



Short communication

Transamidation of carboxamides with amines over nanosized zeolite beta under solvent-free conditions



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ABSTRACT

A highly efficient approach to transamidation of carboxamides with amines over nanosized zeolite beta under solvent-free conditions has been successfully demonstrated. Transamidation of a variety of amides with amines produced the respective *N*-alkyl amides in moderate to excellent yields.

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Amide bond is one of the most important linkages in nature and also they have been intensively investigated in organic synthesis [1–3]. Furthermore, it represents a significant functional group that has ubiquitous applications in natural products, pharmaceuticals, fine chemicals and polymers [4]. In general, substituted amides are synthesized by the coupling of carboxylic acid derivatives with amines or aryl/alkyl halides with primary amides [5–6]. However, these procedures have some drawbacks, such as the lability of the activated acid derivatives and tedious experimental procedures [7]. Alternatively, some name reactions (i.e., Ritter [8], Schmidt [9], Beckmann [10], Ugi [11], Wolff [12], etc.) and metal catalyzed reactions have been developed for their synthesis [13–16].

However, reactions of amide group with nucleophiles usually requires harsh reaction conditions due to the poor electrophilic character of the amide group, which makes the transamidation of amides with amines, an alternative and attractive method for obtaining the substituted amides. Amides are relatively inert when compared with other acyl donors and therefore uncatalyzed transamidation reactions require forcing conditions [17–18]. Y. L. Khmelnsky et al. reported the enzyme-mediated transamidation, but it requires highly evolved enzymes, long reaction times and limited scope [19]. To overcome these drawbacks, new homogeneous [20–24] and heterogeneous [25–30] catalysts have been recently reported. In present days, environmental and economical considerations have raised strong interest in

redesigning commercially important processes to avoid the use of harmful reagents and the generation of toxic waste. In this regard, heterogeneous catalysts can play a key role in the development of eco-friendly processes in petroleum chemistry and production of chemicals. Unfortunately, most of the heterogeneous methods suffer from one or more disadvantages such as limited substrate scope, harsh reaction conditions, need of a solvent and strong base. Considering these, the development of environmentally benign and efficient transamidation approach towards the synthesis of higher amides is still challenging.

Zeolites are uniform microporous crystalline materials and have widespread applications both in petroleum and fine chemical industries due to their unique physical and chemical properties, such as uniform channel size, large internal surface area, unique molecular shape selectivity, strong acidity and good thermal/hydrothermal stability. Zeolite H β has received much attention because of the large available micropore volume, large-pore channel system and the presence of active sites in different concentrations that are useful in a number of acid-catalyzed reactions. However, zeolites often show inadequate activity and/or fast deactivation because of poor diffusion efficiency [31]. The slow transport in the zeolite micropores leads to unwanted secondary side reactions or slow reaction rates. In order to get additional benefits from the unique sorption and shape-selectivity effects in the micropores, the diffusion path length in the micropores should be extremely small.

Nanozeolites are a type of zeolites which have narrow particle size distributions with sizes of less than 200 nm. Reducing the particle size from micrometer to nanometer scale, leads to a significant change in

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Table 1Optimization of reaction conditions for the transamidation of benzamide with benzylamine.^a

$\text{Ph}-\text{C}(=\text{O})\text{NH}_2 + \text{Ph}-\text{CH}_2\text{NH}_2 \xrightarrow[24\text{ h}]{\text{Catalyst}} \text{Ph}-\text{C}(=\text{O})\text{N}(\text{CH}_2\text{Ph})\text{H}$			
	1a	2a	3a
Entry	Catalyst	Temp °C	Yield ^b (%)
1	HZSM (40)	135	26
2	H-mordenite	135	57
3	HY	135	36
4	NaY	135	8
5	H β	135	72
6	MCM-41	135	49
7	Montmorillonite K10	135	56
8	Absence of catalyst	135	25
9	Nanosized zeolite beta	135	92
10	Nanosized zeolite beta	100	46
11	Nanosized zeolite beta	120	70
12	Nanosized zeolite beta	140	92
13	Nanosized zeolite beta	135	78 ^c
14	Nanosized zeolite beta	135	88 ^d
15	Nanosized zeolite beta	135	93 ^e
16	Nanosized zeolite beta	135	68 ^f
17	Nanosized zeolite beta	135	40 ^g

^a Reaction conditions: **1a** (1 mmol), **2a** (2 mmol), catalyst (100 mg), 135 °C, 24 h.^b Isolated yields.^c **2a** (1 mmol).^d **2a** (1.5 mmol).^e **2a** (2.5 mmol).^f Catalyst (50 mg).^g Catalyst (25 mg).

material characteristics and their applications in catalysis and adsorption. The number of atoms in the unit cell increases as particle size decreases and therefore, nanozeolites have large external surface area. The diffusion path lengths also shortened in nanozeolites as compared to that in the conventional micrometer zeolites [32–34].

In continuation of our efforts towards the development of novel and eco-friendly synthetic protocols using zeolites [35] herein, we report a

Table 3Transamidation of benzamide with different amines over nanosized zeolite beta.^a

$\text{Ph}-\text{C}(=\text{O})\text{NH}_2 + \text{R}-\text{CH}_2\text{NH}_2 \xrightarrow[135\text{ }^\circ\text{C, neat, 24 h}]{\text{nanosized zeolite beta}} \text{Ph}-\text{C}(=\text{O})\text{N}(\text{CH}_2\text{R})\text{H}$		
Entry	R	Yield ^b (%)
1	4-MeOC ₆ H ₄	91
2	4-MeC ₆ H ₄	93
3	4-FC ₆ H ₄	96
4	4-ClC ₆ H ₄	97
5	2-ClC ₆ H ₄	90
6	4-BrC ₆ H ₄	96
7	1Me-Ph	45
8	2-Naphthyl	62
9	3-C ₅ H ₄ N	92
10	2-C ₄ H ₃ O	60
11	2-C ₄ H ₃ S	62
12	CH ₂ -Ph	65
13	Cyclohexyl	60
14	C ₅ H ₁₁	62
15	C ₁₅ H ₃₁	58

^a Reaction conditions: benzamide (1 mmol), amines (2 mmol), nanosized zeolite beta (100 mg), 135 °C, 24 h.^b Isolated yields were calculated based on benzamide.

simple and efficient method for the transamidation of amides with amines over nanosized zeolite beta under solvent-free conditions. To the best of our knowledge, nanosized zeolite beta catalyzed transamidation has been not yet reported. Nanosized zeolite beta was prepared according to the procedure described in our earlier report, which was systematically characterized by various spectroscopic techniques (SEM, TEM, XRD, FT-IR, MAS-NMR, NH₃-TPD and ²⁷Al NMR) [35].

In the initial investigation, the reaction of benzamide with benzylamine (2 equiv.) was selected as a model system to find out the best reaction conditions. In order to choose the best catalyst first, the reaction was subjected with various zeolites, MCM-41 and montmorillonite K10 at 135 °C (Table 1, entries 1–7). Among the various catalysts investigated, H β zeolite exhibited the best catalytic activity and afforded

Table 2Transamidation of carboxamides with benzylamine over nanosized zeolite beta.^a

$\text{R}-\text{C}(=\text{O})\text{NH}_2 + \text{Ph}-\text{CH}_2\text{NH}_2 \xrightarrow[135\text{ }^\circ\text{C, neat, 24 h}]{\text{nanosized zeolite beta}} \text{R}-\text{C}(=\text{O})\text{N}(\text{CH}_2\text{Ph})\text{H}$		
Entry	R	Yield ^b (%)
1	Ph	92
2	4-MeOC ₆ H ₄	72
3	3-MeOC ₆ H ₄	94
4	4-MeC ₆ H ₄	74
5	3-MeC ₆ H ₄	73
6	4-BrC ₆ H ₄	82
7	2-ClC ₆ H ₄	65
8	4-NO ₂ C ₆ H ₄	65
9	3-NO ₂ C ₆ H ₄	68
10	3-CF ₃ C ₆ H ₄	93
11	PhCHCH	82
12	2-C ₄ H ₃ S	65
13	2-C ₅ H ₄ N	98
14	3-C ₅ H ₄ N	68
15	2,5-C ₄ H ₃ N ₂	96
16	H	98 ^c
17	CH ₃	99 ^c
18	C ₂ H ₅	99 ^c

^a Reaction conditions: amides (1 mmol), benzylamine (2 mmol), nanosized zeolite beta (100 mg), 135 °C, 24 h.^b Isolated yields were calculated based on amide.^c Reactions were carried out at 100 °C.

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