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Highly Selective Phosgene Free Synthesis of Methylphenylcarbamate from Aniline and Dimethyl Carbonate over Heterogeneous Catalyst

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Abstract : Organic carbamates are versatile compounds widely employed as pesticides, fungicides, herbicides, dyes, pharmaceuticals, cosmetics and in the synthesis of polyurethanes. Carbamates can be easily transformed into isocyanates by thermal cracking. Isocyantes are used as precursors for manufacturing agrochemicals, adhesives and polyurethane elastomers. Manufacture of polyurethane foams is a major application of aromatic ioscyanates and in 2007 the global consumption of polyurethane was about 12 million metric tons/year and the average annual growth rate was about 5%. Presently Isocyanates/carbamates are manufactured by phosgene based process. However, because of high toxicity of phoegene and formation of waste products in large quantity; there is a need to develop alternative and safer process for the synthesis of isocyanates/carbamates. Recently many alternative processes have been investigated and carbamate synthesis by methoxycarbonylation of aromatic amines using dimethyl carbonate (DMC) as a green reagent has emerged as promising alternative route. In this reaction methanol is formed as a by-product, which can be converted to DMC either by oxidative carbonylation of methanol or by reacting with urea. Thus, the route based on DMC has a potential to provide atom efficient and safer route for the synthesis of carbamates from DMC and amines. Lot of work is being carried out on the development of catalysts for this reaction and homogeneous zinc salts were found to be good catalysts for the reaction. However, catalyst/product separation is challenging with these catalysts. There are few reports on the use of supported Zn catalysts; however, deactivation of the catalyst is the major problem with these catalysts. We wish to report here methoxycarbonylation of aniline to methylphenylcarbamate (MPC) using amino acid complexes of Zn as highly active and selective catalysts. The catalysts were characterized by XRD, IR, solid state NMR and XPS analysis. Methoxycarbonylation of aniline was carried out at 170 °C using 2.5 wt% of the catalyst to achieve >98% conversion of aniline with 97-99% selectivity to MPC as the product. Formation of N-methylated products in small quantity (1-2%) was also observed. Optimization of the reaction conditions was carried out using zinc-proline complex as the catalyst. Selectivity was strongly dependent on the temperature and aniline:DMC ratio used. At lower aniline:DMC ratio and at higher temperature, selectivity to MPC decreased (85-89% respectively) with the formation of N-methylaniline (NMA), N-methyl methylphenylcarbamate (MMPC) and N,N-dimethyl aniline (NNDMA) as by-products. Best results (98% aniline conversion with 99% selectivity to MPC in 4 h) were observed at 170oC and aniline:DMC ratio of 1:20. Catalyst stability was verified by carrying out recycle experiment. Methoxycarbonylation preceded smoothly with various amine derivatives indicating versatility of the catalyst. The catalyst is inexpensive and can be easily prepared from zinc salt and naturally occurring amino acids. The results are important and provide environmentally benign route for MPC synthesis with high activity and selectivity.

Keywords : aniline, heterogeneous catalyst, methoxycarbonylation, methylphenyl carbamate
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