

Discussion

Comment on the paper “Zeolite-promoted selective mono-*N*-methylation of aniline with dimethyl carbonate” by T. Esakkidurai and Kasi Pitchumani, School of Chemistry, Madurai Kamaraj University, India
[*J. Mol. Catal. A: Chem.* 218 (2004) 197–201]

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In the past seven years, our group has extensively investigated the combined use of alkali metal exchanged faujasites Y and alkyl methyl carbonates [ROCO₂Me, R = Me, MeO(CH₂)₂O(CH₂)₂] for the selective synthesis of mono-*N*-methyl anilines (ArNHMe) [1]. Hence, directly related to this topic, I was genuinely interested in the paper of Pitchumani and Esakkidurai, published in the last issue of the *Journal of Molecular Catalysis (A: Chemical)* [2].

However, after a careful reading, I feel compelled to say that most of the research reported in this work, contains neither synthetic novelties nor new concepts inherent to the reaction of anilines with dialkyl carbonates and faujasites Y. This is for several reasons:

- (i) The authors claim the use of lower reaction temperatures (100 °C) as well as lower amounts of dimethyl carbonate (DMC) as the methylating agent, providing that benzene is used as the reaction solvent. However, we already reported that in the presence of NaY as the catalyst, highly selective mono-*N*-methylation of anilines (even deactivated by stereoelectronic effects, such as XC₆H₄NH₂, X = *o*- and *p*-CONH₂) with DMC do take place also at 90 °C [1f]. Moreover, DMC is a non-toxic compound, which is even cheaper with respect to benzene [3]. To be honest, I cannot see any advantage both from synthetic, economic, and most of all environmental standpoints, in replacing DMC with benzene!
- (ii) The authors report the need of using apolar solvents to allow the presence of aniline within the polar cages of

the Y catalysts. No support is given to this statement. However, for liquid phase reactions catalyzed by Y zeolites, the solvent effect was investigated by us and by others [1d,4]. Data indicate that non-polar solvents may improve the reaction rate with respect to polar solvents (DMF, glycols) because they do not adsorb competitively with the substrate, into the catalyst. This effect however, especially in the case of the *N*-methylation of anilines [1d], is not appreciable when the methyl carbonate acts both as reagent and solvent.

- (iii) The authors claim the use of dibenzyl carbonate (PhCH₂OCO₂CH₂Ph) for selective mono-*N*-benzylation of aniline; though the same result was reported by us three years ago [1c].
- (iv) The authors report that primary aromatic amines substituted by both electron-withdrawing and electron-donating groups (XC₆H₄NH₂; X = *p*-Cl, *p*-NO₂, *p*-Me, *p*-OMe, *p*-CO₂H) are less reactive with respect to aniline, towards mono-*N*-methylation with DMC. Also this result was already reported and discussed by us [1a,d–e].

Overall, I repeat, it is my firm opinion that this paper does not present any significant novelty, and another major concern is that, despite the authors knew and reported our work on dialkyl carbonates up to 1997 [5], our recent and most relevant references [1b–e] were not indicated.

References

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- [5] It should be noted however, that Ref. [1a] was cited improperly: in that paper, experiments were carried out at 120–150 °C under batch-wise conditions, and not—as indicated by the authors of Ref. [2]—at 180 °C and under continuous flow conditions.