Selective nitration of aromatic compounds by solid acid catalysts

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High activity and *para*-selectivity in the nitration of aromatic compounds is achieved by a high density of acidic sites and ready formation of the *para*-isomer in the pores of zeolite beta with low Si/Al ratio as revealed by molecular modeling studies.

Nitration of aromatic compounds is a ubiquitous reaction to realise organic intermediates required in large tonnages for the fine chemical industry. The conventional nitration process,¹ employing a nitrating mixture of nitric and sulfuric acid, for the last 150 years has remained unchallenged in the commercial arena owing to uneconomical alternative options. Selective synthesis of the desired isomer in the nitration of substituted aromatic compounds is of topical interest to reduce pollution caused by unwanted isomers and specifically to respond to market demand. Earlier we reported selective nitrations by employing a solid acid, Fe³⁺ montmorillonite in the presence of acetic anhydride-nitric acid.² Later, various novel options, meeting international environmental laws, and also avoiding the recovery of the spent acid in the conventional mixed acid process have been explored that include Laszlo's³ claycop (copper nitrate impregnated on K10 montmorillonite) acetic anhydride and recently claycop-nitric acid-acetic anhydride, Smith's⁴a mordenite-benzoyl nitrate, Kwok's⁵ ZSM-5-propyl nitrate and Olah's⁶ Nafion-H-n-butyl nitrate. However these options fall short of expectations to commercial realisation in view of low space time yields, high dilution, and use of expensive mixtures in the form of acetic anhydride-nitric acid or expensive acyl or alkyl nitrate whereas Sato's7 and Prins's8 vapour phase nitrations of benzene conducted employing clays and mordenite zeolite provided low space time yields. The

zeolite beta-acetic anhydride-nitric acid system developed later by Smith *et al.*,^{4b,c} afforded good space time yields but required great care in large scale operations. Barrett and coworkers^{4d} employed La(III) triflates as recyclable catalysts for aromatic nitrations but such systems required longer reaction times to obtain good yields without any explicit selectivity towards *o*-/ *p*-isomer.

Herein, we present a unique methodology for the nitration of aromatic compounds that offers high space time yields, near zero emission of effluents, especially high *p*-selectivity for monosubstituted products, essential for commercial processes, employing nitric acid at a concentration of 60–90%, with reuse of the solid acid catalysts being possible by azeotropic removal of water formed in the reaction and present in nitric acid.[†]

We executed a two-fold approach employing modified clays and zeolites to realise a high space time yield as well as high selectivity of the desired *p*-isomer as indicated in Table 1. In an earlier investigation,⁹ a series of different metal-exchanged and pillared clay catalysts were prepared¹⁰ and employed in the nitration reactions of aromatic compounds under identical conditions. Fe³⁺ montmorillonite catalyst was found to be the most active owing to its high metal content and highly acidic sites. This catalyst (entry 1) is far superior in terms of space time yield, when compared even with gas phase reactions conducted with various metal-exchanged montmorillonites⁷ and mordenite.⁸ In the nitration of benzene, mononitrobenzene is obtained selectively without formation of any di- or poly-nitrobenzenes and the *p*-selectivities in the nitration of monosubstituted benzenes are improved.

Our main emphasis is to achieve higher *p*-selectivity to meet market demand. Accordingly, various zeolites which have well

Table 1 Selective nitration of aromatic comp	ounds
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Entry	Arene	Catalyst	HNO ₃ (%)	Product yield ^a (%)	STY ^b	Product distribution ^c		
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1	C ₆ H ₆	Fe ³⁺ mont.	90	88	22.8	_	_	_
2	C_6H_6	Al ³⁺ mont. ^{d}	60	48,e 95f	0.6		_	
3	C ₆ H ₅ Me	Mixed Acid	90	_	_	58	4	38
4	C ₆ H ₅ Me	Fe ³⁺ mont.	90	89	26.0	53	3	44
5	C ₆ H ₅ Me	K10 mont.	60	53	9.1	45	3	52
6	C ₆ H ₅ Me	Zeolite beta-I ^g	60	68, 96 ^f	10.6	30	3	67
		5th recycle	60	$67,95^{f}$	10.3	33	3	64
7	C ₆ H ₅ Me	Zeolite beta-II ^g	60	$40, 95^{f}$	6.8	41	4	55
8	C ₆ H ₅ Me	ZSM-5	60	32	5.6	49	7	44
9	C ₆ H ₅ Me	Mordenite	60	35	6.0	56	6	38
10	C ₆ H ₅ Me	HY	60	32	5.4	54	7	39
11	C ₆ H ₅ Me	TS-1	60	30	5.0	56	6	38
12	C ₆ H ₅ Cl	Fe ³⁺ mont.	90	77	26.0	36		64
13	C ₆ H ₅ Cl	Zeolite beta-I	60	$51, 98^{h}$	12.0	10		90
14	$C_6H_5Br^i$	Zeolite beta-I	70	51, 96^{h}	15.8	18		82
15	$C_6H_5I^i$	Zeolite beta-I	70	52	19.8	28	_	72
16	$C_6H_5Pr^i$	Zeolite beta-I	70	51	12.8	19		81
17	C ₆ H ₅ OMe	Zeolite beta-I	70	49, 96 ^h	11.4	25		75

^{*a*} Product yield based on total amount of HNO₃ used. ^{*b*} Space time yield: kg product/kg catalyst/h. ^{*c*} By GC. ^{*d*} Results from ref. 7. ^{*e*} Yields based on benzene. ^{*f*} Yields calculated based on HNO₃ actually consumed, *i.e.* subtracting the amount of nitric acid azeotropically distilled out from the reaction vessel and collected in the Dean–Stark trap from the total amount of nitric acid used. The nitric acid collected is reused after adjusting to the desired concentration. ^{*g*} Zeolite beta-I, II:SiO₂/Al₂O₃ molar ratio = 22, 27. ^{*h*} Yields based on aromatics with aromatic compound and HNO₃ in 1:2 ratio. ^{*i*} Dichloroethane used as solvent.

defined pore structures and channels that are derived from the networking of SiO₂ and Al₂O₃ making them attractive candidates for shape selective catalysis¹¹ were employed¹² to achieve higher shape selectivity in the nitration of substituted aromatics. Zeolite beta-I¹³ (entry 6) is found to the best catalyst for the nitration of aromatic hydrocarbons to nitroaromatics with high p-selectivity. When compared with the selectivities obtained using classical mixed acid, zeolite beta-I catalyst displayed a major shift towards *p*-selectivity as is evident, for example; for toluene: from 38 to 67%, for cumene: 58 to 81%, for chlorobenzene: 64 to 90%, for anisole: 40 to 75% (Table 1). The production of the *p*-isomer in higher ratio for toluene and cumene meets the timely demand of the market and at the same time avoids the burning of undesired o-isomers occasionally resorted to by the manufacturers which causes environmental pollution. Increased formation of the p-isomer in the nitration of chlorobenzene eases the isomeric separation to a considerable extent and helps to save energy. Whereas the change from methyl (toluene) to the larger isopropyl (cumene) substituent increases the *para* selectivity, the reverse applies for halogens, for which the best para selectivity is obtained with the smaller substituent, namely chlorine owing to electronic factors.

We carried out nitration of toluene with various zeolite catalysts and zeolite beta of different Si/Al ratios (Table 1). Zeolite beta proved to be the best catalyst among the zeolites used in terms of space time yield and p-selectivity. On decreasing the Si/Al ratio in zeolite beta, an increase in pselectivity as well as overall activity is observed (entry 6 and 7). An increased number of Bronsted acid sites reduces the available space in the pore and this result substantiates our inference that the formation of o-isomer, which requires more space, is unfavourable. These observations are in accord with the results observed by Bellussi et al. in alkylation reactions.14 It is also found that with an increase of catalyst concentration the *p*-selectivity of toluene nitration increased further to 73%. Zeolite beta catalyst showed consistent activity and selectivity even after five cycles (entry 6). Careful analysis of the regenerated catalyst after recycling it five times showed no change in the Si/Al composition indicating that no dealumination of catalyst has taken place.

Sorption studies of the reactant and isomers of the product and their intermediates (transition states) undertaken using the sorption module of Cerius² which implements rapid Monte Carlo statistical mechanical calculations¹⁵ clearly predicted high *p*-selectivity possible with ease of formation of the intermediate of the *p*-isomer in the pores. The result of shape selectivity observed employing zeolite beta derives further support from the results obtained with metal exchanged clays, wherein mesopores of montmorillonite formed due to acid treatment also induced some shift in *p*-selectivity (entries 4 and 5). The higher shape selectivity for the zeolite is ascribed to the induction of larger steric effects by the 3D structure of zeolite beta in comparison to the 2D structure of clay catalysts.

Nitration involves electrophilic attack on the aromatic ring by the nitronium ion, NO₂⁺. Bronsted acidic sites are responsible for the generation of NO_{2⁺} ion from nitric acid. Reaction conducted with fuming nitric acid without azeotropic removal of water is totally inhibited after some time owing to a poisoning effect of water formed in the reaction. It is necessary to scavenge the water out of the reaction zone formed during the reaction to facilitate regeneration of active acid sites on the catalyst. The rate of addition of nitric acid to the reactor containing powder catalyst and substrate is matched with the rate of removal of water present in nitric acid and the reaction zone through extractive distillation with a Dean-Stark apparatus using the substrate as the solvent or chlorohydrocarbon solvent for high boiling aromatic compounds to afford optimum selectivity, activity and protection of the catalyst from degradation. This protocol envisages the instant reaction of added nitric acid and establishes that the solid acid catalysts used here act as bifunctional catalysts generating the electrophile, nitronium ion, as well as acting as an instant adsorbent for water formed during the reaction.

On the other hand ZSM-5 under such conditions affords low space time yield and selectivity (entry 8) in the nitration of toluene when compared to the high *p*-selectivity obtained by Kwok *et al.*⁵ employing acyl nitrate as nitrating agent. This is attributed to low diffusion of aqueous HNO₃ in the hydrophobic pores of ZSM-5 and the resulting density of acidic sites is too low to promote the generation of nitronium ions from nitric acid. Therefore the reaction on ZSM-5 mainly takes place on the surface of the zeolite.

In conclusion, a simple methodology for nitration employing solid acids dispensing with the use of acetic anhydride or acyl nitrate described here leading to high space time yields and high *p*-selectivities, appears to be a promising alternative to the conventional acid mixture of nitric and sulfuric acid. Enhanced *p*-isomer formation to meet market demands, dispensing the use of sulfuric acid, achieving near zero emission of effluents, noncorrosivity and low water requirement are other attractions.

Notes and references

 \dagger General procedure for the nitration of monosubstituted aromatics: A mixture of toluene (161 ml; 1.5 mol) and zeolite beta-I catalyst (10 g) were added to in a 1 litre-reactor flask equipped with stirring rod and Dean–Stark apparatus. 60% nitric acid (120 ml, 1.5 mol) was added in a controlled manner with an infusion pump over a period of 80 min to the above mixture, which was preheated to the refluxing temperature. The liberated water collected into the Dean–Stark apparatus was continuously removed. After completion of the reaction, the catalyst was filtered off and the reaction mixture was concentrated to obtain the mixture of nitrotoluenes. Nitration of other aromatic hydrocarbons was similarly carried out on a 76 mmol scale.

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