoxide which is supported by the reactivity conferred to the Al-PILC. It is important to remark that the lack of (*hkl*) reflections in the XRD patterns assigned to orthorhombic V_2O_5 indicates that vanadium oxide is incorporated into PILCs as poorly crystalline phases, or as very small crystals in VAPCs with the further calcination step. It should be taken into account that V_2O_5 xerogel is thermally transformed into the orthorhombic V_2O_5 phase by heating at temperatures greater than 200 °C [ref. 17(*c*)].

The characteristic vibration modes of V_2O_5 could be detected in the IR spectra only after incorporation of significant amounts of such species into both PILCs and pre-PILCs. Fig. 4 shows the IR spectra of an Al-PILC before (Fig. 4A) and after (Fig. 4C) loading with 30% V_2O_5 together with the spectrum of a pre-PILC incorporating the same percentage of V_2O_5 (Fig. 4B). In the last two spectra the presence of bands at around 1010 and 770 cm^{-1} is observed; these are assigned to V=O and V–O stretching vibration modes, respectively, which are characteristic of V^V bonded to oxygen atoms in both the V_2O_5 xerogel and the orthorhombic anhydrous phase.

Between 60 and 170 °C the TG–DTA plots of VAPCs show a weight loss assigned to water molecules belonging to both the Al-PILC and the V_2O_5 xerogel. Above 400 °C the weight loss is attributed to hydroxyl groups of the system. The total weight loss depends upon previous thermal treatments applied to the VAPC samples (*i.e.*, drying, calcination, *etc.*). Beside the two characteristic endothermic peaks, at about 110 °C and about 640 °C, which are associated with the two types of processes indicated above, the samples containing the highest V_2O_5 content exhibit an exothermic peak at about 415 °C and an endothermic peak at about 760 °C in the DTA curves (Fig. 5). The exothermic peak appears as a small signal that can be ascribed to the crystallisation of V_2O_5 from the xerogel phase to the orthorhombic structure, whereas the peak at 760 °C can be tentatively assigned to the melting of small crystals of V_2O_5 or eventually to rearrangement processes involving V and Al oxides located in the interlayer region of the silicate. None of these last peaks are detected in the DTA curves of the pristine Al-PILC, or in VAPCs with low V_2O_5 content. These results suggest that a part of the V_2O_5 remains associated with the PILCs, retaining the characteristics of the xerogel phase. We have tested the application of VAPCs to the oxidation of alcohols, in particular benzyl alcohol. It is proved that these new nanocomposites can act as mild oxidants in the conversion of benzyl alcohol to benzaldehyde [eqn. (1)].



(1)

Thus, we initially tested this reaction at 25 °C and found reasonable oxidative reactivity (37% yield) at such temperature. Despite the rather low yield and the long reaction time (a few days) it is important to note the good selectivity of the reaction that exclusively gives benzaldehyde without further oxidation towards benzoic acid. The reaction yield increases markedly with temperature. Table 3 presents results showing this temperature effect on benzyl alcohol oxidation using VAPCs under our defined standard conditions (*i.e.*, containing 30% V_2O_5, with CH_2Cl_2 as the selected solvent and a 2:1 V_2O_5–benzyl alcohol ratio). Raising the reaction temperature has a considerable effect on the oxidative conversion of benzyl alcohol, the yield of benzaldehyde at 45 °C being almost twice the yield at 25 °C. It is remarkable that complete conversion of benzyl alcohol to benzaldehyde is reached after 24 h at 55 °C. A similar effect is achieved for higher temperatures (for instance at 65 °C), requiring shorter reaction times.

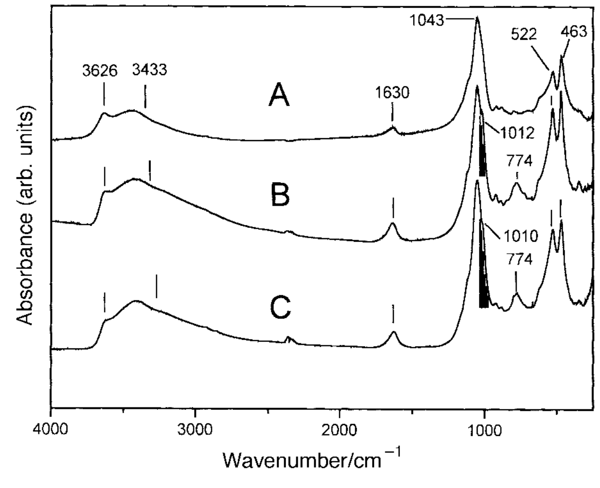


Fig. 4 IR spectra of: A, Al-PILC from Wyoming montmorillonite; B, pre-PILC loaded with 30% V_2O_5 (without further calcination); C, VAPC derived from the PILC A containing 30% V_2O_5 (without further calcination).

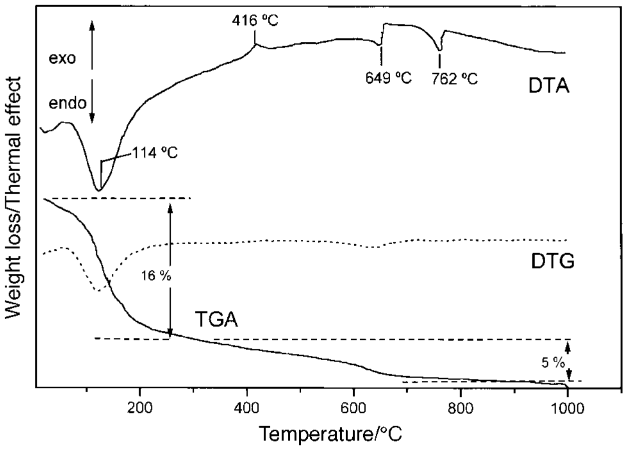


Fig. 5 TG, DTG and DTA plots of a VAPC material derived from Wyoming Al-PILC containing 30% V_2O_5 (without further calcination).

Table 3 Effect of temperature on the oxidative conversion of benzyl alcohol using: VAPCs based on 30%V_2O_5–Al-PILC. Molar ratio of V–benzyl alcohol = 2:1; solvent CH_2Cl_2

Reaction time/h	Reaction temperature/°C	Yield of benzaldehyde (%)
24	25	37
24	45	75
24	55	100
6	65	100

Table 4 Comparison of oxidant activity of VAPCs and other reagents based on V_2O_5 in the conversion of benzyl alcohol to benzaldehyde. Experimental conditions: 24 h at 55 °C; solvent $CHCl_3$ except for [a]CH_2Cl_2; molar ratio of V–benzyl alcohol = 2 : 1

Oxidant	Yield of benzaldehyde (%)
VAPC (30% V_2O_5–Al-PILC)	98
VAPC (30% V_2O_5–Al-prePILC)	100
V_2O_5 xerogel (dried at 50 °C)	39
V_2O_5 orthorhombic	14
30% V_2O_5–montmorillonite[a]	41

Silica gel appears to be unable to produce good V_2O_5 supported reagents *via* the method described here. Moreover, the V_2O_5/montmorillonite systems are found to be not selective towards the oxidation of benzyl alcohol. Compared to both commercial vanadium pentoxide (orthorhombic V_2O_5 phase) and the vanadium pentoxide xerogel (dried at 50 °C), we found that the VAPC compounds are more effective oxidant materials towards benzyl alcohol (Table 4).

As indicated above, EDX analyses show that the V_2O_5 content in VAPCs remains practically unchanged after use in the oxidation reactions of benzyl alcohol (Table 2). The corresponding XPS spectra show that a small fraction of V^{V} in VAPCs is reduced to V^{IV} after use in such reactions, according to the development of a V(2p) signal at 515.3 eV assigned to V^{IV} species.

It appears also that the oxidative behaviour of VAPCs is very similar for materials prepared from montmorillonites and those from saponites. A small decrease in the activity has been observed for the calcinated nanocomposites compared to uncalcinated VAPCs. In addition, the nanocomposites obtained by the reaction of vanadium pentoxide xerogel with the pre-pillared clays are also shown to exhibit excellent oxidative reactivity.

The oxidative reactivity of VAPCs towards some different alcohols was tested to determine the applicability of these materials as general reagents for fine chemical purposes. Thus, it is found that some secondary alcohols can be oxidised by VAPCs in low yield as shown by cyclohexanol which is oxidised to the corresponding carbonyl with only about 10% yield (Table 5). Diphenyl carbinol (Ph_2CHOH) gives a side reaction consisting of the dehydration process resulting in a yield of only about 38% of the corresponding carbonyl compound. Such a decrease in the yield when voluminous substrates are used also suggests that a shape selective effect may affect the distribution of reaction products in view of their greater steric hindrance compared to the benzyl alcohol. It is shown that a primary alcohol, such as hexan-1-ol, is not oxidised under these conditions, in the same way as in oxidations carried out using conventional MnO_2. Thus, this last reagent exhibits behaviour similar to our VAPC materials, acting as a mild oxidant for selective oxidation of benzyl alcohols but without significant activity towards saturated primary alcohols such as hexan-1-ol. Note that other 'classical' oxidant reagents such as potassium permanganate and dichromate in acid media, oxidise primary alcohols ($>C_4$) as well as benzylic alcohols to the corresponding carboxylic acids instead of to the aldehydes.

Table 5 Oxidative reactivity of VAPCs with different alcohols under the experimental standard conditions: solvent CH_2Cl_2; reaction time 24 h; reaction temperature 55 °C; molar ratio of V–alcohol = 2 : 1

Alcohol	Carbonyl compound yield (%)
$PhCH_2OH$	100
$CH_3(CH_2)_4CH_2OH$	0
$C_6H_{11}OH$	10
Ph_2CHOH	38

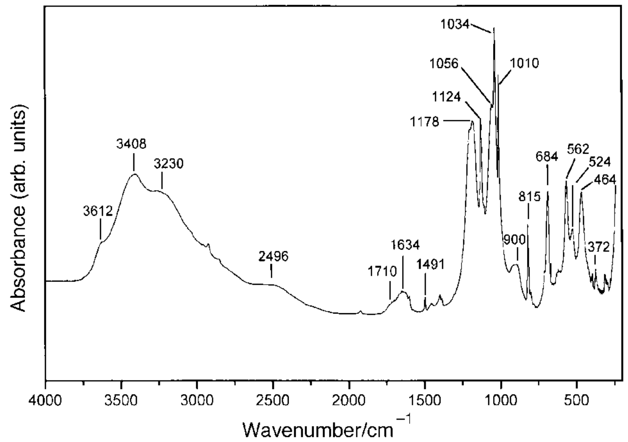


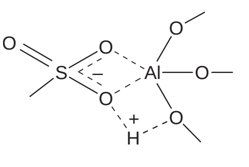
Fig. 6 IR spectrum of a TSPC containing 2.1 mmol of *p*-toluenesulfonic acid per g of Al-PILC.

TSPC nanocomposites

The synthesis of the TSPC materials was carried out by treatment of organic solutions of *p*-toluenesulfonic acid (2.5 mmol per g of PILC) with Al-PILCs at room temperature. The solvent most frequently used was acetone which was removed under vacuum to recover the organic–inorganic nanocomposites which were then stored to avoid contact with humid air.

The resulting TSPC materials derived from montmorillonite Al-PILC show typical chemical analyses (%): C, 18.1; H, 2.66; S, 6.94; Mg, 0.48; Al, 10.25; Si, 10.34; Fe, 0.47; O, 50.76. The content of *p*-toluenesulfonic groups deduced from these analyses (%C and %S) is 2.1 mmol per g of TSPC indicating that the incorporation of such groups is very efficient (84%). By comparing the XRD patterns of PILCs before and after *p*-toluenesulfonic acid adsorption no significant change is observed. This fact indicates that *p*-toluenesulfonic acid is inserted into the pores of the pillared clays without any apparent alteration of the alumina pillars. The IR spectra show some of the specific bands of *p*-toluenesulfonic acid, in particular the very intense bands at 1010 and 1034 cm^{-1} which correspond to the stretching vibrations of S=O bonds. The bands around 1700 and 2500 cm^{-1}, which can be assigned to vibrations of H_3O^+ species, are clearly defined, corroborating the strong acid character of the TSPC materials (Fig. 6). So, it can be inferred that at least a part of the sulfonic groups remain unaltered, although it can also be proposed that a fraction of such species are involved in the interaction with the alumina pillar, probably as postulated in Scheme 1. Proton catalysed reactions are assured, either by the free sulfonic groups or by the sulfo-alumina species.

Thermal analyses (under N_2) of different TSPC materials show a series of bands appearing from 55 to 118 °C in the DTA curves (endothermic effects) of some representative samples. In the corresponding TG curves, the first weight loss (5.3%) is observed at about 110 °C which should be related to the release of water molecules. In the temperature region between 120 and 250 °C the DTA curves show an endothermic



Scheme 1 Proposed interaction of sulfonic groups with the alumina pillar.

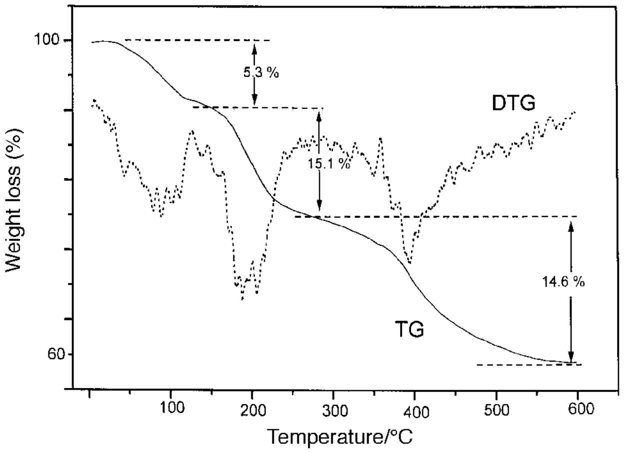


Fig. 7 TG and DTG plots of a TSPC containing 2.1 mmol of *p*-toluenesulfonic acid per g of Al-PILC.

peak at about 220 °C with a weight loss of 15.1% that can be related to the loss of sulfur trioxide (theoretically, 17.5%). A significant weight loss occurs around 400 °C meaning that most of the organic component (methylbenzene framework) has been decomposed by the heating (theoretical: 20.4%; experimental: 14.8%). The overall weight loss in the 25–600 °C temperature range is about 35.0% (Fig. 7). The most significant feature derived from the thermal analyses is the determination of the thermal stability range in which the sulfonic groups remain adsorbed (over 100 °C), which is an interesting characteristic in view of different potential applications.

The electrochemical impedance technique has been applied both to characterise TSPC solids and also to study the experimental conditions under which the maximum proton conductivity is reached, to try and find a correlation between proton conductivity and H^+ availability of the system that may be related to the acid catalytic activity.

Nyquist plots obtained by this technique (Fig. 8) show a semicircle at high frequencies followed by an arc at low frequency values. The ionic conductivity is deduced from the diameter of these semicircles.[18] This last parameter is related to the ionic (H^+) mobility.[19] The low frequency arc is ascribed to polarisation phenomena close to the electrodes. Fig. 9 shows the conductivity evolution with temperature in a characteristic TSPC sample derived in this case from Al-Fulcat montmorillonite. As we report below, the temperature range of the maximum conductivity value ascribed to H^+ mobility (70–100 °C) almost corresponds to the temperature of the maximum acid catalytic activity for MTBE and bisphenol A syntheses (Fig. 10).

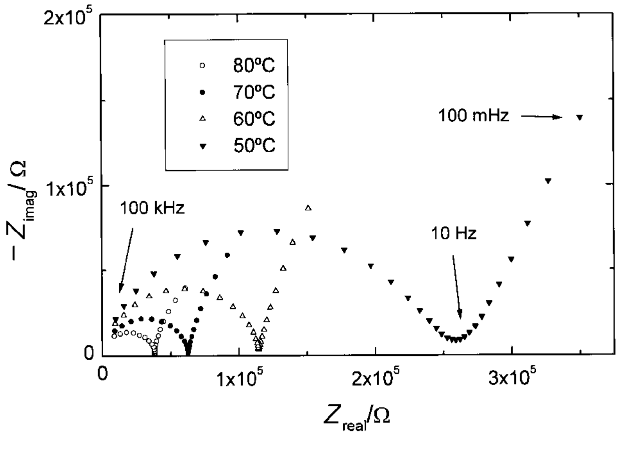


Fig. 8 Evolution of Nyquits plots *versus* temperature for a TSPC containing 2.1 mmol of *p*-toluenesulfonic acid per g of Al-PILC.

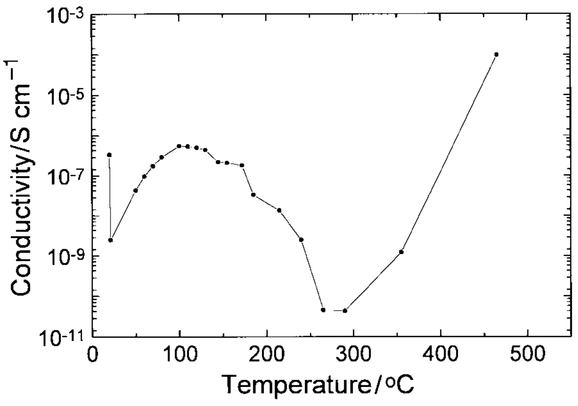


Fig. 9 Evolution of electrical conductivity *versus* temperature for a TSPC containing 2.1 mmol of *p*-toluenesulfonic acid per g of Al-PILC.

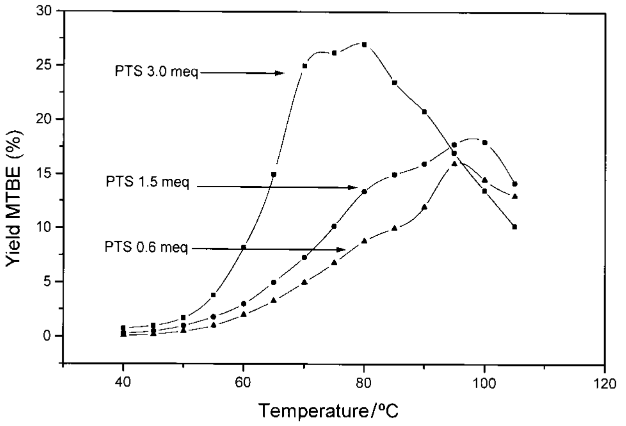


Fig. 10 Catalytic activity of TSPCs based on Al-PILC (FULCAT) in the MTBE synthesis. The content of *p*-toluenesulfonic acid (PTS) is indicated.

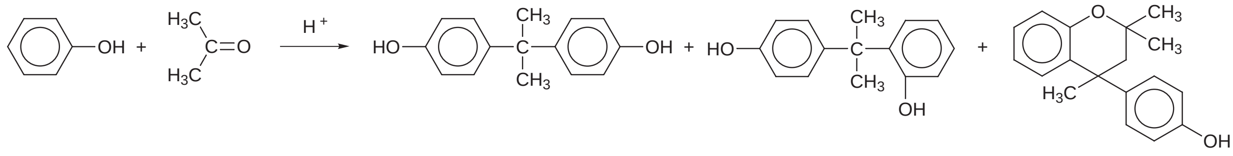
From the data showed in Fig. 9 the following points may be proposed. (1) The water elimination at room temperature produced by flowing dry N_2 causes a marked decrease of the conductivity values. (2) Heating between 20 and 100 °C produces a progressive increase of the conductivity, whereas exceeding the last temperature results in a strong decrease of the conductivity. In this temperature range, Arrhenius behaviour ($E_a = 0.66$ eV) can be ascribed to the proton activation. (3) Heating between 100 and 300 °C causes a drastic decrease of the conductivity values, *i.e.* from 10^{-6} to 10^{-10} S cm. This change is associated with a significant weight loss detected in the TG curves (Fig. 7) which can be assigned to water and sulfonic group elimination. (4) Above 300 °C a significant increase of the conductivity is observed. The corresponding Nyquist plots intercept the real axis indicating a predominance of electronic conductivity over ionic (protonic) conductivity, which can be explained by the formation of carbonaceous materials (like graphite) as a result of the acid auto-catalysed degradation of the organic matter included in the Al-PILC.

TSPC materials were successfully used for the catalytic synthesis of bisphenol A, *i.e.* 2,2-bis(4-hydroxyphenyl)propane, a product widely used (>300 000 tons per year in Western Europe and USA) for synthetic resins (epoxy) and thermoplastic (polycarbonate) preparations.[20] The industrial manufacture consists of the reaction of phenol and acetone which is proton catalysed either by mineral acids (H_2SO_4 or dry HCl and methylmercaptan as a promoter) or, better, by arylsulfonic resins, such as Amberlyst and Dowex.

The usefulness of TSPC materials as catalysts for bisphenol A preparation was tested under different experimental conditions, *i.e.* varying the time of treatment, the reagents, the catalyst ratio and the reaction temperature *etc.* The selected temperature, optimal for the conversion rates of the considered reaction, ranges from 80–110 °C. Note that in this temperature range the highest proton conductivity of TSPC solids as deduced from the impedance studies, is also observed. Bisphenol A was the predominant product of the reaction of phenol and acetone in the presence of TSPCs as indicated by chromatographic analyses, although at least two by-products identified as 2-(4-hydroxyphenyl)propane (I), 2-(1-hydroxyphenyl)propane (II) and 4,4′-hydroxyphenyl-2,2,4-trimethylchroman (known as Dianin's compound) (III) are also detected [eqn. (2)].

Table 6 Synthesis of bisphenol A from acetone (Ac) and phenol (Ph) catalysed by a TSPC containing 2.1 mmol of *p*-toluenesulfonic acid per g of Al-PILC

Reagents ratio Ac/Ph (%)	Yield (referred to acetone conversion) (%)	Selectivity (Product/by-products)
5	64	5.3
10	88	1.5
20	57	1.3
35	20	1.3

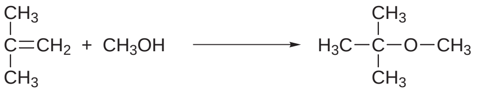


(2)

I II III

Similar compounds have already been reported[21] when using commercial arylsulfonic resins as catalysts. After different experiments varying the time, temperature, reagents and catalyst ratio, *etc.*, we found that the best experimental conditions to enhance the yield of the reaction, as well as to increase the selectivity, are as follows: time of reaction between 24 and 48 h, temperature in the 90–100 °C range, optimal reagents and catalyst ratio: (Ac + Ph)/Cat ≈ 50 (acetone: Ac, phenol: Ph; catalyst: Cat), and Ac/Ph ratio in the 5–10% range (Table 6). It appears that TSPC materials act as catalysts for bisphenol A synthesis with similar or higher activity than commercial arylsulfonic resins such as Amberlyst 15, under our experimental conditions. In addition, larger amounts of by-products result when such resins are involved as catalysts in place of TSPCs. The origin of this different catalytic behaviour should be related to the special textural characteristics of the TSPC organic–inorganic material compared with those of the Amberlyst sulfonated polymer.

The TSPCs have also been tested as catalyst for methyl *tert*-butyl ether (MTBE) synthesis from methanol and isobutene [eqn. (3)] which is an important product used in gasoline blending (reduction in lead antiknock usage).[22]



$$\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{=}CH_2 + CH_3OH \longrightarrow H_3C{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}O{-}CH_3 \qquad (3)$$

Fig. 10 shows the yield of MTBE *vs.* reaction temperature for TSPCs derived from Al-PILCs containing different quantities of *p*-toluenesulfonic acid (0.6, 1.5 and 3.0 mequiv. g^{-1}). The maximum yield of MTBE is attained for TSPCs containing the largest amount of *p*-toluenesulfonic acid. Interestingly, the temperature corresponding to the maximum activity found for these catalysts (75 °C) coincides with the temperature corresponding to the maximum value of their electrical conductivity determined by the impedance technique. Taking into account that the main contribution to the electrical transport is ascribed to H^+ conductivity, this result indicates the correlation between this parameter and the catalytic activity of the TSPC materials.

Commercial catalysts such as Amberlyst 15 are more active than TSPCs under identical experimental conditions (52% *vs.* 27% yield). However, TSPCs show comparable or better catalytic behaviour than zeolites (Y zeolite, mordenite, Ω zeolite, ZSM-5, *etc.*).[23]

Conclusions

We reported initial work on the synthesis and application of a new class of nanocomposite materials derived from pillared clays exhibiting designated chemical reactivities. Vanadium pentoxide could be incorporated into Al-PILCs by a partial filling of its galleries, giving materials able to act as mild oxidants for selective oxidation of benzyl alcohol to benzaldehyde and for other alcohol oxidations to carbonyl compounds. This oxidant can be successfully used in aprotic polar solvents, such as methylene dichloride. These new nanocomposite reagents are easily prepared, not expensive, easily separated and recovered after the reaction and exhibit good thermal stablity. So they may be applied as mild oxidants on the laboratory scale and, potentially, in industrial fine organic chemical syntheses.

In addition, a new acidic catalyst has been obtained by the inclusion of *p*-toluenesulfonic acid into aluminium oxide pillared clays while avoiding the rapid degradation of the reagent upon exposure to moisture. These materials exhibit excellent catalytic activity and good selectivity towards the syntheses of both bisphenol A, from acetone and phenol, and MTBE, from isobutene and methanol. Electrochemical impedance appears as a promising technique to detect the maximum activity of these proton catalysts as a function of the temperature, with potential applications in the prediction of the activity of other acid catalysts. Here a new approach has been applied to the preparation of systems in which their acidity may be improved by the synergetic action between H^+ furnished by a strong acid and the alumina environment assured by the pillar surface. Nevertheless, these TSPC materials exposed to the atmosphere for long time periods lose activity due to progressive degradation caused by the moisture. This is an important point limiting their applications.

Apparently the nature of the starting silicates (montmorillonites and saponites) does not affect the VAPC and TSPC reactivities, but it could be interesting to investigate the influence of the nature of the pillars (*e.g.* Zr or Ti oxides) on the chemical activity of the corresponding nanocomposites.

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