

# Regioselective methanesulfonylation of toluene catalysed by cation-exchanged zeolite $\beta$

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**The reaction of methanesulfonic anhydride with toluene over various cation exchanged zeolite beta catalysts affords higher *para*-selectivity and better yields of methyl tolyl sulfone than standard Friedel–Crafts sulfonylation utilising aluminium chloride.**

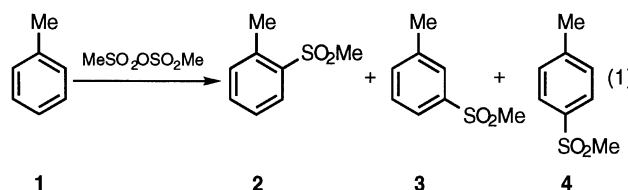
In recent years many selective electrophilic aromatic substitutions have been carried out with the help of solid or solid-supported catalysts.<sup>1–10</sup> In particular, zeolite catalysts impose regioselectivity through their microporous structures, consisting of pores and channels of molecular dimensions, which can render *ortho* and *meta* substitution difficult. However, little use has been made of this approach for the sulfonylation of toluene and other aromatic compounds.

The best known method for methanesulfonylation of toluene involves aluminium chloride as the catalyst and methanesulfonyl chloride as reagent, but affords a yield of only 52% with an *o*:*m*:*p* isomer distribution of 53:14:33.<sup>11</sup> Furthermore, the aluminium chloride cannot be recovered and creates an effluent problem. A truly catalytic sulfonylation method for alkylbenzenes using inexpensive and non-polluting reagents is therefore highly desirable, particularly if it can be rendered highly *para*-selective. A supported Lewis acid catalyst has been recommended for selective sulfonylations,<sup>12</sup> but yields and selectivities were still not good in our hands when the recommended catalyst was used for the reaction of toluene with methanesulfonyl chloride. The best *para*-selectivity to date, reported in the patent literature, was obtained by the use of the protonated form of zeolite  $\beta$  as catalyst with methanesulfonyl chloride as reagent, which in the most favourable cases gave methyl tolyl sulfone in a yield of 14%, of which 81% was the *para*-isomer.<sup>13</sup> We therefore undertook a broader study of the latter reaction in the hope of finding a better catalyst/reagent system for the selective *para*-methanesulfonylation of toluene.

Initially, different methanesulfonylating agents were tested

with a small number of selected solid catalysts in refluxing toluene. Methanesulfonyl chloride gave much better yields than methanesulfonyl chloride in these tests, while other reagents tried produced negligible yields of sulfonylated products. The anhydride was therefore chosen for further study. With this reagent the yield of methyl tolyl sulfones was highest when the catalyst was Synclyst 13, an amorphous silica–alumina. Under standard conditions (0.6 g of catalyst, 1.2 g of anhydride in 15 ml of refluxing toluene, 18 h) the yield was 85%, but it could be raised to 91% by the use of a dry bag during transfer of the anhydride and by addition of a little phosphorus pentoxide to the reaction mixture. Unfortunately, although the yield (based on anhydride) was excellent, the regioselectivity was unexceptional (*o*:*m*:*p* = 56:10:34). Attention was therefore turned to the use of zeolite catalysts in the hope of gaining shape-selectivity.

Preliminary screening of a range of proton-form zeolites suggested that zeolite  $\beta$  offered the best *para*-selectivity (*o*:*m*:*p* = 37:11:53) and a good yield (79%). Therefore, a range of cation-exchanged forms of zeolite  $\beta$  was prepared by the use of a standard procedure. [The supplied material, following calcination at 550 °C to remove the template, was stirred in a 1 M refluxing aqueous solution of the corresponding metal chloride (10 ml g<sup>-1</sup>) for 1 h, then filtered, washed with water, subjected to a second exchange, washed with water until halide-free, and then calcined at 400 °C. No attempt was made to estimate the degree of cation exchange in individual cases.] These zeolites were then tested as catalysts in the reaction [eqn. (1)]. The results are reported graphically in Fig. 1.



		M <sup>n+</sup> Yield <i>para</i>															
H <sup>+</sup> 79 53																	
Li <sup>+</sup> 51 55	Be <sup>2+</sup> 52 67																
Na <sup>+</sup> 14 97	Mg <sup>2+</sup> 69 43														Al <sup>3+</sup> 69 47		
K <sup>+</sup> 12 53	Ca <sup>2+</sup> 62 61			Ti <sup>3+</sup> 72 44		Cr <sup>3+</sup> 73 50	Mn <sup>2+</sup> 68 45	Fe <sup>3+</sup> 46 54	Co <sup>2+</sup> 77 55	Ni <sup>2+</sup> 72 45	Cu <sup>2+</sup> 65 55	Zn <sup>2+</sup> 66 48		Ga <sup>3+</sup> 60 45			
Rb <sup>+</sup> 3 79	Sr <sup>2+</sup> 33 62			Zr <sup>4+</sup> 75 43										Cd <sup>2+</sup> No Rxn	In <sup>3+</sup> 1 71	Sn <sup>4+</sup> 77 40	
Cs <sup>+</sup> 1 67	Ba <sup>2+</sup> 50 71	La <sup>3+</sup> 62 46												Hg <sup>2+</sup> 28 77	Tl <sup>3+</sup> 66 43		
				Ce <sup>3+</sup> 68 50													

Fig. 1 Total yield (after isolation by distillation) of 2, 3 and 4 (%) and proportion (%) of the product corresponding to 4 for reactions according to eqn. (1) with different cation forms of zeolite  $\beta$

Several features of interest emerge from Fig. 1. Within group 1 the yields decrease down the group as the cations become larger. The larger cations presumably block entry to the pore system of the zeolite, spoiling its potential as a catalyst. However, the restriction of the pore size might also be expected to lead to an increase in *para*-selectivity, which is apparent with sodium but tails off thereafter. With the larger cations it may be that a substantial proportion of the product arises from reaction at the external surface, thereby reducing the regioselectivity and also limiting the yield because of the relatively small number of available sites.

For Group 2 the yields are higher than their Group 1 counterparts in every case. Presumably the smaller divalent cations allow easier entry into the pore network, which would be consistent with the increased yields. There is also a general increase in *para*-selectivity going down the group as the cations get larger, but again at the expense of overall yield.  $\text{Be}^{2+}\beta$  appears to be an exception, giving a lower yield and higher selectivity than the  $\text{Mg}^{2+}\beta$  analogue.

With the exception of  $\text{In}^{3+}$ , all trivalent and tetravalent cation cases produced reasonable yields (typically 60–70%) and *para*-product proportions in the range 40–50%. This is consistent with the idea that small cations allow more space for reaction and the results are fairly similar to those obtained with proton-exchanged zeolite. The divalent cations of the first transition series provided rather similar results also, with yields typically 70% and *para*-proportions typically 50%.

The cases which provided results that were out of line may have arisen from poor exchange, impurities or pore-blocking, however the benefits to be gained from more careful scrutiny of them could not justify the amount of work involved in such a study. It is clear that overall there is a broad correlation between cation size and both yield and selectivity. Unfortunately, there is also a trade-off between the two, with those cases providing highest *para*-selectivity also giving rather poor yields. Nevertheless, the sodium-exchanged case offers the possibility of very high *para*-selectivity if the yield based on the anhydride is not critical (methanesulfonic acid can be recovered after work-up). Alternatively, reasonable *para*-selectivity can be achieved in

quite good yield by use of proton, calcium, barium or cobalt(II) exchanged forms of zeolite  $\beta$ . All of these cases provide much better *para*-selectivity than the published reaction with aluminium chloride and methanesulfonyl chloride and in most cases the yield is substantially improved too. With the additional advantages of easy catalyst recovery and the lack of a metal-containing waste stream, this approach should prove attractive for sulfonylation reactions.

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