Friedel–Crafts sulfonylation of aromatics catalysed by solid acids: An eco-friendly route for sulfone synthesis

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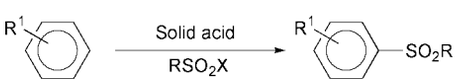
A mild and efficient catalytic method for Friedel–Crafts sulfonylation of arenes to the corresponding sulfones using a catalytic amount of reusable solid acid and arene- or alkanesulfonyl chlorides, sulfonic anhydrides and sulfonic acids as sulfonylating agents is described. Solid acids enable formation of a sulfone by the reaction of a sulfonic acid and an arene for the first time. In pursuit of the development of the best catalytic system, various metal-exchanged K10 montmorillonites and synthetic zeolites such as zeolite beta, zeolite Y and ZSM-5 have been screened for Friedel–Crafts sulfone synthesis. Fe^{3+}-montmorillonite in the family of clays and zeolite beta in the family of zeolites exhibit higher activity. The activity is correlated to the presence of the right mix of Brønsted and Lewis acidic sites. The regioselective sulfonylation of toluene and naphthalene are studied in which *para* and beta selectivities are observed respectively.

Introduction

Sulfones are useful intermediates in a wide range of fields such as agrochemicals,[1] pharmaceuticals[2] and polymers.[3] The sulfonyl group is a widely used synthon for synthetic organic chemists,[4] and sulfones have many industrial applications.[5] Aryl sulfones are synthesised through Friedel–Crafts sulfonylation of arenes using conventional Lewis acid catalysts,[6] such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, $SbCl_5$, $SnCl_4$, BF_3, silver triflate, bismuth(III) triflate and Brønsted acids, for example polyphosphoric acid[7] or triflic acid.[8] The inherent disadvantages encountered in the use of conventional soluble acid catalysts for Friedel–Crafts sulfonylation are (1) generation of a large amount of effluent, (2) inability to recycle reagents in the process, (3) difficulty in handling of the moisture-sensitive and hazardous Lewis acids, (4) highly corrosive conditions, (5) large requirement for water in the work-up involved after the reaction and finally, (6) offers lower selectivity of *para*/*ortho* sulfonylated isomers. In this connection, the use of heterogeneous catalysts in the liquid phase offers several advantages compared with their homogeneous counterparts, including ease of recovery of products, recyclability of reagents, regioselectivity and enhanced stability.

Solid acid catalysts

The solid acids having both Brønsted and Lewis acidities in their natural and cation-exchanged forms catalyse various organic transformations.[9] The contributions made by Clark, Laszlo and Moreau are significant in the development of solid acid catalysts. Expandable-layer lattice clays such as natural montmorillonite and its acid-treated counterpart, commercially known as K10 montmorillonite, have H_0-values between 1.5 and −8.2 and their acidities may be tuned further by metal-ion exchange with the introduction of a large number of Lewis acidic sites. The zeolites, which also possess Brønsted and Lewis acidic sites, exhibit shape selectivity owing to their crystalline porous structure which provides molecular-sized channels and/or cavities.[10] Wide use of solid acids for various organic transformations such as Friedel–Crafts alkylations and acylations,[11] rearrangements, esterification[12] and condensation[13] reactions have been documented. The sulfonylation of *o*-xylene with TsCl and toluene with MsCl using zinc supported on montmorillonite has been reported.[14a] Methanesulfonylation of toluene in the presence of cation-exchanged zeolite beta has also been reported.[14b,c] Recently we found sulfonylation of aromatics occurs by Fe^{3+}-montmorillonite, employing arenesulfonyl chlorides.[15] We now present a detailed study on the efficacy of the various solid acids in sulfonylation of arenes. This was mediated by employing modified natural clay catalysts and synthetic zeolites and varying sulfonylating agents such as sulfonyl chloride, sulfonic anhydride or sulfonic acid to afford high *para*-selectivity and excellent yields (Scheme 1). Further, the best solid acid catalysts with compatible Lewis and Brønsted acid sites required for effective Friedel–Crafts sulfonylation of arenes are realized through tuning the process of modification of clays and by employing the right choice of zeolites. We also highlight the synthesis of useful sulfone intermediates accessible through the process described here.



R = CH_3, Ph, tolyl
X = Cl, OH, OSO_2R

Scheme 1

Results and discussion

Generally the reactions were conducted at reflux temperatures with an excess of arene as a solvent. Initially, we undertook studies on the sulfonylation of *m*-xylene with various solid acid catalysts and a variety of sulfonylating agents to identify the best sulfonylating system (Table 1). *m*-Xylene was chosen as a substrate since only one isomer is expected to form in the reaction and the temperatures can be studied at up to 138 °C. The order of reactivity of sulfonylating agents is: Toluene-*p*-sulfonic anhydride (Ts_2O) > toluene-*p*-sulfonyl chloride (TsCl) > toluene-*p*-sulfonic acid (TsOH). The highest yields were obtained with Ts_2O. Sulfonic acids gave the corresponding sulfones in moderate yields albeit at longer reaction times. Incidentally, this is the first example of sulfonylation using sulfonic

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Table 1 Tolune-*p*-sulfonylation of *m*-xylene by various solid acid catalysts

Entry	Sulfonylating agent	Catalyst	Time (*t*/h)	Temp. (*T*/°C)	Product yield[a] (%)
a	TsCl	Fe^{3+}-mont	6	120	85
b	Ts_2O	Fe^{3+}-mont	6	120	92 (90,[b] 52[c])
c	TsOH	Fe^{3+}-mont	24	138	63
d	Ts_2O	Al^{3+}-mont	6	120	54
e	Ts_2O	Zn^{2+}-mont	6	120	80
f	Ts_2O	Cu^{2+}-mont	6	120	72
g	Ts_2O	K10 mont	6	120	41
h	Ts_2O	zeolite beta	6	120	85
i	Ts_2O	zeolite Y	6	120	68
j	Ts_2O	ZSM-5	6	120	50

[a] Isolated yield of (2,4-dimethylphenyl) *p*-tolyl sulfone **4**. [b] With used catalyst for 5th cycle. [c] With catalyst calcined at 550 °C.

Table 2 Sulfonylation of toluene catalysed by solid acids with various sulfonyl chlorides, sulfonic anhydrides and sulfonic acids

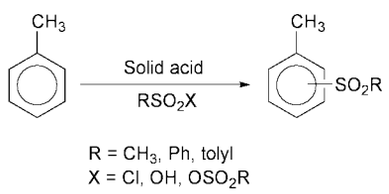
Entry	Sulfonylating agent	Catalyst	Time (*t*/h)	Yield[a] (%)	Isomer distribution[b] *o*:*m*:*p*
a	Ms_2O	Fe^{3+}-mont	6	81	47:19:34
b	Ms_2O	zeolite beta	6	78	42:21:37
c	Ms_2O	ZSM-5	6	60	48:14:38
d	Ms_2O	zeolite Y	6	54	50:15:35
e	$PhSO_2Cl$	Fe^{3+}-mont	6	84	5:0:95
f	$PhSO_2Cl$	zeolite beta	6	72	11:3:86
g	TsCl	Fe^{3+}-mont	6	86	1:0:99
h	TsCl	zeolite beta	6	53	1:0:99
i	TsOH	Fe^{3+}-mont	24	42	13:7:80
j	TsOH	zeolite beta	24	50	12:5:83
k	Ts_2O	Fe^{3+}-mont	6	84	11:6:83
l	Ts_2O	zeolite beta	6	88	14:6:80

[a] Yield refers to the mixture of isomeric products. [b] Isomers distribution based on ^{1}H NMR study of crude sulfones.

acids catalysed by solid acids. A Dean–Stark trap was employed to remove the water generated in the reactions in which a sulfonic acid has been used as an electrophile. We studied the catalytic activity of various metal-exchanged K10 montmorillonites and synthetic zeolites in order to identify the best catalyst. Fe^{3+}-montmorillonite was found to be superior to the Zn^{2+}-, Cu^{2+}-, and Al^{3+}-exchanged montmorillonites in sulfonylation and the sequence is $Fe^{3+} > Zn^{2+} > Cu^{2+} > Al^{3+} > K10$. The order of activity is in consonance with the results observed in Friedel–Crafts alkylations.[16] In case of zeolites, zeolite beta showed better activity than the other zeolites (zeolite beta > zeolite Y > ZSM-5). The catalyst was recovered by simple filtration. The used catalyst was oven-dried at 120 °C for 3 h before reuse and this protocol offered consistent activity of the catalyst for several cycles. However, catalyst calcined at higher temperatures showed only moderate activity (Table 1, entry b).

Regioselectivity

Various solid acid catalysts were screened for sulfonylation of toluene to evolve the best catalyst in terms of regioselectivity and activity (Scheme 2, Table 2). The reactions were conducted



Scheme 2

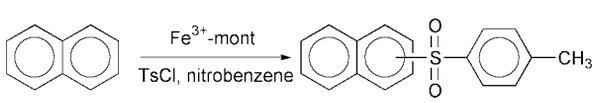
at 120 °C with excess of toluene as a solvent. The various sulfonylating agents employed here gave good yields. Fe^{3+}-mont is superior to zeolite beta in the sulfonylation reaction. The selectivity obtained with these solid acids in the methanesulfonylation of toluene was similar to that obtained with the conventional anhydrous aluminium chloride method wherein a 33% yield of the *para* isomer was obtained. A tremendous enhancement of *para* selectivity was observed, giving as high as 99% *para* isomers in the arenesulfonylation of toluene in contrast to 86% by the conventional method.[6c] The sulfonylation of toluene with sulfonyl chlorides afforded better selectivity than with sulfonic anhydrides or sulfonic acids. However, a better reuse of catalyst was observed in non-chloride-containing systems.

Table 3 Tolune-*p*-sulfonylation of naphthalene using TsCl and Fe^{3+}-montmorillonite

Entry	Temp (*T*/°C)	Time (*t*/h)	Yield[a] (%)	Isomer distribution[b] α:β
a	100	6	65	77:23
b	130	6	78	47:53
c	160	6	84	28:72
d	180	3	82	11:89
e	200	3	86	6:94

[a] Isolated yields. [b] Isomers distribution based on ^{1}H NMR study of crude sulfones.

Furthermore, regioselectivity was also observed in sulfonylation of naphthalene with TsCl (Scheme 3, Table 3). In the case



Scheme 3

of naphthalene at low temperatures the α-isomer was the major product. With an increase in reaction temperature the selective formation of β-isomer reached 94% at 200 °C as identified by the ^{1}H NMR spectra in which the methyl protons of the tolyl group appear at δ 2.36 and δ 2.38 for α-isomer and β-isomer, respectively. However at room temperature there was no reaction even after 48 h.

Table 4 Fe^{3+}-montmorillonite-catalysed sulfonylation of arenes with sulfonic acids and sulfonic anhydrides

Entry	Arene	Sulfonylating agent	Product and isomers	Temp (T/°C)	Time (t/h)	Yield[a] (%)
a	benzene	Ms_2O	**1**	80	6	82
b	benzene	$PhSO_3H$	**2**	80	24	61
c	benzene	Ts_2O	**3**	80	6	82
d	*m*-xylene	TsOH	**4**	138	24	63
e	*m*-xylene	$PhSO_3H$	**5**	138	24	68
f	*m*-xylene	MsOH	**6**	138	24	23
g	*p*-xylene	Ms_2O	**7**	120	6	78
h	*p*-xylene	MsOH	**7**	138	24	25
i	*p*-xylene	Ts_2O	**8**	120	6	94
j	*p*-xylene	TsOH	**8**	138	24	60
k	*p*-xylene	XsOH[b]	**9**	138	24	52
l	mesitylene	Ms_2O	**10**	120	6	85
m	mesitylene	Ts_2O	**11**	120	6	94
n	anisole	Ts_2O	**12**(21 : 79)[c]	120	6	86
o	chlorobenzene	Ms_2O	**13**(26 : 74)[c]	120	6	82
p	chlorobenzene	$PhSO_3H$	**14**(17 : 83)[c,d]	133	24	64
q	chlorobenzene	Ts_2O	**15**	120	6	88
r	bromobenzene	Ts_2O	**16**	120	6	75[e]

[a] Yield refers to the isolated products. [b] *p*-Xylenesulfonic acid. [c] *ortho* and *para* isomers based on ^1H NMR spectroscopy. [d] By GLC. [e] 0.4 g of the catalyst was employed.

In Table 4, we extended the examples towards a series of arenes, in the presence of Fe^{3+}-montmorillonite using various alkyl and aryl sulfonylating agents. Fe^{3+}-montmorillonite is capable of catalysing not only the sulfonylation of activated arenes (entries d–n) but also that of deactivated arenes such as chlorobenzene and bromobenzene. Monosulfonylated products were invariably obtained in sulfonylation reactions. However, the *para*-isomer only is formed in the sulfonylation of chloro- and bromobenzene, when Ts_2O was employed as sulfonylating agent, whereas anisole afforded mixture of *ortho* and *para* isomers.

The sulfones obtained in this process were useful intermediates; for example, diphenyl sulfone (Table 4, entry b) is an intermediate for dapsone, an antileprosy drug.[2a] *p*-Chlorophenyl phenyl sulfone (Table 4, entry p) is used as an insecticide.[5] Methyl *p*-tolyl sulfone (Table 2, entries a–d) is an intermediate for a herbicide.[1] The halogenated aromatic sulfone compounds can be used as monomers in the production of high-temperature arylene sulfide sulfone polymers.[3c]

For homogeneous catalysis of Friedel–Crafts sulfonylation, Lewis acids are more effective than Brønsted acids as is evident from the superior activity of anhydrous aluminium chloride[6c] over polyphosphoric acid.[7] In order to elucidate the nature of the active sites of solid catalysts that induce sulfonylation of arenes, several modified clays and zeolites have been screened. Among the family of metal-exchanged montmorillonites, Fe^{3+}-montmorillonite was found to be superior in the sulfonylation reaction, while zeolite beta is very active in the family of zeolites. Acid-treated montmorillonite, commercially known as montmorillonite K10, with a highly mesoporous structure compatible for large reacting molecules and a high density of acidic sites as such showed moderate activity in sulfonylation of arenes (Table 1, entry g). Therefore, metal-exchanged montmorillonites were conceived and prepared using commercial K10 as a support. The activity of the metal-exchanged K10 montmorillonites in the sulfonylation of arenes is higher than the commercial K10 montmorillonite used as supplied. This result indicated that the mere presence of a higher number of Brønsted acidic sites per unit volume, predominantly at broken edges of the layered structure of montmorillonite K10, was not adequate to afford optimum yields of sulfone product.

In the hydrated montmorillonite, metal aquo-complexes generate protons and the number of protons generated is directly proportional to the ratio of ionic charge/ionic radius of exchanged metal ion.[17] Accordingly, an intercalated Fe^{3+} complex generates a higher number of protons than the other metal ions employed in this study. The order of activity $Fe^{3+} > Zn^{2+} > Cu^{2+} > Al^{3+} > K10$ observed in this reaction supports the above. However, Al^{3+} ion shows activity inferior to divalent ions such as Zn^{2+} and Cu^{2+}. This may be ascribed to the weak acidic sites generated by Al^{3+}. Lewis acidic sites are also introduced by exchange of metal cations in K10 montmorillonite. The higher Friedel–Crafts sulfonylation activity of the Fe^{3+}-montmorillonite, conducted with an oven-dried sample, is therefore ascribed to the presence of a higher density of Lewis acidic sites through the exchange of Fe^{3+} in the montmorillonite and Brønsted acid sites as described. As indicated in our experiments, the Fe^{3+}-montmorillonite calcined at higher temperature in air shows less activity. This can be explained that upon calcination, the catalyst loses preferentially Brønsted acidic sites and retains the Lewis acidic sites.[18] From these results it was inferred that the compatible mixture of Brønsted and Lewis acidity plays a vital role in the reaction.

In case of zeolites, zeolite beta showed the highest activity in the sulfonylation of *m*-xylene and the activity follows the sequence zeolite beta > zeolite Y > ZSM-5. A similar order of activity was observed by Corma *et al.* in the acylation of anisole and cyclohexene.[19] With regard to the influence of the zeolite structure, it indicated that medium pore sized ZSM-5 is less active than the tridirectional Y and beta zeolites under similar experimental conditions (Table 1). The zeolite beta and Y have both Lewis and Brønsted acidic sites. However, the higher activity of zeolite beta over zeolite Y may be attributed to the increased number of Lewis acidic sites per unit volume.[18] On the other hand ZSM-5 shows moderate activity due to presence of Brønsted acidic sites only.[20] Therefore, the Lewis and Brønsted acidic sites both in clays and zeolites have similar effects on the activity, and correct admixtures of these sites show optimum activity. It is impressive to note that these compatible Lewis and Brønsted acidic sites of the solid acids, make the formation of electrophiles from sulfonic acid in the sulfonylation reaction, which is a difficult task, possible.

Conclusions

In summary, the simple methodology for sulfonylation of arenes with sulfonyl chloride, sulfonic anhydride or sulfonic acid as sulfonylating agent, catalysed by a small amount of reusable solid acid catalyst, presented here offers superior economic viability over currently practiced Friedel–Crafts sulfonylation conducted with large amounts of waste-generating Lewis acids. The higher activity of Fe^{3+}-montmorillonite in the family of clays and zeolite beta in the family of zeolites is due to a compatible mixture of Lewis and Brønsted acid sites in large

number per unit volume. Steric crowding of the supported catalyst influences higher *para* selectivities observed in the sulfonylation of toluene. Further, the other striking advantages offered by our methodology include (1) high atom economy, (2) minimization of effluents, (3) simple work-up procedure, (4) reusable catalysts. From these salient features it can be termed as an eco-friendly process for sulfone synthesis.

Experimental

IR spectra were recorded on a Nicolet 740 FTIR spectrometer for samples as KBr pellets. ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz instrument for solutions in $CDCl_3$ with TMS as an internal standard. Mass spectra were recorded on VG micromass 7070H and Finnigan MAT 1020 mass spectrometers. TLC was performed on silica gel 60 F_{254} plates procured from E-Merck. Toluene-*p*-sulfonyl chloride, toluene-*p*-sulfonic anhydride, methanesulfonyl chloride, methanesulfonic anhydride (Aldrich), benzenesulfonic acid (E-Merck), benzenesulfonyl chloride and toluene-*p*-sulfonic acid (SRL, India) were used without further purification. *p*-Xylenesulfonic acid was prepared. K10 montmorillonite was purchased from Fluka. Zeolite beta and zeolite Y were commercial ZEOLYST products with SiO_2/Al_2O_3 molar ratios of 22 and 5.1, respectively. ZSM-5 was a commercial product of United Catalysts India Ltd with SiO_2/Al_2O_3 molar ratio of 150. All reactions were run in flame-dried glassware under a nitrogen atmosphere. Mps were measured on a V Scientific digital melting point apparatus and are uncorrected.

Preparation of metal-exchanged montmorillonites[16]

To 1 L of 1 M aqueous metal chloride solution was added 80 g of K10 montmorillonite. Stirring was maintained for 16–30 h in order to saturate the exchange capacity of K10 montmorillonite. The clay suspension was centrifuged and the supernatant solution was discarded. The clay catalyst was washed each time with fresh distilled water until free of chloride ions as indicated by the $AgNO_3$ test. The catalyst was dried overnight in an oven at 120 °C and finely ground in a mortar. The metal content of Fe^{3+}-, Zn^{2+}-, Cu^{2+}-, Al^{3+}-exchanged montmorillonite catalysts was analysed according to Vogel's procedure[21] and found to be Fe = 6.32, Zn = 1.79, Cu = 1.28, Al = 7.82%.

Sulfonylation of arenes. General procedure

In a typical experimental procedure, to a solution of arene (5 mL) and sulfonylating agent (3 mmol) was added 0.2 g of solid acid catalyst. The reaction was maintained at reflux temperature. On completion of the reaction, the reaction mixture was cooled and filtered. The catalyst was rinsed with diethyl ether followed by methanol. The filtrate was washed successively with dil. aq. $NaHCO_3$ (2 × 10 mL) and water (10 mL). The organics were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the product.

Sulfonylation of naphthalene

To a solution of naphthalene (0.3 g, 3 mmol) and toluene-*p*-sulfonyl chloride (0.57 g, 3 mmol) in nitrobenzene (10 mL) was added Fe^{3+}-montmorillonite (0.2 g, 0.22 mmol of Fe) and the mixture was heated in a two-necked flask under nitrogen atmosphere. On completion of the reaction, the reaction mixture was cooled and filtered. The filtrate was taken into 20 mL of diethyl ether and washed successively with dil. aq. $NaHCO_3$ (2 × 10 mL) and water (10 mL). The organics were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the product. Recrystallisation from ethanol afforded pure naphthyl *p*-tolyl sulfone as a white solid.

All the products have been characterised by their mps and spectral (IR, ^{1}H NMR and mass) data. These data are presented below.

Methyl *o*-, *m*- and *p*-tolyl sulfone (Table 2, entry a). ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.40 (s, ArMe, *p*), 2.41 (s, ArMe, *m*), 2.65 (s, ArMe, *o*), 3.18 (s, SO_2Me, *p*), 3.20 (s, SO_2Me, *m*), 3.21 (s, SO_2Me, *o*), 7.43–7.93 (m, ArH).

Phenyl *o*- and *p*-tolyl sulfone (Table 2, entry e). ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.39 (s, Me, *p*), 2.45 (s, Me, *o*) 7.29 (2 H, d), 7.48 (3 H, m), 7.83 (2 H, d), 7.94 (2 H, d).

Di(*p*-tolyl) sulfone (Table 2, entry g). Solid, mp 155 °C (lit.,[7a] 156 °C); IR (KBr) 1161, 1310 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.39 (6 H, s, 2 × CH_3), 7.26 (2 H, d, *J* 9.0 Hz), 7.79 (2 H, d, *J* 9.0 Hz); MS (EI) *m*/*z* 246 (M^+), 139 (100%), 107, 91, 65.

α- and β-Naphthyl *p*-tolyl sulfone (Table 3, entry e). Solid, mp 114 °C (lit.,[7a] 121 °C); IR (KBr) 1152, 1312 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.36 and 2.38 (CH_3, 2 s, α and β isomers), 7.27 (2 H, d), 7.59 (2 H, m), 7.78 (1 H, d), 7.83 (2 H, d), 7.87 (1 H, m), 7.93 (1 H, d), 7.97 (1 H, d), 8.52 (1 H, s).

Methyl phenyl sulfone 1. Solid, mp 86 °C (lit.,[22] 84–85 °C); IR (KBr) 1136, 1296 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 3.02 (3 H, s, CH_3), 7.57 (3 H, m), 7.92 (2 H, d); MS (EI) *m*/*z* 156 (M^+), 141, 77 (100%), 51.

Diphenyl sulfone 2. Solid, mp 124 °C (lit.,[7a] 121 °C); IR (KBr) 1148, 1287 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.50 (6 H, m), 7.88 (4 H, m); MS (EI) *m*/*z* 218 (M^+), 125 (100%), 77, 51, 50.

Phenyl *p*-tolyl sulfone 3. Solid, mp 127 °C (lit.,[7a] 125 °C); IR (KBr) 1153, 1307 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.39 (3 H, s, CH_3), 7.29 (2 H, d), 7.48 (3 H, m), 7.83 (2 H, d), 7.94 (2 H, d); MS (EI) *m*/*z* 232 (M^+), 139, 125, 107, 91, 77, 65, 51 (100%), 39.

(2,4-Dimethylphenyl) *p*-tolyl sulfone 4. Solid, mp 50 °C (lit.,[7a] 49 °C); IR (KBr) 1155, 1310 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.36 (3 H, s, CH_3), 2.38 (3 H, s, CH_3), 2.40 (3 H, s, CH_3), 6.99 (1 H, s), 7.13 (1 H, d), 7.23 (2 H, d), 7.70 (2 H, d), 8.03 (1 H, d); MS (EI) *m*/*z* 260 (M^+), 242, 194, 91, 77 (100%), 51.

(2,4-Dimethylphenyl) phenyl sulfone 5. Solid, mp 86 °C (lit.,[7a] 85 °C); IR (KBr) 1151, 1306 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.32 (3 H, s, CH_3), 2.37 (3 H, s, CH_3), 6.99 (1 H, s), 7.16 (1 H, d), 7.46 (3 H, m), 7.81 (2 H, d), 8.07 (1 H, d); MS (EI) *m*/*z* 246 (M^+), 228, 180, 103, 91, 77 (100%), 51.

(2,4-Dimethylphenyl) methyl sulfone 6. Solid, mp 54 °C (lit.,[5] 56 °C); IR (KBr) 1143, 1302 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.40 (3 H, s, CH_3), 2.67 (3 H, s, CH_3), 3.01 (3 H, s, CH_3), 6.94 (1 H, s), 7.13 (1 H, d), 7.90 (1 H, d).

(2,5-Dimethylphenyl) methyl sulfone 7. Solid, mp 44 °C (lit.,[6e] 45 °C); IR (KBr) 1139, 1298 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.38 (3 H, s, CH_3), 2.63 (3 H, s, CH_3), 3.01 (3 H, s, CH_3), 7.18 (1 H, d), 7.27 (1 H, d), 7.79 (1 H, s); MS (EI) *m*/*z* 184 (M^+), 169, 121, 105 (100%), 77, 51.

(2,5-Dimethylphenyl) *p*-tolyl sulfone 8. Solid, mp 104 °C (lit.,[23] 108–110 °C); IR (KBr) 1146, 1300 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.36 (3 H, s, CH_3), 2.41 (6 H, s, 2 × CH_3), 7.06 (1 H, d), 7.21 (1 H, d), 7.26 (2 H, d), 7.72 (2 H, d), 7.98 (1 H, s); MS (EI) *m*/*z* 260 (M^+), 242, 225, 194, 151, 104, 91, 77 (100%), 65.

Bis(2,5-dimethylphenyl) sulfone 9. Solid, mp 142 °C (lit.,[7a] 143 °C); IR (KBr) 1149, 1305 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ 2.30 (3 H, s, CH_3), 2.46 (3 H, s, CH_3), 7.08 (1 H, d), 7.28 (1 H, d), 7.99 (1 H, s).

Mesityl methyl sulfone 10. Solid, mp 129 °C (lit.,[6e] 130 °C); IR (KBr) 1126, 1295 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 2.30 (3 H, s, CH_3), 2.64 (6 H, s, 2 × CH_3), 3.0 (3 H, s, CH_3), 6.93 (2 H, s).

Mesityl *p*-tolyl sulfone 11. Solid, mp 123 °C (lit.,[7a] 117 °C); IR (KBr) 1155, 1310 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 2.29 (3 H, s, CH_3), 2.41 (3 H, s, CH_3), 2.58 (6 H, s, 2 × CH_3), 6.90 (2 H, s), 7.24 (2 H, d), 7.65 (2 H, d); MS (EI) *m*/*z* 274 (M^+), 256 (100%), 208, 193, 165, 117, 91, 65.

(4-Methoxyphenyl) *o*- and *p*-tolyl sulfone 12.[7c] Solid; IR (KBr) 1156, 1315 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 2.36 and 2.43 (Me, 2 s, *p*-**12** and *o*-**12**), 3.78 and 3.81 (MeO, 2 s, *o*-**12** and *p*-**12**), 6.91 (2 H, d), 7.24 (2 H, d), 7.78–7.87 (4 H, 2 d).

2- and 4-Chlorophenyl methyl sulfone 13.[6e] Liquid; IR (film) 1154, 1316 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 2.96 and 3.17 (CH_3, 2 s, *p*-**13** and *o*-**13**), 7.47–8.05 (m, 4 H).

(4-Chlorophenyl) phenyl sulfone 14.[6h] Solid; IR (KBr) 1152, 1318 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 7.50 (5 H, m), 7.85 (4 H, m).

(4-Chlorophenyl) *p*-tolyl sulfone 15.[6h] Solid; IR (KBr) 1153, 1315 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 2.39 (3 H, s, CH_3), 7.27 (2 H, d), 7.45 (2 H, d), 7.77 (2 H, d), 7.84 (2 H, d); MS (EI) *m*/*z* 268 [M^+(^{37}Cl), 19%], 266 [M^+(^{35}Cl), 51], 161, 159, 139 (100), 107, 91, 65.

(4-Bromophenyl) *p*-tolyl sulfone 16. Solid, mp 134 °C (lit.,[6h] 135–136 °C); IR (KBr) 1152, 1314 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 2.40 (3 H, s, CH_3), 7.28 (2 H, d), 7.61 (2 H, d), 7.78 (2-,2′-, 6-,6′-H, m); MS (EI) *m*/*z* 312 [M^+(^{81}Br), 21%], 310 [M^+(^{79}Br), 23], 205, 203, 139 (100), 107, 91, 79, 77, 76, 65, 75, 50.

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References

1 W. J. Michaely and G. W. Kraatz, *US Pat.*, 4 780 127, 1988 (*Chem. Abstr.*, 1989, **111**, P129017a).
2 (*a*) J. Weijlard and J. P. Messerly, *US Pat.*, 2 385 899, 1945 (*Chem. Abstr.*, 1946, **40**, P180); (*b*) A. Padwa, W. H. Bullock and A. D. Dyszlewski, *J. Org. Chem.*, 1990, **55**, 955.
3 (*a*) S. M. Mackinnon and J. Y. Wang, *Macromolecules*, 1998, **31**, 7970; (*b*) F. Paolo, M. Giorgio, M. Patrizia, P. Concetto and S. Filippo, *Macromol. Chem. Phys.*, 1996, **197**, 1007; (*c*) R. L. Robsein, J. J. Straw and D. R. Fahey, *US Pat.*, 5 260 489, 1993 (*Chem. Abstr.*, 1994, **120**, P165200z).
4 (*a*) P. D. Magnus, *Tetrahedron*, 1977, **33**, 2019; (*b*) L. Field, *Synthesis*, 1978, 713.
5 K. M. Roy, in *Ullmann's Encyclopedia of Industrial Chemistry*, ed. W. Gerhartz, VCH, Weinheim, Germany, 1985, vol. A25, pp. 487–501.
6 (*a*) F. R. Jensen and G. Goldman, in *Friedel–Crafts and Related Reactions*, ed. G. Olah, Wiley-Interscience, New York, 1964, vol. III, pp. 1319–1367; (*b*) R. Taylor, in *Comprehensive Chemical Kinetics*, ed. C. H. Bamford and C. F. H. Tipper, Elsevier, New York, 1972, pp. 77–83; (*c*) G. A. Olah, S. Kobayashi and J. Nishimura, *J. Am. Chem. Soc.*, 1973, **95**, 564; (*d*) G. A. Olah and H. C. Lin, *Synthesis*, 1974, 342; (*e*) J. A. Hyatt and A. W. White, *Synthesis*, 1984, 214; (*f*) M. Desbois, *US Pat.*, 4 554 381, 1985 (*Chem. Abstr.*, 1985, **103**, P141625q); (*g*) F. Effenberger and K. Huthmacher, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 409; (*h*) S. Repichet, C. L. Roux, P. Hernandez and J. Dubac, *J. Org. Chem.*, 1999, **64**, 6479.
7 (*a*) B. M. Graybill, *J. Org. Chem.*, 1967, **32**, 2931; (*b*) H. J. Sipe, Jr., D. W. Clary and S. B. White, *Synthesis*, 1984, 283; (*c*) M. Ueda, K. Uchiyama, T. Kano, *Synthesis*, 1984, 323.
8 (*a*) F. Effenberger and K. Huthmacher, *Chem. Ber.*, 1976, **109**, 2315; (*b*) M. Ono, Y. Nakamura, S. Sato and I. Itoh, *Chem. Lett.*, 1988, 395.
9 (*a*) J. H. Clark and D. Macquarrie, *Chem. Soc. Rev.*, 1996, **25**, 303; (*b*) M. Balogh and P. Laszlo, *Organic Chemistry using Clays*, Springer-Verlag, New York, 1993; (*c*) A. Finiels, P. Geneste, J. Lecomte, F. Marichez, C. Moreau and P. Moreau, *J. Mol. Catal. A: Chem.*, 1999, **148**, 165; (*d*) T. J. Pinnavaia, *Science*, 1983, **220**, 365; (*e*) R. S. Drago and E. E. Getty, *J. Am. Chem. Soc.*, 1988, **110**, 3311; (*f*) J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 913; (*g*) R. A. Sheldon, *Chem. Ind.* (*London*), 1997, 12.
10 S. E. Sen, S. M. Smith and K. A. Sullivan, *Tetrahedron*, 1999, **55**, 12657.
11 (*a*) B. M. Choudary, M. Sateesh, M. L. Kantam and K. V. R. Prasad, *Appl. Catal. A.*, 1998, **171**, 155; (*b*) B. M. Choudary, M. L. Kantam, M. Sateesh, K. K. Rao and P. L. Santhi, *Appl. Catal. A.*, 1997, **149**, 257.
12 (*a*) A. X. Li, T. S. Li and T. H. Ding, *Chem. Commun.*, 1997, 1389; (*b*) D. E. Ponde, V. H. Deshpande, V. J. Bulbule, A. Sudalai and A. S. Gajare, *J. Org. Chem.*, 1998, **63**, 1058.
13 F. Bigi, L. Chesini, R. Maggi and G. Sartori, *J. Org. Chem.*, 1999, **64**, 1033.
14 (*a*) S. J. Barlow and C. Calvert, *Environmentally-Friendlier Catalysts Using Non-Toxic Supported Reagents*, BACS Symposium at Chemspec Europe, 1993; (*b*) K. Smith, G. M. Ewart and K. R. Randles, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1085; (*c*) S. Daley, K. A. Trevor, K. R. Randles and B. D. Gott, *PTC Int. Appl.* WO93 18. 000, 1993 (*Chem. Abstr.*, 1994, **120**, P54320u).
15 B. M. Choudary, N. S. Chowdari, M. L. Kantam and R. Kannan, *Tetrahedron Lett.*, 1999, **40**, 2859.
16 P. Laszlo, A. Mathy, *Helv. Chim. Acta*, 1987, **70**, 577.
17 R. D. Laura, *Clay Min.*, 1976, **11**, 331.
18 C. Cativiela, F. Figueras, J. M. Fraile, J. I. Garcia, J. A. Mayoral, L. C. de Menorval and E. Pires, *Appl. Catal. A.*, 1993, **101**, 253.
19 (*a*) A. Corma, M. J. Climent, H. Garcia and J. Primo, *Appl. Catal. A.*, 1989, **49**, 109; (*b*) E. Armengol, A. Corma, L. Fernandez, H. Garcia and J. Primo, *Appl. Catal. A.*, 1997, **158**, 323.
20 Y. Isaev and J. J. Fripiat, *J. Catal.*, 1999, **182**, 257.
21 A. R. Vogel, *Textbook of Quantitative Inorganic Analysis*, ed. G. H. Jaffery, J. Bassett, J. Mendham and R. C. Denney, Longman, London, 5th edn., 1989, p. 417.
22 W. E. Truce and C. W. Vriesen, *J. Am. Chem. Soc.*, 1953, **75**, 5032.
23 H. Drews and S. Meyerson, *J. Am. Chem. Soc.*, 1961, **83**, 3871.