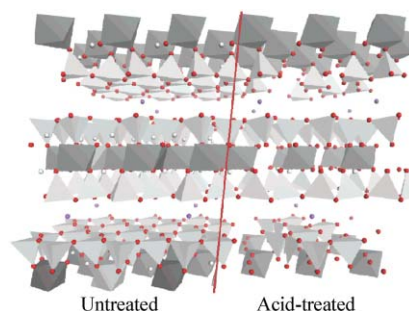


Assessing and improving the catalytic activity of K-10 montmorillonite

Philip J. Wallis, Will P. Gates, Antonio F. Patti,
Janet L. Scott and Euneace Teoh

Procedures for assessing the catalytic activity of K-10 montmorillonite utilising physical and synthetic techniques are described. Significant and reproducible enhancements in K-10 reactivity can be obtained by acid treatment of the clay.



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1 **1** Assessing and improving the catalytic activity of K-10 montmorillonite†

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K-10 montmorillonite, commonly used as a heterogeneous acid catalyst, was found to vary in the extent of acid-treatment, with some batches exhibiting significantly reduced catalytic activity in Brønsted acid-catalysed reactions. K-10 was thus further treated with HCl of varying concentrations to increase its activity in acid-catalysed reactions. Acid-treated clays exhibited significant enhancements in catalytic activity in three test reactions; tetrahydropyranlation of ethanol, diacetylation of benzaldehyde and esterification of succinic anhydride. Acid-treatment of K-10 was shown to result in protonation, and loss of layer stacking of the clay structure, as determined by powder X-ray diffraction, inductively coupled plasma–optical emission spectroscopy (ICP-OES), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and Brunauer–Emmett–Teller (BET) specific surface area measurements. Quantifiable physical changes to the K-10 correlated with measurable increases in catalytic activity. Standard procedures for assessing acid-treated montmorillonite clay catalysts, such as K-10, and procedures for obtaining the most effective catalyst for acid-catalysed reactions, involving analytical and synthetic techniques, were devised.

Introduction

K-10 montmorillonite is a commercially available smectite clay, which has been acid-treated with sulfuric acid, and is used as a catalyst in organic synthesis. K-10 has featured prominently in clay-mediated organic synthesis for many years: it is an effective catalyst for a range of reactions, is safe to handle and is easily separated from reaction mixtures. The utility of clays as catalysts in organic synthesis is reflected in a huge number of reports of synthetic procedures utilising such catalysts, and the reader is referred to a number of recent reviews.¹ Specifically, K-10 montmorillonite is widely considered to be a green heterogeneous catalyst.² Chemists often employ K-10 as purchased, without any further treatment of the clay and accepting the consequences of its use without question. However, in our experience, different batches of K-10 montmorillonite “fresh” from the bottle give highly variable results. Thus, to ensure product quality for laboratory experimentation, we find that K-10 should be characterised and possibly acid-treated before use.

Montmorillonite clay is a hydrated 2 : 1 layered dioctahedral aluminosilicate of the smectite group of clays.³ It is composed of two tetrahedral (predominantly silicate) sheets which are bonded to either side of an octahedral (predominantly aluminate) sheet. Isomorphous substitution of Mg²⁺ for the

octahedral aluminium, and of Al³⁺ for the tetrahedral silicon, results in charge deficit. This layer charge is balanced by hydrated exchangeable cations (*e.g.*, Na⁺ or Ca²⁺) which occupy the surfaces between clay layers, termed the interlayer.³

With respect to catalytic applications, various aspects of acid-activation of montmorillonite have been studied in depth,⁴ however, where previous studies have focused on acid treatment of virgin montmorillonite, the aim of this study is to assess commercially acid treated montmorillonite. Acid activation results in at least four significant changes in the smectite: (1) exchange of the hydrated interlayer charge compensating cations for H⁺ and their release into solution; (2) delamination, or loss of layer stacking of individual clay platelets into dis-oriented aggregates; (3) dissolution of the individual clay platelets and release of the constituent cations into solution; and (4) formation of a hydrous, poorly crystalline and highly porous phase.⁵ In general, changes 1 and 2 precede 3 and 4 in time, but harsh acid-treatment can result in all occurring simultaneously. The final acid activation products arising from the acid-treatment of smectites are hydrous and poorly crystalline silica that may or may not contain some aluminium.⁶ Prolonged acid-treatment can result in complete structural breakdown of the smectite component as inferred from changes in the infrared spectra.⁷ The process of ‘autotransformation’, whereby acid-treated clays are found to self-digest in the solid state, and thus increase the proportion of exchange sites occupied by Al³⁺ or Mg²⁺, is also a significant process relevant to acid-treated clay catalysts.⁸ Autotransformation of acid treated montmorillonite must be considered when using old batches of K-10, as the catalytic activity will decline over time.

The extent of acid-treatment has profound implications for the use of clays as acid catalysts, particularly in synthetic organic chemistry where researchers may use an acid-treated

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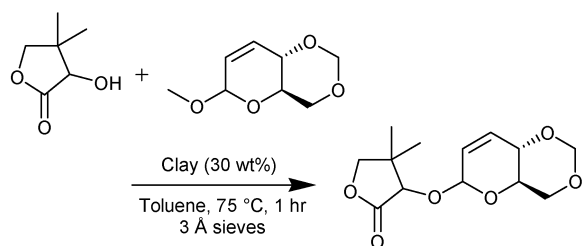
† Electronic supplementary information (ESI) available: Additional experimental data. See DOI: 10.1039/b701504f

1 clay catalyst as-purchased and uncharacterised. Dissolution of
the clay and formation of hydrous, amorphous, silica-rich
phases in part, promote the catalytic activity of the acid-
treated material for either Brønsted and Lewis acid-catalysed
reactions.^{8,9} The ability of clay catalysts to promote Brønsted
or Lewis acid-catalysed reactions, depends on the exchange-
able cations present. Thus, products can be created with
properties ranging from an *acidic clay*, represented by H⁺
exchange and delamination, to an *acid digested product*,
represented by formation of hydrous silica.

In our study, recently purchased K-10 montmorillonite
(referred to herein as K-10A) was treated with hydrochloric
acid at various concentrations and temperatures. Treated and
untreated clays were utilised in well described acid-catalysed
reactions, including tetrahydropyranylation of ethanol,^{10,11}
acetylation of benzaldehyde¹² and esterification of succinic
anhydride.¹³ Tetrahydropyranylation was included to demon-
strate the importance of exchangeable H⁺ to the reaction,
where the solvent, ethanol, was also a reagent and thus access
to reactive sites was not limited. The acetylation reaction,
using reagents dissolved in a solvent, was included to demon-
strate the need for greater exposed surface area caused by
stronger acid treatment. Finally, the esterification example
was selected from the literature where low conversions were
obtained with as-supplied K-10, which could be improved by
further acid treatment of K-10 to illustrate that the acid
treatment proposed in this paper has merit. The important
alterations in clay structure and composition were probed
using powder X-ray diffraction (XRD), diffuse reflectance
infrared Fourier transform (DRIFT) spectroscopy, Brunauer–
Emmett–Teller (BET) method for specific surface area,¹⁴ and
inductively coupled plasma optical emission spectroscopy
(ICP-OES) analysis of supernatants post acid-treatment. The
objective of this study was to perform an in-depth assessment
of acid-treated K-10 montmorillonite by a variety of physical
and synthetic techniques, in order to provide synthetic “green”
chemists with tools to achieve the optimal performance of acid
activated clay catalysts.

Results and discussion

A routine experiment, the transacetalisation of pantolactone
with an auxiliary (Scheme 1), usually catalysed by K-10, was
attempted using a batch of K-10 as received (K-10A).¹⁵ Under
standard reaction conditions, only starting materials were
recovered. Further attempts using more rigorously dried



Scheme 1 Transacetalisation of pantolactone with methyl-2,3-dideoxy-4,6-*O*-methylene- α -D-erythro-hex-enopyranoside, under standard conditions for catalytic comparison.

solvents and K-10A dried at 120 °C under vacuum, again
yielded only starting materials. Repeating the reaction using
a different batch of K-10 (K-10B) resulted in high (98%)
conversion, but only when reactions were allowed to proceed
overnight (>12 hours).

To determine possible differences in the composition of the
two K-10 batches, powder XRD diffraction patterns were
collected. Both K-10A and K-10B were composed predomi-
nantly of montmorillonite, with significant quantities of
muscovite, quartz and opalised silica and small quantities of
feldspar. The most notable difference was that of the relative
intensity and location of the basal 001 reflections. With
increasing acid-treatment, a decrease in intensity of the basal
001 peak corresponds to disruption of the layered structure of
the clay. Relative intensity is reported with respect to other
clay reflections in the XRD pattern which are not affected
by acid-treatment. The powder XRD pattern of K-10A
exhibited an intense basal reflection at 5.74° 2 θ , corresponding
to a *d*-spacing of 15.40 Å, whereas K-10B exhibited a weak
reflection at 5.94° 2 θ corresponding to a *d*-spacing of 14.88 Å.
These differences are likely to be a result of acid-treatment, as
the intensity of the basal reflection of montmorillonite relates
to the preservation of aggregates composed of well oriented
stacks of individual clay platelets.⁴ Higher intensity basal
reflections indicate a greater number of repeating clay platelets
within the aggregate. A lower intensity indicates a loss of
laminar stacking due to poorer orientation of clay platelets,
dissolution of the clay platelets and an increased presence of
acid digestion products, and possibly the interstratification of
numerous interlayer spacings.

Mild acid-treatment can potentially affect the specific
surface area, where more strongly delaminated and partially
dissolved clays exhibit higher external specific surface areas (as
measured by the BET technique). Also, the slight difference in
the size of the interlayer (0.52 Å) indicated a possible difference
in the composition of cations present: intercalation of protons
would result in a smaller interlamellar spacing than intercala-
tion with either hydrated Ca²⁺ or Na⁺. In terms of reactivity,
the lack of available protons would fail to promote any
Brønsted acid-catalysed reactions at the basal surfaces, and
the lower surface area may affect the rate of reaction due to
diffusion limitations.

In a pilot study, two acid-treatments were performed on
K-10A utilising HCl at 1.0 M and 10 M. The clay was
subjected to acid-treatment for six hours at room temperature
(21 °C) and recovered by centrifugation. The sample was then
repeatedly washed with deionised water until Cl⁻ could no
longer be detected by a silver nitrate test, and dried at 120 °C.
The materials thus prepared were analysed by powder XRD,
and notable differences included a significant shift to a smaller
interlayer spacing (change of 0.69 Å), as well as a decrease in
the intensity of the basal 001 reflection (at 6.01° 2 θ corres-
ponding to a *d*-spacing of 14.71 Å). When the acid-treated
clays were compared with the batch K-10A and K-10B for
catalytic activity using the synthetic reaction previously
described (with a standard set of conditions less forcing than
those previously used), K-10A (10 M HCl) yielded significantly
higher conversion to product (Table 1) compared with K-10B
(23% versus 3%) under these conditions, as determined by GC

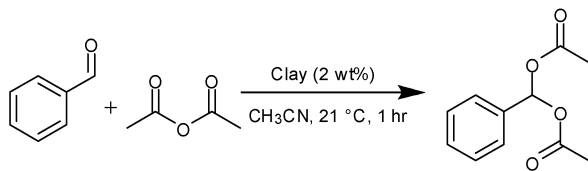
Table 1 Transacetalisation of pantolactone with methyl-2,3,-dideoxy-4,6-*O*-methylene- α -D-erythro-hex-enopyranoside, conversion at 60 minutes

Catalyst	Conversion (%)
K-10A	0
K-10B	3
K-10A (1.0 M HCl treated)	7
K-10A (10 M HCl treated)	23
Silica gel	0
Silica gel (0.1 M HCl)	0

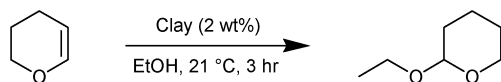
analysis. Furthermore, in general, transacetalisation reactions with other alcohols were complete within 3 hours using K-10A (10 M HCl), as compared with overnight (>12 hours) using K-10B.

These results prompted a more comprehensive study of the acid-treatment procedure, including analysis by ICP-OES of the acidic supernatants post-treatment, and acid-treated clays by XRD, IR and N₂ adsorption isotherms for surface area determination. Four acid-treatments, ranging in severity, were performed: 0.1 M HCl, 1.0 M HCl, 10 M HCl at 21 °C and 5 M HCl at 80 °C. All treatments were for 6 hours. Treatments were performed in duplicate, using 10 g of K-10A and 200 ml of acid in each case. The resulting acid-treated clays obtained are herein designated: (K-10A) untreated K-10, (K-10A1) 0.1 M HCl treated K-10, (K-10A2) 1.0 M HCl treated K-10, (K-10A3) 10 M HCl treated K-10, (K-10A4) 5 M HCl at 80 °C treated K-10, (K-10B) an additional batch of untreated K-10, and (K-10C) a further additional batch of untreated K-10. The rationale for these treatments was that the 1.0 M HCl and 10 M HCl treatments had improved the catalytic activity of the clay previously, 0.1 M HCl was used to determine whether a fairly dilute acid could be used to cost effectively and more safely achieve an effect for syntheses requiring mildly acidic clays, and 5 M HCl at 80 °C had been used by others to effect a more thorough digestion of montmorillonite.^{6,7}

All four treated clays, as well as K-10A and K-10B, were utilised in two common examples of acid-catalysed transformations: the diacetylation of benzaldehyde (Scheme 2), used to protect aldehydic functional groups and previously shown to be catalysed by acidic clay,¹² and the tetrahydropyranylation of ethanol (Scheme 3).¹⁶



Scheme 2 Clay-catalysed diacetylation of benzaldehyde to form phenylmethylene diacetate.



Scheme 3 Clay-catalysed tetrahydropyranylation of ethanol to form 2-ethoxy-tetrahydro-2H-pyran.

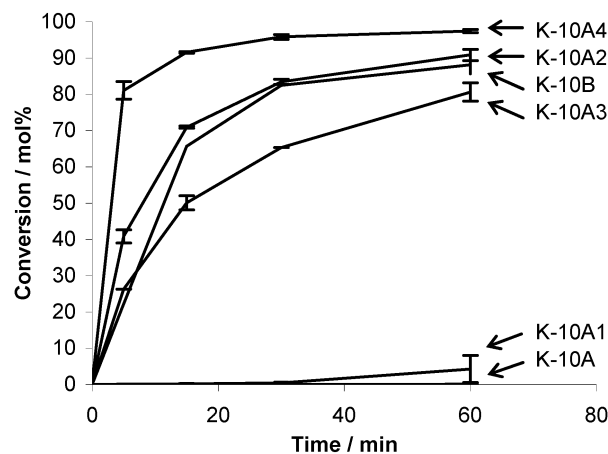


Fig. 1 Diacetylation of benzaldehyde, promoted by: untreated K-10A, 0.1 M HCl treated K-10A1, 1.0 M HCl treated K-10A2, 10 M HCl treated K-10A3, 5 M 80 °C HCl treated K-10A4 and untreated K-10B.

Results for the diacetylation of benzaldehyde (Fig. 1) and the tetrahydropyranylation of ethanol (Fig. 2) show negligible conversion using the untreated K-10A, to quantitative conversion for the strongly acid-treated K-10A4. The changes in reactivity with acid-treatment are significant, and follow the general trend of increasing catalytic activity with stronger acid-treatment of the clay. The two different reactions exhibit different trends of reactivity; the tetrahydropyranylation of ethanol is rapidly promoted by all catalysts, even the lightly acid-treated K-10A1, whereas the degree of diacetylation of benzaldehyde by different treated clays is more differentiated by the degree of acid-treatment, with the weakly treated K-10A1 giving almost no conversion. This may be due to different reaction limiting processes, with the tetrahydropyranylation limited by the availability of protons at the clay surface, and the diacetylation limited by the accessibility of active sites.

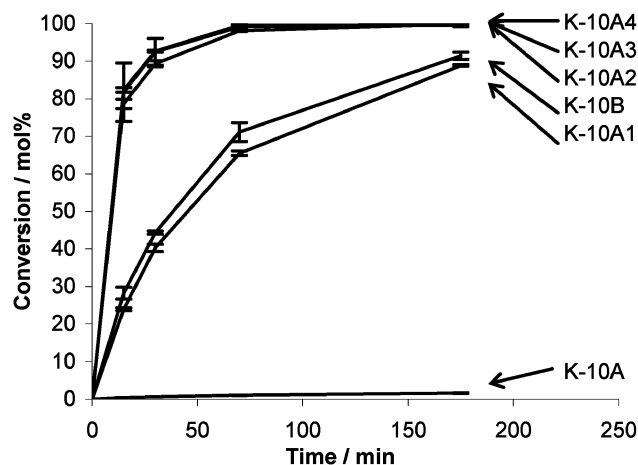


Fig. 2 Tetrahydropyranylation of ethanol, promoted by: untreated K-10A, 0.1 M HCl treated K-10A1, 1.0 M HCl treated K-10A2, 10 M HCl treated K-10A3, 5 M 80 °C HCl treated K-10A4 and untreated K-10B.

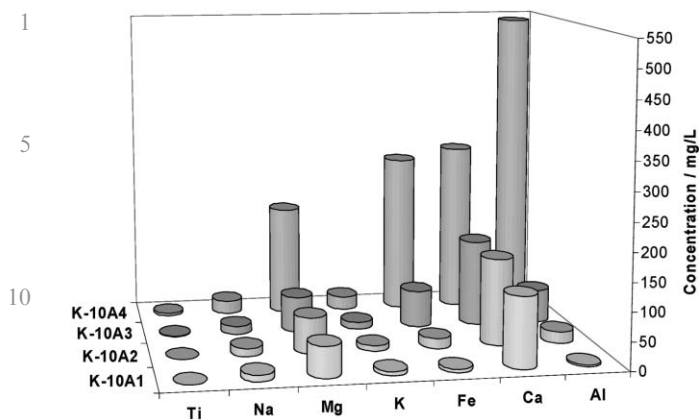


Fig. 3 Concentrations of cations from acidic supernatants (K-10A1–K-10A4) as determined by ICP-OES. Concentration of analytes in mg L^{-1} from 0.7 L of supernatant, treating 10 g of K-10A.

Analysis of the acid-treatment supernatants by ICP-OES (Fig. 3) revealed significant differences in the amount of leaching between acid-treatments. With K-10A as the starting material, we observed that significant amounts of Ca^{2+} and Mg^{2+} were released with light acid treatment (K-10A1). The high levels indicate that the original clay material may have been Ca^{2+} saturated and that this batch of clay largely escaped acid-treatment during the industrial preparation of K-10. Mg^{2+} can be both an exchange cation and a structural cation, but its ready removal, with even the 0.1 M HCl treatment, indicated the presence of a significant amount of exchangeable Mg^{2+} .

With stronger acid-treatments, removal of additional Mg^{2+} occurred, most likely originating from the clay structure. The Al^{3+} was progressively removed from the octahedral sheets with increasing acid-treatment, with the harshest conditions leaching significant quantities from the clay. Fe^{3+} followed the same trend as Al^{3+} . The rate and extent of clay dissolution has previously been found to increase with the degree of Mg^{2+} and Fe^{3+} substitution for Al^{3+} in the octahedral sheet.⁷ Small amounts of Na^+ and K^+ were leached from the material, most likely originating from the feldspar and muscovite impurities, respectively, but possibly also arising from the smectite interlayers. The peak corresponding to muscovite in the powder XRD was relatively unaltered, which is consistent with the resistance of muscovite to acid attack. Negligible, but measurable, levels of Ti^{4+} were also leached from the clay.

Powder XRD provided a means for assessing the extent of delamination with acid-treatment (Fig. 4). As acid-treatments increased in severity, the layered structure of the clay was lost, as evidenced by the decrease in intensity of the basal 001 peak. The retention of other clay-related peaks, including the two-dimensional hk index pairs 02–11 20–13 and 06–33,¹⁷ indicated some preservation of the two-dimensional lattice. Note that these decreased, but were still present in the harshest treatment. The quartz impurity was significant in all of the K-10 samples analysed, and was retained despite acid-treatment. From a visual comparison of the powder XRD spectra, it appeared that untreated K-10B lay somewhere between the two stronger acid-treatments K-10A3 and K-10A4, in terms of structural disruption and surface area,

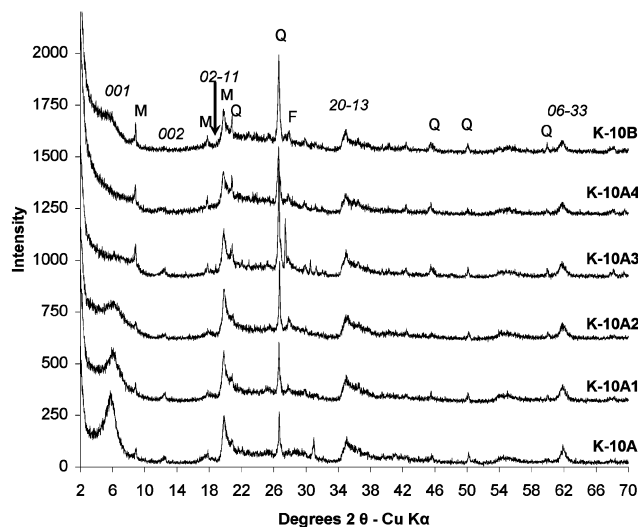


Fig. 4 Stacked powder XRD spectra of treated (K-10A1, K-10A2, K-10A3, K-10A4) and untreated (K-10A, K-10B), indicating impurities (Q: quartz, M: muscovite, F: feldspar) with reflections and hk index pairs attributed to montmorillonite.

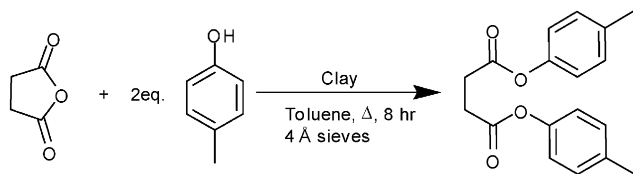
although this did not give an idea of the saturation of protons at the surface. Indeed, acid-treated montmorillonite may undergo partial auto-transformation in the solid state when in storage, where the surface protons attack octahedral sites, and are replaced at exchange sites with metals from the lattice.⁸ Therefore, clays which are determined to have been highly acid-treated by powder XRD, but are still of sub-optimal catalytic activity, could in theory be rejuvenated by a simple acid-wash with a dilute mineral acid.

The external specific surface area of the clay increased with increasing severity of acid-treatment. In this context, external specific surface area, as determined from N_2 adsorption isotherms using the BET method, can also be used to estimate the extent of dissolution of the clay structure.¹⁰ From specific surface measurements made of our acid-treated clays (Table 2) it could be seen that the surface area of K-10A increased from a relatively low $83 \text{ m}^2 \text{ g}^{-1}$ to $270 \text{ m}^2 \text{ g}^{-1}$ for the strongest acid-treatment. The surface area of K-10B was between that of the 10 M HCl (K-10A3) and 5 M HCl at 80°C (K-10A4) treatments, in agreement with the powder XRD data.

Specific surface area measurements give a good indication of the degree of clay acid-treatment, however, they do not allow quantification of the proportion of surface sites saturated with protons. As discussed above, clay that has been strongly acid-treated will have reduced catalytic activity if the remaining exchangeable cations are not protons, a situation which may arise through the process of autotransformation.⁸ In this

Table 2 Specific surface area of treated clays determined by N_2 BET

Clay	Specific surface area/ $\text{m}^2 \text{ g}^{-1}$
K-10A untreated K-10	83
K-10A1 (0.1 M HCl K-10A)	88
K-10A2 (1.0 M HCl K-10A)	110
K-10A3 (10 M HCl K-10A)	130
K-10A4 (5 M 80°C K-10A)	270
K-10B untreated K-10	220



Scheme 4 Clay-catalysed esterification of succinic anhydride to form the succinic acid di-*p*-tolyl ester.

context, an example was found in the literature where a strongly acid-treated clay gave significantly reduced catalytic activity compared with other H^+ exchanged clays.¹³ In this published example, the esterification of succinic anhydride (Scheme 4), K-10 montmorillonite with a specific surface area of $254.6 \text{ m}^2 \text{ g}^{-1}$ yielded 10% of the di-ester, whereas H^+ -montmorillonite with a specific surface area of $33.3 \text{ m}^2 \text{ g}^{-1}$ gave 71% yield under the same conditions.¹³ This result indicated that the K-10 used may not have had sufficient protons at exchange sites when used straight from the bottle, whereas the freshly treated H^+ -montmorillonite, despite having a much lower specific surface area, most likely had a full complement of protons at exchange sites.

The esterification of succinic acid was thus performed using untreated (K-10A-C) and treated (K-10A1-4) K-10 montmorillonite under conditions (see Experimental) similar to those published.¹³ The results are presented as a percentage of conversion from succinic anhydride *versus* time (Fig. 5).

The results show that untreated K-10A gives 9% conversion to the di-ester, in accordance with the literature example.¹³ However, the acid-treated clays gave up to 91% conversion (K-10A4), which was a clear indication that whilst loss of layer

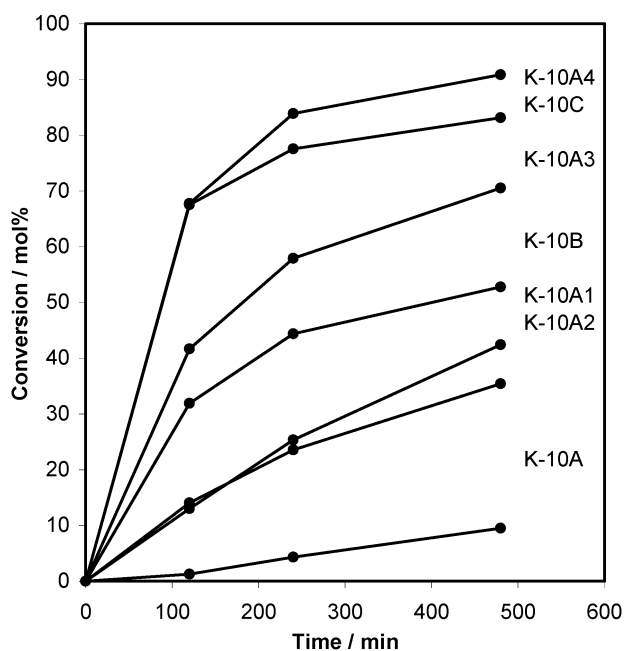


Fig. 5 Esterification of succinic anhydride, promoted by: untreated K-10A, 0.1 M HCl treated K-10A1, 1.0 M HCl treated K-10A2, 10 M HCl treated K-10A3, 5 M 80 °C HCl treated K-10A4, untreated K-10B and untreated K-10C.

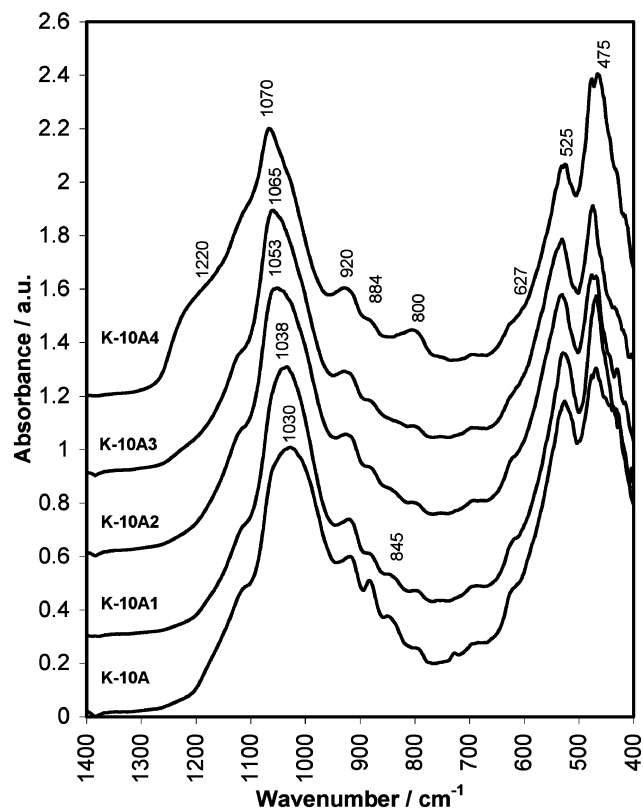


Fig. 6 DRIFT spectra of treated and untreated clays: untreated K-10A, 0.1 M HCl treated K-10A1, 1.0 M HCl treated K-10A2, 10 M HCl treated K-10A3 and 5 M 80 °C HCl treated K-10A4. Spectra have been normalised to Si-O stretch, smoothed using a 7-point boxcar function, and stacked.

stacking is important in optimising activity, protonation of the available exchange sites is essential for the reaction to proceed.

Some further effects of acid-treatment of clay can be observed using FTIR.^{4,7} Infrared spectra of clays were obtained using DRIFT, and spectra were normalised with regards to intensity to the Si-O stretch at $\sim 1030 \text{ cm}^{-1}$, in order to compare the appropriate wavenumber shifts and changes in intensity (Fig. 6). The clearest trend is the shift to higher wavenumber of the main Si-O stretch associated with silica tetrahedra in the clay.^{18,19} As the acid-treatment increases in severity, this peak shifts from $\sim 1030 \text{ cm}^{-1}$ to $\sim 1070 \text{ cm}^{-1}$, indicative of changes to the bonding environment surrounding the tetrahedra. In this case the loss of layer charge due to the removal of (1) substituted cations that provide layer charge and (2) loss of interlayer exchangeable cations that neutralised that charge. The result is Si-O in a different environment due to internal (1) and external (2) factors.²⁰ The most strongly acid-treated clay (5 M HCl 80 °C) showed the greatest shift, and also the appearance of a large shoulder centred on 1220 cm^{-1} next to the Si-O band, and a new band near 800 cm^{-1} , both characteristic of amorphous silica.¹⁸ The peaks relating to AlAl-OH (920 cm^{-1}), AlFe-OH (884 cm^{-1}) and AlMg-OH (845 cm^{-1}) deformation bands,¹⁸ decreased in intensity with increasing acid-treatment, with the Mg leaching out rapidly in agreement with ICP-OES data. Furthermore, the Si-O-Al (525 cm^{-1}) lattice deformation

band decreased in intensity in relation to the Si–O–Mg (475 cm^{-1}) lattice deformation band.

Infrared can be used to estimate the degree of acid digestion, and hence the potential reactivity of montmorillonite, by observing the location of the Si–O stretch, ranging from 1030 cm^{-1} to 1070 cm^{-1} . In summary, the IR spectra show that the acid-treatment mostly caused exchange of interlayer exchangeable cations, delamination of the layer stacking, and only partially show destruction of the layers. The 5 M HCl at $80\text{ }^{\circ}\text{C}$ for 6 hours is not a harsh enough treatment to completely convert the clay to amorphous silica, which would be characterised by a shift of the Si–O stretch closer to 1100 cm^{-1} , and the complete disappearance of the Al–OH, AlFe–OH, AlMg–OH, Si–O–Al and Si–O–Mg bands.¹⁸

In summary, the physical effects of the treatment of K-10 montmorillonite with HCl includes protonation of surface exchange sites, proton attack at sites of isomorphous substitution and the resulting removal of Mg^{2+} , dissolution of octahedral sites resulting in removal of Fe^{3+} and Al^{3+} , and the resulting increase in surface area associated with delamination of the smectite and formation of a poorly crystalline silica phase.

Conclusion

In our laboratory we found that acid-treated K10 montmorillonite had variable catalytic activity. Acid-treatment improved the catalytic activity of untreated K-10. Analysis of acid-treated materials by IR, XRD and BET specific surface area indicated that only the harshest acid-treatment resulted in significant dissolution of the smectite and production of hydrous silica.

In general, acid-treatment of K-10 improved the catalytic activity for three synthetic reactions: (1) diacetylation of benzaldehyde, (2) tetrahydropyranlation of ethanol and (3) esterification of succinic anhydride. One batch of untreated K-10 (K-10A) yielded no product conversion in acid-catalysed reactions, whereas other untreated batches yielded moderate (K-10B) and high (K-10C) conversion to product in acid-catalysed reactions. These differences in reactivity reflect either differences in the degree of initial acid treatment by the manufacturers or differences in age of the K-10 product. Reaction yields of both diacetylation and esterification generally increased with strength of acid-treatment, indicating the importance of a highly acid-treated material for this reaction. In contrast, even the mildest acid-treatment provided a material with significantly enhanced catalytic activity for tetrahydropyranlation reactions. Thus, acetylation or esterification is suitable for determining the degree of clay delamination, and tetrahydropyranlation is suitable for determining the degree of clay protonation.

Experimental

Materials and methods

Benzaldehyde, 3,4-dihydro-2H-pyran, pantolactone, acetic anhydride, silver nitrate, succinic anhydride, *p*-cresol and K-10 montmorillonite (K-10A batch 03412CA, K-10B batch 11007BI, K-10C batch 13721JD) were purchased from

Sigma–Aldrich chemical company. Ethanol (99.7%), acetonitrile, HPLC-grade acetone, toluene and hydrochloric acid (34%) were purchased from Merck. All reagents and solvents were used as purchased from the supplier without any further purification.

Powder XRD spectra were collected on a Philips PW1140 diffractometer from $2\text{--}70^{\circ} 2\theta$ at $4^{\circ}\text{ min}^{-1}$ with a step size of 0.02° using a Cu $K\alpha$ source ($\lambda = 1.54\text{ nm}$). A 1° divergence slit, 1° receiving slit and 0.2° scatter aperture were used. Samples were prepared as front-loaded packed powders in aluminium sample holders.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected using a “Harrick” single bounce mirror assembly on a BIORAD Excalibur Series FTS 3000MX Fourier transform spectrophotometer. A cooled DTGS solid-state detector was employed with an extended KBr beamsplitter, and the sample compartment was purged with dry nitrogen gas prior to and during collection. Spectra were collected in the mid-IR region ($400\text{--}4000\text{ cm}^{-1}$) at a resolution of 2 cm^{-1} with 1024 scans co-added. Powdered clay samples were diluted (2.5%) in solid KBr, with KBr as the reference background.

Gas chromatography (GC) was performed on an Agilent 6850 Series II Network GC System, equipped with an FID detector and an HP-1 column ($30\text{ m} \times 0.32\text{ mm ID}$). Helium was used as a carrier gas at a flow-rate of 2.0 ml min^{-1} , and a temperature program of $100\text{--}300\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ was employed. Detector response factors (from multiple-point calibration curves) were determined for all of the starting materials and reaction products.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out using a Varian VistaPro ICP-OES with simultaneous CCD and axial view torch detectors. Specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method. Nitrogen vapour adsorption data was obtained for the vapour pressure range (P/P_0) of 0.05 to 0.25. Samples were degassed at $105\text{ }^{\circ}\text{C}$ overnight under vacuum. Surface area was determined based on the linear portion of the BET plot. A silver nitrate (AgNO_3) test was used to determine the presence of chloride ions in washing supernatants after treatment of the clay samples. If halide ions are present, the insoluble precipitate AgCl is formed, and can be visually detected.

Acid-treatment procedures

K-10 montmorillonite (K-10A) (10 g) was placed in a 250 ml round-bottom flask. 0.1 M hydrochloric acid (200 ml) was added, and the suspension was stirred at room temperature ($21\text{ }^{\circ}\text{C}$) for 6 h. The mixture was added to a 1 L polypropylene centrifuge tube containing 250 ml of deionised water, and the residues were washed with a further 250 ml of deionised water. The clay was centrifuged (5000 rpm) for 5 min, and a sample of the supernatant taken for analysis by ICP-OES, and refrigerated until analysis, which occurred within 7 days. The remaining supernatant was discarded, and the clay repeatedly resuspended in deionised water until no Cl^- could be detected in the supernatant by a silver nitrate test, and then washed once more. The clay was recovered, dried in a vacuum oven at

120 °C overnight, then ground in a mortar and pestle and ball-milled for 2 minutes. The final material was a finely divided powder with a beige colour. This procedure was performed in duplicate for each acid-treatment, including 0.1 M HCl, 1.0 M HCl, 10 M HCl at 21 °C and 5 M HCl at 80 °C.

General procedure for transacetalisation of pantolactone with methyl-2,3,-dideoxy-4,6-*O*-methylene- α -D-erythro-hex-enopyranoside

Pantolactone (450 mg, 3.49 mmol) and methyl-2,3,-dideoxy-4,6-*O*-methylene- α -D-erythro-hex-enopyranoside (200 mg, 1.16 mmol) were dissolved in dry toluene (5 mL) followed by the addition of 10 M HCl treated K-10 montmorillonite (60 mg, 30% by weight) and 3A molecular sieves. The reaction mixture was heated to 75 °C. After 20 h the clay was filtered off, and the solvent was evaporated to give a yellow oil. The ratio of *R*- α : *S*- α = 68 : 32 was assessed by GC, which showed 93% conversion.

General procedure for diacetylation of benzaldehyde¹²

Benzaldehyde (1.0 g, 9.4 mmol) and acetic anhydride (1.44 g, 14 mmol) were added together in a test-tube. K-10 (0.0220 g \pm 0.0002 g) was added, the tube sealed, and the mixture stirred at room temperature (21 °C) for 1 h. GC samples were taken at 5, 15, 30 and 60 min by removing a drop of the reaction mixture, diluting with HPLC-grade acetone, and filtering through a Teflon disc filter (0.45 μ m) directly into a GC vial.

General procedure for tetrahydropyranylation of ethanol^{10,11}

Ethanol (1.38 g, 30 mmol) and 3,4-dihydro-2*H*-pyran (2.53 g, 30 mmol) were added together in a test-tube. K-10 (0.0500 \pm 0.0002 g) was added, the tube sealed, and the mixture stirred at room temperature (21 °C) for 3 h. GC samples were taken at 15, 30, 70 and 175 min by removing a drop of the reaction mixture, diluting with HPLC-grade acetone, and filtering through a Teflon disc filter (0.45 μ m) directly into a GC vial.

General procedure for esterification of succinic anhydride with *p*-cresol¹³

Succinic anhydride (0.5080 g) was dissolved in toluene (32.5 ml) with heating. The hot solution was pipetted in portions (8 \times 3.25 ml) into test-tubes. *p*-Cresol (1.6231 g) was dissolved in toluene (17.5 ml) and pipetted in portions (8 \times 1.75 ml) into each tube. The mixtures were heated to reflux (111 °C), and two 4A molecular sieve pellets were added to each tube. K-10 (0.0500 g \pm 0.0002 g) was added to each tube, and stirred at reflux for 8 hours. GC samples were removed at 2, 4 and 8 h,

diluted with HPLC-grade acetone and filtered through a Teflon disc filter (0.45 μ m) directly into a GC vial.

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