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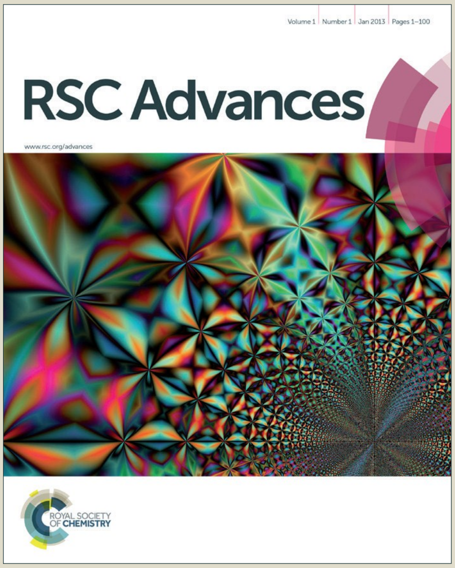

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Surface modification of polyhedral nanocrystalline MgO with imidazolium carboxylates for dehydration reactions: A new approach

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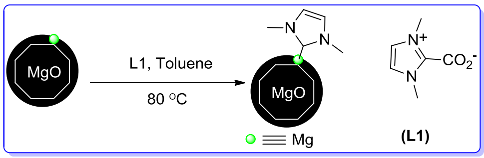
The surface modification of nanomaterial with organic molecules and the utilization of modified materials in various applications is equally important. Here we demonstrate, the surface modification of polyhedral nano MgO with imidazolium carboxylate, which generates NHC stabilized material MgO-[NHC]. The resultant material was successfully utilized in the catalytic dehydration of glucose under heterogeneous conditions. Further, it was demonstraed in the dehydration of nitro alcohol to the olefins in high yields. In addition, the surface modified catalyst was characterized by using various techniques like XRD, FE-SEM, TEM, FT-IR, XPS and AES analysis.

The nanostructured materials possess a unique property like high surface area and accessibility of various active facets. Their catalytic activity dependent on the structure and composition of the surface, both can change by modifying the surface.[1-3] The utilization of nanomaterials in various directions is increasing rapidly after surface modification due to change of their environment and hence properties at the surface.[4] Various methods have been employed for the surface modification of nanomaterials using silane, polymers primary amines, long chain carboxylic acids and recently dicarboxylic acids.[5] There are large number of surface modified nanomaterials, including metal oxides, metal nanoparticles with various chiral and achiral moieties.[6] To develop a new material for catalytic application after surface modification of nanomaterials is still quiet interesting.[7]

N-heterocyclic carbenes (NHCs) are rapidly expanding area of research in transition metal catalysis as well as in organo catalysis.[8,9] The coordination of NHC ligands is not only limited to transition metals, but also to non-transition metals.[10] It is worth noting that the manipulation of free carbenes are quite difficult due to their highly reactive nature.[11] Recently, the use of CO_2 adducts of NHCs attracted much attention in organocatalysis as well as in the synthesis of NHC-metal complexes.[11] Since *N,N'*-disubsituted imidazolium carboxylates are readily available and moreover NHC-CO_2 adducts are air and water stable reagents, we have selected them as a choice of surface modifiers on nanomaterial. Due to high thermal stability in nature, robustness and high accessibility, nano MgO is selected in the present study as a promising nanomaterial to modify the surface.[12]

Herein, we report the covalent surface modification of nano MgO with Imidazolium carboxylates, (zwitterions) which leads to the formation of MgO-[NHC] complex (Scheme 1).



Scheme 1 Surface modification of nano MgO with L1 to generate MgO-[NHC]

This method represents a novel and is having more advantage towards environmental concern compared with earlier reported Mg-NHC complexes with organometallic reagents, which are highly expensive and lot of waste could be generated after the reaction.[13,14] To the best of our knowledge, non-transition metal-NHC complexes have not been used under heterogeneous catalysis.[15] The resultant MgO-[NHC] complex was used as a versatile heterogeneous catalyst in the dehydration of glucose to 5-hydroxymethylfurfural (5-HMF) and also in the dehydration of nitro alcohol to alkenes (Scheme 2).

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Electronic supporting information is available. [XPS, AES, elemental mapping, FTIR spectrum and HPLC are available.]
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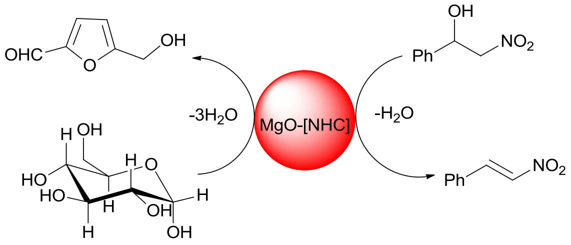

Scheme 2 MgO-[NHC] complex catalyzed dehydration reactions.

The nano MgO was prepared by the so-called solvothermal method as reported in the literature.[16] To open the doors for application of nano MgO, its surface was modified by imidazolium carboxylate in toluene at 80 °C. The catalytic properties of the surface modified nanomaterial was initially evaluated in the dehydration of glucose in DMF at 100°C. This transformation provides valuable compound, 5-hydroxymethylfurfural (HMF), which is a well known component of biofuel. [17-19] We were pleased to identify the conversion of glucose is 99% with 92% selectivity towards HMF. To understand clearly, the role of surface modifier, we performed the reaction separately in the presence of nano MgO (without surface modification) and also using imidazolium carboxylate (without MgO). Notably, neither nano MgO nor organic ligand catalysed the conversion of glucose. The dehydration of glucose has been catalyzed by using various acid and base catalysts under homogeneous conditions as well as under heterogeneous conditions.[20]

Later the dehydration reaction was performed in different solvents like water and DMSO, which are commonly, used. The dehydration reaction in aqueous medium furnished the full conversion of glucose with expected product, HMF in 23%, along with a significant number of by-products, one of which was identified as levulinic acid (46%). Surprisingly, in DMSO higher selectivity was observed upto 73% towards HMF, with less conversion upto 52% at 100 °C. The heterogeneous nature of this catalyst system was demonstrated by recycling of the catalyst. The surface modified catalyst was used three times without any significant decrease in activity and selectivity. After completion of the first reaction, the catalyst was washed several times with ether dried for 2 h. A new reaction is then performed with fresh glucose using the recovered catalyst under the same conditions.

The MgO-[NHC] complex was characterized by X-Ray Diffraction (XRD). The chromatograms were comparable to JCPDS (card number 45-0946). No significant change was observed in the plane position of MgO-[NHC] and MgO (Fig. 1). However, the decrease of particle size of MgO-[NHC] was highly remarkable. This may be due to the interaction of Mg-C than Mg-Mg interactions and prevents the agglomeration of nano MgO. In addition, the XRD data of MgO-[NHC] indicated the decrease in intensity of (220) and (200) planes due to the interaction of ligand preferentially, whereas the intensity of (111) and (110) planes remain same (Fig. 1). There was no significant change in the XRD data of recycled catalyst in the dehydration of glucose (Fig. 1c). The crystallite size was calculated using Debye-Scherer equation and it was observed that 8.2, 5.4 and 6.2 nm for freshly prepared MgO, MgO-[NHC] and the recycled catalyst respectively.

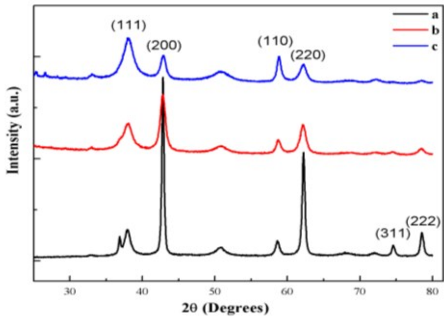

Fig. 1. XRD pattern of (a) nano MgO (b) MgO-[NHC] (c) after recycling of the catalyst.

Remarkably, the particle size increases to 50.84% after three recycles from 45.97% before recycling (Table 1.)

Table 1. Relative crystalline size of nano MgO

Parameter	MgO	MgO-[NHC-L1]	MgO-[NHC-L1] (recycling)
β (HWFM)	0.464	1.01	0.914
Relative Particle size	0.92	0.42	0.47
% of particle size	100 %	45.97 %	51.08 %

The field emission scanning electron microscopy (FE-SEM) images of nano MgO and MgO-[NHC] shows distinct differences of surface structure. The unmodified MgO nanoparticles are self assembled to form 3D flower like morphology. However the MgO-[NHC] results the incorporation of organic moieties inside the 3D flowers (Fig. 2). Further the elemental distribution was carried out from the elemental mapping energy dispersive X-ray (EDX) analysis (Fig. S1 and S2). The representative elemental mapping of the MgO-[NHC] indicating the presence of carbon, nitrogen along with magnesium and oxygen confirming the surface modification with ligand.

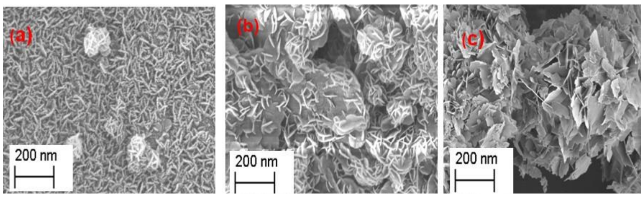

Fig. 2. SEM of (a) nano MgO (b) nano MgO treated with L (c) after recycling of the catalyst

The FE-SEM image of MgO-[NHC] after recycling shows well dispersed flower-like structures in the range of 1-50 µm and open-flakes of flowers in less than 100 nm (Fig. 2). Additionally, the transmission electron microscopy (TEM) indicates that nanomaterials are of 20-50 nm in diameter for MgO-[NHC] complex (Fig. S3). The distinct ring diffraction pattern shown as insect of figure S3 further suggests that the crystalline nature of the MgO-[NHC]. Moreover the chemical

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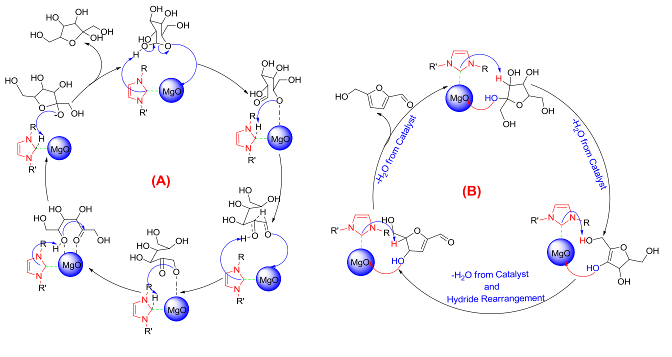
modification of nano MgO was confirmed from X-ray photo electron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). The successful modification was indicated by XPS from the most important characteristic of heteroatom sites (nitrogen) of imidazolium moiety at 400 eV (Fig. S4). The N1s binding energy near to 400 eV was earlier reported by Glorius and co-workers for imidazolium salts modified magnetite nanoparticles.[4d] Notably, binding energies of Mg 2p, C1s are at 49.6 and 295 eV respectively (for complete XPS of each element, see the supporting information Fig. S4). In addition Auger electron spectroscopy (AES), further confirms the presence of nitrogen and carbon along with magnesium and oxygen in the surface modified MgO (Fig. S5) and observed that 3.3% of nitrogen was present.

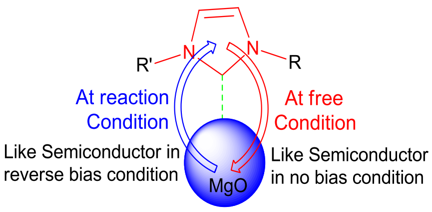
The FTIR spectrum of surface modified MgO materials further confirmed the presence of ligand on surface of nano MgO. Of particular note was that the absence of stretching frequency of $\nu(CO_2)$ at 1615 cm^{-1} suggests that released carbon dioxide is not adsorbed on nano MgO surface (Fig. S6). Interestingly, the surface hydroxyl groups are not affected (3600 cm^{-1}) even after surface modification with imidazolium salts (MgO-[NHC]). The stretching frequency at 772 cm^{-1} is may be due to the Mg-C bond of surface modified MgO. Apart from these differences, there is a good agreement with rest of the spectrum, suggesting the remaining molecular identity is retained after modification. These results further confirm that an organic layer exists and the linkage between inorganic material and organic nuclei is covalent linkage. The FT-IR of the recycled catalyst MgO-[NHC] shows the stretching frequency at 3612 cm^{-1} is due to the adsorption of water molecules.

The reaction from glucose to HMF is generally assumed to involve isomerisation of glucose to fructose followed by dehydration to HMF. The plausible mechanism for the synthesis of 5-HMF from glucose is shown in the Scheme 3. Initially, the isomerisation of glucose to fructose may takes place in the presence of MgO-[NHC] (Scheme 3A) and then from fructose to 5-HMF (Scheme 3B) using the same catalyst. In MgO-[NHC] complex the electron cloud is towards electron deficient MgO from electron rich NHC (like in the semi conductor in zero bias system).



Scheme 3 Plausible mechanism for the dehydration of glucose using MgO-[NHC] complex (A) glucose to fructose (B) fructose to HMF.

When the glucose was added, it may be in the reverse direction due to NHC abstract the acidic proton of sugar and simultaneously the MgO of MgO-[NHC] abstract the hydroxyl group of the sugar (like in reverse bias condition) (Scheme 4).



Scheme 4 nano MgO-[NHC] complex like in semiconductor.

Finally water is removed from biomass followed by the hydride rearrangement to produce dehydrated product in high yields. Later, the dehydration of nitrolacohol was performed using MgO-[NHC-L1] complex and the results are shown in the table S1. The dehydration nitro alcohol is very important since the resultant compounds, nitro alkenes are used as key intermediates in the synthesis of natural products.[21] In addition, nitro alkenes have been using as a receptors of Michael addition reaction.[22] In the present system, nano-MgO itself catalyze the dehydration of β-nitro alcohol, gave nitro alkene in 82% yield at 80°C. The surface modified catalyst increase the rate of reaction and nitro alkene was isolated in 85% yield after 2 h (Table S1). To the best of our knowledge, our work is the first report of using NHC-CO_2 adducts as surface modifiers, and also as stabilizer for nano MgO.[23]

As a part of our ongoing research towards the synthesis of enantiopure secondary alcohols under heterogeneous conditions, our quest is finding an efficient, environmentally friendly protocol for the synthesis of secondary alcohol.[24] Therefore, the chiral imidazolium salts were used as modifiers on the surface of nano MgO to generate chiral catalysts MgO-[NHC-L2*] and MgO-[NHC-L3*]. These two L2 and L3 were selected due to easily isolable and which play a major role in asymmetric heterogeneous catalysis and moreover chiral NHCs are known to stabilize nanoparticles (Fig. 3).[25]

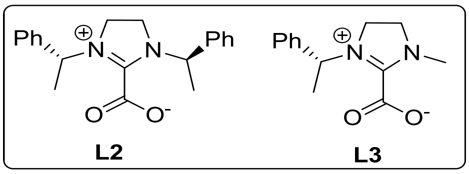
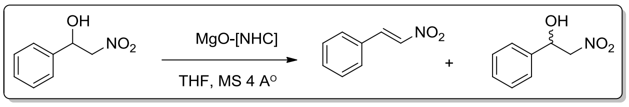


Fig. 3. Chiral imidiazolium salts on nano MgO used for dehydration of nitro alcohols.

The dehydration of nitro alcohol was then performed using both chiral catalysts MgO-[NHC-L2*] and MgO-[NHC-L3*]. Notably, when the simple (±)-nitroalcohol was reacted with 5mol% of chiral catalyst, MgO-[NHC-L2*], at 25°C, the dehydration took 48 h for giving 28% of nitroalkene in THF solvent. In this asymmetric reaction, 61% of nitroalcohol was recovered with 32% enantiomeric excess (ee) (Table 2). When the same reaction was performed at 60 °C, 81% of nitroalkene was isolated provided the recovered nitroalcohol in 4% without ee. However, in the presence of MgO-[NHC-L3*], at 25°C, asymmetric reaction took 48 h and nitroalkene was isolated in 18% without ee in THF (Table 2). Moreover, when the dehydration reaction was performed in water, no reaction was observed either using MgO-[NHC-L2*] or MgO-[NHC-L3*]. This may be due to not proper dispersion of surface modified nano MgO in the reaction medium.

Table 2 Dehydration of nitro alcohol catalyzed by asymmetric catalysts MgO-[NHC-L2*] and MgO-[NHC-L3*]



Entry	Catalyst	Time (h)	Temp(° C)	Yield (%)	Ee(%)
1	Mg-NHC-L2	48	25	28	32
2	Mg-NHC-L2	12	60	81	-
3	Mg-NHC-L3	48	25	18	-
4	Mg-NHC-L3	20	60	85	-

MgO-[NHC] complex: 20.0 mg, THF: 3.0 mL, nitro alcohol (1.0 mmol)

In conclusion, the present study demonstrates the formation of MgO-[NHC] complex using zwitterionic salts. This modified material with its new ensemble of catalytically active entities catalyzed dehydration of glucose to HMF. Further work will try to elucidate the underlying active principle of this new class of heterogeneous catalysts for surface modification and catalysis.

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Surface modification of polyhedral nanocrystalline MgO with N-Heterocyclic Carbene (NHC) for Dehydration Reactions: A New Approach

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