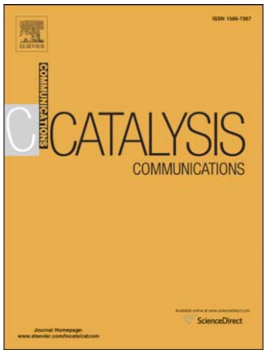

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G. Sampath, S. Kannan

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Fructose dehydration to 5-hydroxymethylfurfural: Remarkable solvent influence on recyclability of Amberlyst-15 catalyst and regeneration studies

G. Sampath and S. Kannan[*]

Discipline of Inorganic Materials & Catalysis, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), GB Marg, Bhavnagar - 364 002, India

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[*]**Manuscript Correspondence**:

Dr. S. Kannan

Discipline of Inorganic Materials & Catalysis

Central Salt and Marine Chemicals Research Institute

Council of Scientific and Industrial Research (CSIR)

Bhavnagar - 364 002

India

Tel: +91-278-2567760 Ext. 7030

FAX: +91-278-2567562

E-mail: skannan@csmcri.org ; kanhem1@yahoo.com

Abstract

Dehydration of fructose to 5-hydroxymethylfurfural (HMF) using Amberlyst-15 catalyst showed significant loss in activity upon reuse in N,N-dimethylformamide (DMF) while no activity loss in dimethylsulphoxide (DMSO) even up to seven cycles. The activity variation was monitored through HMF yield, pH and acidity of the catalyst. The loss in activity is attributed to neutralization of amine groups of DMF with acid sites as supported by FT-IR and elemental analysis measurements. Simple dilute acid treatment on the dead catalyst restored activity in DMF. Incidentally, the initial activity increased upon simple mechanical scrubbing of catalyst particles.

Keywords

Fructose dehydration; Amberlyst-15; 5-Hydroxymethylfurfural; Recyclability; Re-activation; Solvent effect

1. Introduction

With diminishing petroleum resources and increasing demand for fuels and chemicals, it is necessary to look for alternative renewable resources such as biomass. 5-hydroxymethylfurfural (HMF) is one of the promising intermediate chemicals derived from biomass that finds diverse applications such as fuel additive (2,5-dimethylfuran), polymer precursors e.g., alternative for terephthalic acid (2,5-furandicarboxylic acid (FDCA) and 2,5-diformylfuran (DFF)) and as platform molecule for value-added chemicals [1]. It is produced from hexose sugars through acid catalyzed dehydration [2]. Besides homogenous catalysts, one of the well-studied catalysts for this reaction is Amberlyst-15 [2-7], an inexpensive, commercially available solid acid catalyst. Amberlyst-15, is the commercial/trade name of a macroporous cation exchange resin, which is a co-polymer of styrene and divinylbenzene with sulfonic acid groups attached developed 50 years ago [8]. It can be functionalized by different methods using fuming or concentrated sulphuric acid as a reagent [9]. Owing to its structural stability, high acidic strength and surface area, it was found to be an efficient catalyst compared to many other commercial resins for many organic reactions [10-13]. In the synthesis of HMF from sugars, many attempts were made to improve the process efficiency with this catalyst. One of such attempts is continuous removal of water from the reaction mixture during the reaction [5]. An attempt was also made to increase the yield of HMF by decreasing the resin particle size by crushing and sieving to obtain powdered form with particle diameter 0.15-0.053 mm and explained based on improved mass transfer where adsorption-desorption is faster with reduced particle size [5]. Among the sugars, dehydration of fructose to HMF is facile as fructofuranoic structure is more reactive for dehydration [6, 14]. This reaction is reported using Amberlyst-15 catalyst in various solvents namely N,N-dimethylformamide (DMF) [6], dimethylsulphoxide (DMSO) [5], 1,4-dioxane [15,16] and ionic liquids [4, 17]. Among them, DMF and DMSO are suitable as these solvents are reported for value addition of the platform chemical HMF to useful products such as DFF and FDCA, that would inadvertency avoid intermittent solvent separation [17]. Although Amberlyst-15 is reported for catalytic dehydration of fructose to HMF in DMF and DMSO solvents, the efficiency of this catalyst in these solvents in terms of the recycle ability has not been studied.

In the present work, Amberlyst-15 catalyst was studied for dehydration of fructose to HMF in these two polar basic solvents to understand the following for the first time:

a. Does the solvent have an effect on the catalyst reusability?
b. Is there a method to reactivate the dead catalyst?
c. Does the particle size of the catalyst have a role on the catalytic activity?
d. Is there any way by which one can improve the yield with this catalyst?

2. Experimental

Chemicals namely Amberlyst-15(dry) from Lancaster, DMF from Ranbaxy, India, fructose (>99%), DMSO and mineral acids from s d fine-chemicals Ltd, India and HMF (>98%) from Aldrich were used as received.

2.1 Catalyst treatment

As-received Amberlyst-15 granules were scrubbed using a domestic mixer grinder for 10 min to expose the freshly prepared catalyst surface. For particle variation studies, granules were ground to obtain different sizes by passing through sieves (BSS) of mesh numbers 300, 200, 150, 100, 72, 52 and 30 (particle size ranging from 75 to 500 µm). For recycle studies, the catalyst was separated from the reaction mixture by centrifugation and used as such without further washing. Acid treatment of catalyst was done by adding 0.1 g of catalyst to 3 ml of H_2SO_4 of desired concentration taken in a beaker, stirred at room temperature for 5 h and washed with distilled water until no sulphate ions were found with $BaCl_2$ solution in the washed solution, and washed subsequently with methanol (two times; 3 ml each) and dried in an oven at 85 ^oC for 1 h.

2.2 Catalytic activity studies

All reactions were conducted in batch mode using a preheated oil-bath either with 1:1 or 4:1 substrate:catalyst weight ratio using 0.1 g of catalyst and 3 ml of solvent in a 10 ml round bottom flask. Fructose conversion was determined using Waters-HPLC system equipped with RI detector using Supelcogel-610H column, and the yield of HMF was determined by using Kromasil C18 column with multi-wavelength detector connected to JASCO-HPLC (PU-2089 Plus) system. For both fructose and HMF, standard solutions were made and calibration graphs were drawn for computing the conversion and yield. Analysis and calculation procedure are given in supplementary information.

2.3 Catalyst characterisation

Estimation of acid sites was done by adding excess amount of 0.1M NaOH solution to the catalyst and titrating against 0.1M HCl with phenolphthalein as an indicator. The acid site concentration for fresh catalyst is 4.2 meq/g. pH of the reaction mixture before and after the reaction was measured with a pH meter (Toshniwal instruments CL 54). Fourier transformed-infrared (FT-IR) spectra were recorded in a Perkin-Elmer FT1730 instrument using KBr pellets. Specific surface area and pore size analysis of the samples were measured by nitrogen adsorption at –196 ^oC using a sorptometer (ASAP-2010, Micromeritics). The samples were degassed at 80 ^oC for 4 h prior to measurements. Scanning electron microscopy (SEM) of the samples was analysed in a microscope (Leo Series VP1430) of Oxford Instruments. Surface area of all samples (both as received and crushed) was found to be similar (~42 m^2/g; see supporting information). CHNS elemental analyses were performed by using Elementor's Vario Microcube instrument.

3. Results and discussion

In order to investigate the influence of solvent on the activity and recycle efficiency of Amberlyst-15 catalyst, fructose dehydration was conducted in DMF and DMSO. Using a substrate to catalyst weight ratio of 1:1, 100% fructose conversion with 82% yield of HMF was obtained in both solvents at 120 ^{o}C for 30 minutes. However, in DMF the yield of HMF drastically decreased after second recycle as shown in Figure 1. Further, at higher substrate to catalyst weight ratio (4:1), HMF yield was observed only for first use and decreased drastically thereafter in DMF (*vide infra*). In general, the reduction in the catalytic activity of Amberlyst-15 was attributed by leaching of acid sites in polar solvents at higher temperature [18]. To check the influence of temperature, experiments were carried out under other optimised condition (100 ^{o}C for 2 h). Under this condition also, same trend was observed (Supporting Information, Table 1S) indicating that temperature is not responsible for deactivation. To study the effect of reaction components like, reactant, intermediates or products on the acid sites in the reaction mixture, pH of the reaction mixture was measured before and after the reaction. Figure 2 showed a gradual increase in pH with catalyst recycle suggesting a decrease in the acidity of reaction medium.

During the fructose dehydration reaction, water and soluble brown polymers are formed as side products. As catalyst is moisture sensitive, to delineate the effect of water and brown polymers on the deactivation, reactions were carried under similar conditions however, by washing the catalyst with methanol after each cycle and dried at 85 ^{o}C for 1 h before reuse. However, such treatment could not restore the activity of the catalyst. Similar set of reactions were carried out using DMSO, an efficient solvent compared to many other solvents reported for fructose dehydration [19]. Interestingly, the catalyst remained active even for up to seven cycles exhibiting similar HMF yields even at higher substrate amount (4:1 substrate to catalyst ratio). Further, no change in pH of the reaction medium was observed upon catalyst recycling (Table. 1). It is worth mentioning here that it is possible to extract HMF from DMSO/fructose reaction mixtures using simple adsorption using porous carbons [20].

The concentration of acid sites of the catalyst after successive runs in both solvents is given in Table 1. It clearly showed that the acidity of the catalyst decreased significantly upon recycle in DMF while no change in the acidity was observed in DMSO, suggesting the loss of activity in DMF is due to decrease in the concentration of acid sites. It is also intriguing to note that the basicity of solvents does not play a role as sustained activity is bestowed by DMSO which is more basic (pH = 11.4) than DMF (pH = 9.2). Further SEM images of used catalysts in both solvents showed similar morphology (Supporting Information, Figure 1S) indicate non-influence of morphology.

To understand the catalyst deactivation in DMF, FT-IR was recorded for fresh and used catalysts in both solvents, given in Figure 3. Used catalyst in DMF (Figure 3b) showed multiple broad bands around 2400-3300 cm^{-1} confirms the formation of ammonium ion [21]. This suggests neutralization of acidic sites of the catalyst with the basic amine groups of DMF. The presence of ammonium ions was further supported by the higher nitrogen content (4.5%) determined by CHNS analysis while no nitrogen was present in the fresh catalyst.

Control experiments in the absence of Amberlyst-15 catalyst were conducted to check the solvent effect. In DMSO solvent 53% of HMF yield was observed while DMF yielded only 3%. DMSO is reported to participate in this reaction wherein it interacts strongly with HMF through solvation and stabilize thereby restricting its contact with the intermediates and water molecules to avoid further hydrolysis of HMF to levulinic acid and polymers formation [19]. The results disclosed here further augment the potential of DMSO as an efficient solvent for fructose dehydration using Amberlyst-15 catalyst. In addition, it is less expensive and safer than many costlier solvents like ionic liquids reported in literature.

Although better solvent (here DMSO), can be chosen from various solvents for a given reaction, it is also necessary to overcome the drawback of other solvents, here DMF, for practical reasons. It was reported earlier, that DMF is preferred for direct conversion of glucose to HMF by combining Amberlyst-15 with hydrotalcite catalyst [22]. With this backdrop, efforts were then made to improve the efficiency of the catalyst in DMF.

After the catalyst is deactivated in DMF (after four recycle), catalyst was washed with methanol, dried and treated with dilute H_2SO_4 (1M). Interestingly, the catalyst showed similar activity as that of fresh catalyst giving similar yields of HMF up to next 3 cycles and a loss in the activity was observed upon further cycling (Figure 1). This re-sustenance of the activity of the catalyst could be repeated by this simple dilute acid treatment. In addition, 1MHCl or 1M HNO_3 (3 ml) have also reactivated the catalyst indicating that sulfonation is not the factor for reactivation. The reason for regain in the activity of the dead catalyst is probably due to the removal of ammonium ions in acid medium. This is corroborated by a decrease in the N content of the catalyst (0.8% from 4.5%) and absence of ammonium group as elucidated from FT-IR after acid treatment (Figure 3d).

Further, it was observed that as-received granular catalyst showed lesser HMF yield (73 %) for the first cycle, and the yield increased in the next cycle (80 %). This is similar to the results reported earlier for thehydration of dicyclopentadiene reaction and attributed to an increase in the hydrophobicity with recycle [23]. However, the increase in the HMF yield here is probably due to an increase in the accessibility of active sites (better mass transfer effects) owing to swelling of the particles in the solvent (Supporting Information, Table 2S). However, simple scrubbing of the catalyst surface increased the yield of HMF (83 % with 1:1 catalyst to substrate weight ratio), and is probably due to better diffusion of product through external pores thereby avoiding condensation-polymerisation of the product with intermediates. This is supported by SEM images of the particle surface (Figure 4) that showed generation of rough porous morphology of the scrubbed catalyst while smooth morphology for fresh catalyst. However, such increase was noted only for the first cycle and followed similar trend upon recycling as that of original catalyst (Supporting Information, Table 2S). Catalyst was macerated to different sized particles which showed same yield as that of scrubbed. However, irrespective of the particle size, the recycle efficiency of the catalyst in DMF was similar (Supporting Information, Table 3S). Further, the size of the particles was not stable regardless of the initial size of catalyst particle which decreased on recycle and became almost fine powder after third cycle.

4. Conclusions

The remarkable solvent influence on the recycle efficiency of Amberlyst-15 catalyst for dehydration of fructose to 5-hydroxymethyl furfural was observed wherein in DMSO, a stable activity was noted for even up to seven cycles, while in DMF, the activity deteriorated significantly upon recycling. The loss in the activity in DMF is due to neutralization of acid sites forming ammonium ions as inferred from FT-IR and CHNS measurements. To circumvent this deactivation, a method of regeneration of the dead catalyst is proposed by treating it with dilute acid. Simple scrubbing of particles (as-received commercial sample) is sufficient and grinding of particles, an energy intensive process is not necessary for obtaining higher yields of HMF.

Promising results in DMSO further encourages its use in conversion of HMF to value added furan derivatives such as FDCA or DFF thereby avoiding intermittent solvent separation.

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Table 1 Variation in activity and acidity of Amberlyst-15 catalyst upon recycling in DMF and DMSO solvents and pH of the reaction mixture[a]

Cycle	In DMF solvent			In DMSO solvent		
	HMF yield(%)	(pHafter reaction)	Acidity(meq/g)	HMF yield(%)	(pHafter reaction)	Acidity(meq/g)
1	64	4.2	2.2	83	3.6	3.6
2	11	6.5	1.2	84	3.8	3.8
3	02	7.0	0.8	83	3.8	3.8
4	0.4	7.1	0.8	80	3.9	3.8
5	nd	nd	nd	81	3.9	nd
6	nd	nd	nd	80	3.9	nd
7	nd	nd	nd	80	3.9	nd

[a] 0.4 g fructose; 0.1 g 30-mesh sieved Amberlyst-15; 3 ml solvent;120 ^{o}C; 1 h; Errors in % HMF yield is ± 1%, pH is ± 0.1 and for acidity is ± 0.1meq/g; (nd - Not determined)

Figure Captions:

Figure 1 Yield of HMF in DMF with catalyst recycle. 0.1 g fructose; 0.1 g 30-mesh sieved Amberlyst-15; 3 ml DMF, 120 ^{o}C; 30 min; (1M H_2SO_4 treatment was done after fifth and ninth cycle)

Figure 2 pH of the reaction mixture. 0.1 g fructose; 0.1 g 30-mesh sieved Amberlyst-15; 3 ml DMF; 120 ^{o}C; 30 min (1M H_2SO_4 treatment was done after fourth cycle)

Figure 3 FT-IR spectra of Amberlyst-15: a) fresh catalyst; b) catalyst after using for 4 cycles in DMF; c) catalyst after using for 4 cycles in DMSO; d) after acid treatment of (b)

Figure 4 Scanning electron microscopic images showing the surface of Amberlyst-15: a) as-received; b) scrubbed (inset shows single granule)

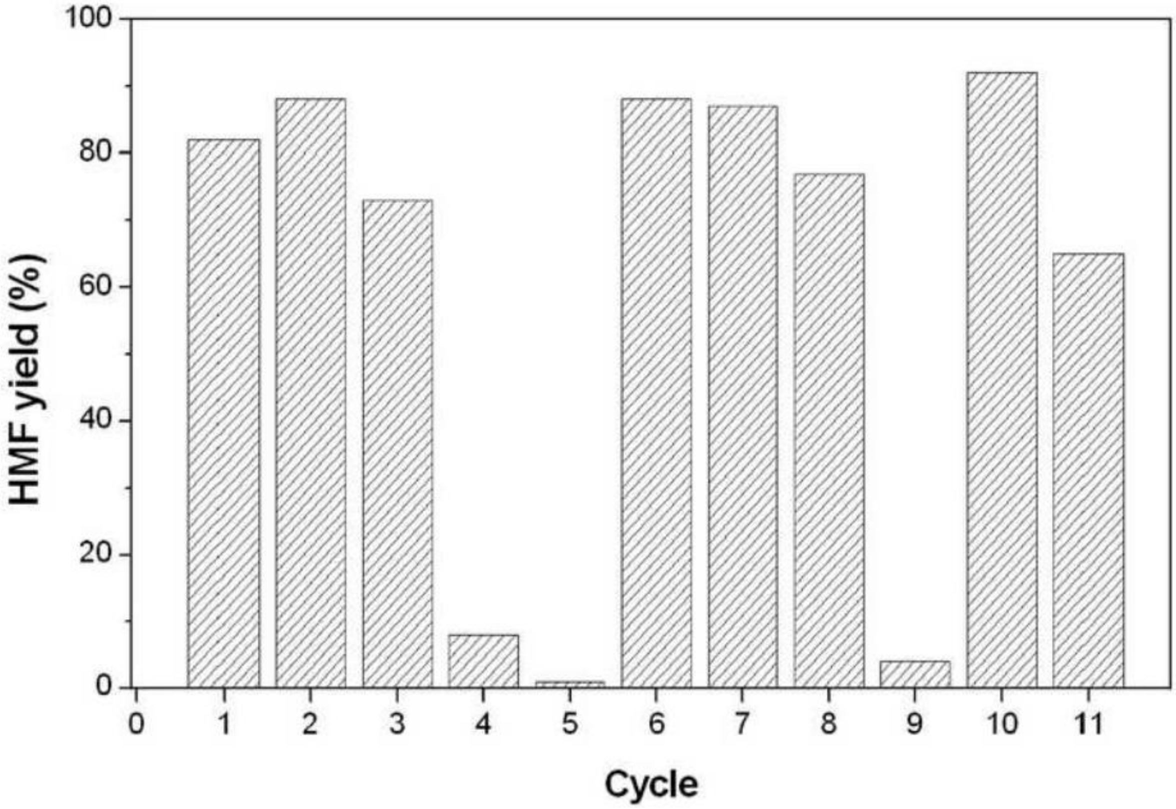


Figure 1

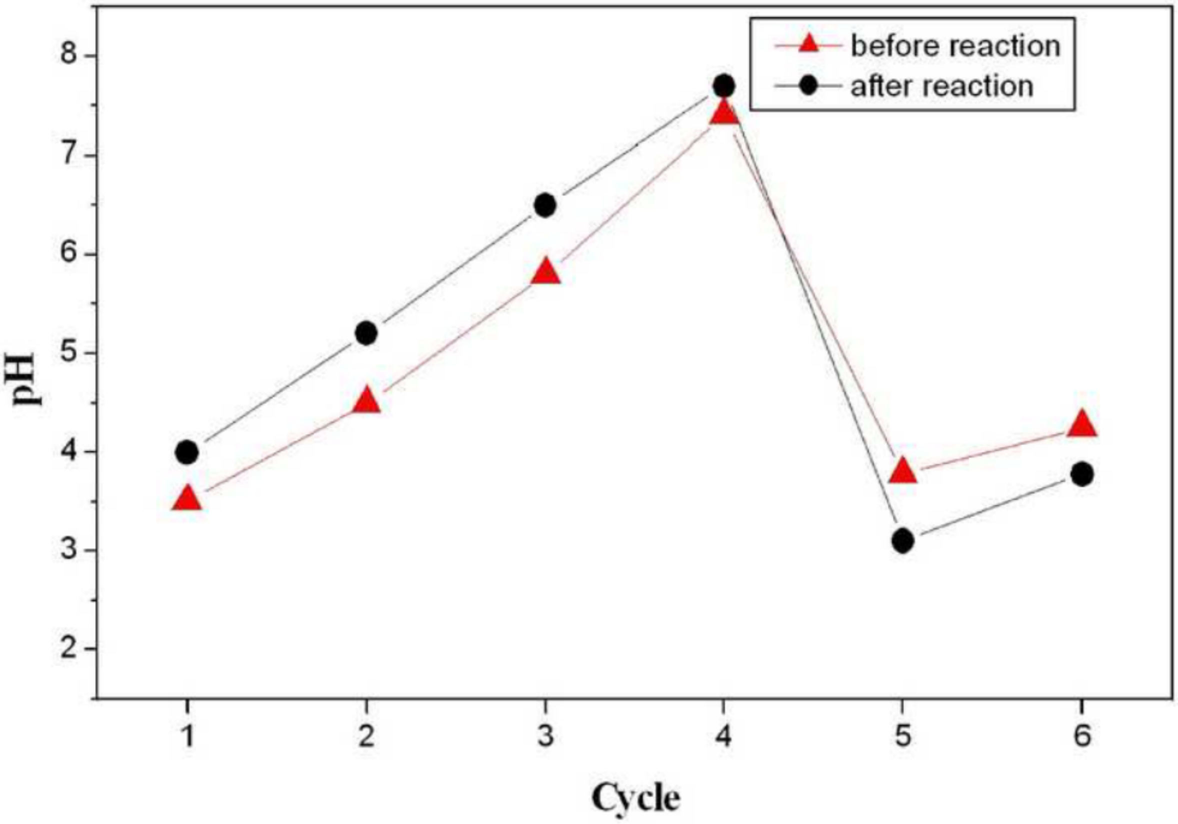


Figure 2

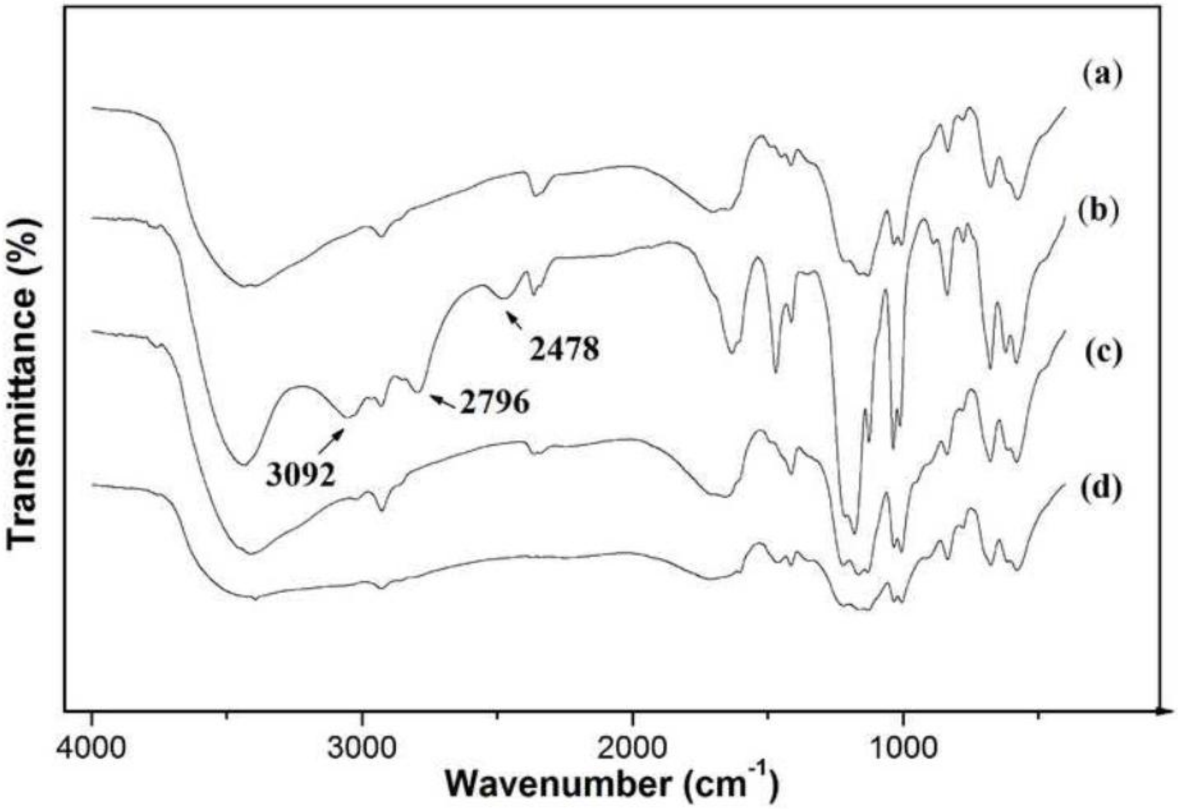

(a)
(b)
(c)
(d)
2478
2796
3092
Transmittance (%)
4000
3000
2000
1000
Wavenumber (cm^{-1})

Figure 3

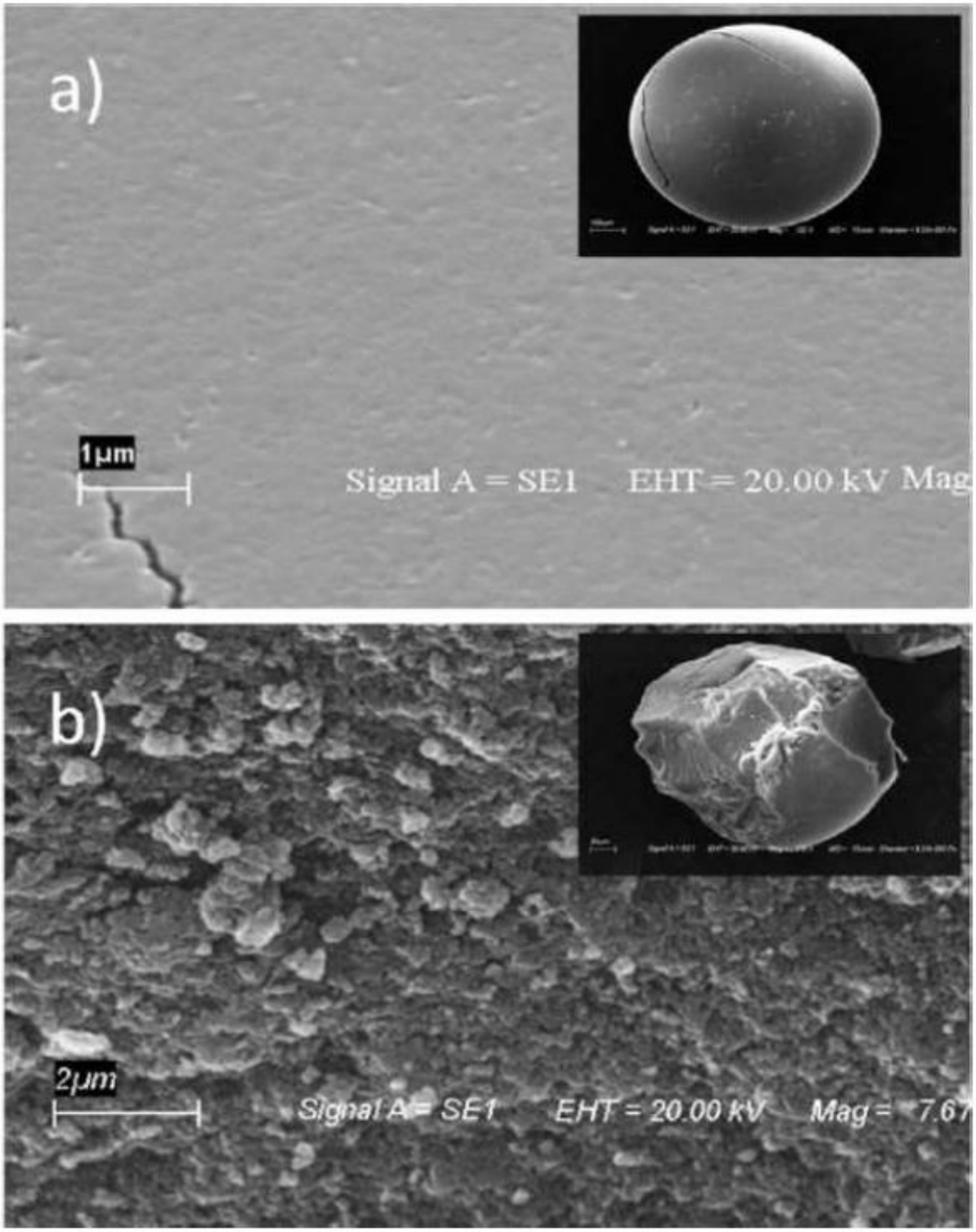
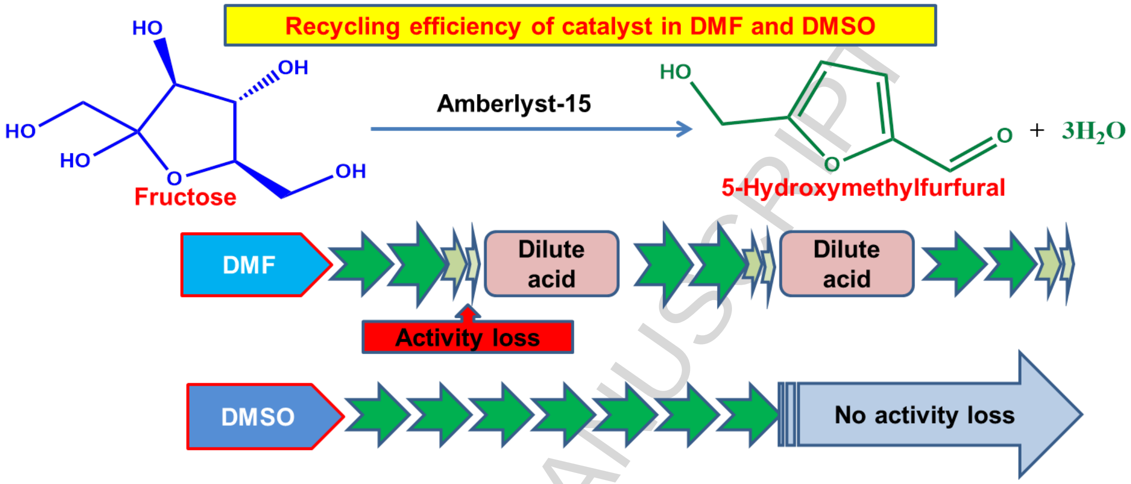

a)
1µm
Signal A = SE1
EHT = 20.00 kV
Mag
b)
2µm
Signal A = SE1
EHT = 20.00 kV
Mag = 7.6

Figure 4

Graphical abstract



Research Highlights

- Fructose dehydration to 5-hydroxymethylfurfural using Amberlyst-15 was studied in DMF and DMSO solvents
- Dimethylsulphoxide (DMSO) is more efficient than N,N-dimethylformamide (DMF) in terms of catalyst recycling
- The activity of the dead catalyst was regenerated by dilute acid treatment
- Yield of HMF increased by simply scrubbing the catalyst particle surface