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Zeolite-promoted selective mono-*N*-methylation of aniline with dimethyl carbonate

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Abstract

Selective mono-*N*-methylation of aniline with dimethyl carbonate is carried out over faujasite Y zeolites. This one pot protocol is highly selective, favouring mono-*N*-methylation. Benzylation with dibenzyl carbonate is also found to be very selective, resulting in exclusive monobenzylation. Other advantages such as lower temperature, less rigorous reaction conditions, absence of C-alkylation products, etc., are also highlighted.

Keywords: Aniline; Mono-*N*-methylation/benzylation; Faujasite zeolites

1. Introduction

Selective mono-*N*-alkylation of primary aromatic amines is a reaction of interest for the synthesis of pharmaceuticals and dyes [1] as alkylanilines are useful intermediates and *N*-ethylaniline is an important dyestuff. However, the utility of this reaction for synthetic purposes is limited due to its their poor selectivity, when common alkylating agents (alkyl halides/alcohols) are used. In addition, the high nucleophilicity of the amine nitrogen results in the formation of mixture of secondary and tertiary amines along with the corresponding ammonium salts [2]. Previously, vapour phase alkylation at high temperatures and pressures are reported [3] over solid acid catalysis such as oxides, clays and zeolites and also on their modified forms.

To improve the yield of selective alkylation under liquid phase conditions, several approaches are made including use of zeolites and other media. Selective mono-*N*-alkylation of aniline (**I**) has been reported using different alkyl halides in the presence of suitable X and Y-type zeolites [4–6]. However, preparation of mono-*N*-methylanilines (**II**) in this way is severely restricted due to the low steric hindrance of the methyl group and sizable amount of *N*,*N*-dimethyl derivatives are always observed, when methyl halide or dimethyl sulphate is used as the alkylating agent. Moreover, when alkyl halides are used, an additional problem is encountered, wherein the co-product HX rapidly deactivates the zeolites [7].

Alkylation of aniline (**I**) with isopropanol over basic zeolites [8] leads to the formation of both *N*-alkylated and C-alkylated products. Prasad and Rao [9] have studied aniline (**I**) alkylation over $AlPO_4{}^{5-}$ catalysts and suggested that during the methylation of aniline (**I**), formation of *N*-methylaniline is favoured at low temperature. This is subsequently methylated to *N*,*N*-dimethylaniline (**III**), which undergoes isomerization to *N*-methyltoluidine at high reaction temperatures. Alkylation of **I** with ethanol has been reported using solid acid catalysts, in which *N*-ethylaniline is formed at 573 K and leads to the formation of *N*,*N*-diethylaniline at 693 K and finally at 723 K, C-alkylation takes place. In alkylation of **I** with methanol, [Al]-KL molecular sieves [10] exhibit an improved *N*-methylaniline (**II**) selectivity and more stable activity than NaX, NaY and Naβ zeolites under the same experimental conditions. Incorporation of an appropriate amount of Fe into the framework of zeolite L can enhance the reactivity without loss of monoalkylation selectivity and this is attributed to an increase in basicity.

However, the use of strong acid catalysts at high temperature and pressure poses corrosion and pollution problems. In

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addition, many undesired byproducts including C-alkylated products are obtained. The unreacted raw materials cannot be recycled and in this context vapour phase systems still seem preferable. In a recent work, which employs dimethyl carbonate (DMC) as the alkylating agent, a continuous flow reaction of **I** with DMC has been reported to lead to high mono-*N*-methyl selectivity, alkali cation-exchanged zeolites being used as the catalysts at 180 °C [11,12]. It is interesting to note that dimethyl carbonate behaves as a very selective C-methylating agent for a variety of active methylenic compounds [13–17] and allows selective mono-*N*-methylation of primary aromatic amines [18] as well (under gas–liquid phase transfer catalysis at 180 °C in the presence of K_2CO_3 and polyethylene glycol as phase transfer agents). Though no *N*,*N*-dialkylated byproducts are formed, *N*-methyl-*N*-aryl carbamates are observed (3–25%) under steady state conditions. To avoid this drawback, a batch synthesis of **II** has been developed based on the formation of *N*-methylurethanes during the reaction of dimethyl carbonate with primary amines in the presence of K_2CO_3 and phase-transfer agents (onium salts and crown ethers) [19]. These results have prompted the selective mono-*N*-methylation under batch conditions [20]. Other examples of mono-*N*-alkylation such as alkylation of aniline with dimethyl carbonate in the presence of spinel type mixed oxides [21,22] and alkylation of aniline with ethanol over HY and dealuminated HY zeolites [23] are also reported.

However, the above selective mono-*N*-methylation of anilines using Y- and X-faujasites with dimethyl carbonate as the alkylating agent is performed in an autoclave at a temperature of 120–150 °C. Dimethyl carbonate is also used in very large amounts (20-fold excess) since it acts both as a reagent and as a solvent. Our interest in utilizing zeolites as media for selective transformations in photochemical [24–26] and thermal [27–29] reactions has prompted us to explore the title reaction for milder and more selective reaction conditions. In the present study, the reaction of dimethyl carbonate with **I** has been investigated in the presence of different cation-exchanged faujasite zeolites and the salient features are discussed below.

2. Experimental

Faujasite NaY, NaX, and NH_4Y zeolites were obtained from Aldrich and used after activation at 450 °C. The cations of interest (K^+, Ni^{2+}, Ba^{2+}, Ca^{2+}, Zn^{2+} and Mg^{2+}) were exchanged into the NaY powder (10 g) by stirring with the corresponding nitrate (100 ml, 10%) solution at 90 °C for 12 h. The exchange was repeated at least four times. Each time, after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. In a similar manner to an earlier report [30], cation exchange capacities were determined by extraction of exchangeable cations with 1 M ammonium acetate solution at pH 7.0. Fifty milligrams of the zeolite sample was shaken with 10 ml of ethanol, 10 ml of ammonium acetate solution was added, and the extracts were collected after 24 h. 10 ml of distilled water added to the solids and the extracts were collected after an additional 24 h. This process was repeated at least five times, and all extracts obtained from the same sample were combined and analyzed by atomic absorption spectroscopy (AAS). The values were between 66 and 74% for Ni^{2+}, Ba^{2+}, Zn^{2+} and Mg^{2+}. It is relevant to note that in literature report [31], exchange levels were found to be between 62 and 84%. All the cation-exchanged zeolites were activated at 450 °C for about 10 h prior to use. Zeolite HY was obtained by the thermal deammonification of NH_4Y at 450 °C.

In a typical methylation reaction, 0.27 ml of **I**, 0.5 ml of dimethyl carbonate and 0.4 g of calcined (at 450 °C) zeolite were taken in 5 ml of benzene and stirred in an oil bath at 100 °C for 1/2–3(1/4) h. The benzene portion was filtered and the zeolite portion was extracted with dichloromethane. The combined benzene and dichloromethane portions, after evaporation of the solvent were analyzed by GC. In benzylation, 0.27 ml of **I**, 0.34 ml of benzylchloride and 0.4 g of calcined (at 450 °C) zeolite taken in 5 ml of benzene/*iso*-octane were stirred in an oil bath at 100 °C for 5 h. The benzene/*iso*-octane portion was filtered and the zeolite portion was extracted with dichloromethane. The combined benzene/*iso*-octane and dichloromethane portions, after evaporation of the solvent, were analyzed by GC.

The reaction mixture was analyzed by capillary gas chromatography (Shimadzu 17A model, SE-30 10% capillary column, FID detector and high purity nitrogen as carrier gas). Retention time of aniline was taken as the internal reference. Products were identified by their GC retention times and also by coinjection with authentic samples. In all the cases the recovered mass balance was about 90%.

3. Results and discussion

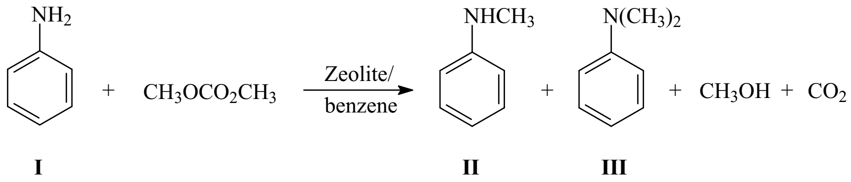
In the present study, benzene (non-polar) is chosen as the solvent of choice to ensure the presence of the substrate predominantly inside the more polar cages/channels of the zeolite. This is in contrast to the earlier study [20], where dimethyl carbonate is taken in large excess, which plays the role of the solvent. Methylation is carried out in NaY, NaX and also various cation-exchanged faujasites.

The results shown in Table 1 indicate that highly selective formation of mono-*N*-methylaniline (**II**) (Scheme 1) is observed and that very small amount of *N*,*N*-dimethylaniline (**III**) is obtained under the present experimental conditions. Control experiments show that there is no reaction in the absence of zeolite. Also, with potassium carbonate as the base, the percentage conversion is poor, indicating that zeolitic medium offers an ideal environment for the selective *N*-methylation. The reaction is also carried out with different time intervals. The formation of **II** increases with increasing time and reaches a maximum after 2 h.

Table 1
Percentage conversion and yields of products in the mono-*N*-methylation of aniline with dimethyl carbonate[a,b]

Zeolite	Time (min)	Conversion (%)	Product proportion of		Selectivity (%) (mono-/di-)[c]
			II	**III**	
None	365	Nil	–	–	–
K_2CO_3	365	8	100	–	100
NaY	90	54	98	2	98
NaY	60	67	99	1	99
NaY[d]	60	29	100	–	100
NaY	90	75	97	3	97
NaY	120	99	91	9	91
NaY	205	93	98	2	98
KY	60	48	100	–	100
KY	205	98	99	1	99
NaX	60	48	96	4	96
Mol. sieve 5A	60	Nil	–	–	–
NiY	205 (360)[e]	8 (20)[e]	100 (95)[e]	(5)[e]	100 (95)[e]
BaY	205	7	86	14	86
CaY	205	45	92	8	92
HY	205	2	100	–	100
None	60	Nil	–	–	–

[a] Reactions are carried out with 0.27 ml (3 mmol) of **I**, 0.5 ml of dimethyl carbonate and 0.4 gm of preactivated zeolite at 100 °C in an oil bath.
[b] Analyzed by GC: error limit ±2%.
[c] The percentage mono-/di-selectivity is calculated as per the expression $\{\mathbf{II}/\mathbf{II}+\mathbf{III}\}\times 100$.
[d] At 70 °C.
[e] In *iso*-octane medium.

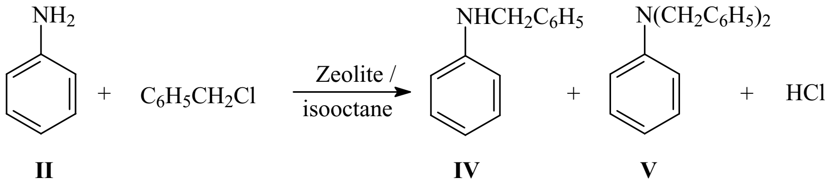


Scheme 1.

It is clear that NaY, KY and NaX zeolites are very efficient catalysts for the alkylation of **I**, with dimethyl carbonate as the alkylating agent. With a 5A molecular sieve, there is very little reaction under the experimental conditions. Similarly to acidic HY and CaY zeolites (more Brönsted acidity), the reaction is very slow, as aniline is now protonated. The reaction is also slower with zeolites possessing Lewis acidity such as NiY, BaY as the lone pair in aniline nitrogen is likely to be coordinated with the metal ions.

Similar experiments are also carried out with different substituted anilines (X-PhNH$_2$, where X = *p*-CH$_3$, *o*-CH$_3$, *p*-OCH$_3$, *p*-Cl, *p*-NO$_2$ and *p*-COOH). Unlike simple anilines, the reaction with substituted anilines is very slow and the yield of the corresponding mono-*N*-methylated product is very poor (<6%). While anilines with electron-withdrawing groups are deactivated and hence are poorly reactive, anilines with electron-releasing groups are sufficiently basic and hence protonated by the residual Brönsted acidic sites of the faujasite zeolites (Scheme 2).

The efficiency of dialkyl carbonates is also evident, when dibenzyl carbonate is employed as the alkylating agent (Table 2). Monobenzylated aniline (**IV**) is produced exclusively as in the case of dimethyl carbonate. NaY as well as NaX is found to be efficient towards benzylation. With acidic zeolites such as HY and NiY, the reaction is very slow. However, when benzyl chloride is employed as



Scheme 2.

Table 2
Percentage conversion and products distribution in *N*-benzylation of aniline with dibenzyl carbonate/benzyl chloride[a,b]

Solvent	Zeolite	% Conversion	% of		Selectivity (%) (mono-/di-)[c]
			IV	**V**	
Dibenzyl carbonate					
Benzene	NaY	73	100	–	100
Benzene	NiY	32	100	–	100
Benzene	NaX	77	100	–	100
Benzene	HY	8	100	–	100
iso-Octane	NiY	3	100	–	100
Benzyl chloride					
Benzene	NaY	30	70	30	70
Benzene	NiY[d]	Nil	–	–	–
Benzene	NiY	7	86	14	86
iso-Octane	NiY[d]	4	90	10	90
iso-Octane	NiY	18	89	11	89
iso-Octane	NiY[e]	32	55	45	55

[a] Reactions are carried out with 0.27 ml (3 mmol) of **I**, 0.34 ml dibenzyl carbonate/benzyl chloride, and 0.4 g of preactivated zeolite at 100 °C in an oil bath.

[b] Analyzed by GC: error limit ±2%.

[c] The percentage mono-/di-selectivity is calculated as per the expression $\{\mathbf{IV}/\mathbf{IV}+\mathbf{V}\}\times 100$.

[d] Reaction carried out at 25 °C.

[e] Reaction carried out for 540 min.

the alkylating agent, not only the reactivity decreases but also the monoselectivity drops significantly. This indicates clearly that dialkyl carbonates can serve as much better and selective alkylating agents than other related reagents such as RCl/ROH.

Thus, reduction in reactivity and selectivity in benzylation using benzyl chloride may be attributed to an increase in the amount of the acidic by-product HCl, which not only protonates aniline but also deactivates the basic sites of zeolites. The data presented in Table 2 also highlight the utility of dialkyl carbonates as much more selective and better alkylating agents than RCl/ROH.

4. Conclusions

We have developed a much simpler one-pot waste-free environmentally benign procedure for the preparation of mono-*N*-methylaniline. Thus, the present atom efficient and greener method also offers several advantages over other zeolite-mediated selective *N*-alkylation protocols: simpler work-up much improved monoselectivity, lower reaction temperature (100 °C), lesser amount of dimethyl carbonate (only a two-fold excess) as that of the amount of aniline taken compared to a 20-fold excess reported earlier [20], less rigorous reaction conditions (absence of autoclave and high pressure), absence of C-alkylation products and *N*-aryl carbamates, etc.

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