# Cation-exchanged Montmorillonite Clays as Lewis Acid Catalysts in the Fries Rearrangement of Phenyl Toluene-*p*-sulphonate

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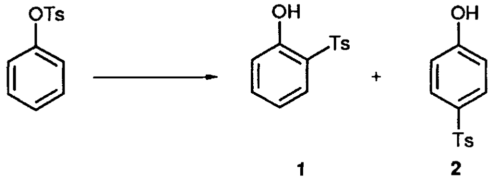
Cation-exchanged montmorillonite clays catalyse the Fries rearrangement of phenyl toluene-*p*-sulphonate to give selectively 2- and 4-hydroxyphenyl *p*-tolyl sulphones as major and minor products respectively.

The use of clays as catalysts and catalyst supports has received considerable attention recently.[1–4] Expandable layer lattice clays such as montmorillonites have $H_0$ values between 1.5 and −3 and their acidities may be enhanced further by ion-exchange. Acidic cation-exchanged montmorillonites are efficient catalysts in a number of proton-assisted reactions.[1] Such catalysts are interesting because the acidity is confined to the interlayer, the catalyst is easily separated from products, and the reactivity and selectivity may be different from those in homogeneous solution. We felt that cation-exchanged montmorillonite clays may function as effective Lewis acid catalysts in the place of conventional catalysts like anhydrous

**Table 1** Products distribution in the Fries rearrangement of phenyl toluene-*p*-sulphonate with various cation-exchanged montmorillonites

| Clay | Conversion (%; ±5%) | Yield (%)[b] 1 | 2 | Conditions[a] |
|---|---|---|---|---|
| Natural | No reaction | — | — | $CH_2Cl_2$, 120 °C, 3 h |
| 'Collapsed'[c] | No reaction | — | — | 160 °C, 3 h |
| $Na^+$-montmorillonite[d] | No reaction | — | — | 160 °C, 3 h |
| Natural | 100 | 88 | 12 | |
| $Al^{3+}$-montmorillonite | 100 | 92 | 8 | |
| $Fe^{3+}$-montmorillonite | 100 | 89 | 11 | |
| $Co^{2+}$-montmorillonite | 100 | 96 | 4 | |
| $Cr^{3+}$-montmorillonite | 100 | 79 | 21 | |
| $Cu^{2+}$-montmorillonite | 100 | 93 | 7 | |
| $H^+$-montmorillonite[e] | 100 | 86 | 14 | |
| $H^+$-montmorillonite | 100 | 81 | 19 | 180 °C, 6 h |
| $H^+$-montmorillonite | 100 | 65 | 35 | 180 °C, 12 h |
| Anhydrous $AlCl_3$[f] | 40 | Not reported | | 140 °C, $CS_2$, 90 min |

[a] Reactions were carried out at 180 °C (2 h) unless specified otherwise. [b] HPLC yield. [c] Prepared by heating natural clay at 160 °C overnight. [d] Also carried out with dichloromethane and acetic acid solvents. [e] With other cation-exchanged montmorillonites longer reaction times do not alter the product distribution. [f] Ref. 5.



aluminium chloride for Fries rearrangement, and we now report our results on the rearrangement of phenyl toluene-*p*-sulphonate.

Fries rearrangement of sulphonate esters has received little attention, despite its potential utility to produce precursors for organosulphur compounds. Heating of phenyl benzenesulphonate to 120 °C with anhydrous aluminium chloride gave a mixture of 2- and 4-hydroxydiphenyl sulphone in 12% yield.[5] At 160 °C, the yield of the isomer mixture was 45%. Heating of phenyl toluene-*p*-sulphonate with anhydrous aluminium chloride in the presence of carbon disulphide for 90 min at 140 °C gave a mixture of 2- and 4-hydroxyphenyl *p*-tolyl sulphone, in only about 40% yield.

We have studied this rearrangement in the presence of several cation-exchanged montmorillonite clays prepared as reported.[1] In a typical experiment, an intimate mixture of a cation-exchanged montmorillonite (0.2 g) and the substrate (0.2 g) was heated to 180 °C in an oil bath for 2 h, followed by extraction with diethyl ether and analysis by HPLC. The results (Table 1) demonstrate that natural as well as other cation-exchanged montmorillonite clays (cations include $Al^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Cr^{3+}$ and $H^{+}$) cause complete conversion of the substrate and also show high selectivity, the *ortho*-isomer **1** being the major product (~90% yield), indicating the superiority of cation-exchanged montmorillonites over anhydrous aluminium chloride as Lewis acid catalysts. With the acid-washed clays, the proportion of the *para*-isomer **2** increases after longer reaction times, a feature not observed for the other clays. The rearrangement does not take place with $Na^{+}$-montmorillonite and with a 'collapsed' clay, and there is no reaction between natural clay and the substrate in dichloromethane solvent.

The reactivity of these cation-exchanged clays provides qualitative support to previous conclusions regarding their acidities[1,2] and their ability to serve as efficient solid acid catalysts. Chemisorbed aluminium chloride has recently been shown to be useful for hydrocarbon cracking.[6]

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