Development of a system for clean and regioselective mononitration of aromatic compounds involving a microporous solid, dinitrogen tetroxide and air†

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Nitration of aromatic compounds using a zeolite as a solid inorganic catalyst and a combination of dinitrogen tetroxide and oxygen or air as the nitrating reagent, in open or sealed systems, leads to high yields and significant *para* selectivities for halogenobenzenes and other aromatics in a relatively clean process. The material used as catalyst has a strong influence on the reaction.

Introduction

Electrophilic aromatic substitution reactions are of considerable importance in the production of fine chemicals. However, many traditional processes suffer serious disadvantages, including low selectivity for the desired product and the requirement for large quantities of mineral or Lewis acids as activators. The use of such acids causes plant corrosion and generates large volumes of spent reagents, which, given the current environmentally conscious climate, are increasingly unacceptable. Major efforts are therefore being made to develop processes with lower environmental impact.

Inorganic solids can offer significant benefits by providing both effective catalysis and, in some cases, enhanced selectivity.[1] For example, in our own research we have utilised zeolites to enhance the *para* selectivity in chlorination,[2] bromination,[3] acylation[4] and methanesulfonylation[5] reactions of simple aromatic substrates. In addition, such solids are easily removed from reaction mixtures and can often be recycled. Therefore, study of the use of inorganic solids as catalysts for electrophilic aromatic substitution reactions can make an important contribution to green chemistry.

Aromatic nitration is a particularly important problem since nitro compounds represent versatile chemical feedstocks for a wide range of industrial products, including pharmaceuticals, agrochemicals, dyestuffs, and explosives. Traditional nitration with a mixture of nitric and sulfuric acids (the mixed acid method)[6] is notoriously unselective for nitration of substituted compounds, and disposal of the spent liquors presents a serious environmental concern.[7] Consequently, there is intense international effort to address these problems and several alternative methods for aromatic nitrations have been developed.[8–15] None of these methods, however, is totally devoid of disadvantages.

At present, the best combination of high yield, high *para* selectivity and low solvent use is achieved using a reagent system comprising nitric acid, zeolite Hß as catalyst, and acetic anhydride (for moderately active aromatics)[12] or trifluoroacetic anhydride (for deactivated aromatics)[13] as activator. Even these systems, however, produce at least two molar equivalents of carboxylic acid as by-product.

Another approach towards clean nitration involves the use of dinitrogen tetroxide in combination with oxygen or ozone as an oxidant.[14] The method where ozone is employed most likely

involves dinitrogen pentoxide, as this is known to be a highly active nitrating agent. The method utilising oxygen is less clear cut and requires the use of tris(pentane-2,4-dionato)iron(III) (Fe(acac)$_3$) as a catalyst in an organic solvent.[15] In principle, this could lead to a highly atom-efficient process (eqn. (1)), but it is not regioselective. Therefore, we decided to study the use of dinitrogen tetroxide as a nitrating agent in the presence of microporous solids, in order to determine if such solids were able to catalyse the process and impart *para* selectivity.

$$4\,ArH + 2\,N_2O_4 + O_2 \xrightarrow{\text{Catalyst}} 4\,ArNO_2 + 2\,H_2O \qquad (1)$$
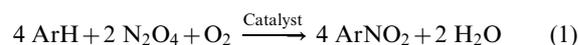
Zeolites have been used before in the nitration of aromatic compounds using nitrogen dioxide. However, the patented process was conducted at high temperature in the vapour phase, did not involve oxygen, was complicated, required a high flow rate for the carrier gas (N$_2$, 880 ml min^{-1}) and showed poor *para* selectivity.[16] In preliminary communications we have reported that certain zeolites can indeed catalyse the process of nitration with dinitrogen tetroxide at low temperature in the liquid phase, whilst simultaneously providing enhanced *para* selectivity.[17,18] We now report the details of this work.

Experimental

A PU 4400 gas chromatograph (Philips) fitted with a Carbowax column (30 m × 0.32 nm × 0.25 μm) was used to analyse reaction mixtures. Octadecane or hexadecane was added as an internal standard to allow quantification.

Zeolites

Commerical zeolites were purchased from Aldrich Chemical Company or provided as a gift by Zeolyst International.

Nitration procedure: nitration using zeolite Hß/N$_2$O$_4$/O$_2$ in a solvent system

The reaction of chlorobenzene illustrates the general procedure for the nitration process. In an ice–water cooling bath was placed a 100 ml round-bottom flask containing a mixture of chlorobenzene (10 mmol), zeolite (1.0 g), and 1,2-dichloroethane (30 ml). The flask was flushed with oxygen gas for 20 min at 0 °C. Liquid dinitrogen tetroxide (*ca.* 10 ml, *ca.* 165 mmol) was added quickly all at once to the stirred mixture, and the flask was connected to a balloon filled with oxygen gas. After 50 h stirring at 0 °C, the mixture was filtered through a

medium porosity sintered glass funnel, and the filtrate was diluted with water. It was extracted with 1,2-dichloroethane and the organic phase was separated and dried over magnesium sulfate. The isomer distribution was determined by GC.

Nitration procedure: nitration using zeolite Hß/N_2O_4/air in a solvent-free system

The reaction of chlorobenzene illustrates the general procedure for the nitration process. The zeolite (3 g) was placed in a 450 ml autoclave, followed by chlorobenzene (3.71 g, 33 mmol). Liquid dinitrogen tetroxide (*ca.* 1.4 ml, *ca.* 23 mmol) was added quickly to the mixture, the autoclave was sealed and pressurised to 200 psi with air, and the mixture was stirred at room temperature for 14 h. The autoclave was then opened and the product was extracted with dichloromethane (200 ml). The extract was washed with water (50 ml), dried (MgSO₄) and concentrated under reduced pressure to give the product, which was analysed by GC. [Identical results were obtained if the zeolite was extracted with diethyl ether or ethyl acetate instead of dichloroethane; acetone was also a useful extraction solvent, but the solvent then had to be replaced before aqueous washing could be accomplished. In a commercial process, the product would probably be isolated without recourse to solvent extraction.]

Results and discussion

Aromatic nitration using a zeolite/N_2O_4/O_2/solvent system

Initially, an attempt was made to reproduce approximately the conditions of Suzuki for nitration of chlorobenzene.[15] Liquid N_2O_4 (approx. 10 ml) was condensed into a trap at −78 °C and was then warmed to 0 °C. Fe(acac)₃ (0.355 g) and chlorobenzene (10 mmol) were then added, the system was flushed with oxygen and the mixture was stirred at 0 °C for 48 h. The product thus obtained contained nitrochlorobenzenes in proportions (2- : 3- : 4-nitrochlorobenzene proportions of 32 : <1 : 67) that approximated to those reported by Suzuki, but also showed significant quantities of a product based upon nitration of acetylacetone.

We then carried out similar reactions in which various zeolites were used as catalysts instead of Fe(acac)₃ in an attempt to determine which zeolite, if any, would be the most applicable to *para* selective aromatic nitration. Zeolite ß and zeolite Y have three-dimensional channels and large pore sizes and were selected on this basis. Mordenite, which has linear large pores, and ZSM-5, which has a medium pore size, were chosen for comparison. Additionally, variation of the cation type was undertaken, with H^+, Na^+, K^+ and NH_4^+ being used in the case of zeolite β, and H^+ and Na^+ in the case of zeolite Y. Finally, zeolite ZSM-5 was tested with two specific Si/Al ratios. Thus, the effects of pore size, channel structure, acidity, cation size and Si/Al ratio could all be assessed. A reaction in the presence of chromatographic silica was also included for comparison. The results are shown in Table 1.

As shown in Table 1, reaction occurred in the presence of all of the solids, and all of the reactions gave higher yields than in the absence of any catalyst. The large, three-dimensional-pore zeolites gave higher yields, comparable with those achieved with Fe(acac)₃ as catalyst, but the medium pore zeolites and the linear large pore zeolite gave lower yields, as did the silica. All of the zeolites demonstrated higher *para* selectivity than that obtained with Fe(acac)₃, except for NH₄β. This last result may reflect the fact that this was the only zeolite not calcined (heated in air to a high temperature), since this would have caused loss of ammonia and formation of Hβ.

Mordenite and ZSM-5 gave lower *para* selectivities as well as lower yields, which probably reflects more restricted diffusion through the pores, allowing greater opportunity for

Table 1 The effect of zeolite type on the nitration of chlorobenzene with N_2O_4 and O_2 in dichloroethane[a]

Zeolite	Si/Al	Time/ h	Conversion[b] (%)	Yield[b] (%)	Proportions[b] (%)		
					ortho	*meta*	*para*
None[c]	—	50	6	2	39	0	61
SiO₂[c]	—	50	40	28	29	<1	70
Hβ	12.5	50	100	90	14	<1	85
Naβ	12	50	100	96	15	0	85
Kβ	12	50	97	92	21	0	79
NH₄β	12.5	50	76	70	30	1	69
HY	30	50	100	91	16	2	82
NaY	28	50	100	91	16	1	83
HMordenite	10.5	50	36	28	27	0	73
HZSM-5	50	72	44	42	28	2	70
HZSM-5	150	72	48	32	20	<1	79

[a]All reactions were carried out with zeolite (1.0 g), chlorobenzene (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (*ca.* 10 ml) at 0 °C. [b]Calculated by quantitative GC. [c]For comparison.

competition from reaction at the external surface of the solid. The selectivity was also low for the reaction in the presence of silica. The ZSM-5 sample with the higher Si/Al ratio gave a higher *para* selectivity than that with the lower ratio, possibly because it would have been produced by the process of dealumination, which would have opened up the pore structure of the zeolite, causing it somewhat to resemble the larger pore systems. However, the yield with the higher Si/Al ratio sample was less, possibly because of the lower density of active sites. Interestingly, the nature of the cation present appeared to have a negligible effect on the reactions, the H^+, Na^+ and K^+ forms of the zeolites giving very similar results for each reaction where comparison was possible. Evidently, the process does not rely upon strong acid catalysis and does not depend significantly on cation size. Perhaps the role of the active site is merely to bring together the reagents and substrates within the confines of the pores by simple co-adsorption.

Zeolites Hß and Naß produced the greatest selectivity for *para*-chloronitrobenzene (85%) and the highest yields (90% and 96%, respectively). Therefore, zeolite Hß was tested with a range of other substrates. The results are shown in Table 2.

The results in Table 2 are interesting in a number of ways. After 24 hours toluene had been completely consumed and produced a reasonable yield of mononitrotoluenes (85%). The *para* selectivity was fairly low, though greater than for mixed acid nitrations. By contrast, the reaction with benzene was rather slow, being only *ca.* 50% complete after 48 hours, while all of the halogenobenzenes gave good yields and reasonable *para* selectivities within 48 hours. Although the reactions were not conducted in such a way as to allow true kinetic comparisons, it is clear that the relative rates are not in line with expectations for a classical electrophilic aromatic substitution reaction. Also, the *para* selectivities in all cases

Table 2 Nitration of various substrates with N_2O_4, O_2 and zeolite Hß in 1,2-dichloroethane[a]

Substrate	Time/ h	Conversion[b] (%)	Yield[b] (%)	Proportions[b] (%)		
				ortho	*meta*	*para*
Toluene	24	100	85	53	2	45
Benzene	45	55	50	—	—	—
Fluorobenzene	48	100	95	7	0	93
Chlorobenzene	48	98	95	14	<1	85
Bromobenzene	48	>99	94	22	<1	77
Iodobenzene	48	99	95	37	1	62

[a]All reactions were carried out with zeolite (1.0 g), substrate (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (*ca.* 10 ml) at 0 °C. [b]Calculated by quantitative GC.

were somewhat higher than for the comparable mixed acid nitrations, but not to the extent that has been seen in zeolite-catalysed nitrations with acetyl nitrate, where it is believed that a classical electrophilic substitution step is involved.[12] The patterns of reactivity and selectivity observed suggest a change in the orbital control of the reaction from that for electrophilic aromatic substitution, as happens, for example, in radical aromatic substitution reactions.

At this point we had demonstrated some of the aims of the work. The reactions could be catalysed by zeolites, in some cases to give a rate of reaction higher than that for the comparable reaction catalysed by Fe(acac)$_3$, and the *para* selectivities observed were higher than for comparable mixed acid reactions, albeit not as high as for some other zeolite-catalysed nitration reactions. However, the method was not viable as an environmentally benign preparative procedure. It was not desirable to have to maintain a low temperature over such long periods of time, nor to require such a large excess of dinitrogen tetroxide to be employed. Also, the reaction involved use of a halogenated solvent. Therefore, we sought to improve the procedure by avoiding the need for cooling, decreasing the excess of dinitrogen tetroxide used and eliminating the solvent. It appeared that the driving force behind the use of all of these features, which were based on the initial Suzuki conditions,[15] was the volatility of dinitrogen tetroxide (bp 21 °C). Simply containing the reaction mixture in a sealed system capable of withstanding a modest pressure might enable the desired improvements. We therefore undertook a study of solvent-free reactions carried out in an autoclave.

Aromatic nitration using zeolite Hß/N$_2$O$_4$/air in a solvent-free system

A mixture of zeolite HBEA (Hβ), dinitrogen tetroxide and chlorobenzene at room temperature was placed in an autoclave and pressurised to 200 psi with oxygen. The reaction proceeded readily and relatively quickly to give a mixture of chloronitrobenzenes in high yield. Furthermore, when oxygen was replaced by air in an otherwise similar situation, the reaction was still efficient. With air it was slower, requiring about 12 hours to go to completion, though still quicker than with oxygen under the previous conditions. By contrast, when the pressurising gas was nitrogen, virtually no nitration occurred and almost all of the chlorobenzene was recovered, demonstrating the necessary involvement of oxygen in the reaction.

It was of interest to identify the reaction stoichiometry, since it was not known whether the by-product was water, nitric acid or a mixture of the two. Eqn. (2) ($n = 0$–6) is a general one that covers the various possibilities. In the case of $n = 0$, the equation simplifies to eqn. (1), which involves production of water but no nitric acid, whereas if $n = 6$, the by-product would be entirely nitric acid with no water.

$$24\ ArH + (12 + 2n)\ N_2O_4 + (6 + n)\ O_2 =$$
$$24\ ArNO_2 + 4n\ HNO_3 + (12 - 2n)\ H_2O \quad (2)$$
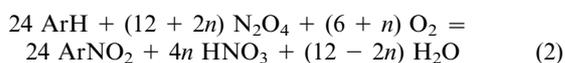
In order to gain information about the value of n, a series of reactions involving different proportions of chlorobenzene to dinitrogen tetroxide was allowed to react to completion (2 days). The results are shown in Table 3.

The results obtained showed that reaction of chlorobenzene (33 mmol) with dinitrogen tetroxide (16.5 mmol, *i.e.* equivalent to 33 mmol of nitrogen dioxide) gave only 69% of the theoretical conversion of substrate into nitration products. The results of leaving a similar mixture of 4 equivalents of chlorobenzene with 2 equivalents of N$_2$O$_4$ under air pressure for double the time (4 days, see Table 3) revealed only a small increase in yield, to a figure (73%) that was almost exactly three quarters of the theoretical maximum. Titration of the solution

Table 3 Effect of dinitrogen tetroxide amount on chlorobenzene nitration^a

Amount of N$_2$O$_4$			Conversion of PhCl^b	Yield of nitro compounds^b	Proportions^b (%)		
/ml	/mmol	Time/h	(%)	(%)	*ortho*	*meta*	*para*
0.5	8.3	46	41	33	14	<1	85
1.0	16.5	46	74	69	16	<1	84
1.0	16.5	168	75	73	15	<1	85
1.4	23.1	46	100	96	15	<1	84
2.0	33.0	46	100	92	19	<1	81

^{a}All reactions were carried out with zeolite Hß (3.0 g), chlorobenzene (33.0 mmol), under air pressure (200 psi) at room temperature. ^{b}Calculated by quantitative GC.

obtained by washing the latter reaction mixture with water revealed the presence of acid corresponding to 22% of the N$_2$O$_4$ used. These observations suggested that ArH (3 mole equivalents) had reacted with N$_2$O$_4$ (2 mole equivalents) to give nitro product (3 mole equivalents). We therefore conclude that the most likely value of n (eqn. (2)) is 2, leading to the simplified stoichiometry of eqn. (3).

$$3\ ArH + 2\ N_2O_4 + O_2 = 3\ ArNO_2 + HNO_3 + H_2O \quad (3)$$

On the assumption that the stoichiometry was as shown in eqn. (3), various types of zeolites, with different pore structures, counter-cations and Si : Al ratios, were examined under the new conditions to see if there were any changes from the observations made previously under the original conditions. The results are shown in Table 4.

As shown in Table 4, all of the zeolites tested catalysed the reaction and provided a modest increase in *para* selectivity compared to reaction in the absence of catalyst. Zeolite Hß provided a somewhat faster reaction and greater *para* selectivity than the others, but the differences were not major. Interestingly, the yield and selectivity were both significantly lower when the cation associated with zeolite β was the very large Cs cation rather than when a smaller cation was present. In the case of Csβ the selectivity was no better than for smaller pore zeolites. This suggests that the reaction derives its albeit modest *para* selectivity from that portion of the reaction taking place within the pores of the zeolite.

Based on these results, zeolite Hß was chosen for further study and was tested with a range of other substrates. The

Table 4 The effect of zeolite type on the solvent-free nitration of chlorobenzene^a

Zeolite	Si/Al ratio	Time/ h	Conversion^b (%)	Yield^b (%)	Proportions^b (%)		
					ortho	*meta*	*para*
None	—	24	38	34	34	<1	65
Hβ	12.5	14	100	97	15	<1	84
Liβ^c	12.5	24	95	91	17	<1	82
Naβ	12	24	90	80	19	1	80
Mgβ^c	12.5	24	80	72	21	<1	79
Feβ^c	12.5	24	94	88	21	<1	79
Znβ^c	12.5	24	91	83	19	<1	80
Csβ^c	12.5	24	78	61	31	<1	69
NH$_4$β	12.5	24	58	44	24	<1	75
HY	30	24	80	75	27	<1	72
NaY	28	21	76	68	25	<1	74
HMordenite	10.5	24	81	70	29	1	70
HZSM-5	50	24	86	82	26	1	74
HZSM-5	150	24	89	78	24	<1	76
HZSM-5	1000	24	70	54	27	<1	72

^{a}Reactions were carried out with zeolite (3.0 g), chlorobenzene (33.0 mmol), and dinitrogen tetroxide (1.4 ml, *ca.* 23.1 mmol), under 200 psi air pressure at room temperature. ^{b}Calculated by quantitative GC. ^{c}Reactions were carried out at half scale.

Table 5 The nitration of various substrates with N_2O_4, zeolite Hß and air[a]

| Substrate	Time/h	Conversion[b] (%)	Yield[b] (%)	Proportions[b] (%)		
				ortho	meta	para
Toluene	24	86	76	50	3	47
Benzene	22	100	97	—	—	—
Fluorobenzene	16	100	95	9	<1	91
Chlorobenzene	14	100	97	15	<1	84
Bromobenzene	14	97	90	19	<1	80

[a]Reactions were carried out with zeolite Hß (3.0 g), substrate (33.0 mmol), and dinitrogen tetroxide (1.4 ml, ca. 23.1 mmol), under 200 psi air pressure at room temperature. [b]Calculated by quantitative GC.

results are shown in Table 5. The results show that all of the substrates tested gave good yields of nitration products, with modest increases in the amounts of *para* isomer in comparison with traditional methods. The trends were generally similar to those observed in the reactions carried out in solvent at atmospheric pressure. Again, the relative reactivities of the substrates did not appear to be consistent with a normal electrophilic aromatic substitution mechanism. A sample of zeolite Hß was recovered from one of the reactions and washed with water to remove nitric acid. After calcination, the zeolite was re-used in an identical reaction and gave virtually identical results.

In an attempt to get further information about the system, we investigated the simple adsorption of N_2O_4 on zeolite Hß as a function of temperature. We discovered that the amount adsorbed drops steadily as temperature increases, but that there is still some adsorption even at 80 °C and that the amount adsorbed at 20 °C is in the region of 1.53 mmol N_2O_4 per gram of zeolite. By employing excess zeolite we were able to conduct a reaction in ordinary glassware at 20 °C and near-atmospheric pressure, which enabled direct observation of the reaction mixture. Adsorption of N_2O_4 alone onto the zeolite imparted a pale brown colour to the solid. However, when benzene was then allowed into the system, the colour of the adsorbed material immediately became much darker. Following admission of oxygen the reaction proceeded slowly to give the nitrated products.

We speculate that the dark colour is indicative of an adsorbed intermediate formed by interaction of the substrate with N_2O_4, and that its conversion into product requires another reactive species to be formed more slowly between oxygen and the excess N_2O_4. The relative reactivities of different substrates and the small differences in the catalytic activities of proton and sodium forms of the same zeolites do not seem to be in line with an acid-catalysed electrophilic substitution reaction under these conditions. We therefore suspect that the reaction is radical in nature. Scheme 1 gives a tentative mechanism that is consistent with the apparent stoichiometry. A similar overall result would be produced if NO_2 radicals were to abstract the first hydrogen atoms and the HNO_2 produced were then to react with oxygen to give $HOONO_2$. However, in that event it would not be easy to understand why the amount of nitration product obtained in the absence of oxygen is negligible.

There have been previous reports of nitrations of aromatic compounds using dinitrogen tetroxide and zeolites in the absence of solvent, but generally the reactions have been conducted at elevated temperatures in the gas phase.[19,20] In those reports, it was assumed that the stoichiometry was as shown in eqn. (1). If the assumed stoichiometry was indeed correct, it appears likely that some of the product was formed by the action of nitric acid on the substrate at the elevated temperatures. Therefore, the product may be formed by several different routes within the same mixture, so that conclusions about the reaction mechanism based solely on the overall
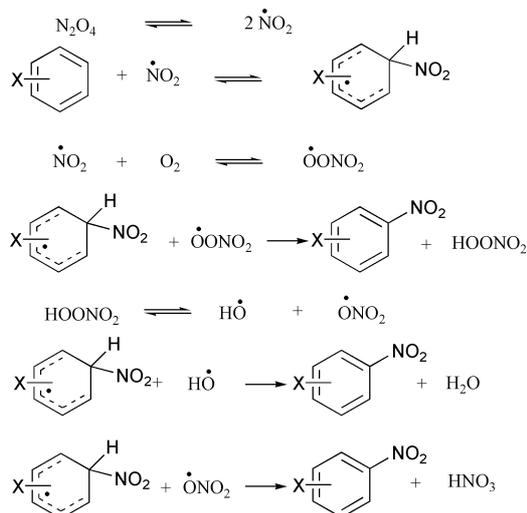
Scheme 1 A speculative mechanism for the reaction. Any or all of the reaction steps involving reaction of the substrate–NO_2 adduct with another radical could proceed by either of two mechanisms: (i) direct hydrogen atom abstraction; or (ii) electron abstraction to give a Wheland intermediate and an anion, followed by proton abstraction from the Wheland intermediate by the anion. Whether the zeolite would play an active part in catalysing any of the processes or merely assist through stabilisation of intermediates by adsorption is an open question.

results may need to be treated with caution. It is also not clear that the mechanism of any part of the reaction mixture would be the same at the elevated temperatures used in those reports as for the reactions described herein, which occur at room temperature and at above atmospheric pressure, under which conditions the reagent would be primarily liquid dinitrogen tetroxide rather than the gaseous nitrogen dioxide prevalent at elevated temperatures.

In the recent work of the Suzuki group, superior selectivities for production of *para* isomers were achieved at low conversion using H-ZSM-5 as the zeolite and the substrate as its own solvent in the liquid phase.[21] In the present work we have shown how it is possible to carry out the reaction to give high yields, with modest *para* selectivities, without solvent, with only the stoichiometric quantity of dinitrogen tetroxide, using air instead of oxygen, and under mild conditions (ambient temperature and a modest pressure). Under these conditions the reaction is rather slow, but simply raising the temperature to 30–40 °C in the sealed system used can reduce the required reaction period dramatically. Therefore, only two remaining obstacles prevent this reaction from fulfilling all the desired criteria. One is the relatively low *para* selectivity (though already better than for traditional methods). The other is the production of a modest amount of nitric acid as by-product, which can deactivate the zeolite by adsorption or reaction, limits the efficiency of usage of the dinitrogen tetroxide and could lead to plant corrosion. We continue to search for ways to overcome these remaining disadvantages.

Conclusions

Our aim in this research has been to develop aromatic nitration methods that potentially improve upon the environmental impact of current commercial methods. Indeed, we have developed a method that fulfils many of our objectives. Among the advantages of the method are the following: the reaction occurs at ambient temperature, so does not require the input of much energy; it uses dinitrogen tetroxide and oxygen or air as the reagent, thereby minimising the problems of corrosion and the need to treat large quantities of acidic wastewater that occur with mixed acid methods; there is some improvement in

para selectivity compared to traditional methods; and the substrate is converted quantitatively into nitration products by use of just a stoichiometric amount of dinitrogen tetroxide. Furthermore, the reaction does not require a solvent and the zeolite can be recovered and re-used at least once without loss of performance.

The results of experiments in which dinitrogen tetroxide and benzene were adsorbed onto the zeolite, together with the observed stoichiometry of the nitration reaction of chlorobenzene, have encouraged the proposal of a speculative mechanism by which this reaction might occur. We continue to investigate the reaction in order to try to understand it better. By so doing we hope to find ways to overcome the remaining disadvantages associated with the reaction, namely the production of one mole equivalent of nitric acid for every three mole equivalents of nitrated substrate and the relatively low *para* selectivity.

Acknowledgements

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