

Oxidative coupling of carboxylic acids using transition metal hydrotalcite catalysts

Samudrala Shanthi Priya ^{1,2}, Theegala Srinivas ^{1,2}, Deepa K. Dumbre ², Suresh K. Bhargava ²,
Komandur V. R. Chary ¹, Mannepalli Lakshmi Kantam ³

¹Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road,
Hyderabad,-500007, India

²Centre for Advanced Materials & Industrial Chemistry (CAMIC), School of Applied Sciences, RMIT University,
GPO BOX 2476, Melbourne-3001, Australia

³Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai-400019, India
Corresponding author Email: lk.mannepalli@ictmumbai.edu.in

Keywords: Oxidative coupling, Cu-Al/HT, carboxylic acids, substituted amides

Introduction:

Amide linkages (–CONH–) are of great significance in biological systems as a principal constituent of proteins. Amide compounds are widely used as precursors in various fields such as pharmaceuticals, natural products, polymers and chemical industry [1, 2]. To date, several research efforts have been focused on the synthesis of substituted amides by oxidative cross coupling reactions of carboxylic acids over different catalytic systems. However, owing to the emerging importance of these amides in several fields, development of an alternate and convenient method involving less expensive metal catalysts and eliminating harsh reaction conditions is highly desirable as well as challenging. In this regard, a simple and recyclable catalytic protocol for the synthesis of substituted amides from carboxylic acids using various transition metal (Cu-Al, Cu-Fe, Mg-Al, Mg-Fe, Ni-Fe, Ni-Al) hydrotalcite catalysts is described.

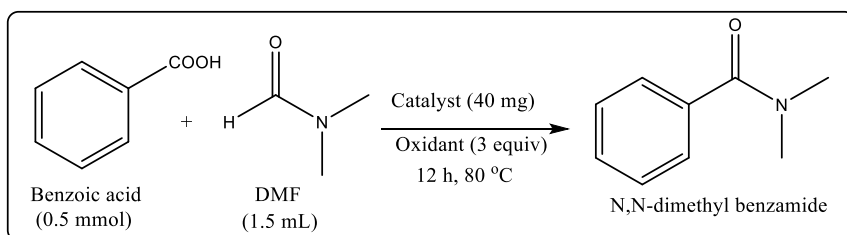
Experimental:

A series of transition metal containing hydrotalcites (X-Y/HT; X-Y: Cu-Al, Cu-Fe, Mg-Al, Mg-Fe, Ni-Fe, Ni-Al) were prepared by co-precipitation method [3, 4] by using respective metal nitrate precursors. The as prepared catalysts were systematically characterized using TEM, XRD and XPS. Typical procedure for synthesis of substituted amides using X-Y/HT catalyst involves a 10 mL round bottomed flask charged with 0.5 mmol of carboxylic acids, 40 mg of catalyst, DMF (1.5 mL) and drop wise addition of TBHP (3 equiv) under stirring at RT for 10 min. The temperature was raised gradually to 80 °C and the reaction was continued for 12 h. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 x 20 mL). The filtrate was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give the crude products and purified by flash silica gel (100-200 mesh) column chromatography using a mixture of ethyl acetate and hexane as eluents to afford the desired products in good yields.

Results & Discussion:

Initially a preliminary reaction was carried out on a 0.5 mmol scale with benzoic acid employing X-Y/HT catalyst (40 mg) and 3 equiv. TBHP in 1.5 mL DMF at 80 °C for 12 h. As expected, the reaction proceeded smoothly and provided good yields of N, N-dimethylbenzamide. Thereafter, the reaction is optimised by various reaction parameters such as the effect of catalyst, effect of oxidant, effect of substrate. Moreover, the catalyst is easily recovered after the reaction and reused.

Scheme 1: Oxidative coupling reaction of benzoic acid with DMF



Conclusion:

Amongst all the catalysts tested, the Cu containing hydrotalcite catalysts exhibited good catalytic activity and hence these are the promising catalysts for the oxidative coupling reaction of carboxylic acids.

References:

- [1] S. Priyadarshini, P. J. Amal Joseph, M. L. Kantam, RSC Adv. 3 (2013) 18283.
- [2] V. R. Pattabiraman, J. W. Bode, Nature. 480 (2011) 471.
- [3] P. R. Likhar, R. Arundhathi, M. L. Kantam, Tetrahedron Letters. 48 (2007) 3911.
- [4] Bo Qiao, Le Zhang, Rong Li, RSC Adv. 5 (2015) 93463.