Supporting Information

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

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1. Experimental techniques

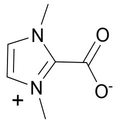
Reactions were performed in oven-dried glassware. All chemicals were purchased from Aldrich and used directly as received; Reactions were monitored by HPLC from Shimadzu company with dual pump using C-18 column. Concentrations (*c*) are given in g/100 mL. Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers of recorded IR-signals are quoted in cm^{-1}. ^{1} H- was recorded in $CDCl_3$ or using Bruker ARX-300, AV-300 or AV-400 spectrometers. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform and $CDCl_3$ (^{1}H δ7.28) as internal standard on the δ scale. Field emission scanning electron microscopy (FE-SEM) was used to study the surface morphology of as prepared catalyst. The FE-SEM images were captured in a Zeiss MERLIN electron microscope operated at 5 kV accelerating voltage. Elemental mapping of catalyst surface was analyzed by energy dispersive X-ray spectroscopy (EDX). The EDX mapping was carried out with an EDAX elemental analyzed attached to the FE-SEM. A Tecnai FEI transmission electron microscope (TEM) operated at 200 kV accelerating voltage was utilized to evaluate the microstructure of the as prepared catalyst. The crystallinity and phase analysis was performed using powder X-ray diffraction (PXRD) pattern. The PXRD pattern was recorded in a panalytical High Resolution diffractometer equipped with Cu-$K_{\alpha 1}$ irradiation at a power of 40 kV × 40 mA. The entire PXRD pattern was recorded over a two theta range of 10-80°.

2. Experimenal Conditions:

2.1. Synthesis of nano MgO:

In a typical procedure magnesium nitrate hexahydrate $Mg(NO_3)_2.6H_2O$ (5.0 mmol) and urea (10.0 mmol) were dissolved in 100 mL of ethanol and then the solution was poured into a Teflon lined autoclave of 250 mL capacity. The autoclave was sealed and heated to 150 °C for 30 min. After cooling to room temperature, precipitate was collected and washed with ethanol and water for several times. The nano MgO was obtained after calcination at 500 °C for 4 h. The nano MgO was characterized by XRD, SEM, TEM analysis.

2.2 Synthesis of ligand (L1):



L 1

1,3-dimethyl 2-imidazolium carboxylate was synthesized according to the literature procedure. Dimethyl carbonate (1.5 mL) and 1-methyl imidazole (1.0 mL) were combined and heated in a sealed vial at 120 °C for 24 h. The reaction mixture was cooled to room temperature and dried the resultant solid for 6 h to get ligand. The ligand formation was confirmed through I.R spectroscopy (Fig. 4.)

2.3 Preparation of Surface Modified Nano-MgO

To a solution of L1 (0.35 g) in toluene (5 mL) were added MgO nanoparticles (1.0 g) and the resulting suspension was stirred for 4 h at 80°C. Following cooling to room temperature, the suspension was centrifuged (2500 rpm, approx. 30 min), and the solid residue was washed thoroughly with toluene (50 mL), washed with EtOH (50 mL) and dried *in oven* to furnish the title compound as a free-flowing white powder.(elemental analysis: 48% Mg, 48% O, 2% N and N% C)

2.4 Experimental Procedure for the HMF production:

In a typical run, glucose (180 mg) was added to the sealed tube containing the catalyst (30.0 mg) and it was heated to 100 °C for 30 min. The solid was allowed to cool to room temperature and diethyl ether was added (2 X 10 mL) and product was extracted. Finally, water (5.0 mL) was added to remove unreacted glucose followed by MeOH (5.0 mL) and the catalyst was allowed to dry for 6 h.

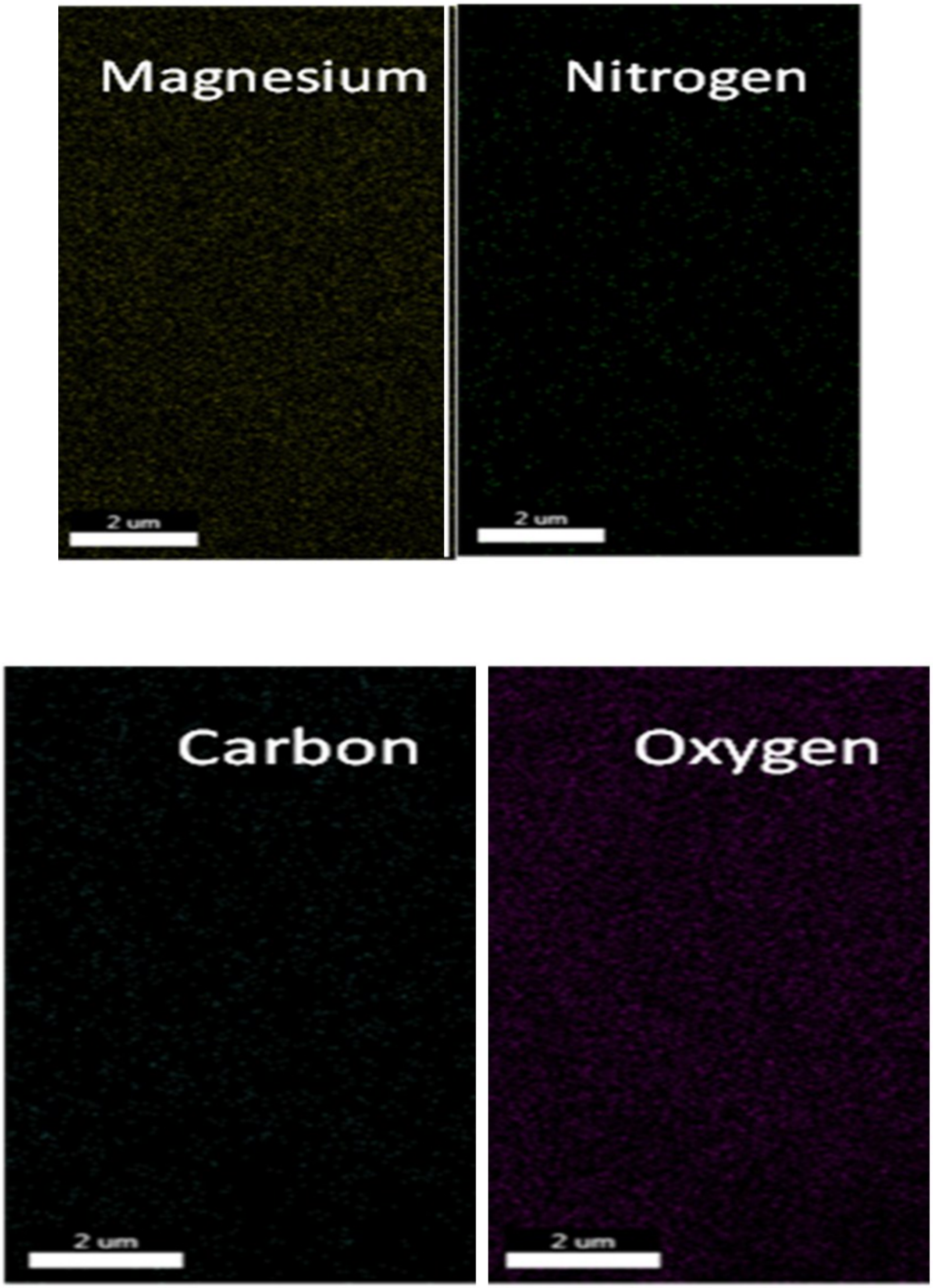


Fig. S1 Elemental mapping analysis after surface modification MgO-[NHC-L1] complex

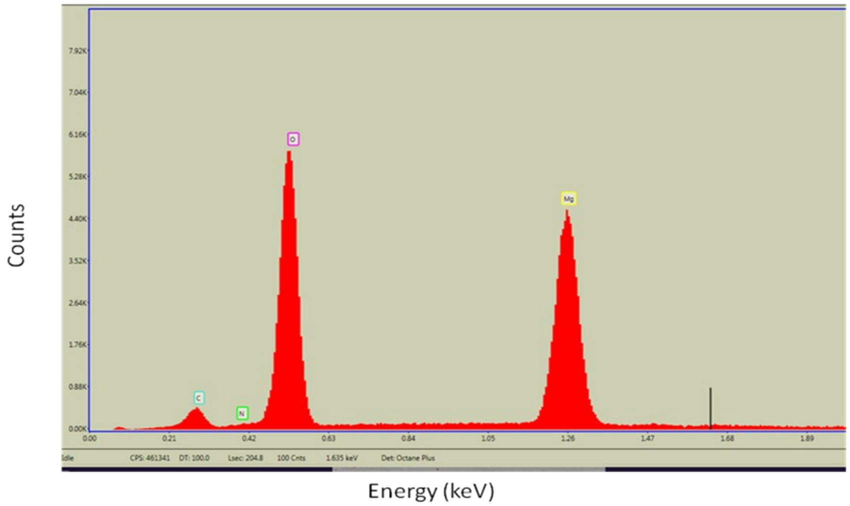


Fig.S2 SEM-EDX analysis of nano MgO after surface modification.

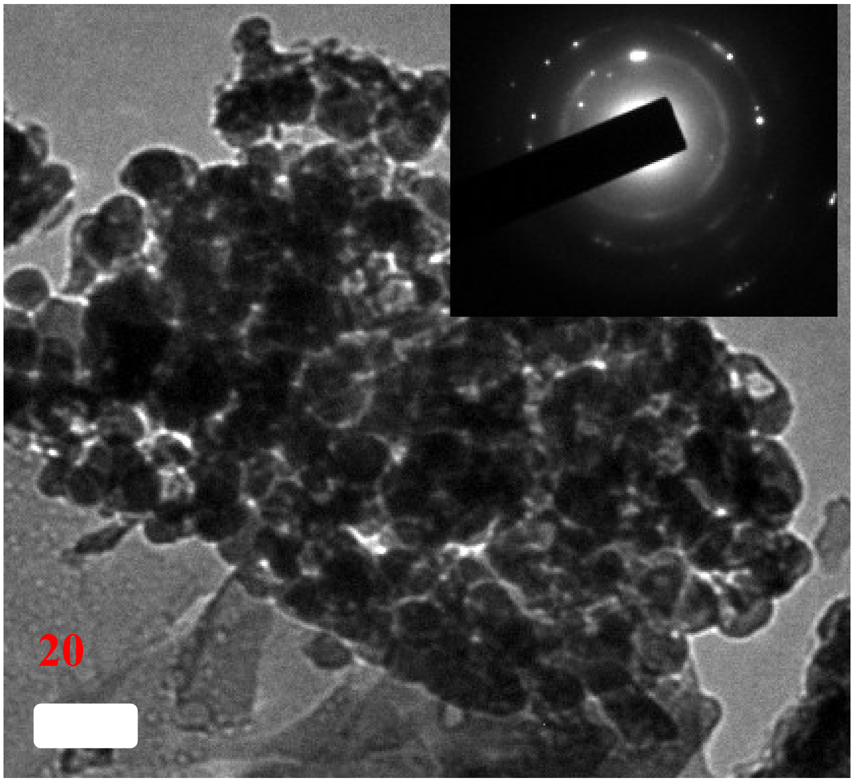
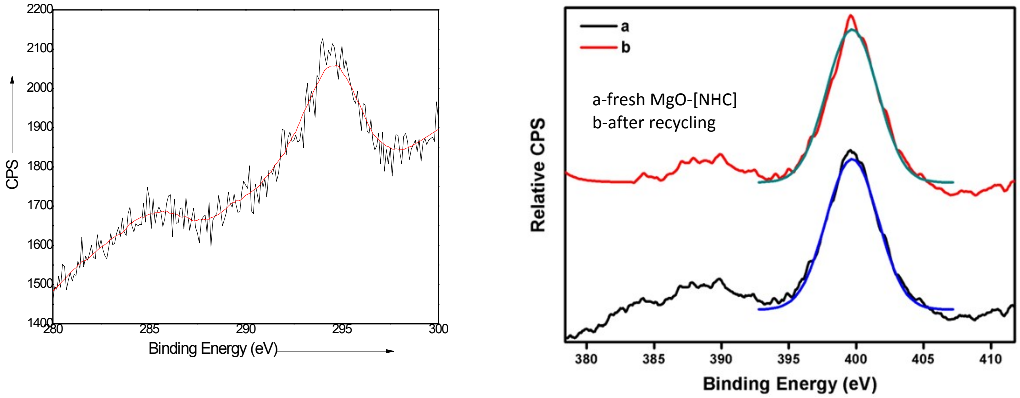
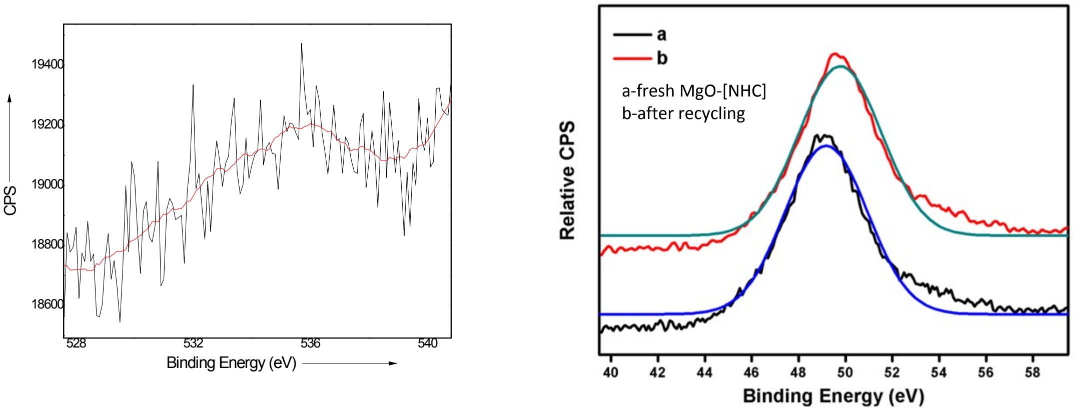


Fig.S3 TEM analysis of surface modified nano MgO (Inset of (c) shows a selected area electron diffraction pattern of corresponding region.)



(a) C 1s emission (b) N 1s emission



(c) O 1s emission (d) Mg 2p emission

Fig. S4 XPS spectrum of a) C 1s emission b) N1s c) Mg 2p d) O1s emission spectra

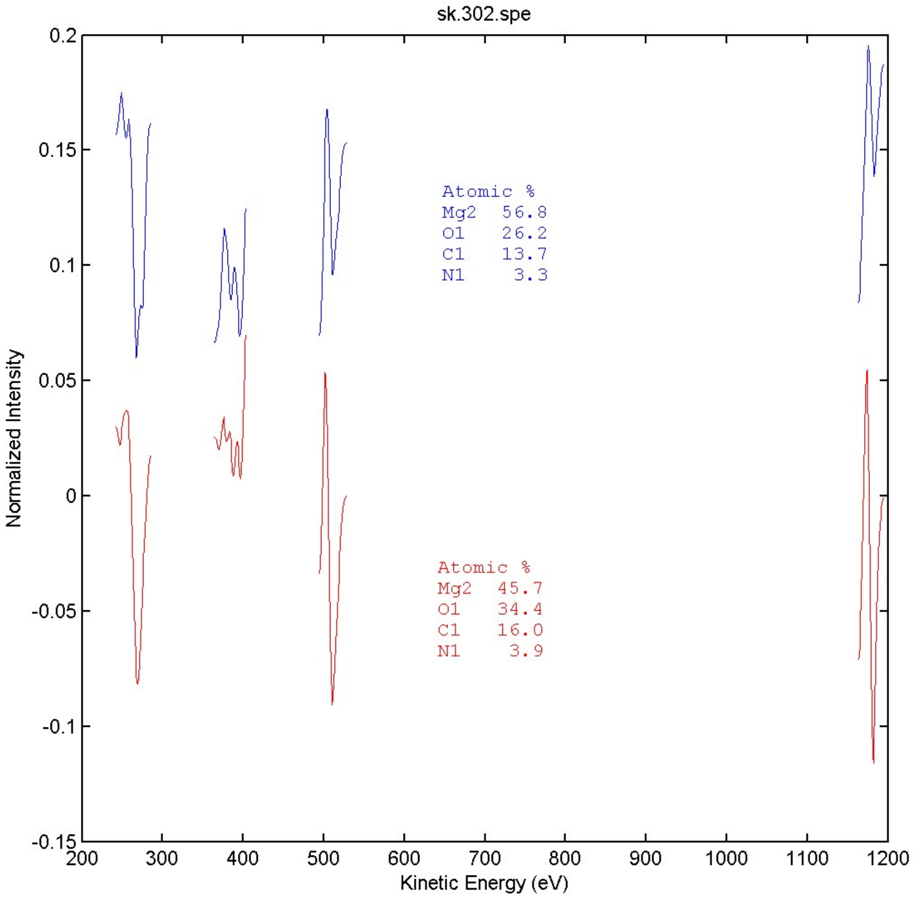


Fig. S5 Auger electron spectrum of surface modified MgO with L1

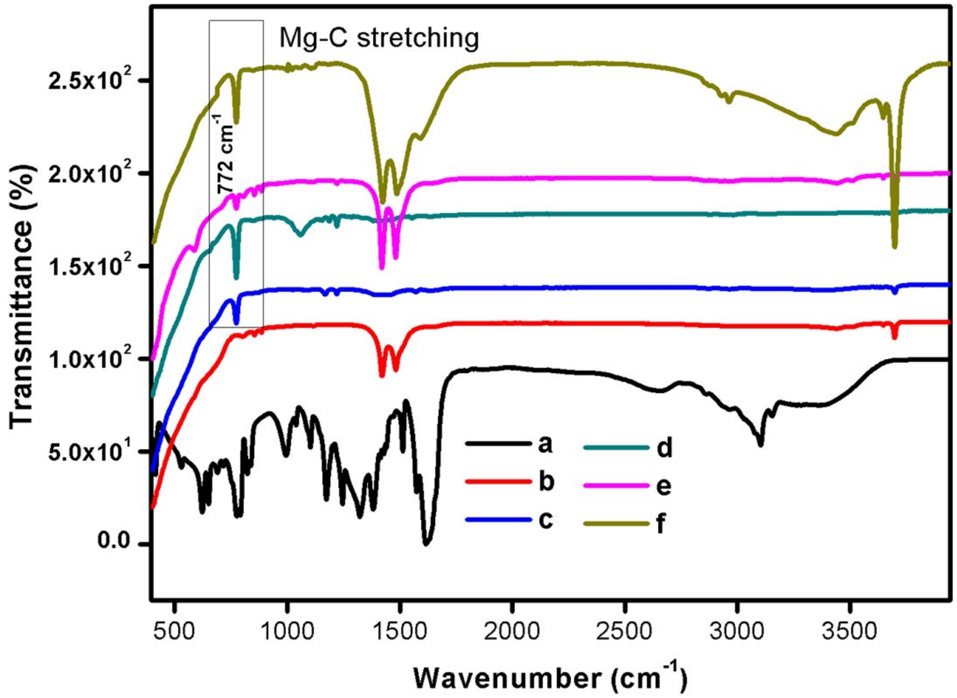


Fig. S6. FTIR analysis of a) ligand L1 b) MgO c) nano MgO modified with L1 (d) with L2 and (e) with L3 (f) after recycle of MgO with L1

Table S1: Dehydration of nitroalcohol catalyzed by MgO-[NHC] complex

Entry	Catalyst	Time (h)	Temp (°C)	Yield (%)
1	Nano MgO	6	80	82
2	Mg-NHC-L1	2	80	85
3	Mg-NHC-L1	1	90	90
4	Mg-NHC-L1	36	25	28

Mg-NHC complex: 20.0 mg, THF: 3.0 mL, nitro alcohol (0.5 mmol)

3.0. The Spectrophotometric method for the determination of HMF:

After completion of the reaction, 0.5μl reaction mixture was diluted up to 50 mL with HPLC water followed by the addition of 0.5 mL of Carrez solution I and 0.5 mL of Carrez solution II. Aliquots of 5 mL were put into 2 tubes; 5 mL of deionized water was added to one tube (sample solution); 5 mL of sodium bisulfite solution 0.2% was added to the second (reference solution). The absorbance (determined using a Lambda 25 double beam spectrophotometer UV/Vis, Shimadzu) of the aqueous reaction sample at 284 nm (A284) was determined versus reference solution, in order to avoid the interference of other components at that wavelength. The absorbance at 336 nm (A336) was read to subtract the background absorbance. The HMF was quantified by using the proposed formula of the original White method.

HMF(mg) = (A284 − A336) × 149.7 × *5/W,* where W is the weight of the fructose, the factor 149.7 is a theoretical value linked to the molar extinction coefficient of HMF at 284 nm, which is 16830. In this work we studied the experimental extinction coefficient of HMF to check the correspondence with the theoretical behaviour of HMF.

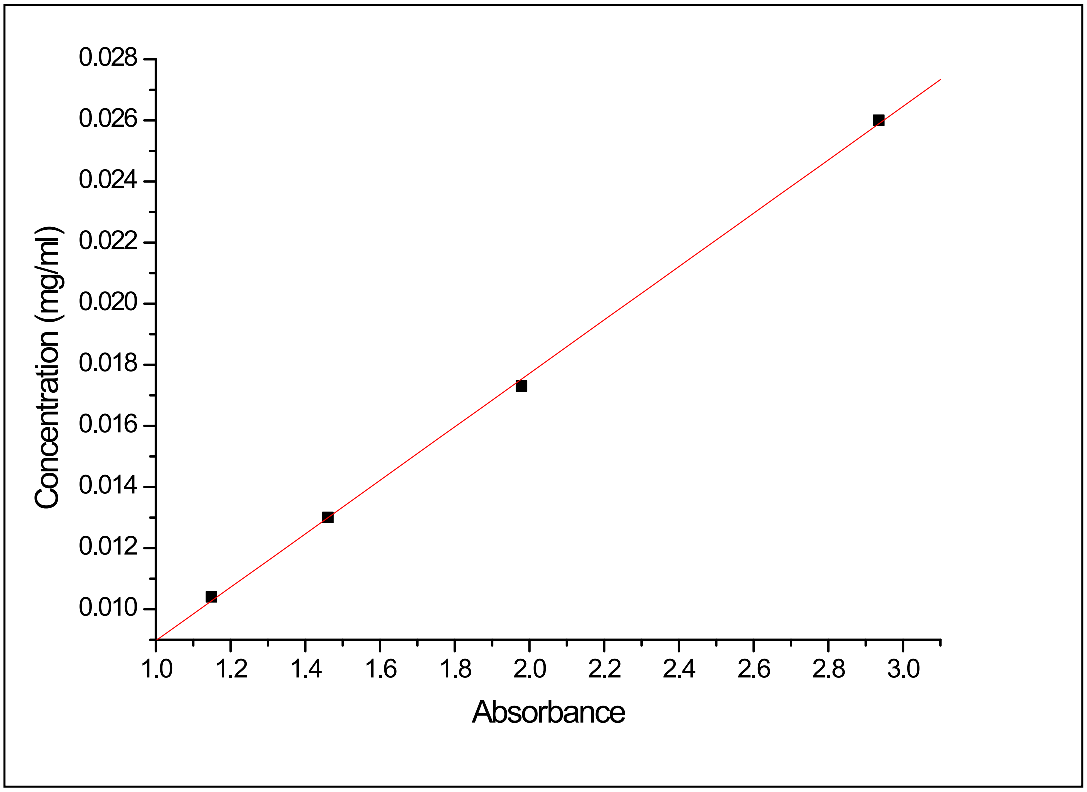


Fig. S7 Calibration Curve for the HMF using UV-spectrometer.

Y= (87.4x10^{-4}) (X) + 2.264x10^{-4}

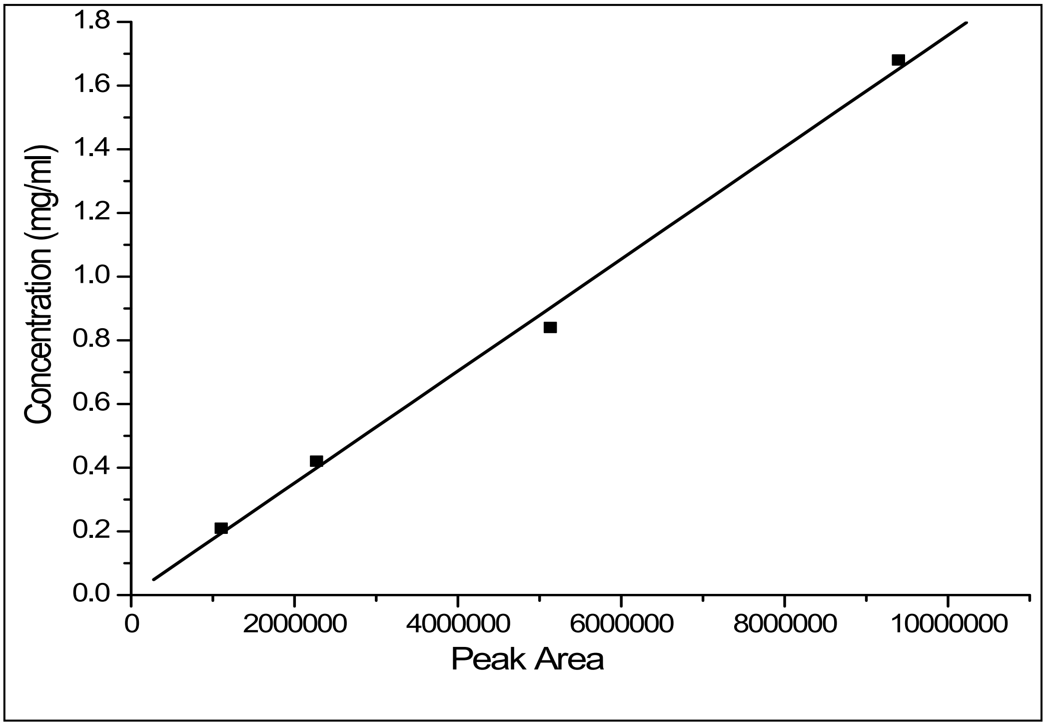
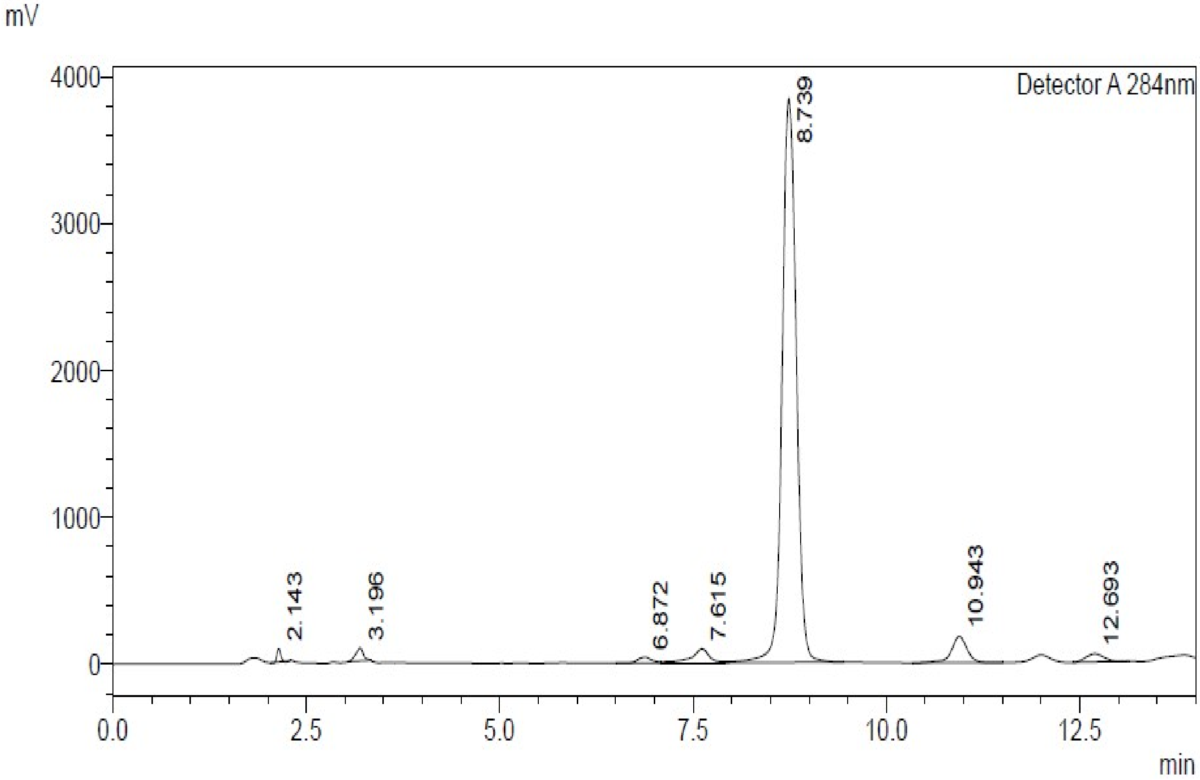


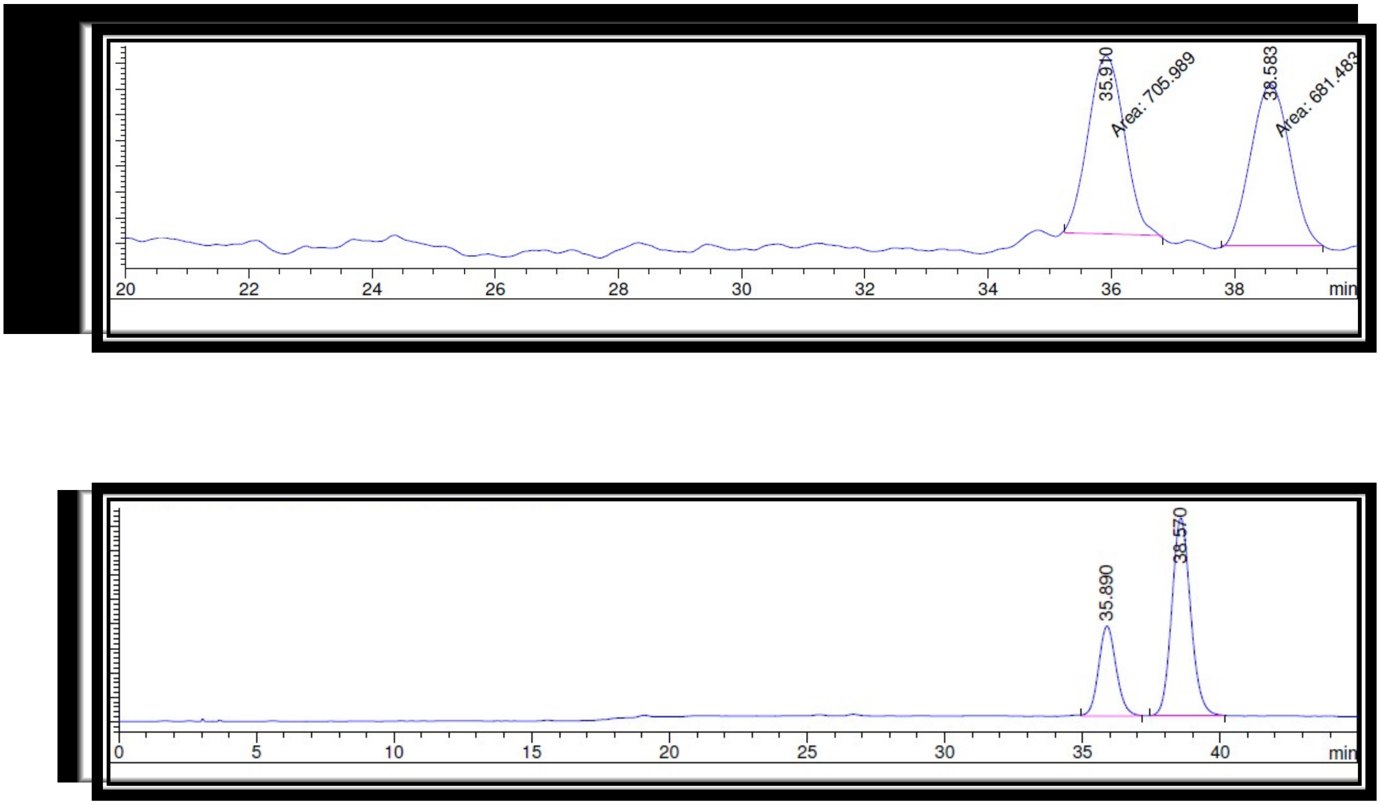
Fig. S8 HPLC-calibration curve for HMF (Y =(1.76x10^{-3} x + 5.2)10^{-4}



Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
2.143	276301	91234	0.501	2.080
3.196	610424	87822	1.107	2.002
6.872	515491	41402	0.935	0.944
7.615	1527490	94820	2.771	2.162
8.739	48790144	3837520	88.513	87.491
10.943	2521431	178545	4.574	4.071
12.693	880864	54836	1.598	1.250
	55122146	4386179	100.000	100.000

Fig. S9. HPLC spectrum of reaction mixture of glucose dehydration using MgO-[NHC-L1] in DMF.



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  35.890 BB    0.6886 8180.98877  184.05731  29.8004
   2  38.570 BB    0.7320 1.92716e4   404.35120  70.1996
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Fig. S10 HPLC spectrum of recovered nitro alcohol product [chiral pak AS-H column; Hexane: *i*-propanol 9:1, flow rate: 1.0 ml/min.]

References

1. C.-Y CaO, J. Qu, F. Wei, H. Liu, W.-G Song *ACS Appl. Mater. Interfaces,* 2012, 4, 4283-4287.
2. J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi and R. D. Rogers, *Chem. Commun*., 2003, 28-29;