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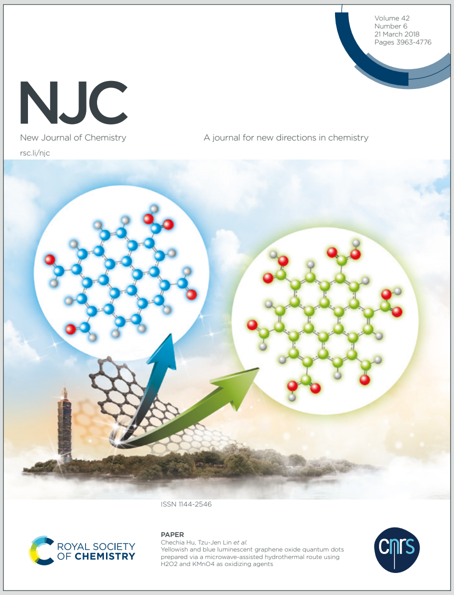

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PAPER
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Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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Iron and chromium MOFs as sustainable catalysts for transfer hydrogenation of carbonyl compounds and biomass conversions

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Abstract: MIL-88B is a class of metal-organic framework (MOF) which is widely explored in catalysis. Iron- and chromium-based MIL-88B MOFs were prepared and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N_2 adsorption/desorption measurements. The MOFs (MIL-88B) were investigated as catalysts for transfer hydrogenation (TH) of carbonyl compounds (ketones and aldehydes) and biomass derivatives (levulinic acid and furfural) with 2-propanol as a hydrogen donor. Their conversion and selectivity were excellent. The recovered catalyst was reused for ten times, with no significant loss in catalytic activity. Recovered catalyst after the tenth run retained its original crystallinity and morphology, which were confirmed by SEM and powder XRD studies. Catalyst reusability for levulinic acid (LA) conversion was also studied. The activation energy for the transformation of LA to *γ*-valerolactone (GVL) was 25.44 KJmol^{-1}. The catalytic performance of MIL-88B(Fe) was compared with that of MIL-53(Fe).

Keywords

Metal-organic frameworks; MIL-88B; Transfer hydrogenation; Acetophenone; Levulinic acid; *γ*-valerolactone

1. Introduction

Reduction of C=O and N=O is one among the fundamental transformations in the nature to form alcohols and amines.[1, 2] Enzymes which catalyze such reductions are termed as oxidoreductases. Oxidoreductases such as horse liver alcohol dehydrogenase catalyze transfer hydrogenation of carbonyl compounds to alcohols,[3] which contain zinc[4] as the metal centre to transfer hydride from an alcohol.[5, 6] The reduction of carbonyl and nitrosyl groups to their respective alcohols and amines is one of the most scientifically popular processes, which is predominantly carried out in chemical industries. The catalytic hydrogenation of C=O

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group is usually performed using a precious metal (Pd, Au, Pt, Ag, Rh, Ru or Os)[7, 8] and/or a non-precious metal (Cu or Ni) catalyst(s) along with H_2 gas.[9] The use of molecular hydrogen has drawbacks such as the requirement of high pressure and temperature, safety issues during transportation and storage, and it also increases the demand for hydrogen as a feedstock for chemical processes.[10] Therefore, researchers have made attempts to find alternative sources for H_2 gas for hydrogenation reactions. One of the alternatives is to use hydrogen from an alcohol, a process referred to as transfer hydrogenation (TH). This concept is appealing for the following reasons: (i) Catalytic transfer hydrogenation (CTH) does not require hazardous pressurized H_2 gas, (ii) the hydrogen donors are readily available, inexpensive and easy to handle, (iii) the primary side product can be recycled and (iv) the catalysts that are involved are usually readily accessible and not sensitive.[11, 12]

CTH has recently been employed for the hydrogenation of bioderived compounds such as furfural using metal oxides, including zeolite beta, $Ru/RuO_2/C$, MgO, Al_2O_3, ZrO_2, ZnO and SiO_2 as catalysts. Either, the performance of these catalysts was relatively lower or the reactions employed high temperature (~150-600 °C) and pressure (~2-10 bar). In this scenario, the choice of earth abundant metals such as Fe and Cr will help to reduce the cost of the final product. Iron is known to form stable iron oxides[13] as well as iron hydrides.[14, 15] There are considerably a number of reports on iron based CTH of ketones but most of the good catalysts are either sulphur, oxygen or phosphine-based ligands-embedded iron nanoparticles or their corresponding metal complexes.[16] Chromium, on the other hand remains concealed, wherein its catalytic potential is still to be discovered.[17-19] However, giving importance to its abundancy and low cost, recent trend has been shifted towards Cr-based catalysts for hydrogenation reactions.[20-22]

Crystalline porous materials are extremely important for developing catalytic systems with high scientific and industrial impact.[23] Metal-organic frameworks (MOFs) show unique features that are yet to be fully exploited. MOFs are generally formed by metal and an organic di or tri topic linker, the coordination is extended in all three-directions, creating a uniform porous structure. MOFs have the advantage of tunability in the organic linker to impart specific functions such as chirality and electronic property.[24-26] MIL-88B is one such MOF which has the property of breathing in presence of different solvents *i.e.*, it can increase its pore volume up to 270 times the normal in solvents such as pyridine.[27] Thus, MIL-88B has the ability to accommodate a bigger molecule too. The mechanism of swelling was investigated

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and explained by Ferey *et al.*,[28] in which they inferred that "polar solvents interact with the metal trimers through hydrogen bonding" which gave us the clue that MIL-88B can transport hydrogen from one molecule to another.[29] MOFs were widely experimented for catalytic oxidation reactions.[30] There are only limited reports on usage of MOFs for CTH reactions. CTH of ethyl levulinate to γ-valerolactone (GVL) using zirconium-based MOFs was reported by Valekar *et al.* whereas Rojas-Buzo *et al.* described the use Hf-based MOFs for the CTH of biomass derived carbonyls.[31, 32] Reduction of the carbonyl attached to a heterocycle remains challenging, because heterocyclic molecule may either give poor selectivity or poison the catalyst. We have extended the simple CTH to the conversion of biomass derivatives such as levulinic acid (LA) and furfural to value-based products GVL and furfuryl alcohol respectively with an absolute selectivity. Further, to understand the importance of MIL-88B in catalysis, its catalytic efficiency was compared with that of MIL-53(Fe) which also has swelling property but possesses a different morphology.

2. Experimental section

2.1 Materials

1,4-Benzenedicarboxylic acid (H_2BDC), 2-amino-1,4-benzenedicarboxylic acid ($H_2BDC-NH_2$), $CrCl_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, hydrofluoric acid (HF), dimethylformamide (DMF), ethanol and 2-propanol (HPLC grade) were obtained commercially and used without any further purification. MOFs were synthesized according to the published procedures[33, 34] and activated under *vacuum* at 150 °C for 12 h before the characterization and catalysis (**Schemes S1-S3**).

2.2 Physical methods

Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Nicolet iS5 FT-IR spectrometer using iD3 ATR mode in the range of 4000-550 cm^{-1}. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a PAN analytical B.V.-Empyrean diffractometer using CuKα radiation (40 kV, 40 mA). Scans were performed over the 2θ range from 5 to 80° at the rate of 0.3°/min. The specific surface areas were determined from N_2 adsorption/desorption isotherms at liquid N_2 temperature by using a Belsorp Max system with the Brunauer-Emmett-Teller (BET) method.

2.3 Catalysis

All the MOFs were explored as catalysts for the TH of ketones and aldehydes, and conversion of biomass derivative LA to GVL. MIL-88B/NH_2-MIL-88B (3 mg), 2-propanol (3 mL), substrate (1 mmol) and NaOH (1 mmol) were placed in a 10 mL round bottom flask fitted with a reflux condenser, and heated at the desired temperature for a specific time. Having acetophenone as a model substrate and MIL-88B(Fe) as a test catalyst, the CTH reaction was investigated under various temperatures, time, amounts of the base, catalyst loadings and hydrogen donors to arrive at an optimized reaction condition. The catalyst was separated by centrifugation for 20 min at 1800 rpm. The supernatant was decanted, extracted with ethyl acetate and concentrated to 3 mL.[35] 300 µL of the concentrate was diluted with 1.5 mL of 2-propanol and subjected to GC/GC-MS analysis. GC and GC-MS analyses were done with Shimadzu GC-2010 and Shimadzu GC-MS QP 2010 Ultra instruments respectively, equipped with ZB-5M plus Phenomenex column of 30 m length and 0.25 mm inner diameter, and the relative conversion and selectivity were calculated from the area under the peak. Mass was matched with NIIST and Wiley libraries. All the GC-MS results have similar retention index irrespective of time. Mass was analyzed by scan mode (m/z from 45 to 750).

2.4 Mercury drop test

Catalyst MIL-88B(Fe) (3 mg, 0.0039 mmol), 2-propanol (3 mL, 39.43 mmol), acetophenone (117 µL, 1 mmol), NaOH (40 mg, 1 mmol) and two drops of Hg were placed in a 10 mL round bottom flask fitted with a reflux condenser at 90 °C for 12 h. The product was extracted and subjected to GC-MS analysis.

2.5 Hot filtration test and atomic absorption spectrometry analysis

Hot filtration test was performed with MIL-88B(Cr). In a typical reaction, MIL-88B(Cr) (3 mg, 0.0042 mmol), 2-propanol (3 mL, 39.43 mmol), acetophenone (117 µL, 1 mmol) and NaOH (40 mg, 1 mmol) were taken in a round bottom flask, and the reaction was proceeded for 5 h at 90 °C. Then the reaction mixture was centrifuged, and the catalyst was separated off by a simple filtration process.[36] Filtrate was divided into two parts. One part was refluxed under the identical conditions as the former for another 15 h, and the sample was extracted with ethyl acetate and analyzed by GC. The other part was used for GC and atomic absorption spectrometry (AAS) analyses. GC analysis gave conversion at 5 h. AAS analysis gave the amount of leached metal ion. The standard solutions (1, 2, 5, 10 and 15 ppm) were prepared by dissolving $CrCl_3 \cdot 6H_2O$ in 2-propanol.

2.6 Reuse of the catalysts

All the four catalysts were reused for 10 cycles. The recycling of the catalysts was performed by following a specific process. Firstly, after the reaction, the catalyst was

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separated by centrifugation. The supernatant was processed and subjected to GC-MS analysis. The catalyst was washed twice with water and acetone, dried and reused.

3. Results and discussion

3.1 Synthesis and characterization of the catalysts based on MIL-88

We have synthesized four MIL-88B materials, namely MIL-88B(Cr), NH_2-MIL-88B(Cr), MIL-88B(Fe) and NH_2-MIL-88B(Fe). All the four catalysts were isostructural but differed in the transition metal (Cr^{3+} or Fe^{3+}) and anions present in the cavity, F is present in MIL-88B(Cr) and NH_2-MIL-88B(Cr) whereas NO_3 is present in MIL-88B(Fe) and NH_2-MIL-88B(Fe).[37] F and NO_3 in the pores acted as counter ions for the charge balance and also gave structural rigidity to the material (**Table S1**). Powder XRD patterns of the prepared catalysts matched well with the simulated patterns. All the catalysts showed signature peaks at 2θ values 9.53±0.5° and 10.50±0.5°, which corresponded to 100 and 101 planes respectively (**Figs. 1a and S1**).[38] Introduction of electron-donating group (NH_2) in 1,4-benzenedicarboxylic acid (BDC) significantly altered the physio-chemical properties by providing additional basicity to the framework, resulting enhanced CTH activity (According to Noyori's outer sphere mechanism, presence of NH_2 in the catalyst favours CTH).[33] N_2 adsorption measurement was carried, and specific surface area was found to be 40 m^2/g (**Figs. 1b and S2**). SEM and TEM analyses of the catalysts showed uniform bipyramidal hexagonal prism-like morphology (**Figs. 2, S3-S8**).[39, 40] A sharp peak around 1590 cm^{-1} was observed in their FT-IR spectra, which corresponded to C=O stretching.[41] The disappearance of OH stretching frequency confirmed the bonding of COOH with Cr^{3+} or Fe^{3+}. Moreover, the weak and sharp peak at 757 cm^{-1} indicated the presence of metal-oxygen (Cr^{3+}–O/Fe^{3+}–O) bonds. In the spectra of catalysts NH_2-MIL-88B(Cr) and NH_2-MIL-88B(Fe), NH_2 stretching and N–H bending frequencies were observed at 3470-3327 and 1253 cm^{-1} respectively **(Fig. S9)**.[42, 43] With all these spectral and analytical studies, the structure and morphology of all the four catalysts were confirmed. We also synthesized MIL-53(Fe),[44, 45] and characterized by powder XRD and SEM (**Figs. S10 and S11**). All the catalysts were activated at 150 °C under *vacuo* for 6 h.

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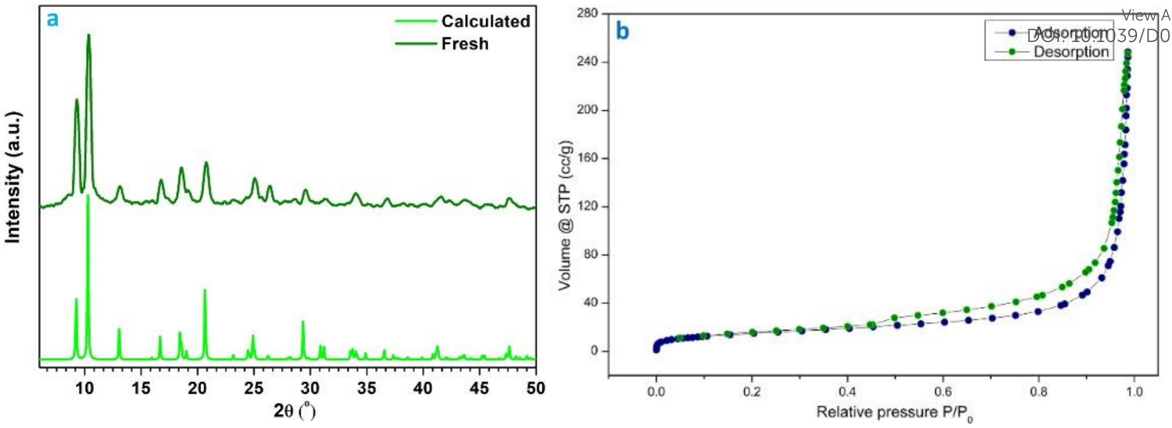

Figure 1 Powder XRD patterns [**a**] and N_2 adsorption and desorption isotherm [**b**] of catalyst NH_2-MIL-88B(Fe)

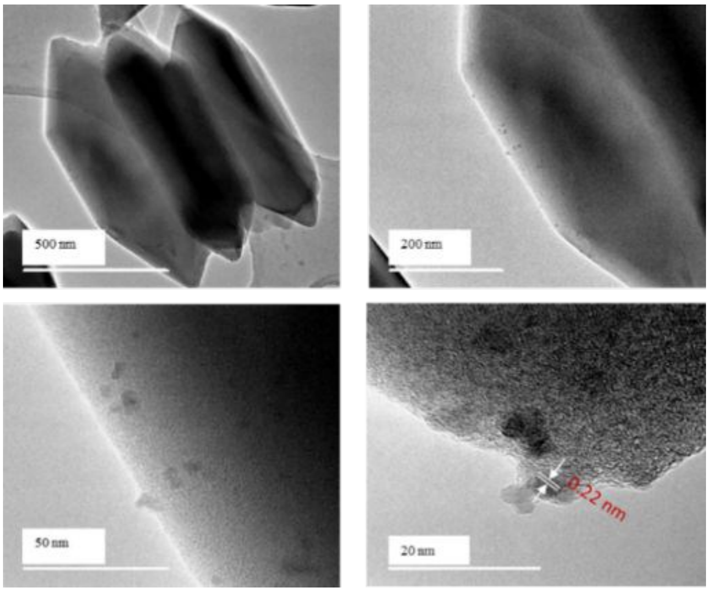

Figure 2 TEM images of catalyst NH_2-MIL-88B(Fe)

3.2 Catalytic properties of MIL-88B

3.2.1 CTH of acetophenone to 1-phenylethanol

Various parameters such as time, temperature, quantity of catalyst, base and solvent for CTH of acetophenone (substrate) to 1-phenylethanol (product) were optimized using 2-propanol (hydrogen donor) and NaOH (base).

3.2.2 Effect of reaction temperature and time

The temperature dependence of this reaction was studied in the range of 25-100 ^{o}C. The yield of 1-phenylethanol at room temperature (25 ^{o}C) was meagre (8 %), reflecting the need for thermal energy for the substrates to cross the activation barrier to form 1-phenylethanol (product). When the temperature was increased to 60 ^{o}C, the yield also increased proportionally to 66 %. Further increase in temperature to 100 ^{o}C gave a better yield of 96 % (**Fig. S12**). However, further rise in temperature (above 100 ^{o}C) decreased the selectivity of 1-phenylethanol due to the formation of the corresponding acetate.

We have also studied the influence of reaction time on the CTH of acetophenone to 1-phenylethanol at 100 ^{o}C. Aliquots were taken at a specific time interval and subjected to GC analysis. At a shorter reaction time of 1 h, the yield was as low as 5 %, whereas the increase in reaction time increased the yield of 1-phenylethanol, and the maximum yield of 96 % was obtained after 10 h of the reaction (**Fig. S13**).

3.2.3 Effect of bases

Further, the effect of various bases on CTH of acetophenone was evaluated. Weak bases such as K_2CO_3 and Et_3N gave very less conversion, whereas strong bases such as NaOH, KOH and KO^{t}Bu accelerated the process with the conversion up to 96, 92 and 83 % respectively (**Fig. S14**). From the above results, it was evident that the strong bases because of higher basicity favoured deprotonation of alcohol (hydrogen donor), which in turn led to easy formation of alkoxide.

3.2.4 Effect of hydrogen sources

In the same way, various hydrogen donors were screened. $HCOOH/Et_3N/H_2O$ failed to donate hydrogen in the presence of all the catalysts (1 % conversion). When ethanol was used, better conversion was obtained (18 %). However, the well-known hydrogen donor – 2-propanol gave an excellent conversion (96 %). 2-propanol was used both as solvent and hydrogen donor to eliminate the interference of solvent in the system. It is also evident from the previously reported computational study that secondary alcohols interact more efficiently with the MIL-88B class of MOFs.[46]

3.2.5 Effect of functional group in the benzene ring of acetophenone

All the catalysts exhibited comparable activity towards the conversion of acetophenone up to 98 % (**Table 1, entries 1-4**). Effect of substitution was examined with electron-withdrawing and -donating groups (**Scheme 1**). Electron withdrawing group (phenyl or halogen) substituted acetophenones were converted into their respective alcohols quickly (8-9 h) when compared to acetophenone (10 h). Among them, benzophenone (phenyl substitution) was converted

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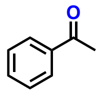
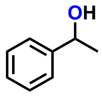
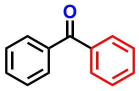
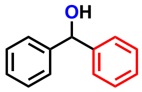
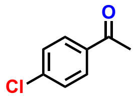
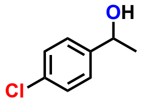
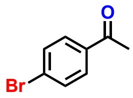
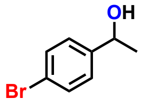
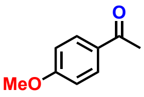
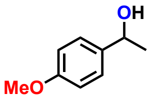
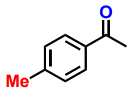
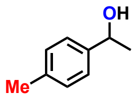
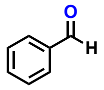
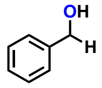
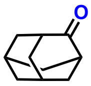
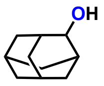
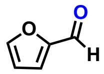
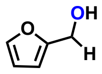
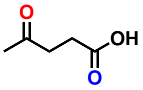
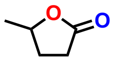
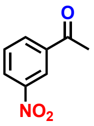
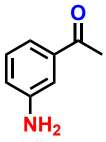
Table 1 TH of different substrates catalyzed by the MIL-88B catalysts

Entry	Substrate	Product	Catalyst	S/C ratio*	% Yield^{a}	TOF (h^{-1})
1			MIL-88B(Cr)	240	94	11.2
2			NH$_2$-MIL-88B(Cr)	255	99	12.6
3			MIL-88B(Fe)	258	98	12.6
4			NH$_2$-MIL-88B(Fe)	273	99	13.5
5			MIL-88B(Cr)	240	94$^{\#}$	14.1
6			NH$_2$-MIL-88B(Cr)	255	91$^{\#}$	14.5
7			MIL-88B(Fe)	258	92$^{\#}$	14.8
8			NH$_2$-MIL-88B(Fe)	273	88$^{\#}$	15.0
9			MIL-88B(Cr)	240	92‡	12.2
10			NH$_2$-MIL-88B(Cr)	255	87‡	12.4
11			MIL-88B(Fe)	258	97‡	13.9
12			NH$_2$-MIL-88B(Fe)	273	100‡	15.2
13			MIL-88B(Cr)	240	97‡	12.9
14			NH$_2$-MIL-88B(Cr)	255	98‡	13.9
15			MIL-88B(Fe)	258	94‡	13.5
16			NH$_2$-MIL-88B(Fe)	273	95‡	14.4
17			MIL-88B(Cr)	240	58	4.6
18			NH$_2$-MIL-88B(Cr)	255	73	6.2
19			MIL-88B(Fe)	258	69	5.9
20			NH$_2$-MIL-88B(Fe)	273	81	7.4
21			MIL-88B(Cr)	240	95§	7.6
22			NH$_2$-MIL-88B(Cr)	255	93§	7.9
23			MIL-88B(Fe)	258	62§	5.6
24			NH$_2$-MIL-88B(Fe)	273	62§	5.6
25			MIL-88B(Cr)	240	92‡	12.3
26			NH$_2$-MIL-88B(Cr)	255	93‡	13.2
27			MIL-88B(Fe)	258	96‡	13.7
28			NH$_2$-MIL-88B(Fe)	273	92‡	13.9
29			MIL-88B(Cr)	240	98	11.7
30			NH$_2$-MIL-88B(Cr)	255	97	12.4
31			MIL-88B(Fe)	258	97	12.5
32			NH$_2$-MIL-88B(Fe)	273	96	13.1
33			MIL-88B(Cr)	240	100 (99)^{b}	11.9
34			NH$_2$-MIL-88B(Cr)	255	100 (99)^{b}	12.7
35			MIL-88B(Fe)	258	100 (99)^{b}	12.9
36			NH$_2$-MIL-88B(Fe)	273	100 (99)^{b}	13.6
37			MIL-88B(Cr)	240	100 (99)^{b}	11.9
38			NH$_2$-MIL-88B(Cr)	255	100 (99)^{b}	12.7
39			MIL-88B(Fe)	258	100 (99)^{b}	12.9
40			NH$_2$-MIL-88B(Fe)	273	100 (99)^{b}	13.6
41			MIL-88B(Cr)	240	100	11.9
42			NH$_2$-MIL-88B(Cr)	255	90	11.8
43			MIL-88B(Fe)	258	81	12.9
44			NH$_2$-MIL-88B(Fe)	273	86	13.6

Reaction conditions: Substrate (1.0 mmol), catalyst (3 mg, ~0.004 mol %), NaOH (40 mg, 1.0 mmol), 2-propanol (3 mL), 100 ^{o}C and 10 h, $^{\#}$ 8 h, ‡ 9 h, § 15 h, ^{a} GC-MS yield, ^{b} Isolated yield, * Calculation is given in ESI - Eq. S3.

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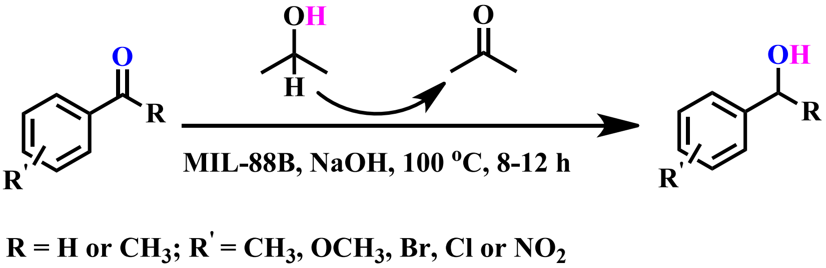
into diphenylmethanol in 8 h (**Table 1, entries 5-8**), whereas 4-chloro or 4-bromo acetophenone (halogen substitution) was converted into 4-chloro or 4-bromo-1-phenylethanol within 9 h (**Table 1, entries 9-16**). Only when the reaction time was extended to 15 h, substrates with electron-donating substituent (methyl or methoxy) gave good conversions (90 or 80 % respectively) (**Table 1, entries 17-24**). The scope was further extended to benzaldehyde and substituted benzaldehyde molecules (**Table 1, entries 25-28**). In general, CTH of aldehydes (benzaldehyde) was faster when compared to ketones (acetophenone). It was evident from these observations that electron-withdrawing substituents enhance the reaction rate by making the target carbonyl group electron deficient. Further, to check the versatility, 2-adamantanone (an alicyclic bicyclic compound) was used as a substrate. 2-adamantanone was converted into 2-adamantanol (**Table 1, entries 29-32**). This showed the compatibility of the catalysts with bicyclic carbonyl compounds. GC-MS chromatogram are given in **Figs. S15-S25**.



Scheme 1 CTH of carbonyl compounds

3.2.6 CTH of furfural and levulinic acid

Further, CTH was extended for the conversion of value-added biomass derivatives such as furfural and LA. Complete conversion (100 %) of furfural to furfuryl alcohol (**Scheme 2**) was achieved with an excellent selectivity (99 %) (**Table 1, entries 33-36**). The hydrodeoxygenation of LA to GVL is of great importance in the valorisation of biomass. Also, GVL is a platform chemical for fuel additives and drugs. To our delight, with MIL-88B based catalysts, LA was converted into GVL (**Scheme 3**) with an excellent selectivity (99 %) (**Table 1, entries 37-40**), and all the catalysts exhibited good substrate to catalyst ratio (S/C). The best S/C values were 240, 255, 258 and 273 for MIL-88B(Cr), NH_2-MIL-88B(Cr), MIL-88B(Fe) and NH_2-MIL-88B(Fe) respectively.

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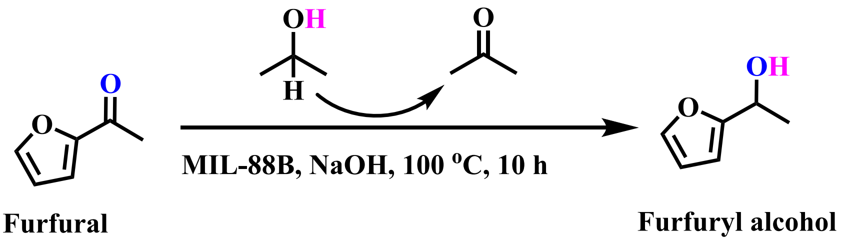
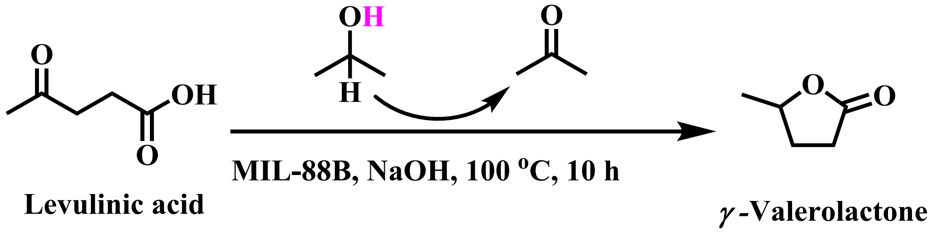


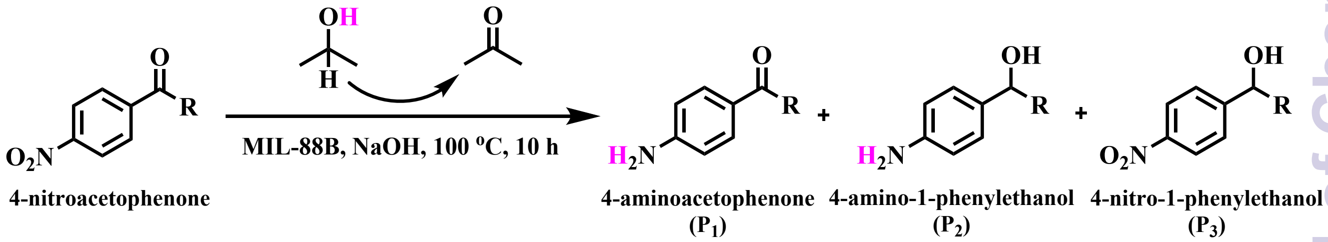
Scheme 2 CTH of furfural to furfuryl alcohol



Scheme 3 CTH of LA to GVL

3.2.7 Chemoselective reduction of nitro over carbonyl *via* CTH

3-Nitroacetophenone was chosen to study the chemoselectivity. It was observed that nitro functional group was preferentially reduced over carbonyl functional group (**Table 1, entries 41-44**) to form 3-aminoacetophenone selectively. Except NH_2-MIL-88B(Cr), all the other catalysts gave excellent selectivity (97-100 %) towards nitro group reduction (**Scheme 4**).



Catalyst	Selectivity (%)		
	P_1	P_2	P_3
MIL-88B(Cr)	100	-	-
NH_2-MIL-88B(Cr)	97	3	-
MIL-88B(Fe)	100	-	-
NH_2-MIL-88B(Fe)	100	-	-

Scheme 4 Chemoselective CTH of 4-nitroacetophenone to 4-aminoacetophenone

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3.2.8 Gram scale synthesis of GVL and furfuryl alcohol

Further, to explore the catalyst activity at higher volume, we have performed reactions with 20 mmol of LA (2.3222 g) or furfural (1.9216 g). Quantity of MIL-88B(Fe) and other reagents were increased accordingly. After the reaction, the catalyst was removed by centrifugation, and crude was passed through a short silica column and extracted with excess of ethyl acetate. After the removal of ethyl acetate by self-evaporation, we have obtained 1.98 g of GVL or 1.96 g of furfuryl alcohol. Activity and selectivity of the catalyst remained the same, even on the gram scale. GVL and furfuryl alcohol were isolated and confirmed by NMR analyses (**Figs. S26-S29**).

3.2.9 Mechanism of CTH in the presence of MIL-88B

For illustration, we have considered catalyst MIL-88B(Fe) (**Fig. 3**). Initially, 2-propanol is deprotonated by the base to form isopropoxide which interacts *via* C–O with the Fe centre of the catalyst (Step 1). Addition of substrate leads to the interaction of carbonyl carbon with the Fe–H formed through the elimination of acetone (Step 2). In step 3, hydride is transferred to carbonyl carbon.[47, 48] This intermediate might be stabilized by the π-π interaction between aromatic ring in the substrate and terephthalic acid in the framework.[35, 49, 50] Simultaneously proton already removed from 2-propanol attacks the oxygen, and alcohol is given out.

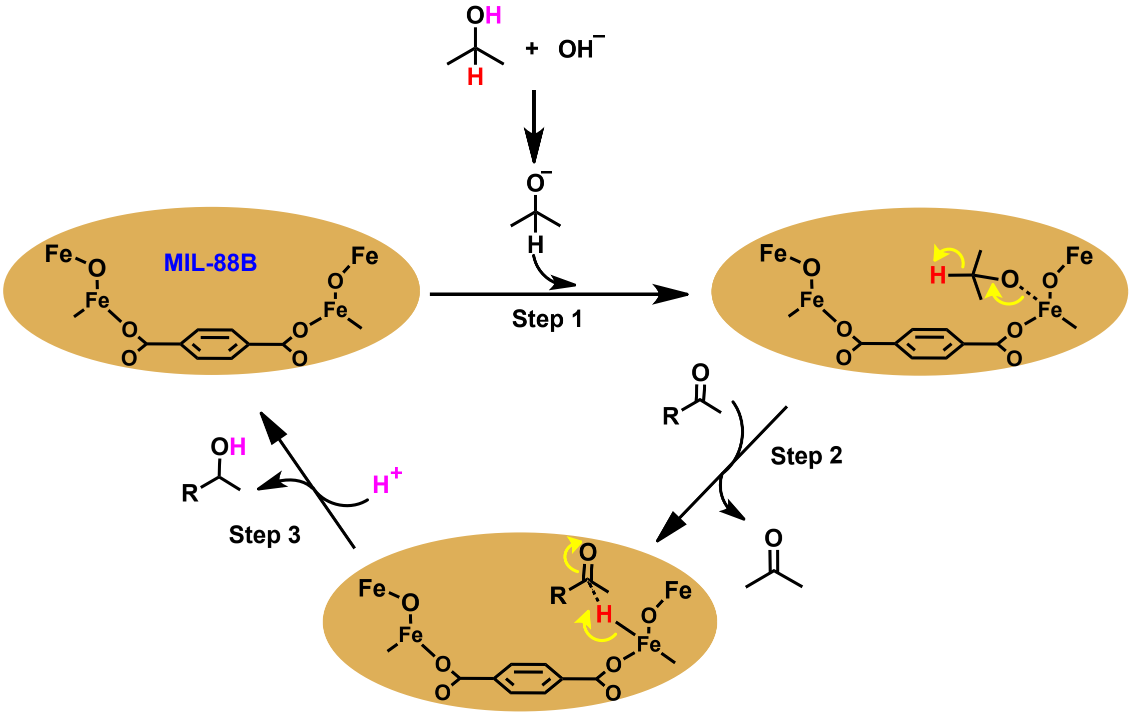

Figure 3 Plausible reaction mechanism for the CTH of carbonyl compound

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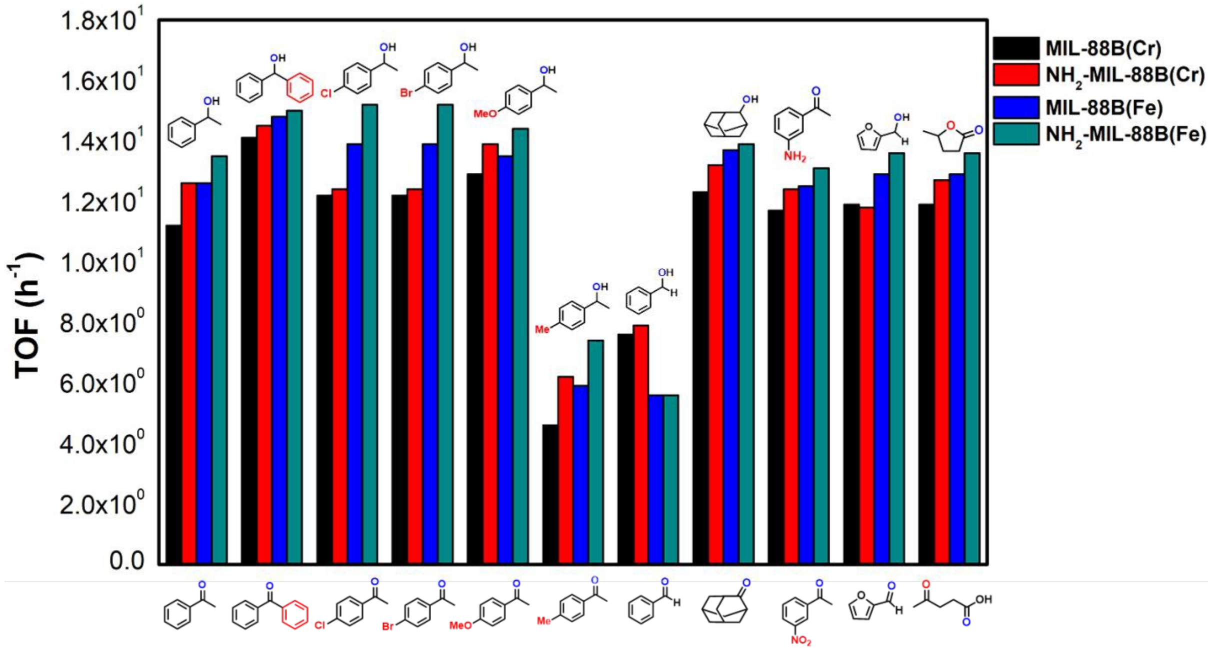
3.2.10 Effect of metal centre and NH_2-substitution

In accordance with the TOF values obtained with various substrates (**Fig. 4**), Fe^{3+} based MOFs showed higher catalytic efficiency than their Cr^{3+} counterparts, presumably due to the higher Bronsted acidity of Fe^{3+}. Also, the NH_2 incorporated MOFs displayed better activity, because of the additional basicity provided by NH_2 group, which might stabilize the generated isopropoxide.



TON and TOF calculations are given in ESI (Equations S1 and S2)

Figure 4 Influence of the metal centre and NH_2-substitution on the TOF values

3.2.11 Efficiency of the MIL-88B catalysts

Conversion of LA to GVL was tested under the optimized conditions with MIL-53(Fe), and the results are given in **Table 2**. From the results, it was evident that MIL-53(Fe) exhibited very less catalytic activity (TOF, 1.8 h^{-1}) as compared to MIL-88B(Fe) (TOF, 12.9 h^{-1}). The superior activity of MIL-88B(Fe) was attributed to its higher magnitude of swelling [51] and surface area (BET surface area: MIL-88B(Fe), 40 m^2/g; MIL-53(Fe), 12 m^2/g).[52]

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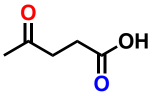
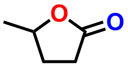
Table 2 Conversion of LA to GVL catalyzed by the MOFs

Entry	Substrate	Product	Catalyst	% Yield[a]	TOF (h^{-1})
1			MIL-53(Fe)	52	1.8
2			MIL-88B(Fe)	100	12.9

Reaction conditions: LA (1.0 mmol), catalyst (3 mg), NaOH (40 mg, 1.0 mmol), 2-propanol (3 mL), 100 °C and 10 h, [a] GC-MS yield.

Catalytic performance of the MOFs was compared with other catalysts in the literature. CTH is generally performed in two ways: one with molecular H_2 and other with hydrogen donors (2-propanol, HCOOH, etc.). Thus, MIL-88B was compared with both kinds of catalysis. From **Tables S2 and S3**, it was seen that MIL-88B showed better selectivity. Noble metal catalysts gave good selectivity at low temperature or at shorter reaction time. Still, most of the non-noble metal catalysts (Ni, Fe or Cu) require either high temperature or extended reaction time. From the viewpoint of the reaction conditions, cost of the raw materials and the convenience of preparation, MIL-88B based catalysts have advantages compared to the noble and other transition metal catalysts.

3.2.12 Stability of the MIL-88B catalysts

All the four catalysts were recycled 10 times with various substrates. The catalysts were reused after solvent washing and activation. In the first five cycles, acetophenone was tested. The reused catalysts showed similar activity as that of the fresh catalyst, and the conversion of 95 % was obtained even after the fifth cycle. In the sixth and seventh cycles, CTH of benzaldehyde and benzophenone was tested respectively. There was no decrease in the catalytic activity, *i.e.*, conversion and selectivity remained unaltered. The eighth cycle was performed with 4-methoxy acetophenone which gave 70 % conversion. Ninth and tenth recycling of the catalysts were tested for the conversion of furfural and 2-bromobenzaldehyde respectively; conversion was 98 % for both the substrates (**Fig. 5**). From the recycling experiments, we confirmed that the catalysts were not poisoned (*i.e.*, the active sites remain unaffected even after extensive use) by the reactants and base, which was also evident from SEM (**Figs. S30-S33**), XRD (**Figs. 6 and S34**) and FT-IR (**Fig. S35**) analyses of the reused catalysts. Moreover, the use of different substrates in different cycles showed the versatile character of the MOFs. Most importantly, the activity did not drop much. This showed a very long catalytic life of the MIL-88B catalysts. Average particle size of the reused

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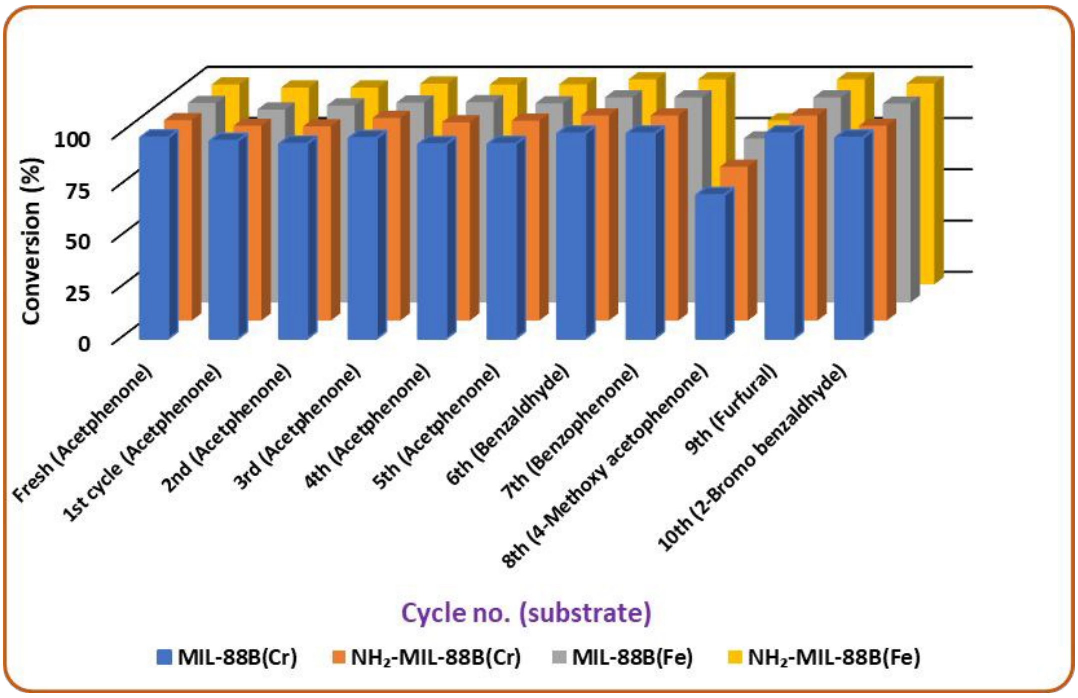
catalyst was smaller than that of the fresh catalyst (**Figs. S7 and S36**, **Table S4**). Large particles of MIL-88B was divided into smaller particles during the catalysis, which exposed fresh surfaces. The newly exposed surfaces might be responsible for the constant activity of the reused catalysts.



Reaction conditions: Substrate, MIL-88B catalyst, NaOH, 2-propanol, 100 °C (Mole ratio of substrate:catalyst:base:solvent was maintained as 1:0.004:1:150).

Figure 5 Reusability of the MIL-88B catalysts

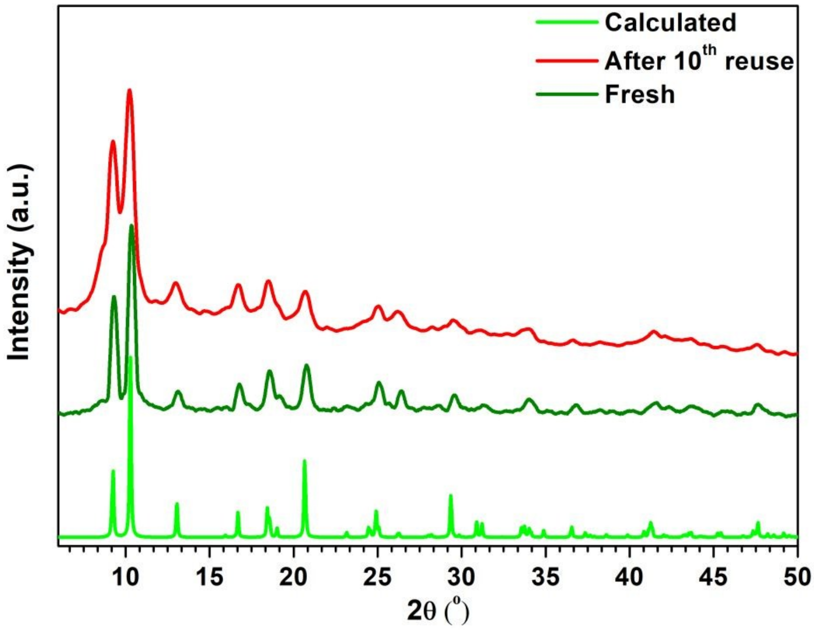


Figure 6 Powder XRD patterns of 10 times reused and fresh NH_2-MIL-88B(Fe)

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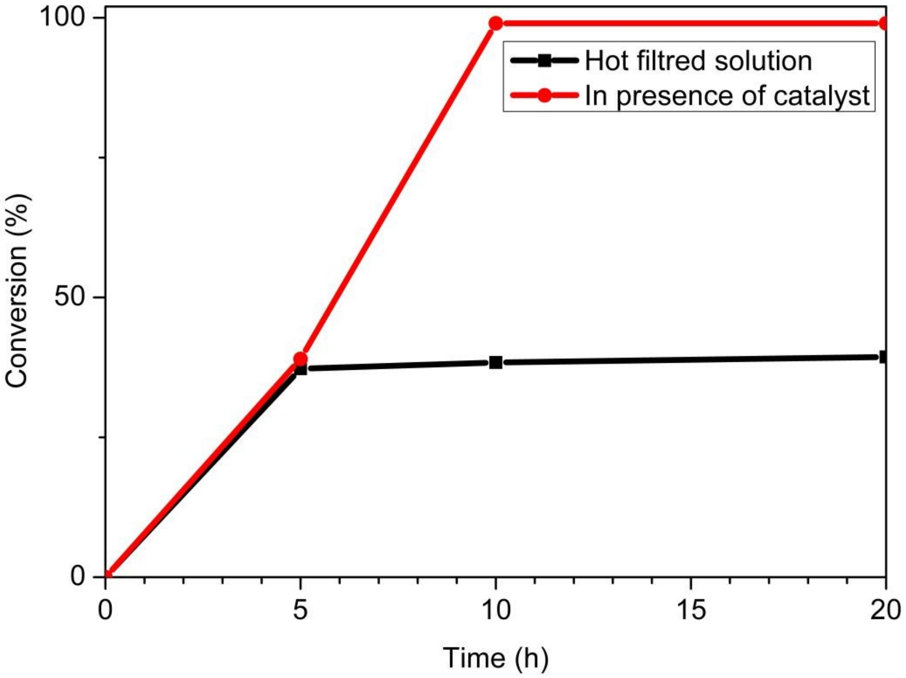
3.2.13 Heterogeneity tests

Hot filtration test results showed that the conversion of acetophenone remained almost the same after separating MIL-88B(Cr) from the reaction mixture. Thus, it was evident that the MOF functioned as a heterogeneous material (**Fig. 7**). Part of the reaction mixture after hot filtration test was analyzed by AAS, and Cr leaching was found to be 3.52 ppm. This trace leaching of the metal was one of the causes for the meagre increase in the conversion in the absence of the catalyst. Further, the conversion remained unaffected (96%) in the presence of mercury drops [Hg(0)], which proved that there were no free metal particles formation in the reaction mixture.



Reaction conditions: Acetophenone (117 μL,1.0 mmol), MIL-88B(Cr) (3 mg, 0.004 mol %), NaOH (40 mg, 1.0 mmol), 2-propanol (3 mL) and 100 °C.

Figure 7 Conversion of acetophenone in the presence and absence of MIL-88B(Cr)

3.2.14 Catalyst stability in biomass conversion

Reusability was also performed in the conversion of LA to GVL, to evaluate the reusability in the biomass conversion. As expected, catalyst MIL-88B(Fe) did not lose its activity even with LA. Fresh, 1st, 2nd, 3rd, 4th and 5th cycles gave 100, 100, 98, 99, 100 and 99 % conversions respectively (**Fig. 8**). Though the conversions varied by ± 1 %, the selectivity remained constant in all the cycles. From these results, it was evident that MIL-88B based catalysts are robust for the conversion of biomass derivatives such as LA.

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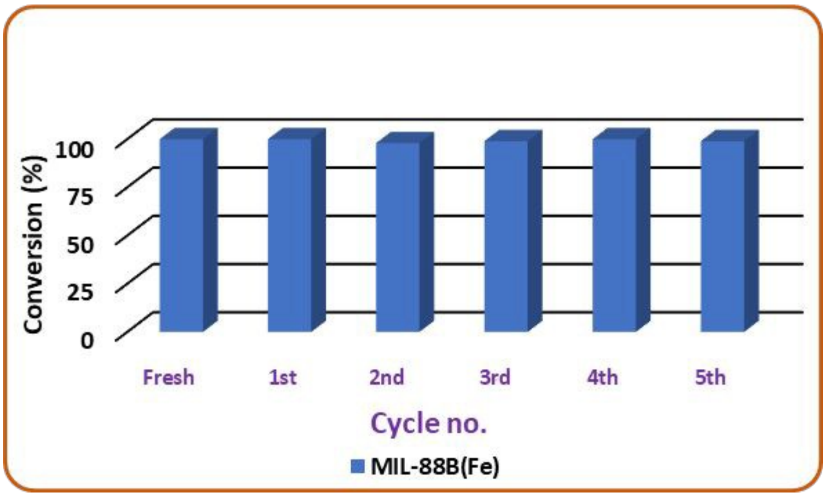

Reaction conditions: LA, MIL-88B(Fe), NaOH, 2-propanol, 100 ºC and 10 h (Mole ratio of substrate:catalyst:base:solvent was maintained as 1:0.004:1:150).

Figure 8 Reusability of catalyst MIL-88B(Fe) for biomass conversion

3.2.15 Kinetics for the conversion of LA to GVL

To understand CTH of LA over MIL-88B, kinetic studies were performed at three different reaction temperatures (60, 80 and 100 °C). In the present system, 2-propanol was used in excess; so that, the reaction kinetics was not affected by the concentration of 2-propanol. CTH of LA was assumed to proceed as a pseudo first order reaction, as a function of LA concentration. **Fig. 9** depicts the plot of $\ln(C_t/C_0)$ *versus* time for the CTH of LA over MIL-88B(Fe), in which C_0 is the initial concentration of LA, and C_t represents the concentration of LA at a particular time. As shown in **Fig. 9**, the reaction followed pseudo first order kinetics at all the studied temperatures, and the rate constant values were determined to be 0.1126, 0.1697 and 0.3030 min^{-1} at 60, 80 and 100 °C respectively. The variation of the rate constant (k) with temperature is shown as an inset in **Fig. 9**. Based on the Arrhenius plot, the activation energy (E_a) was calculated to be 25.44 kJmol^{-1}. The reported activation energy for LA to GVL conversion was 37.4 kJmol^{-1},[53] which was about 1.4 times higher than the present report. Hence, we conclude that CTH of LA to GVL over MIL-88B based catalyst showed higher activity.

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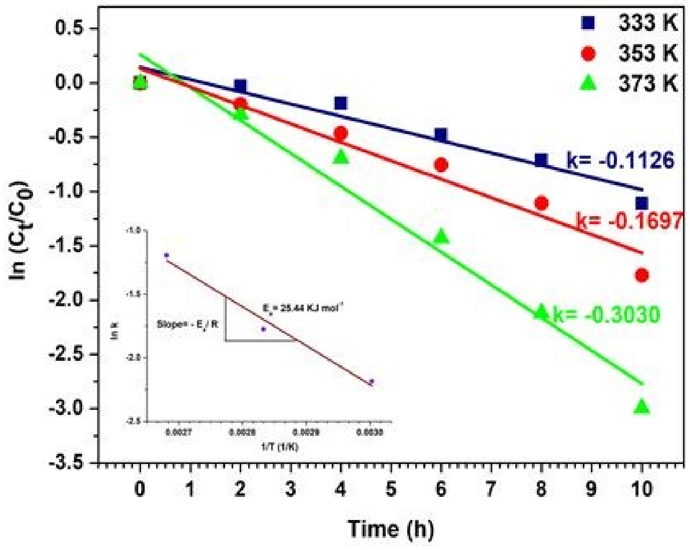

Figure 9 First order kinetic fit for CTH of LA to GVL at different temperatures

Conclusions

Iron and chromium MIL-88B and NH_2-MIL-88B (MOFs) were prepared and characterized. All the four MOFs exhibited MIL-88B morphology (bipyramidal hexagonal prism). They have been successfully applied as catalysts towards catalytic transfer hydrogenation (CTH) of various carbonyl compounds, including biomass derivatives (furfural and levulinic acid). Excellent conversion with low catalyst loading was observed. The MIL-88B catalysts offer many advantages which include high porosity, high activity, recyclability (compatible with various substrates and biomass) and mild conditions in an environmentally benign solvent system with a low activation energy of 25.44 KJmol^{-1} and high S/C of 280. Excellent chemoselectivite reduction of NO_2 was also achieved. The MIL-88B catalysts performed an efficient CTH under mild conditions compared to many of the reported catalytic systems. After a comparative study with MIL-53(Fe), we believe that the interaction of secondary alcohols with metal trimers of MIL-88B catalysts is very similar to the metal hydride bond. Thus, the metal acquired the capacity to transfer hydrogen from secondary alcohol to carbonyl compound. Therefore, along with the swelling property, morphology, crystal structure and surface area are also responsible for the enhanced catalytic activity of MIL-88B. Exploiting such solvent-induced swelling property of the MOFs may open new opportunities in the development of highly active heterogeneous transfer hydrogenation catalysts.

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Graphical abstract

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Fe and Cr bassed MOFs (MIL-88B) act as an efficient and reusable catalyst for transfer hydrogenation of carbonyl compounds including bio-derived substrates.