

Sulfonylation of substituted benzenes using Zn-exchanged zeolites

Paul Laidlaw^a, Donald Bethell^a, Stephen M. Brown^b, Graeme Watson^c,
David J. Willock^c, Graham J. Hutchings^{a,c,*}

^a Department of Chemistry, Leverhulme Centre for Innovative Catalysis, University of Liverpool, Liverpool, L69 3BX, UK

^b Technology and Project Group, Syngenta Limited, P.O. Box A38, Leeds Road, Huddersfield, HD2 1FF, UK

^c Department of Chemistry, Cardiff University, Cardiff, CF10 3TB, UK

Received 9 January 2001; received in revised form 8 March 2001; accepted 14 August 2001

Abstract

The sulfonylation of substituted benzenes is investigated for Zn-exchanged zeolites (ZSM-5, Y, β) using two sulfonating agents (methanesulfonyl chloride and benzenesulfonyl chloride). Zinc-exchanged zeolites are significantly more active than their corresponding proton form. Zinc-exchanged zeolites prepared using zinc acetate give higher level of Zn^{2+} -exchange acid and are more active than those prepared from zinc nitrate. Methanesulfonyl chloride gives similar selectivities for the 2- and 4-substituted products, but benzenesulfonyl chloride gives enhanced selectivity to the 4-product. The highest yields of the 4-product are observed with Zn-H- β as catalyst. For most zinc-exchanged zeolites no leaching of Zn^{2+} is observed and furthermore, the Zn^{2+} that is leached into solution is found to be inactive as a homogeneous catalyst for the reaction. This indicates that the observed reactions are wholly heterogeneously catalysed. The catalytic data are discussed in relation to pore access calculations for the arenium ion intermediates formed during the sulfonylation reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulfonylation; Zn-exchanged zeolites; Sulfones

1. Introduction

Sulfones are an important class of compounds that are typically synthesised using conventional Lewis acid catalysts [1,2]. They are useful intermediates in the pharmaceutical industry, e.g. dimethylsulfone is an intermediate for the synthesis of 4,4'-diaminodiphenyl sulfone [3] which has been used for the treatment of leprosy. The conventional Lewis acid catalysts generate considerable quantities of waste since they

give relatively low yields [4] and now there is a need to identify effective solid catalysts. Clays have been used as catalysts or catalyst supports for electrophilic aromatic substitutions [5–7]. However, very little attention has been given to the sulfonylation of aromatic compounds with this class of catalysts, although, recently, Choudhary et al. [8] has shown that Fe^{3+} -exchanged montmorillonite is effective for the sulfonylation of arenes.

Similarly, zeolites have received very limited attention as catalysts for the sulfonylation of arenes. Daley et al. [9] were the first to show that zeolite H- β could be used as a catalyst for toluene sulfonylation, but a low yield was obtained. Smith et al. [10] reported the

* Corresponding author. Tel.: +44-29-20874805;

fax: +44-29-20874075.

E-mail address: hutch@cardiff.ac.uk (G.J. Hutchings).

use of cation-exchanged zeolite β for the sulfonylation of toluene using methanesulphonic anhydride. Significant improvements in the yield of the 4-substituted product for the zeolite catalysed reactions were observed when compared with the results from the standard homogeneous aluminium chloride catalyst. In this paper we present a study of Zn^{2+} -exchanged zeolites as catalysts for the sulfonylation of substituted benzenes, and in particular, we focus attention on the stability of zinc-exchanged zeolites with respect to leaching of Zn^{2+} into solution.

2. Experimental

2.1. Catalyst preparation

The proton form of the zeolites (H-ZSM-5, H-MOR, H-Y, H- β) were prepared by calcination (500 °C, 24 h) of the corresponding ammonium-exchanged zeolite (NH_4 -ZSM-5, Si/Al = 27, PQ Chemicals; NH_4 -mordenite, Si/Al = 10, Laporte; NH_4 -Y, Si/Al = 2.5, Union Carbide; NH_4 - β , Si/Al = 27, PQ Chemicals). Na-Y (Si/Al = 2.6, Unilever) was used as supplied.

Zinc-exchanged zeolites were prepared according to the following procedure. The dried H/Na-zeolites were stirred in an aqueous solution of zinc acetate or zinc nitrate (0.1 M) at 100 °C for 24 h. The zeolite was recovered by filtration, washed with de-ionised water and dried (200 °C, 5 h). The zinc content was determined using atomic absorption spectroscopy.

2.2. Sulfonylation reactions

The substituted benzene (0.25 mol) and the sulfonylating agent (0.05 mol) were refluxed together under nitrogen with the zeolite catalyst (0.85 g, pre-dried at 200 °C, 5 h). Following reaction, the mixture was cooled to 25 °C and analysed using gas chromatography, following the addition of biphenyl (0.5 g) as an internal standard.

Molecular structures were optimised using the MOPAC program [11] with the PM3 Hamiltonian [12] and the eigenvector follower optimisation routine. The volume available to each molecule in each zeolite was calculated using the occupiable pore volume feature of the InsightII package [13]. We use a fixed

molecular geometry and an all silica model of the zeolite framework. To calculate occupiable volumes the unit cell of the zeolite is overlaid with a grid of points set at 0.5 Å intervals. The probe molecule is placed at each grid point in turn and the point is considered to be within the occupiable volume if any of 60 orientations have no Van der Waals contact with the zeolite.

3. Results and discussion

The sulfonylation of toluene with methanesulfonyl chloride with zeolite catalysts was investigated and the results are given in Table 1. With this sulfonylating agent, under these conditions, the proton form of the zeolites had negligible activity. However, the zinc-exchanged zeolites gave significantly higher conversion. Zn-exchanged zeolites prepared from the acetate generally had higher zinc loadings and gave higher product yields. It is important to note that Zn^{2+} in solution is inactive for this reaction and so this is a clear demonstration that Zn^{2+} -exchanged zeolites are effective heterogeneous catalysts for this reaction. In addition, Zn-H-ZSM-5 and Zn-H-Y catalysts were stable and did not leach any Zn^{2+} into solution. With Zn-H-mordenite and Zn-H- β , ca. 5–10% of the Zn^{2+} leached into solution, however, as noted above, this leached zinc is inactive for this reaction. This is in marked contrast to other Friedel Crafts reactions for which Zn-exchanged zeolites have been used, since for acylation and alkylation Zn^{2+} is active in solution and Zn-exchanged zeolites have been shown to exhibit poor stability giving extensive leaching [14,15]. With respect to selectivity, zeolite Zn-H-Y gives slightly more of the 4-product compared with the other zeolites. This effect cannot be considered to be related to shape selectivity since the pore volume of this zeolite is the highest. However, zeolite Y has the highest density of cation exchange sites and the enhanced selectivity may be related to the proximity of adjacent catalyst sites (whether Zn–Zn or Zn–H).

The sulfonylation of toluene with benzenesulfonyl chloride using zeolite catalysts was also investigated and the results are shown in Table 2. Again, the zinc-exchanged zeolites are stable under these reaction conditions and only minimal leaching is observed. Benzenesulfonyl chloride was more reactive than

Table 1
Sulfonylation of toluene with methanesulfonyl chloride using Zn-exchanged zeolites^a

Catalyst	[M] ^b ($\times 10^{-4}$ mol)		[M] ^c (ppm)	Conversion ^d (%)	Product selectivity (%)		
	Before	After			2-	3-	4-
None	–	–	–	0	–	–	–
H-ZSM-5	–	–	–	0	–	–	–
H-MOR	–	–	–	1	48	9	42
Na-Y	–	–	–	0	–	–	–
H-Y	–	–	–	0	–	–	–
H- β	–	–	–	1	48	10	42
ZnCl ₂	13.0	13.0	2933	0	–	–	–
Zn-H-ZSM-5 ^e	16.3	16.3	–	14	47	11	42
Zn-H-ZSM-5 ^f	1.04	1.04	–	10	47	10	43
Zn-H-MOR ^e	15.7	14.4	295	11	49	9	42
Zn-H-MOR ^f	3.92	3.39	120	8	48	10	42
Zn-H-Y ^e	20.2	20.2	–	12	36	8	56
Zn-H-Y ^f	10.4	10.4	–	1	nd ^g	nd	nd
Zn-H- β ^e	22.1	20.9	275	3	48	10	42

^a Toluene (0.25 mol), methanesulfonyl chloride (0.05 mol), zeolite (0.85 g), 110 °C, 24 h.

^b mol Zn²⁺ in reaction mixture. For zeolite catalyst, before: total mol Zn²⁺ added with zeolite; after: total present at end of reaction. For ZnCl₂ signifies solution Zn²⁺ concentration.

^c ppm Zn²⁺ present at end of reaction in solution.

^d Methanesulfonyl chloride conversion.

^e Prepared using zinc acetate.

^f Prepared using zinc nitrate.

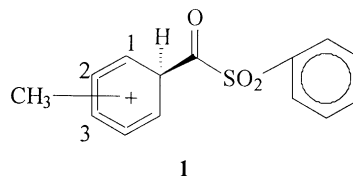
^g nd: Not determined.

methanesulfonyl chloride and, in this case, some activity was observed with the unexchanged zeolites, with H-Y giving very high selectivity for the 4-product. The Zn-exchanged zeolites showed a marked increase in reactivity, with zeolite Zn-H- β giving the highest conversion. However, zeolite Zn-H-Y retained the high selectivity of H-Y giving 82% selectivity to the 4-product. Zn-exchanged zeolites prepared from the sodium exchanged form of zeolite Y were much less active than those prepared from the proton form. Although this may be related to the different zinc loading for the two catalysts, it may also indicate that a combination of the two cations Zn²⁺/H⁺ may be an important feature in the activation of sulfonyl chlorides in this reaction. In general, the selectivity to the 4-product and the overall yields of the sulfones are similar to these reported by Daley et al. [9] and Smith et al. [10].

The sulfonylation using benzenesulfonyl chloride of toluene, ethylbenzene and *t*-butylbenzene was investigated with the zinc-exchanged zeolites and the results are given in Table 3. Although, *t*-butylbenzene showed the highest selectivity to the 4-product (89%),

this substrate was relatively unreactive, presumably, due to the steric hindrance exerted by the *t*-butyl substituent. Ethylbenzene showed the highest reactivity and, with Zn-H- β as catalyst, a yield of 64% of the 4-product was observed.

As a further aspect of this preliminary investigation, pore access calculations were carried out. Sulfonylation reactions are considered to proceed by a positively charged tetrahedral intermediate, an arenium ion **1**:



Only the arenium ion intermediates were considered in this computational study since their volume is significantly greater than the product or reactant molecules. The results are given in Table 4 for the pore access calculations for the arenium ion intermediates from the sulfonylation of toluene with benzenesulfonyl chloride. There is a clear difference between

Table 2

Sulfonylation of toluene with benzenesulfonyl chloride using Zn-exchanged zeolites^a

Catalyst	[M] ^b ($\times 10^{-4}$ mol)		[M] ^c (ppm)	Conversion ^d (%)	Product selectivity (%)		
	Before	After			2-	3-	4-
None	–	–	–	0	–	–	–
H-ZSM-5	–	–	–	1	31	4	65
H-MOR	–	–	–	1	31	4	65
Na-Y	–	–	–	0	–	–	–
H-Y	–	–	–	6	14	4	82
H- β	–	–	–	4	22	4	74
Zn-Cl ₂	13.0	13.0	2640	0	–	–	–
Zn(Oac) ₂	13.0	13.0	2635	0	–	–	–
Zn-H-ZSM-5 ^e	16.3	16.3	–	13	31	4	65
Zn-H-ZSM-5 ^f	1.17	0.91	53	15	31	4	65
Zn-H-MOR ^e	16.3	15.4	184	10	31	4	65
Zn-H-MOR ^f	3.39	3.39	–	1	nd ^g	nd	nd
Zn-H-Y ^e	20.2	19.7	102	21	14	4	82
Zn-Na-Y ^e	16.7	16.7	–	5	14	4	82
Zn-Na-Y ^f	10.4	10.4	–	1	nd	nd	nd
Zn-H- β ^e	22.2	20.9	265	43	22	4	74

^a Toluene (0.25 mol), benzenesulfonyl chloride (0.05 mol), zeolite (0.85 g), 110 °C, 24 h.^b mol Zn²⁺ present in reaction mixture. For zeolite: Zn²⁺ present in zeolite before and after reaction. For homogeneous catalysys signifies the solution Zn²⁺ concentration.^c ppm Zn²⁺ present in solution at the end of reaction.^d Benzenesulfonyl chloride conversion.^e Prepared using zinc acetate.^f Prepared using zinc nitrate.^g nd: Not determined.

Table 3

Sulfonylation of substituted benzenes using benzenesulfonyl chloride^a

Catalyst	Substrate	Conversion ^b (%)	Selectivity		
			2-	3-	4-
Zn-H-ZSM-5	Toluene	14	47	11	42
	Ethylbenzene	32	19	6	75
	<i>t</i> -Butylbenzene	0	–	–	–
Zn-H-MOR	Toluene	11	49	9	42
	Ethylbenzene	36	18	6	76
	<i>t</i> -Butylbenzene	0	–	–	–
Zn-H-Y	Toluene	12	36	8	56
	Ethylbenzene	49	12	9	79
	<i>t</i> -Butylbenzene	8	0	21	79
Zn-H- β	Toluene	3	48	10	42
	Ethylbenzene	86	18	8	74
	<i>t</i> -Butylbenzene	10	0	11	89

^a Substrate (0.25 mol), benzenesulfonyl chloride (0.05 mol), zeolite (0.85 g), 110 °C, 24 h.^b Benzenesulfonyl chloride conversion.

the zeolites, and zeolites Y and β given considerably higher pore accessibility than mordenite and ZSM-5. Consequently, as expected, the arenium ion intermediate is more accessible for the large pore zeolites. This fits with the experimental data for the conversion of toluene ($\beta > Y > \text{Mordenite} > \text{ZSM-5}$) for these zeolites (Table 2) when the zeolites contain similar Zn²⁺

Table 4

Pore accessibility for the arenium ion intermediates for the sulfonylation of toluene with benzenesulfonyl chloride^a

Methyl position ^b	Zeolite (fraction of cell volume that may be occupied by intermediate)			
	β	Y	Mordenite	ZSM-5
1	15.3	48.8	8.2	0
2	9.8	48.7	0	0.8
3	26.9	48.6	14.6	4.5

^a Results quoted as the fraction of the cell volume that may be occupied by each intermediate.^b Methyl group position in intermediate **1**.

concentrations ($1.6\text{--}2.2 \times 10^{-3}$ mol Zn^{2+}) exchanged into the proton form of the zeolite. For mordenite and ZSM-5, these pore access calculations indicate that the 4-product would be preferred. Similarly, for zeolite β , the 4-product is also preferred. However, within the supercage of zeolite Y, all three arenium ion intermediates have similar pore accessibility. This indicates that, on a shape selective basis, zeolite Y should not demonstrate any selectivity to the products. However, this is clearly not the case since Zn^{2+} -exchanged zeolite H-Y gives the highest selectivity for the 3-isomer when benzenesulfonyl chloride is used as the sulfonating agent. These findings suggest that the pore structure of the zeolite is of secondary importance in this reaction, and that the proximity of the adjacent sites is more important. Interestingly, when Zn^{2+} -exchanged zeolite Na-Y is used, the activity is significantly decreased but the selectivity is maintained. In this case (Table 2), the Zn^{2+} concentration is only slightly lower than that for the Zn^{2+} -exchanged zeolite H-Y. From this, we can conclude that the proximity of proton with respect to Zn^{2+} may be important for catalyst activity but further detailed studies are now required to investigate this further.

This study has shown that Zn-exchanged zeolites, in particular zeolites Y and β , can act as stable heterogeneous catalysts for sulfonation of substituted benzenes with sulfonyl chlorides as sulfonating reagents. The turnover numbers, based on $[\text{Zn}^{2+}]$, for the reactions presented in this study vary between 3 and 19

depending on the conversion level achieved, but at this stage no optimisation of the reaction conditions has been attempted.

Acknowledgements

We thank Zeneca for financial support.

References

- [1] G.A. Olah, H.C. Lin, *Synthesis* (1974) 342.
- [2] W.E. Truce, C.W. Vriesen, *J. Am. Chem. Soc.* 75 (1953) 5032.
- [3] T. Weijlard, J.P. Messerly, US Patent 2,385,899 (1945).
- [4] G.A. Olah, S. Kobayashi, J. Nishimura, *J. Am. Chem. Soc.* 95 (1973) 564.
- [5] J.H. Clark, A.P. Kybett, D.J. Macquarrie, S.J. Barlow, P. Landon, *J. Chem. Soc., Chem. Commun.* (1989) 1353.
- [6] P. Laszlo, *Science* 235 (1987) 1473.
- [7] B.M. Choudhary, G.V.M. Sarma, P. Bharathi, *Angew. Chem. Int. Ed. Eng.* 28 (1989) 465.
- [8] B.M. Choudhary, N.S. Chowdari, M.L. Kantam, R. Kannan, *Tetrahedron Lett.* 40 (1999) 2859.
- [9] S. Daley, K.A. Trevor, K.R. Randles, B.D. Gott, *PTC Int. Appl.* WO93, 18000 (1993).
- [10] K. Smith, G.M. Ewart, K.R. Randles, *J. Chem. Soc. Perkin Trans. 1* (1997) 1985.
- [11] J.J.P. Stewart, *J. Comput.-Aided Mol. Design* 4 (1) (1990).
- [12] J.J.P. Stewart, *J. Comp. Chem.* 10 (2) (1989) 209.
- [13] InsightII Release (4.0.0) was obtained from MSI, San Diego.
- [14] E.A. Gunnewegh, S.S. Gopie, H. Van Bekkum, *J. Mol. Catal.* A 106 (1996) 151.
- [15] M. Spagnol, L. Gilbert, D. Alby, *Ind. Chem. Lib.* 8 (1996) 29.