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Macroporous metal oxides as an efficient heterogeneous catalyst for various organic transformations—A comparative study

Harjyoti Thakuria, Ballav Moni Borah, Gopal Das *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

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Abstract

Porous materials have attracted the attention of chemists due to their various applications such as heterogeneous catalysis, chemical separations via adsorption. Macroporous transition metal oxides *viz*. CuO, NiO, CoO, Mn_2O_3, Cr_2O_3 and ZnO were synthesized and used as an efficient, heterogeneous, reusable and eco-friendly catalyst for four different organic transformations *viz*. *N*-formylation, *N*-acylation, *O*-acylation and Friedel Craft acylation under solvent-free conditions in good yields. These results were compared with the literature.

Keywords: Metal oxide; Solvent-free; Heterogeneous catalyst

1. Introduction

Synthetic chemists continue to explore new methods to carry organic transformations. One of the new methods is to perform reactions on the surface of a solid as a heterogeneous catalyst. Inexpensive and commercially available transition metal oxides and zinc oxide are most studied metal oxides as a heterogeneous catalyst for various organic transformations [1]. Metal oxides are important class of heterogeneous catalyst because of their high level of chemo-selectivity, environmental compatibility, simplicity of operation and availability at low cost.

N-Formylation is an important reaction in the formation of formamides. Formamides are again important intermediates in the synthesis of pharmaceutically important compounds [2]. A numerous methods have been reported for the formation of formamides [3]. However, there are several factors such as low yield, difficulties in workup procedure and use of expensive reagents limiting their applications. Very recently ZnO as a heterogeneous solid state catalyst have been reported for *N*-formylation reactions [4].

An acyclic *N*-acylamide core constitutes various natural products such as immunosuppressant microcolin [5] anticancer agent dolastatin 15 [6]. To construct these *N*-acylamide structures, activation of amides and/or acyl donors is generally required. Since the nitrogen atom of amides is less basic than that of the corresponding amines due to amide resonance. Reported methods for the *N*-acylation by a combination of amides and acyl donors are as follows: lithiated amide–acyl chloride [7], trimethylsilylated amide–acyl chloride [8], lithiated amide–pentafluorophenyl esters [9], amide–LiCl–acid anhydride [10]. Recently, ZnO under solvent-free conditions is reported as an efficient catalyst for *N*-acylation [11].

The protection of hydroxyl groups by esterification constitutes the major backbone of many preparations of natural and synthetic products such as perfumes, flavors, food additives, cosmetics, pharmaceuticals, plasticizers and polymers. Generally, esterification is carried out by acylation of alcohols and phenols with carboxylic acids and more conveniently anhydrides or acyl chlorides in the presence of basic catalysts, Bronsted or Lewis acids and metal salts [12]. Amongst the catalysts used for activation of anhydrides and acyl chlorides, pyridine [13] and KF–Al_2O_3 [14] are the most significant, whereas H_2SO_4 [15], and NH_2SO_3H [16] are commonly used acidic catalysts. Recently, other reagents such as distannoxane [17], metal triflates [18], $AlPW_{12}O_{40}$ [19], $ZrCl_4$ [20], $ZrOCl_2·8H_2O$ [21], $BiOClO_4·xH_2O$ [22], metal triflates in ionic liquids [23] and lipase enzymes have been applied for acylation of alcohols and phenols. However, there is always the need for better methodology for these types of widely used reactions. Recently, ZnO under solvent-free conditions have proved to be useful to

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* Corresponding author. Tel.: +91 361 2582 fax: +91 361 2582349.
E-mail address: gdas@iitg.ernet.in (G. Das).

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chemists in the laboratory and industry due to the good activation of adsorbed compounds, reaction rate enhancement, selectivity, easier work-up and recyclability of the supports. These metal oxides are eco-friendly and green in nature [11,23].

The Friedel Craft reaction is an important reaction for C–C bond formation. After over a century of development, it still attracts much research interest in both academia and industry. Brønsted acid or Lewis acid-catalyzed imine or iminium Friedel Craft reactions (aza-Friedel Craft reactions) are important methods to construct a variety of nitrogen containing compounds [24]. The industrial production of various pharmaceuticals and fine chemicals involves the synthesis and further transformation of aromatic ketones. The common routes for preparation of these ketones proceed via the Friedel Craft acylation of the concerned aromatic hydrocarbon with derivates of carboxylic acids. These reactions are traditionally catalyzed by either Lewis acids such as $AlCl_3$, $FeCl_3$ and BF_3 or Brønsted acids such as HF or H_3PO_4 [25]. Recently zinc powder promotes the acylation of activated as well as inactivated aromatics under microwave irradiation [26]. Cheap and commercially available ZnO is also reported recently as a catalyst in solvent-free condition for the reactions described above [27].

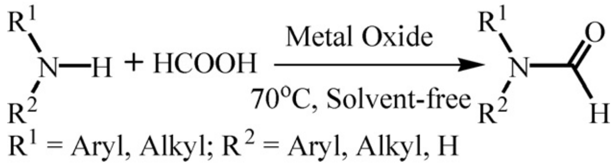
Although numerous methods are known for all these type of organic transformations, newer methods still continue to attract attention for their experimental simplicity and effectiveness. Porous materials have attracted the attention of chemists and materials scientists due to commercial interest in their application in ion exchange, adsorption (for chemical separations) and heterogeneous catalysis. These porous materials have the ability to interact with atoms, ions and molecules not only at their surfaces, but also throughout the bulk of the material, which is responsible for its functional diversities [28].

As the part of our ongoing research, we are trying to synthesize some porous materials having catalytic activities, which are economical for large-scale preparation. We have already synthesized ZnO nano-particles via thermal decomposition [29]. Here we have described the use of five macroporous transition metal oxide (*viz.* CuO, NiO, CoO, Mn_2O_3, Cr_2O_3) and non-transition zinc oxide as a simple and efficient heterogeneous eco-friendly catalyst for different types of organic reactions (*viz.* *N*-formylation, *N*-acylation, *O*-acylation and Friedel Craft acylation). These results were compared with that of already reported commercially available ZnO. To the best of our knowledge, these reactions are never been reported by any group using the porous transition metal oxides.

2. Results and discussion

2.1. Metal oxide-catalyzed formylation of amine

For all the organic transformations, we first prepared the various transition metal hydroxides in presence of agar agar gel as template. Later all these hydroxides were heated to ∼600 °C to transform them to corresponding metal oxides. In case of *N*-formylation (Scheme 1) by macroporous ZnO, we got marginal improvement compared to the reported value [4] as indicated in Table 1.



Scheme 1. *N*-Formylation of amine under solvent-free condition.

Table 1
Comparison of *N*-formylation of aniline (1 mmol) with formic acid (2.5 mmol) by using ZnO as catalyst

Entry	Catalyst	Catalyst (mmol)	Time (min)	Yield (%)[a]	Reference
1	Commercial ZnO	0.50	10	99	[4]
2	ZnO (macroporous)	0.50	08	99	This work
3		0.25	120	55	

[a] Isolated yields.

The reaction conditions were standardized after conducting the *N*-formylation of aniline in different amounts of metal oxides catalyst (Table 2) and reaction time. For *N*-formylation of aniline, 70 °C is proven to be the optimum temperature. This corresponds well with the reported value [4]. Thus under optimum conditions, 1 mmol of aniline was formylated in solvent-free conditions with 2.5 mmol of formic acid using 0.25 mmol CuO, 0.20 mmol NiO, 0.20 mmol CoO, 0.05 mmol Mn_2O_3, and 0.05 mmol Cr_2O_3 as a heterogeneous catalyst. Under similar

Table 2
N-Formylation of aniline (1 mmol) with formic acid (2.5 mmol) at 70 °C

Entry	Catalyst	Catalyst (mmol)	Time (min)	Yield (%)[a]
1	CuO	0.50	25	90
2		0.25	25	95
3		0.25	40	80[b]
4		0.10	40	50
5		0.05	120	–
6	NiO	0.50	60	60
7		0.20	10	99
8		0.20	25	84[b]
9		0.10	20	95
10		0.05	25	80
11	CoO	0.50	45	80
12		0.20	30	99
13		0.20	60	85[b]
14		0.10	40	95
15		0.05	70	85
16	Mn_2O_3	0.50	120	–
17		0.20	60	50
18		0.10	45	74
19		0.05	15	92
20		0.05	35	80[b]
21	Cr_2O_3	0.50	30	80
22		0.20	35	90
23		0.10	25	95
24		0.05	25	90
25		0.05	55	80[b]

[a] Yields are of the isolated compounds.
[b] Reaction performed at 60 °C.