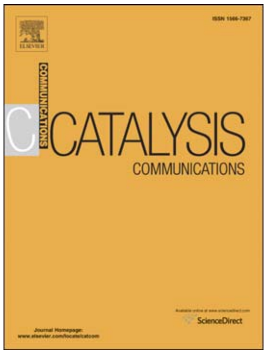

Mg-NHC complex on the surface of nano magnesium oxide for catalytic application

Melad Shaikh, Mahendra Sahu, Pramod Kumar Gavel, Goverdhan Reddy Turpu, Santimoy Khilari, Debabrata Pradhan, Kalluri V.S. Ranganath

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Mg-NHC complex on the surface of nano magnesium oxide for catalytic application

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Abstract: We have developed a simple and eco-friendly protocol for the synthesis of Mg-NHC complexes. The Mg-NHC complex is prepared by reacting nano MgO with imidazolium salts. Thus prepared Mg-NHC complex has been realized in two divergent reactions one in C–C bond formation and other in dehydration reaction. Further, the Mg-NHC catalyst has been characterized by SEM, TEM, XPS, Raman Spectroscopy and XRD analysis.

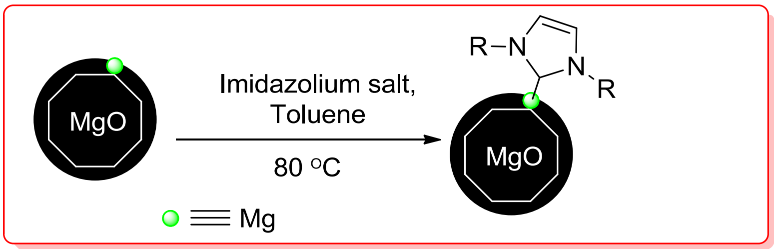
Keywords: Nano MgO, Mg-NHC, C-C bond formation, dehydration, heterogeneous

1. Introduction

The high stability of metal-(N-heterocyclic carbene) NHC complexes and the ability to tune their electronic properties are the attractive features for the development of organometallic materials [1-4]. The coordination of NHC ligands is not only limited to transition metals, but also to non-transition metals [5]. In this direction, the Mg-NHC complex was reported by Arduengo by reacting stable NHCs with dimethyl magnesium [6]. The Mg-NHC complexes have also been realized by using different organometallic reagents such as bis(pentamethylcyclopentadienyl) magnesium, dimethylmagnesium [7], mesitylmagnesium bromide [8], methyl magnesium chloride [9] which leads to the formation of mono and bis Mg-NHC adducts [9]. However, the organometallic reagents used to produce Mg-NHC are highly expensive and a lot of waste could be generated after the reaction. Besides the disadvantage of non-recyclable, Mg-NHCs could not be prepared in large scale, due to economical and environmental concerns. The successful use of Mg-NHCs in catalysis has not been reported on the surface of nanomaterials to the best of our knowledge [10].

Nanostructure materials possess a unique property like high surface area and accessibility of various active facets [11-12]. Because of their chemical activity, robustness and recyclability, nanocrystalline metal oxides have been using in catalysis, either as simple support or even as an active component [13-14].

In the present communication, we report the formation of Mg-NHC on the surface of nano MgO (N-MgO) by reacting with imidazolium salts (Scheme 1) and subsequent application in catalysis under heterogeneous conditions.



Scheme 1: Synthesis of Mg-NHC complex on the surface of nano MgO

2. Experimental:

2.1. Materials:

The nano MgO was prepared as follows:

The metal acetate tetrahydrate (0.05 mol) was initially dissolved in 150 ml of absolute ethanol under constant stirring. The pH of the solution was then adjusted to 5 using 1 M oxalic acid. The mixture was continuously stirred until a thick white gel was formed. The gel formed was left overnight for further gelation process before being dried in an oven at 100°C for 12 h. The dried materials were grounded using mortar and pestle to produce fine powder precursors. Subsequently, the precursors were annealed at 800° C for 24 h to form MgO.

2.2. Synthesis of Mg-NHC complex:

In a typical experiment, nano MgO (0.5 mmol) was added into the round bottom flask containing toluene (3.0 mL) and imidazolium salt (0.05 m.mol). The reaction was stirred at 80 °C for 6 h followed by filtration and dried at 80 °C for 12 h.

2.3. Characterization of Mg-NHC complex:

Mg-NHC complex was characterized by using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-Ray Photo Electron Spectroscopy (XPS) and Raman Spectroscopic techniques.

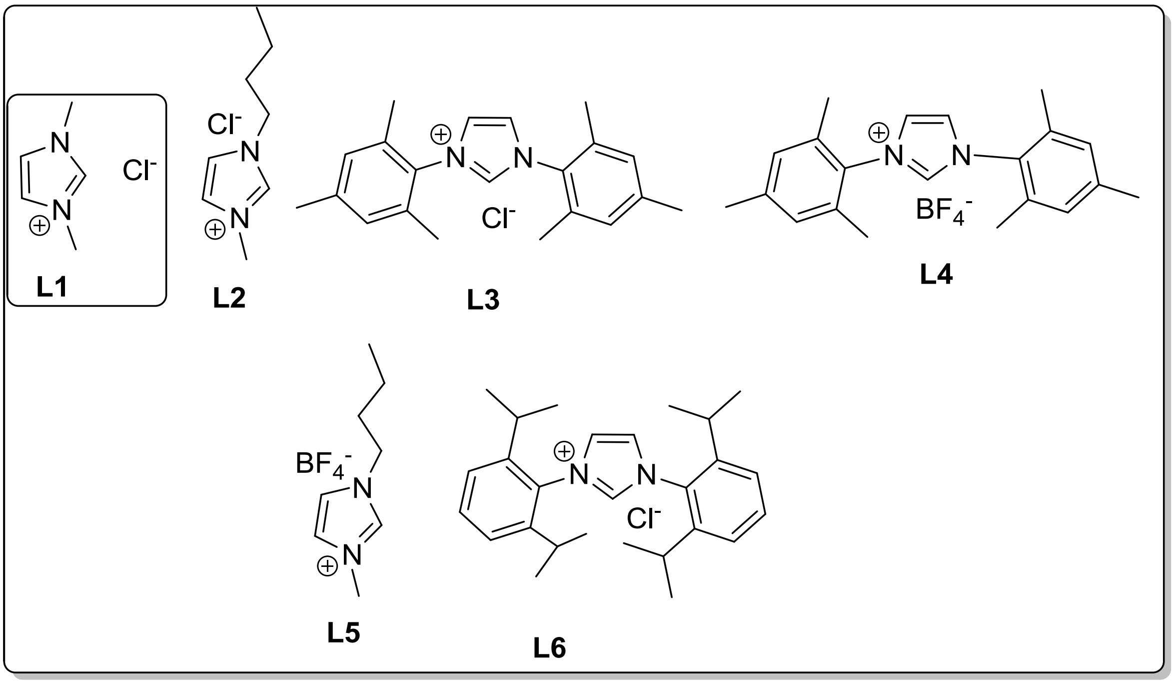
2.4. Catalytic Reaction:

20.0 mg of Mg-NHC was taken into the round bottom flask containing toluene (2.0 mL) and subsequently aldehyde (0.5 mmol) was added. To the resultant mixture nitromethane (2.5 mmol) was added and stirring continued at 60 °C for 12 h. After completion of the reaction, the reaction mixture was filtered to separate the catalyst and purified the product using column chromatography (using Hexane: EtOAc, 9:1)

An oven dried flask was charged with Mg-NHC (0.020 g), glucose (0.180 g). To the flask DMF (3.0 mL) was added and heated to 100 °C with magnetic stirring. After completion of the reaction, the reaction mixture was cooled to room temperature, and catalyst was removed and washed several times with methyl butyl ether and kept at -10°C for 4h to get the crystals of HMF. The reaction mixture was analyzed by using UV-Visible spectroscopy. Final reaction mixture was analyzed by using HPLC using water and methanol: DMF (9:0.5:0.5) using C-18 column.

3. Results and Discussion:

Mg-NHC complexes were prepared using various imidazolium salts on the surface of N-MgO [L1, L2, L3 and L4] as shown in the scheme 2. Initially, the L1-MgO catalyst was characterized by XRD. No significant change was observed in the plane positions after modifying the N-MgO with imidazolium salts (Fig. S1, Supporting Information). However, a small decrease in particle size was observed. The crystallite size was calculated to be 19.6 nm for N-MgO and 16.4 nm for Mg-NHC using Debye-Scherer equation. In the Raman spectroscopy, significant band was observed at 522 cm^{-1}, is the indication for M-O-M or M=O bands [15]. It remains same after surface modification of MgO with 5 mol% of the ligand (L 1) whereas the peak intensity decreases as the concentration of the ligand increases (Fig. 1). No peak corresponding to 522 cm^{-1} was observed using 20 mol% of the L1. This may be due to the coverage of active sites of N-MgO with ligand. At higher concentrations of the ligand, fluorescence can be seen (Fig. S2).



Scheme 2. Various imidazolium salts used for the synthesis of N-Mg-NHC complexes

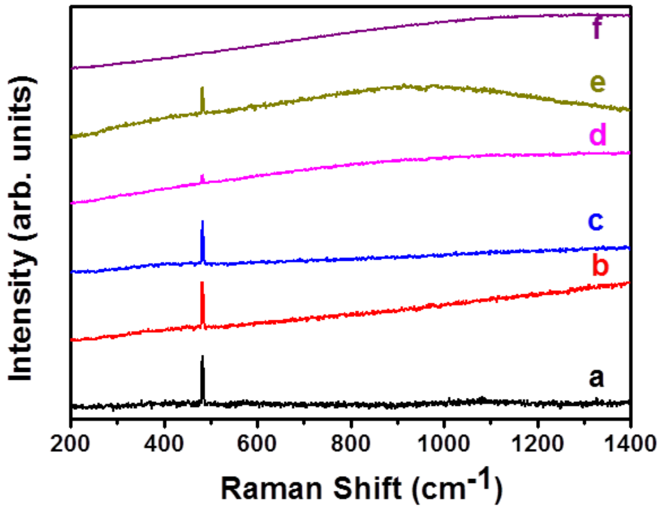


Fig. 1. Raman Spectra a) nano-MgO; b) MgO-L1 (5 mol %); c) MgO- L2 (5mol %); d) MgO-L1 (10 mol %); e) MgO-L3 (5 mol%); f) MgO-L1 (20 mol%)

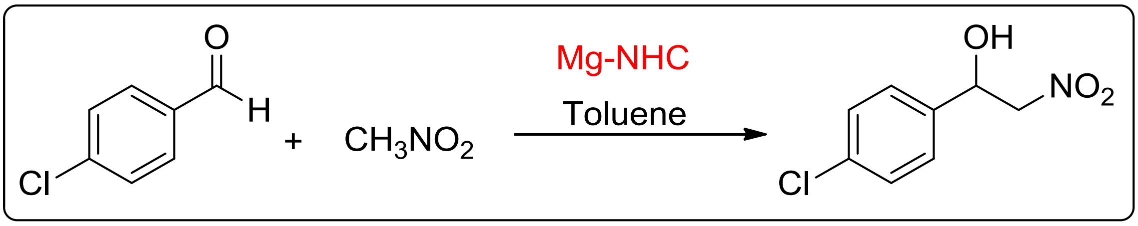
In the SEM of the as synthesized MgO, plate like structures stacked on each other were observed whereas the images of ligand coated samples shows the decoration of particles on the sheets (Fig. S3). Moreover elemental mapping indicates that 2% of nitrogen was present in the sample. The transmission electron microscopy (TEM) of Mg-NHC complex shows MgO particles are of 10-20 nm in diameter (Fig. S4). Further the formation of Mg-NHC complex was confirmed by XPS technique. The N1s emission at 403 e.V of Mg-NHC complex confirms the presence of Mg-NHC (Fig. S5 and S6) whereas the Mg 2p binding energy was observed at 198.6 eV (Fig.S7)

The catalytic properties of the surface modified N-MgO were initially evaluated in the nitroaldol addition reaction between 4-chlorobenzaldehyde and nitromethane, which is an important C-C bond formation reaction (Table 1) [16-17]. The rate of the reaction is very fast using Mg-NHC compared with only nano MgO (< 5%) (Table 1, entry 1). The Mg-NHC L1 acts as a versatile nano heterogeneous catalyst with the yield of up to 55% in toluene at 60°C (Table 1, entry 3). The heterogeneous nature of this catalyst system was demonstrated by recycling of the catalyst for three times. After completion of the first cycle, the catalyst was removed, washed sequentially with toluene, and dried for 30 min. A new reaction was then performed with fresh reactants under the same conditions. To the best of our knowledge, our work is the first report of using N-MgO and NHCs as surface modifiers [10]. As the ligand concentration increases, the rate of reaction increases at the beginning (43% with 5mol% to 55% with 10 mol %) and later on decreases (20 mol %) (Table 1, entry 2, 3, 4 & 5). Further increase in the concentration leads to drastic decrease in the reaction rate and notably there was no reaction with 50 and 100 mol% of L1. This may be due to the surface of N-MgO is completely covered with the imidazolium salts and difficult for activation of carbonyl group of an aldehyde by interaction with the active sites of surface. Effect of temperature has a significant effect on the rate of reaction. Notably, no reaction was observed at room temperature using Mg-NHC complex in the nitroaldol reaction between 4-chlorobenzaldehyde and nitromethane whereas at 80°C, there was no significant change in the yield. Clearly, the success of the reaction will strongly depend on the nature of surface modifier. A screening of various alternative ligands showed pronounced effect on the activity (Scheme 2). Surprisingly, no reaction was observed with L3, L4 and L6 on the surface modified N-MgO whereas with L2, 50% yield was obtained (Table 1). In general, NHC ligands possessing bulky groups show more activity than normal NHCs in catalysis. However, in the present case, the reactivity of linear NHC on the surface of N-MgO is higher than bulk NHCs. This may be due to linear NHCs accommodate properly on the surface of nanomaterials (due to high surface area) and effectively participate in the nitroaldol reaction and hence more reactivity of linear NHCs (Table 1). This clearly indicates, the role of surface chemistry expands into different dimensions towards not only catalysis, but also into the mode of interaction [18] (Fig. S8).

The N-MgO has single crystallite polyhedral structure, which is having the presence of high surface concentrations of edge/corner and various exposed crystal planes (such as 002, 001, 111, 220), leads to inherently high surface reactivity per unit area [19,20]. These active sites may accelerate the nitroaldol reaction in the presence of imidazolium salts with the formation of Mg-NHC complex. In order to test the effectiveness of the Mg-NHC complex in the nitroaldol reaction, various aldehydes containing electron donating and with drawing groups have been examined. Notably, with 4-methoxybenzaldehyde gave the desired product in 52% yield where as benzaldehyde gave 74% yield. Remarkably, when the reaction was performed with 1-naphthaldehyde, reaction went on well with 78% yield in 36 h (Scheme 3). When the reaction was performed with nitroethane, corresponding nitroalcohol product was isolated in 68% yield.

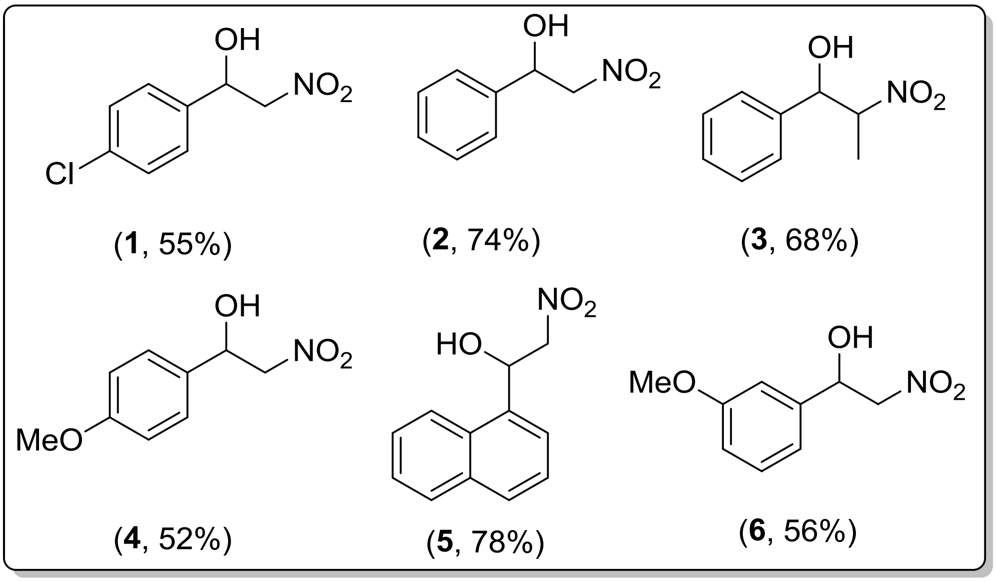
Table 1

Nitroaldol reaction between 4-chlorobenzaldehyde with nitromethane at 60 °C using N-MgO-NHC complex



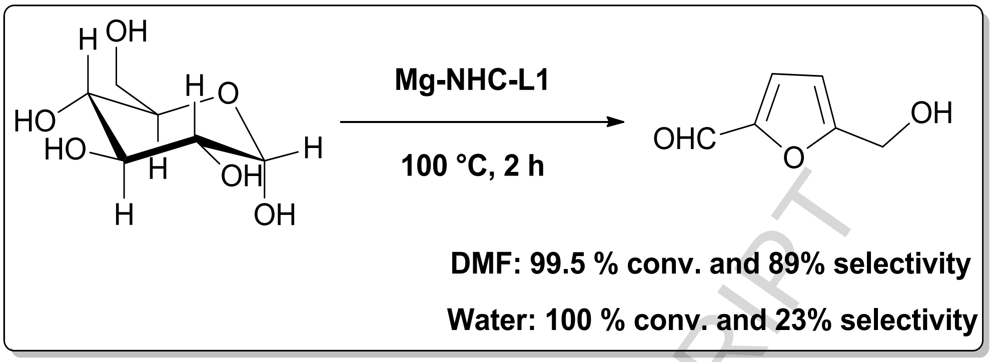
Entry	Catalyst	NHC salt (mol %)	Yield (%)
1	N-MgO	-	< 5%
2	N-MgO-L1	5	43
3	N-MgO-L1	10	55, 52[b], 53[c], 55[d], N.R[e]
4	N-MgO-L1	15	36
5	N-MgO-L1	20	10
6	N-MgO-L1	100	N.R
7	N-MgO-L2	5	50
8	N-MgO-L2	10	38
9	N-MgO-L2	20	34
10	N-MgO-L2	50	N.R
11	N-MgO-L2	100	N.R
12	N-MgO-L3	5	N.R
13	N-MgO-L4	5	N.R
14	N-MgO-L5	5	43
15	N-MgO-L6	5	N.R

Reaction conditions:
[a] aldehyde (0.5 mmol), nitromethane (2.5 mmol), toluene (2.0 mL), catalyst (20.0 mg)
[b] IInd cycle
[c] IIIrd cycle
[d] at 80°C
[e] at room temperature



Scheme 3 Nitroaldol reaction between different aldehydes with nitromethane at 60 °C using Mg-NHC complex

Later, the catalytic properties of Mg-NHC complex was utilized in the glucose dehydration, which leads to the formation of 5-hydroxymethylfurfural (HMF) (Scheme 4). This reaction has emerged as an important transformation, as the resultant compounds represent valuable intermediates for the biofuel [21-23]. The dehydration of glucose has been reported by using various acid and base catalysts under homogeneous conditions as well as under heterogeneous conditions [24]. Therefore the dehydration reaction was performed in different solvents like water and DMF which are commonly, used solvents. Though full conversion was observed in water, however selectivity towards HMF was very less (23%). However, in DMF higher selectivity was observed upto 89% with a conversion of 99.5% at 100 °C in 2 h. However, neither MgO alone nor ligands catalyze the reaction.



Scheme 4 Synthesis of MHF using Mg-NHC complex

4. Conclusion

In conclusion, we have reported the formation of an Mg-NHC on the surface of nano crystalline MgO. This novel catalyst with its new ensemble of catalytically active entities catalyzed C–C bond formation and dehydration reaction. The NHC ligands containing both linear and bulk groups may give the good reactivity. Further work will try to elucidate the underlying active principle of this new class of heterogeneous catalysts for surface catalysis.

5. Acknowledgements

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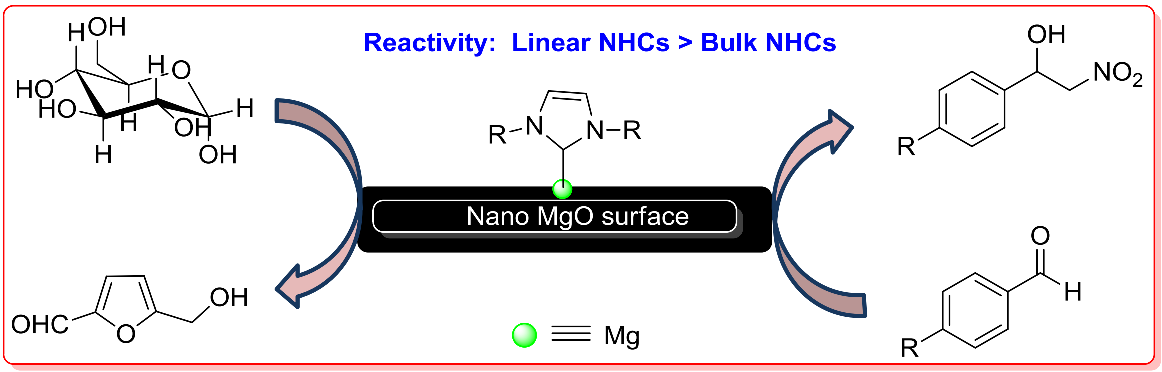
Graphical Abstract



Highlights

- Mg-NHC complex is synthesized on the surface of nano-MgO using simple protocol.
- Mg-NHC complex is used as a heterogeneous catalyst.
- Linear NHCs performed better activity than bulk NHCs.