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LETTERS

Fe(III) Exchanged Montmorillonite: A Mild And Eco-friendly Catalyst For Sulfonylation Of Aromatics

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Abstract: Fe(III) exchanged montmorillonite clay catalyses Friedel-Crafts sulfonylation of arenes with arylsulfonyl chlorides to obtain the corresponding sulfones in excellent yields. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Sulfonylation; Montmorillonite; Arenes; Sulfones.


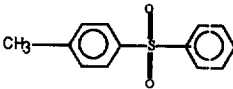
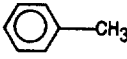
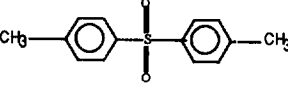
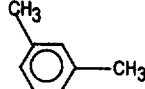
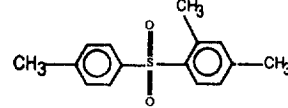
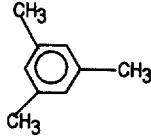
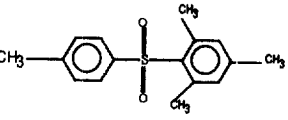

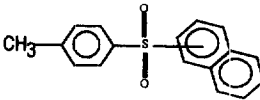

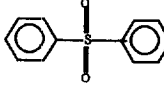
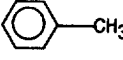
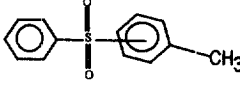
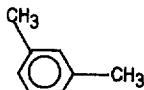
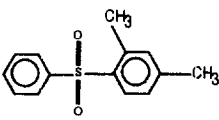
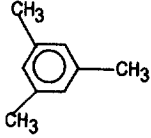
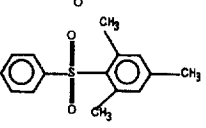
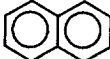
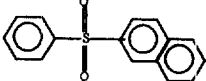
The increasing demand for cleaner processes prompted by stringent environment laws requires the use of ecofriendly and selective catalysts. The use of solid acids to replace waste generating soluble Lewis acids for the alkylation of arenes and acylation of activated arenes represent examples of improved procedures.

Diaryl sulfones are synthesised using conventional Lewis acid catalysts [1-5], for example AlCl_3 , and are useful intermediates for the drug industry. Aluminium chloride is widely used in the laboratory and industry and generates an enormous amount of solid waste. A catalytic sulfonylation method for the synthesis of diaryl sulfones using inexpensive and non-polluting reagents is highly desirable. In recent years the use of clays as catalysts and catalyst supports has received considerable attention [6-11]. Expandable layer lattice clays such as montmorillonites have H_0 values between 1.5 and -3 and their acidities may be tuned further by metal ion exchange with the introduction of a large number of Lewis acidic sites. Acidic cation exchanged montmorillonites are found to be efficient catalysts for electrophilic aromatic substitution reactions [12-14]. We report in this letter sulfonylations by a Fe^{3+} -montmorillonite catalyst for the first time affording high *para*-selectivity and excellent yields (Scheme 1).

Fe^{3+} -montmorillonite clay was prepared in accordance with the literature [13]. The Fe content analysis of the catalyst was carried out according to Vogel's procedure [15] and found to be

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Table 1.
Sulfonylation of Aromatics by Fe³⁺-montmorillonite.

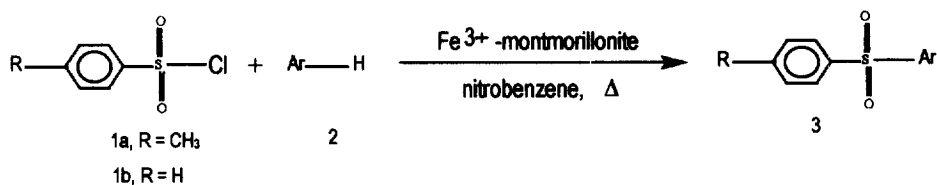
Entry	Sulfonyl chloride	Arene	Sulfone ^a	Reaction conditions time/temperature	Isolated Yield [%]
1	1a			12h/80°C	84
2	1a			6h/110°C	86
3	1a			6h/120°C	85
4	1a			6h/120°C	92
5	1a			3h/200°C	86 ^b
6	1b			12h/80°C	82 ^c
7	1b			6h/110°C	84 ^d
8	1b			6h/120°C	85
9	1b			6h/120°C	89
10	1b			3h/200°C	78

^a All the products were characterised by ¹H NMR, IR and Mass Spectroscopy.

^b Isomers distribution based on ¹H NMR α : β = 6:94.

^c 10 equivalents of benzene was taken. ^d *ortho* : *para* = 5:95.

6.32%.

Scheme 1.

In a typical experimental procedure, to a solution of mesitylene (0.42 ml, 3 mmol) and toluene-*p*-sulfonyl chloride (0.572g, 3 mmol) in nitrobenzene (5 ml), was added Fe³⁺-montmorillonite (200 mg). The reaction was maintained at 120°C for 6h. On completion of the reaction, the reaction mixture was cooled and filtered. The filtrate was taken into 20 ml of ether and washed with dil. NaHCO₃ solution (2x10 ml) and water (10 ml). The organics were dried (Na₂SO₄) and spin dried to give the product. Recrystallization from ethanol afforded pure mesityl tolyl sulfone as a white solid (0.756g, 92% yield).

Results for the sulfonylation of various aromatics are summarised in Table 1. Toluene-*p*-sulfonyl chloride is more reactive than benzene sulfonyl chloride. The *para*-selectivity is impressive in the examples 2 & 7 wherein >95% of the *para*-isomers of ditolyl sulfone and phenyl tolyl sulfone are obtained. On the other hand, aluminium chloride yields mixtures of isomers with the composition of *ortho*: *meta*: *para* = 28:7:65 [16]. Further the improvement in regioselectivity is also observed in sulfonylation of naphthalene with benzene sulfonyl chloride and toluene-*p*-sulfonyl chloride. In the synthesis of diphenyl sulfone, entry 6, an intermediate for DAPSONE (4,4'-diaminodiphenyl sulphone) [17], effective for leprosy treatment, the use of solid acid offers a commercially feasible route with control of solid effluents.

The catalyst can be reused for several cycles with consistent activity for, in example, sulfonylation of *meta*-xylene with toluene-*p*-sulfonyl chloride. Fe³⁺-montmorillonite is found to be superior to the Zn, Cu, Al exchanged montmorillonites in sulfonylation and the higher activity may be ascribed to the Fe in the montmorillonite in conjunction with the Lewis acidity thereby generated and Bronsted acid sites present at the edges of broken layers of the clay.

In conclusion, we have demonstrated a novel inexpensive methodology for Friedel-Crafts sulfonylation of aromatics employing the solid acid catalyst, Fe³⁺-montmorillonite, which has advantages of operational simplicity, environmental acceptability, non-corrosivity, mild conditions and high yields.

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