Contents lists available at ScienceDirect



Applied Catalysis A, General



journal homepage: www.elsevier.com/locate/apcata

# Synthesis of cinnamyl benzoate over novel heteropoly acid encapsulated ZIF-8



# Radhika S. Malkar, Ganapati D. Yadav\*

Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai, 400 019, India

#### ARTICLE INFO

Metal organic framework

Cinnamyl benzoate

Cinnamvl alcohol

Dodecatungstophosphoric acid

Keywords:

Kinetics 1

ZIF-8

ABSTRACT

ZIF-8 is a zeolitic imidazolate framework which is a subclass of metal organic framework (MOF). ZIF-8 is the emerging class of MOF with various applications. Dodecatungstophosphoric acid (DTP) encapsulated ZIF-8 was prepared first time using bottle around the ship strategy. This approach covers ZIF-8 synthesis along with DTP encapsulation in one pot synthesis. The synthesized catalyst shows highest catalytic activity for esterification reaction of benzoic anhydride with cinnamyl alcohol to form cinnamyl benzoate. Heterogeneous catalytic synthesis of cinnamyl benzoate with complete reaction kinetics is presented here for the first time. Cinnamyl benzoate is a famous perfumery and flavoring agent and GRAS listed food additive molecule. Catalyst preparation method is simple, rapid and can be done at room temperature using water as a solvent. DTP@ZIF-8 shows sodalite like structure and it was confirmed by applying several characterization techniques like SEM, TEM, XRD, BET, FTIR, TGA and ammonia-TPD. Duration of DTP@ZIF-8 crystal formation was studied and optimized up to 12.h. Catalyst is thermally stable up to 400 °C and showed reusability for 3 cycles. Reaction kinetics was studied with best fit of Eley-Rideal mechanism.

# 1. Introduction

Metal organic frameworks (MOFs) have been continuously explored in recent era and many efforts are still underway to overcome the shortcomings of previous reports. Due to their excellent properties like high surface area, stable structure, permanent porosity and tunable pore size, MOFs have been explored in various applications such as catalysis, photocatalysis, CO<sub>2</sub> adsorption, storage of hydrogen, etc. [1-3]. There are numerous applications are reported with MOF as catalyst for reactions. Metal organic frameworks serve as excellent supports for catalyst preparation. Yang et al. used MOF-assisted strategy to develop molybdenum phosphide nanoparticles dispersed in porous carbon for hydrogen evolution reaction [4]. Another type of application consists of pyrolysis process for bimetallic Zn/Co MOF in which single Co atom can be reduced by carbonization of the organic linker and Zn is evaporated at high temperature. This kind of catalyst can be used as oxygen reduction reaction catalyst [5]. Efficient electroreduction of CO2 was carried out over single atom catalyst. Herein, they have adopted MOFs to direct the preparation of a catalyst containing single Ni sites [6]. Metal nanoparticles such as Pt have been encapsulated in situ with one step process inside Al MOF. It's increased catalytic activity and selectivity was tested for liquid phase aerobic oxidation of alcohols [7]. There are some bimetallic MOFs; for instance,

Ramezanalizaseh et al. developed mixed Co/Ni MOF for one pot synthesis of substituted imidazoles [8]. These MOFs are classified according to their place of discovery such as HKUST (Hong Kong University of Science and Technology), MIL (Materials of Institute Lavoisier), UiO (Universiteteti Oslo), etc.

Some MOFs possess zeolite like topology which consists of metal ions connected through organic linker usually imidazole rings. Therefore they are abbreviated as zeolitic imidazolate frameworks (ZIF). They are engrossing MOF which is having three dimensional structure with tetrahedral metal ion (Co, Cu, Zn, etc.) linked to imidazolate as a linker. ZIF-8 structure consists of  $Zn^{2+}$  ion linked through N atoms by a ditopic ligand imidazolate to form a framework. It is one of the MOFs produced by BASF in large quantity as Basolite Z1200. These are widely used in catalysis because of ease of preparation with great thermal and chemical stability [9]. Hence they are potential candidates to use as a support in heterogeneous catalysis.

Heteropolyacids are one of the most acidic inorganic compounds and show high catalytic activity. But they cannot be used as such because of their low surface area and higher solubility in most of solvents. Therefore, impregnation and encapsulation over solid support are the two best options to use such molecules in catalysis. Uptill now there are several reports on encapsulation of phosphotungstic acid (PTA) inside MOF. For example, Yang et al. studied heterogeneous Zr based MOF

E-mail address: gd.yadav@ictmumbai.edu.in (G.D. Yadav).

https://doi.org/10.1016/j.apcata.2018.04.038 Received 10 February 2018; Received in revised form 26 April 2018; Accepted 27 April 2018 Available online 30 April 2018

0926-860X/ © 2018 Published by Elsevier B.V.

<sup>\*</sup> Corresponding author.

Nomenclature		k <sub>B</sub>	chemisorptions rate constant for forward reaction
		k' <sub>B</sub>	chemisorptions rate constant for backward reaction
А	reactant species A, cinnamyl alcohol	k <sub>SR</sub>	reaction rate constant ( $cm^6 mol^{-1} g^{-1} s^{-1}$ )
В	reactant species B, benzoic anhydride	K <sub>B</sub>	adsorption equilibrium constant for B (g-cat/mol)
As	chemisorbed A	r <sub>obs</sub>	observed rate of reaction based on liquid phase volume
B <sub>S</sub>	chemisorbed B		$(mol/cm^3. S)$
С	cinnamyl benzoate	Sh	Sherwood number
D	benzoic acid	$D_{AB}$	diffusion coefficient of A in B (cm <sup>2</sup> /s)
S	vacant site	$d_p$	diameter of catalyst particle (cm)
-r <sub>B</sub>	rate of chemisorption of B (mol $\text{cm}^{-3} \text{ s}^{-1}$ )	$k_{\rm SL-A}$	solid-liquid mass transfer coefficient (cm/s)
k <sub>B</sub>	adsorption equilibrium constant for B (cm <sup>3</sup> /mol)	$a_p$	surface area per unit liquid volume (cm <sup>2</sup> /cm <sup>3</sup> )
$C_A$	concentration of A (mol/cm <sup>3</sup> )	$\rho_p$	density of catalyst particle (g/cm <sup>3</sup> )
$C_{AS}$	concentration of A at catalyst surface (mol/g-cat)	$A_o$	concentration of A in bulk liquid phase (mol/cm <sup>3</sup> )
$C_B$	concentration of B (mol/cm <sup>3</sup> )	$C_{wp}$	Weisz Prater parameter
$C_{BS}$	concentration of B at catalyst surface (mol/g-cat)	Μ	mole ratio of A to B
$C_D$	concentration of D (mol/cm <sup>3</sup> )	w	catalyst loading (g/cm <sup>3</sup> )
$C_S$	concentration of vacant sites (mol/cm <sup>3</sup> )	X <sub>B</sub>	fractional conversion of B
$C_{\rm t}$	total concentration of the sites (mol/cm <sup>3</sup> )		

(HPWs@UiO-66) to encapsulate PTA by hydrothermal method [10]. Basically UiO-66 possesses two types of cages: an octahedral cage (1.1 nm, large) which is face sharing with 8 tetrahedral cages and edge sharing (0.8 nm, small) with 8 extra octahedral pores. They have successfully encapsulated Keggin particles of 1.0–1.3 nm in diameter inside large cage of UiO-66. This catalyst was tested on selective oxidation of cyclopentene to glutaraldehyde. Chen et al. studied hydroxyl alkylation of phenol to form bisphenol F over PTA encapsulated in MIL-100(Fe or Cr) and MIL-101 (Fe or Cr) [11]. Synthesis of PTA encapsulated in the chromium based terephthalate metal organic framework (MIL-101) mesocages was also reported by various scientists [12-14]. Synthesized catalyst was fully characterized by various spectroscopic techniques. But there are chances that PTA ions may leach out from the pores of MIL-101 as pore diameter (1.6 nm) of MIL-101 is larger than the PTA molecules (1.3-1.4 nm) [15]. Heteropolyacid functionalized aluminium 2- amino-terephthalate metal organic framework was prepared by Bromberg et al. [16]. It was utilized as a sorbent for vapors of acetaldehyde, acrolein and butyraldehyde. Wee et al. reported convenient method of synthesis of Cu based MOF, i.e. Cu<sub>3</sub>(BTC)<sub>2</sub> encapsulated Keggin heteropolyacid catalyst and its application in catalysis [17]. Cu<sub>3</sub>(BTC)<sub>2</sub> material contains three dimensional pore system with diameters of 1.0 and 1.3 nm which has accessible pore windows of 9.3 and 1.1 nm, respectively. Here they have observed that Keggin ions act as a structure directing agent allowing  $\mathrm{Cu}^{2+}$  ions to assemble around it and form a network. These methods possesses drawback of use of high temperature, long synthesis time and non-green solvents like DMF, DMSO, etc. This will thus add to the cost in production of catalyst and process becomes non eco-friendly. Therefore here we are reporting encapsulation of dodeca-tungstophosphoric acid (DTP) inside ZIF-8 at room temperature using bottle around ship approach. The process is safe, clean and uses water as a solvent. ZIF-8 has previously been used for encapsulation of enzyme [18]. They found that procedure of making ZIF-8 was simple, efficient and rapid wherein the crystals were formed within 20 min.

Keggin type phosphotungstic acid (PTA) molecule possesses relatively larger particle size up to 1.3 to 1.4 nm in diameters [15] whereas pore diameter of ZIF-8 is 1.1 nm so the chances of leaching of DTP molecule from ZIF-8 cage get reduced. There are a very few reports available in literature on encapsulation of DTP in zeolitic imidazole frameworks. Liu et al. studied NiO-PTA supported on ZIF-8 by impregnation method and used for vapor phase hydrocracking of Jatropha oil [19]. Here they have used Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O as a metal precursor for ZIF-8 synthesis. The estimated P and W content was 1.108 atom % and 2.701 atom%. Whereas current in situ approach of encapsulation of DTP inside ZIF-8 showed 2.12 atom% and 5.38 atom% of P and W, respectively. Hence it gets proved that in situ encapsulation provides excellent entrapment of DTP inside the cage of ZIF-8. Ammar et al. recently published such heteropoly acid encapsulated ZIF-67 using cobalt nitrate hexahydrate as a metal precursor [20]. The Friedel-Crafts acylation of anisole with benzoyl chloride was performed over this catalyst and it was found that catalyst was highly stable and reusable up to 5 cycles.

In the present work, catalytic activity of DTP@ZIF-8 was tested in the synthesis of cinnamyl benzoate from cinnamyl alcohol and benzoic anhydride (Scheme 1). Cinnamyl benzoate is one of the popular fragrance compounds used in cosmetics, shampoos, soaps and non-cosmetic products like detergents, house hold cleaners, etc. It is a GRAS (Generally recognized as safe) listed compound and therefore can be added directly in to food. Commercially it is synthesized by acylation of cinnamyl alcohol with benzoyl chloride and pyridine as a solvent. Use of benzoyl chloride produces HCl which is very corrosive. Therefore, finding another green route is always challenging. In this work we are reporting DTP@ZIF-8 as a solid acid catalyst for this esterification reaction. A mechanistic model was developed to deduce kinetics. The process is green, efficient and the catalyst is reusable and active.

# 2. Experimental section

# 2.1. Chemicals

The chemicals were procured from following sources: 1, 4 dioxane, zinc acetate, n-decane (AR grade S.D. Fine Chem. Ltd, Mumbai, India), benzoic anhydride, cinnamyl alcohol (98% Alfa esar), dodeca-tung-stophosphoric acid (Thomas Baker) and 2 methylimidazole (Loba



Scheme 1. Synthesis of cinnamyl benzoate over 18%-DTP@ZIF-8\_12 h.

Cinnamyl alcohol

Benzoic anhydride

Cinnamyl benzoate

Benzoic acid

Chemie). All chemicals were used as received.

## 2.2. Catalyst preparation

DTP encapsulated ZIF-8 was prepared by a reported method with slight modifications [21]. Zn acetate (0.0072 mol) and optimized amount of DTP were mixed in to 20 mL deionized water to prepare solution A. 2 methylimidazole (0.061 mol) were mixed into 20 mL deionized water separately to prepare solution B. A drop wise addition of solution B into a solution A was done to form a white precipitate. The resulting mixture was stirred vigorously at room temperatue for different times (20 min, 6 h, 12 h & 14 h) to study the growth of the structure. Thus the formed precipitate was separated by centrifugation and washed several times with distilled water to remove un-reacted moieties. Afterwards the catalyst was calcined at 300 °C for 3 h. Different weight loadings of DTP i.e. 9%, 18% and 27% were studied for encapsulation. X-ray fluorescence analysis showed 69.34 mass % of Zn and 30.64 mass % of W in 18%-DTP@ZIF-8\_12 h whereas pure ZIF-8 showed 99.9% Zn content in the framework structure (Supplementary Information Figs. S1 and S2).

# 2.3. Reaction set up and analysis

All the experiments were carried out in a glass reactor of 50 ml volume having turbine impeller with standard 6 pitched blades and it was then immersed in oil bath with PID controller for maintaining desired temperature. Benzoic anhydride 1.13 g (0.005 mol), cinnamyl alcohol 3.35 g (0.025 mol) and  $0.16 \text{ g} (0.005 \text{ g mL}^{-1})$  catalyst were added to the glass reactor. Total volume was maintained up to 32 ml made up with 1, 4 dioxane as a solvent. n-Decane was used as an internal standard. The reaction mixture was agitated at 800 rpm at 60 °C. Samples were withdrawn from reaction mixture after attaining the desired temperature. The reaction mixture was analyzed by GC (Thermo Scientific model TRACE 1110) with OV-1701 capillary column and FID detector.

# 2.4. Catalyst characterization methodology

Catalysts were characterized by different techniques using XRD, ammonia TPD, FTIR, BET surface area, SEM, and TEM. As described recently in published literature [22–24]. More details about procedures are provided in supplementary information (ESI). Since 18(wt%) of DTP was found to be giving the best encapsulation into ZIF-8, its complete characterization is presented here. In further discussions, the catalyst has been denoted as X%-DTP@ZIF-8\_Y, where X% is weight % of DTP encapsulated and Y is time of synthesis.

# 3. Results and discussion

## 3.1. Catalyst characterization

# 3.1.1. X-ray diffraction

X-ray diffraction pattern of ZIF-8 and 18%-DTP@ZIF-8\_12 h (Fig. 1) was studied to confirm its rhombic dodeca-tetrahedron structure. ZIF-8 showing peaks at 20, 7.69, 10.76, 13.12, 15.12, 16.88, 18.47, 22.60, 24.98, 26.10, 27.17, 30.17, 31.11, 32.91 correspond to (011), (002), (112), (022), (013), (222), (114), (233), (224), (134), (044), (244), (235). These XRD patterns are in agreement with reported literature [25]. XRD pattern of ZIF-8 and 18%-DTP@ZIF-8\_12 h do not show any differences apart from that the intensity of peaks has been reduced with the entry of guest DTP molecule inside the cage. There is decrease in crystallinity observed in case of 18%-DTP@ZIF-8\_12 h which signifies proper encapsulation of phosphotungstic acid into the pores of ZIF-8. Reused catalyst showed the same pattern of diffraction with slight drop in intensity of crystallinity. Thus the catalyst showed stability in structure even after 3rd reuse. Bulk DTP shows characteristic peaks at

 $2\theta - 10$ , 25 and  $35^{\circ}$ [26]. Absence of characteristic peaks of DTP in the diffraction pattern of 18%-DTP@ZIF-8\_12 h shows molecules are well encapsulated inside the cage of ZIF-8 and they are no more on the surface.

We have also studied duration of crystal formation, in which as the time of nucleation increased, crystallinity found to increase (Fig. 2). The crystallite size was calculated by using Scherrer equation. 18%-DTP@ZIF-8\_12 h showed largest crystal size of 25.72 nm whereas 18%-DTP@ZIF-8\_6 h and 18%-DTP@ZIF-8\_20 min had crystal size of 21.31 nm and 19.76 nm, respectively. On the contrary pure ZIF-8 showed the largest crystallite size 26.59 nm. Reused catalyst after 3rd use showed crystallite size of 23.14 nm. The intensity of the most prominent peak of (011) was found to be increasing with time. Venna et al. reported three stages of ZIF-8 synthesis such as nucleation, growth and stationary phase [27]. Nucleation stage is the step in which ZIF-8 takes time to increase its crystallinity. Hence longer synthesis time is always preferable for getting complete crystallization.

# 3.1.2. Ammonia- temperature programmed desorption (TPD)

Ammonia TPD of pure ZIF-8, virgin 18%-DTP@ZIF-8\_12h and reused 18%-DTP@ZIF-8\_12 hwas carried out between 50-400 °C to study acidic strength of catalysts (Table 1). ZIF-8 possesses Lewis acidic sites because of Zn metal ion whereas basic sites are due to N atom of imidazole ligands [28]. Encapsulation of DTP increases its acidity upto 0.48 mmol/g. NH<sub>3</sub>-TPD curve reveals that pure ZIF-8 possesses weak acidic sites whereas 18%-DTP@ZIF-8\_12 h have weak as well as strong acidic sites (Fig. 3). Reused catalyst showed a slight decrease in acidity. The acidity measurement of PTA-ZIF-67 has not been provided by Ammar et al. [20]. Saikia et al. prepared phosphotungstic acid encapsulated chromium (III) terephthalate MOF having 0.288 mmol/g of total acidic site [12]. Khder et al. prepared heteropolyacid supported MIL-101 catalyst with 50, 70 and 90 wt % loadings. 50 wt% loading showed 0.392 mmol n-butylamine/g of acidity whereas 70 wt % loading showed 0.926 mmol n-butylamine/g. Catalytic activity was tested for three organic reactions such as Pechmann condensation, esterification and Friedel-Crafts reactions [13]. Another group of researchers has prepared Zn, Ni and Cu metal organic frameworks functionalized with phosphotungstic acid for selective adsorptive desulfurization [29]. Total acidity of PTA(0.2)@(Zn, Ni, Cu)-BTC, PTA(0.5)@(Zn, Ni, Cu)-BTC and PTA(1.0)@(Zn, Ni, Cu)-BTC was found to be 0.55, 0.61 and 0.82 mmol/g, respectively. Therefore, the catalyst synthesized in the current work with in situ approach also possesses



Fig. 1. XRD pattern of ZIF-8, 18%-DTP@ZIF-8\_12 h and reused 18%-DTP@ZIF-8\_12 h.



Fig. 2. XRD pattern of 18%-DTP@ZIF-8 synthesized for 20 min, 6 h and 12 h.

Table 1

Ammonia	TPD	of	catalysts.	
---------	-----	----	------------	--

Catalyst	Total acidity in mmol/g
ZIF-8	0.33
18%-DTP@ZIF-8_12 h	0.48
Reused 18%-DTP@ZIF-8_12 h	0.45



Fig. 3.  $\rm NH_3\text{-}TPD$  of ZIF-8, 18%-DTP@ZIF-8\_12 h and reused 18%-DTP@ZIF-8\_12 h.

good acidity as compared to the reported catalysts in literature.

## 3.1.3. Fourier transform infrared spectroscopy (FTIR)

The successful encapsulation of DTP was characterized by FT-IR spectroscopy. Fig. 4 shows FTIR spectra of the pure ZIF-8. The peaks at 3056 and 2900 cm<sup>-1</sup> are representing the aromatic and aliphatic C–H stretch of the imidazole ring, respectively. The out of plane and in plane bending of imidazole ring are present between 692–744 cm<sup>-1</sup> and 950–1177 cm<sup>-1</sup> respectively. The band at 427 cm<sup>-1</sup> is due to stretching of Zn-N. The strong peaks in the region 1300–1450 cm<sup>-1</sup> represents C–N absorption band[30,31].

The infrared spectra of 18%-DTP@ZIF-8\_12 h is presented in Fig. 5. It shows excellent retention of all peaks of ZIF-8. Confirmation of Keggin structure of DTP was done with characteristic peaks showing 994 cm<sup>-1</sup> of W=O stretch of exterior WO<sub>6</sub> octahedron, 820 cm<sup>-1</sup> for W–O–W and 1143 cm<sup>-1</sup> P–O stretching frequency of central PO<sub>4</sub> tetrahedron. Band at 1624 cm<sup>-1</sup> is attributed to the  $\delta$ –OH bending frequency of water molecules associated with catalyst [26,32]. Thus, FTIR confirms the well co-ordination of Zn metal ion with imidazolate molecule.

# 3.1.4. Scanning electron microscopy (SEM)

Jian et al. studied the effect of time required for ZIF-8 formation [33]. They have concluded that it takes longer time for complete crystallization of ZIF-8. Major peak indicated at (011) of sodalite structure of ZIF-8 increases with increase in synthesis time. Considering this fact, SEM analysis of catalyst at different time was carried out to study the structural growth (Fig. 6). Similar to the results found in XRD, no phosphotungstic acid molecules were observed on the surface of 12 h sample indicating that DTP was well encapsulated into the ZIF-8. No structural differences were observed between pure ZIF-8 and DTP encapsulated ZIF-8.

Crystals of 18%-DTP@ZIF-8 started showing hexagonal facets of uneven size within 20 min. At 6 h, surface of crystal became smooth and homogeneous. Finally as the time progresses, evenly distributed rhombic dodecahedron crystals of catalyst were formed. Reused catalyst even after 3 cycles of reaction shows sharp edges of DTP@ZIF-8 crystals. After 3 cycles of reusability, the catalyst started degrading and there was leaching of DTP observed in ICP-AES analysis up to 9%. It may be because of continuous exposure of catalyst to benzoic acid which is formed as co-product in the reaction mixture. It has been reported that external surface of ZIF-8 begins degrading after coming in contact with acidic solution[34]. Hence disturbed structure can be seen in SEM image which has been taken after 3rd cycle of reusability (Fig. 6E).

EDX analysis has been carried out for 18%-DTP@ZIF-8\_12 h to detect the presence of DTP from the catalyst and showed 2.12 atom% and 5.38 atom % of P and W, respectively (ESI Fig. S3). Elemental mapping image revealed the uniform distribution of DTP, i.e. of tungsten and phosphorus inside ZIF-8 cage (Fig. 7).

# 3.1.5. Transmission electron microscopy (TEM)

Fig. 8 shows rhombic dodeca-tetrahedron crystals of 18%-DTP@ ZIF-8\_12 h catalyst. Uniform distribution of DTP inside the ZIF-8 crystals can be seen in the image. It can also be seen that DTP clusters of 2–5 nm have been successfully and evenly encapsulated inside ZIF-8.



Fig. 4. FTIR spectra of ZIF-8.



Fig. 5. FTIR spectra of 18%-DTP@ZIF-8\_12h.

## 3.1.6. Surface area analysis

BET analysis of catalyst was carried out for different time periods of crystal growth (Table 2). ZIF-8 without any encapsulation of DTP showed the highest surface area of  $1306 \text{ m}^2/\text{g}$ . After the entry of DTP



Fig. 7. Elemental mapping image of 18%-DTP@ZIF-8\_12 h.



Fig. 6. SEM analysis of 18%-DTP@ZIF-8 synthesized at (A) 20 min, (B) 6 h, (C)12 h, (D) 18%-DTP@ZIF-8\_12 h 1st Reused, (E) 18%-DTP@ZIF-8\_12 h after 3rd reuse and (F) Pure ZIF-8.



Fig. 8. TEM of 18%-DTP@ZIF-8\_12 h.

Table 2

Surface area analysis of 18%-DTP@ZIF-8 at different synthesis times.

Time of synthesis	BET surface area, m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Pore diameter, nm
20 min	563.9	0.16	6.6
6 h	758.7	0.47	2.4
12 h	1101.6	0.60	1.1
18 h	1176.7	0.67	1.12
Pure ZIF-8_12 h	1306.4	0.61	1.15
Reused 18%-DTP@ ZIF-8-12 h	989.5	0.57	1.1

molecules inside the cage of ZIF-8, thr surface area gets slightly decreased. Results revealed that surface area increases with the time of crystal growth. At 20 min surface area is lower as compared to 12 h and 18 h. After 12 h it remains almost constant for further time. It has been reported in literature that as the synthesis time progresses, the percentage crystallinity of ZIF-8 formation increases [33]. Therefore, pore diameter was found to be decreasing with increase in synthesis time. Because of some adsorbed molecules from reaction mixture, reused catalyst after 3 cycles of reuse showed a slight decrease in surface area and pore volume.

Fig. 9 shows N<sub>2</sub> adsorption desorption curve of ZIF-8,18%-DTP@ ZIF-8\_12 h and reused 18%-DTP@ZIF-8\_12 h. There is an increase in adsorption volume at low relative pressure which shows that the material is microporous in nature with type-I isotherm. ZIF-8 and 18%-DTP@ZIF-8\_12 h do not show any change in shape of isotherm; however, volume of adsorption has decreased in case of 18%-DTP@ZIF-8\_12 h which further confirms that DTP has occupied in the pores of ZIF-8. Reused catalyst even after 3 cycles showed type-I isotherm, retaining its microporous structure.

# 3.1.7. Thermal gravimetric analysis (TGA)

TG analysis of prepared catalyst shows excellent thermal stability. As synthesized ZIF-8, without encapsulation of DTP shows greater thermal stability up to 400 °C. For DTP@ZIF-8 there is a 10–12 % weight loss up to 150 °C because of removal of water molecules from the catalyst. Fig. 10 shows that the catalyst from 20 min batch shows continuous weight loss from 100 °C whereas DTP@ZIF-8\_6 h and DTP@ZIF-8\_12 h shows greater stability up to 400 °C.

# 3.2. Synthesis of cinnamyl benzoate

In all experiments, the selectivity to cinnamyl benzoate was 100%. There was no side reaction. Benzoic acid is a co-product of the reaction.

# 3.2.1. Effect of DTP loading

Different loadings (9, 18 & 27 wt %) of DTP were studied for encapsulation into ZIF-8. All the catalysts were characterized by SEM, XRD and BET. XRD analysis (Fig. 11) shows a slight decrease in intensity of peaks for 18% of loading as compared to 9%. But there was a drastic decrease in crystallinity observed for 27% DTP encapsulation. It was reported that increased loading of DTP increases acidity of the solution and acidic pH is not favorable for ZIF-8 crystal formation [20,35]. Surface area of 489.53 m<sup>2</sup>/g of DTP@ZIF-8\_12 h for 27% loading is the lowest as compared to other two. Uneven growth of ZIF-8 crystals can be seen in Table 3 for 27% loading because of higher loadings of DTP.

Ammonia TPD for different loadings of sample was carried out from 90 to 400 °C to compare the acidity possessed by them (Fig. 12). The low temperature adsorption peaks around 200–300 °C and intermediate peaks around 300–400 °C confirm the acidic nature of the catalysts. As the percentage of DTP was increased, an increase in total acidic sites was observed.

Catalytic activity of all three catalysts was studied for conversion of benzoic anhydride to cinnamyl benzoate (Fig. 13). 18%-DTP@ZIF-8\_12 h shows the best conversion of benzoic anhydride and therefore it was chosen for further reactions. Without catalyst only 5% conversion of benzoic anhydride was observed after 180 min at 60 °C. Pure DTP showed 100% conversion but then it was homogeneously catalyzed reaction. When experiment was conducted with ZIF-8 only there was no product obtained in the reaction mixture.



Fig. 9.  $N_2$  adsorption desorption isotherm of ZIF-8, 18%-DTP@ZIF-8\_12 h and reused 18%-DTP@ZIF-8\_12 h.



Fig. 10. TGA analysis of 18%-DTP@ZIF-8 synthesized at 20 min (a), 6 h (b), 12 h (c) and ZIF-8 (d).



Fig. 11. XRD of 9%-DTP@ZIF-8\_12 h, 18%-DTP@ZIF-8\_12 h and 27%-DTP@ZIF-8\_12 h.

# 3.2.2. Effect of different benzoylating agents

Reaction of benzoic anhydride, benzoic acid and benzoyl chloride with cinnamyl alcohol was tested at the same reaction conditions (Table 4). It was observed that benzoic acid does not react with cinnamyl alcohol at the specified reaction conditions. Reaction with benzoic anhydride always produces benzoic acid as a co-product and hence it confirms that benzoic acid does not play any role in the synthesis of cinnamyl benzoate. Also, the results revealed that benzoic anhydride is more active than benzoyl chloride for this reaction because of its strong adsorption on the catalyst.

## 3.2.3. Effect of speed of agitation

To confirm the absence of mass transfer resistance, reaction was carried out at different agitation speed as 700, 800 and 900 rpm (Fig. 14). It was found that the rate and conversion did not change significantly from 800–900 rpm. Hence, there was an absence of mass transfer resistance beyond 800 rpm. Thus 800 rpm was selected as the optimized speed for further reactions. A theoretical calculation was done to confirm it as reported earlier publications [26].

#### Table 3

Comparative textural properties and SEM study of 9, 18 and 27% DTP@ZIF-8 12 h.

DT loa in 1 (wt	P ding ZIF-8 t %)	Textural Properties	SEM
9		<ul> <li>BET Surface Area = 1179.6 m<sup>2</sup>/g</li> <li>Total Pore Volume = 0.60 cm<sup>3</sup>/g</li> <li>Avg Pore Diameter (4 V/S) = 1.6 nm</li> </ul>	
18		<ul> <li>BET Surface Area = 1101.5 m<sup>2</sup>/g</li> <li>Total Pore Volume = 0.59 cm<sup>3</sup>/g</li> <li>Avg Pore Diameter (4 V/S) = 1.13 nm</li> </ul>	15kU ×5, 600 5mm 1CT
27		<ul> <li>BET Specific Surface Area = 489.5 m²/g</li> <li>Total Pore Volume = 0.30 cc/ gcm³/g</li> <li>Avg Pore Diameter (4 V/S) = 1.4 nm</li> </ul>	
	-0.025		
TCD signal (a.u.)	-0.02		
	-0.015		
	-0.01		
	-0.005		
	U S	50 150	250 350 450
Temperature (oC)			

Fig. 12. NH<sub>3</sub>-TPD curve for different loading of DTP.

# 3.2.4. Proof of absence of external mass transfer resistance

Different controlling mechanisms are reported in literature for solidliquid catalytic reactions. Wilke-Chang equation was used to calculate liquid phase diffusivity of benzoic anhydride (A) at 60 °C [36]. It was found to be  $1.31*10^{-5}$  cm<sup>2</sup>/s. Mass transfer coefficient was calculated by considering 2 as a limiting value for Sherwood number ( $Sh_A = (k_{S-}Ad_{p)}/D_{AB}$ ) [26]. For average particle diameter of 1 µm,  $k_{SL-A}$ , the mass transfer coefficient was calculated as 0.262 cm/s. The particle surface



DTP loading (%)

**Fig. 13.** Effect of DTP loading in ZIF-8: Catalyst loading,  $0.003 \text{ g cm}^{-3}$ , 1:3 mol ratio of benzoic anhydride to cinnamyl alcohol, Temperature: 70 °C, Duration: 90 min, Solvent: 1, 4 diaoxane, Total volume: 32 cm<sup>3</sup>.

#### Table 4

Effect of different benzoylating agents.

Sr No.	Benzoylating agent	Conversion (%)
1. 2. 3.	Benzoic anhydride Benzoyl chloride Benzoic acid	58.17 39.67 No conversion

Reaction conditions: Catalyst: 18%-DTP@ZIF-8\_12 h, Speed of agitation: 800 rpm, 1:3 mol ratio of benzoic anhydride to cinnamyl alcohol, Temp: 70 °C, Duration: 90 min, Solvent: 1, 4 diaoxane, Total volume:  $32 \text{ cm}^3$ .



Fig. 14. Effect of speed of agitation: Catalyst: 18%-DTP@ZIF-8\_12 h, Catalyst loading,  $0.003 \text{ g cm}^{-3}$ , 1:3 mol ratio of benzoic anhydride to cinnamyl alcohol, Temperature: 70 °C, Duration: 90 min, Solvent: 1, 4 diaoxane, Total volume: 32 cm<sup>3</sup>.

per liquid volume was obtained as,

$$a_p = \frac{6w}{\rho_p d_p} = 1601.7 \,\mathrm{cm}^2/\mathrm{cm}^3$$

The observed initial rate of reaction  $r_{obs}$  for benzoic anhydride was calculated as  $2.27 \times 10^{-6}$  mol cm<sup>-3</sup> s<sup>-1</sup> while the mass transfer resistance



**Fig. 15.** Effect of catalyst loading: Catalyst: 18%-DTP@ZIF-8\_12 h, Speed of agitation: 800 rpm, 1:3 mol ratio of benzoic anhydride to cinnamyl alcohol, Temperature: 70 °C, Duration: 90 min, Solvent: 1, 4 diaoxane, Total volume: 32 cm<sup>3</sup>.

for benzoic anhydride,  $k_{SLA} - {}_{A}a_{p}[A_{0}]$ , was calculated as  $1.525 \times 10^{2}$  6.57  $\times 10^{-3}$  mol cm<sup>-3</sup> s<sup>-1</sup>. Thus the comparison of the relevant resistances shows that  $\frac{1}{r_{obs}} > > > \frac{1}{k_{SLA} - {}_{A}a_{p}[A_{0}]}$  i.e. i.e. 4.405  $\times 10^{5} > > > 0.1525 \times 10^{2}$ 

This proved that the reaction is free from external mass transfer resistance. The only other resistance could be the resistance offered by intra-particle diffusion, chemisorption, surface reaction or desorption.

# 3.2.5. Effect of catalyst loading

Catalyst loading was studied from 0.002 to  $0.006 \text{ g/cm}^3$  for the conversion of benzoic anhydride. Fig. 15 shows that the conversion is increasing with increase in catalyst loading. Thus  $0.005 \text{ g/cm}^3$  was optimized for further study because beyond it there was a little difference in the conversion and the number of catalytic active sites available were more than sufficient. Plot of initial rate versus catalyst loading was made (Fig. 16) and it was noted that initial rate was directly proportional to catalyst loading, that is, the number of catalytic active sites. This confirms the absence of intra particle diffusion resistance.

## 3.2.6. Proof of absence of intra-particle resistance

Considering the average particle size of 18%-DTP@ZIF-8\_12 h as 1  $\mu$ m, a theoretical calculation was carried out to compute Wietz-Prater criterion ( $C_{wp}$ ) [37]. The details regarding this calculation has been provided in literature [38–40]. This value was calculated as 2.98 \*  $10^{-5}$  which is far less than unity confirming that the reaction was free from intra particle diffusion resistance. Hence the reaction is kinetically controlled which is further confirmed by the activation energy calculation as given in later Section 3.2.10.

# 3.2.7. Effect of the mole ratio

The mole ratio of two reactants, i.e., benzoic anhydride and cinnamyl alcohol was varied from 1:1 to 1:7. Moles of cinnamyl alcohol were increased by keeping benzoic anhydride as the limiting agent. Excess availability of cinnamyl alcohol favors increased conversion of benzoic anhydride to cinnamyl benzoate (Fig. 17). Benzoic acid was formed as a co-product. There was a marginal difference observed in conversion for 1:5 and 1:7 mol ratio. Therefore, 1:5 was selected as optimum value for further experiments.



Fig. 16. Plot of initial rate versus catalyst loading: Catalyst: 18%-DTP@ZIF-8\_12 h, Speed of agitation: 800 rpm, 1:3 mol ratio of benzoic anhydride to cinnamyl alcohol, Temperature: 70 °C, Duration: 90 min, Solvent: 1, 4 diaoxane, Total volume:  $32 \text{ cm}^3$ .



Fig. 17. Effect of mole ratio: Catalyst: 18%-DTP@ZIF-8\_12 h, Catalyst loading: 0.005 g cm<sup>-3</sup>, Speed of agitation: 800 rpm, Temperature: 70 °C, Duration: 180 min, Solvent: 1, 4 diaoxane, Total volume: 32 cm<sup>3</sup>.

# 3.2.8. Effect of temperature

Temperature always plays an important role in reaction kinetics. Rise in temperature increases the solubility of reacting molecules in solvent, increases diffusivity, reduces viscosity and enhances interaction of reactants and catalyst. For current study the temperature was varied from 40 to 70 °C to assess its effect on conversion of benzoic anhydride (Fig. 18). With rise in temperature, rate of conversion of limiting reactant was increasing up to 60 °C. Above this temperature there was insignificant increase in conversion. Therefore, 60 °C was optimized for further studies. The conversion of benzoic anhydride at this optimum temperature with 1:5 mol ratio of benzoic anhydride to cinnamyl alcohol was found to be 84% at 180 min.

## 3.2.9. Reaction mechanism

The catalyst, 18%-DTP@ZIF-8\_12 h consists of acidic sites (S). Consider benzoic anhydride is adsorbed on the acidic sites. Hydroxyl group of cinnamyl alcohol from bulk phase gets converted to  $- O^-$  which attacks on activated carbonyl group of benzoic anhydride on the surface of the catalyst to give cinnamyl benzoate and benzoic acid. Desorption of adsorbed cinnamyl benzoate and benzoic acid into the reaction mixture from catalytic site makes it free for the next cycle of reaction (Scheme 2).

# 3.2.10. Kinetic model

Kinetic model was developed based on above results for esterification of cinnamyl alcohol with benzoic anhydride to synthesize cinnamyl benzoate. On primary analysis, Eley-Rideal mechanism was supposed to be the best fitted model.Consider, cinnamyl alcohol (A), benzoic anhydride (B), product cinnamyl benzoate (C) and co-product benzoic acid (D). Assuming benzoic anhydride adsorbs on a catalytic site S;

$$(C_6H_5CO)_2 + H^+ \underset{k'_B}{\overset{k_B}{\longleftrightarrow}} C_6H_5C^+O + C_6H_5COOH$$

(B) (S) (BS) (D) The rate of chemisorption of B;

kn

$$-r_B = k_B C_B C_S - k'_B C_{BS} C_D \tag{1}$$

At equilibrium,  $-r_B = 0$ ,

$$k_B C_B C_S = k'_B C_{BS} C_D \tag{2}$$

Since, 
$$K_B = \frac{s_D}{k'_B}$$
  
 $C_{BS} = k_B \frac{C_B C_S}{C_D}$ 
(3)

The reaction between chemisorbed BS and A takes place as follows, The rate equation for reactant B is given by;

$$-\frac{d_{C^B}}{dt} = k_{SR}C_A C_{BS} \tag{4}$$

Substituting C<sub>BS</sub>in above equation,

$$-\frac{d_{C^B}}{dt} = k_{SR}C_A \frac{k_B C_B C_S}{C_D} = k_{SR}k_B \frac{C_A C_B C_S}{C_D}$$
(5)

The total catalytic site can be represented as;



**Fig. 18.** Effect of temperature: Catalyst: 18%-DTP@ZIF-8\_12 h, 1:5 mol ratio of benzoic anhydride to cinnamyl alcohol, Catalyst loading:  $0.005 \text{ g cm}^{-3}$ , Speed of agitation: 800 rpm, Duration: 180 min, Solvent: 1, 4 diaoxane, Total volume:  $32 \text{ cm}^{3}$ .



Scheme 2. Catalytic cycle for reaction of cinnamyl alcohol and benzoic anhydride (S, acidic site of catalyst).

# Table 5 Kinetic parameters of esterification of Benzoic anhydride and cinnamyl alcohol at different temperature.

T (K)	K (cm <sup>6</sup> mol <sup>-1</sup> g <sup>-1</sup> s <sup>-1</sup> )	K <sub>B</sub> (cm <sup>3</sup> /mol)	Activation energy (E) (kcal/ mol)
313 323 333 343	$0.9 * 10^{-5} \\ 0.2 * 10^{-4} \\ 0.3 * 10^{-4} \\ 0.7 * 10^{-3}$	$\begin{array}{c} 0.01 \\ 0.9*10^{-2} \\ 0.8*10^{-2} \\ 0.9*10^{-3} \end{array}$	13.98



Fig. 19. Arrhenius plot.



**Fig. 20.** Reusability of catalyst: Catalyst: 18%-DTP@ZIF-8\_12 h, 1:5 mol ratio of benzoic anhydride to cinnamyl alcohol, Catalyst loading: 0.005 g cm<sup>-3</sup>, Temperature: 60 °C, Speed of agitation: 800 rpm, Duration: 180 min, Solvent: 1, 4 diaoxane, Total volume: 32 cm<sup>3</sup>.

$$C^t = w = C_{BS} + C_{AS} + C_S \tag{6}$$

When, 
$$C_{AS} = 0$$

$$w = C_{BS} + C_S$$

$$C_S = \frac{W}{1 + k_B \cdot \frac{C_B}{C_D}} \tag{7}$$

Substituting value of  $C_S$  from Eq. (7) to Eq. (5)

$$-\frac{d_{C^B}}{dt} = \frac{k_{SR}K_B w C_A C_B}{C_D + K_B C_B}$$
(8)

$$C_B = C_{Bo}(1 - X_B) \tag{8a}$$

$$C_A = C_{Ao} - C_{Bo} X_B = C_{Bo} (M - X_B)$$
 (8b)

$$C_D = C_{Bo} X_B \tag{8c}$$

Substituting in terms of  $X_B$  and integrating Eq. (8) for  $M \neq 1$ , we get;

$$-\ln(1 - X_B) - [K_B(M - 1) - M]ln(\frac{M - X_B}{M}) = [k_{SR}K_B(M - 1)wt]$$
(9)

Experimental values were used for checking the validity of the model. Based upon above equations and using Polymath 6.0 software different rate constants were calculated as presented in Table 5. Arrhenius plot (Fig. 19) was made to calculate activation energy which is 13.98 kcal/mol concluding that the reaction is kinetically controlled.

# 3.2.11. Catalyst reusability and leaching test

After completion of reaction, reaction mixture was centrifuged to separate the catalyst. It was then refluxed with methanol for 3–4 times to get rid off adsorbed reactants and products. Then it was dried in oven for 12 h and reused for next reaction. There was a marginal loss of catalyst quantity during washing. It was made up before each reaction of reusability. Reused catalyst was stable up to two use after that conversion started decreasing (Fig. 20). For 4th reuse there was 10% decrease in conversion. As stated above, exposure to acidic solution makes catalyst weaker and starts disintegrating. Therefore after 3 cycle conversion of benzoic anhydride started decreasing.Therefore the catalyst is stable and reusable upto 3 cycles. ICP-AES analysis was carried out initially of reaction mass and it was found that leaching of tungsten from DTP was below detection level. Whereas reaction mass was again analyzed by ICP-AES after 3rd cycle of reusability and 9% DTP leaching was observed.

Leaching of DTP molecule in the reaction mixture was also studied by a hot filtration test for 1st and and 2nd time reused catalyst. The reaction was stopped after 90 min and the reaction mixture centrifuged to separate the catalyst. Here reaction mass was analyzed by GC to get 57% conversion of benzoic anhydride. The clear reaction mixture was again fed to the reactor and continuously stirred for next 2 h at the same reaction conditions. It was found that there was no change in conversion of benzoic anhydride after 2 h. Thus it proveed that there was no leaching of DTP molecules from ZIF-8 cage.

## 4. Conclusion

Cinnamyl benzoate was synthesized successfully over a DTP encapsulated ZIF-8. For the formation of complete rhombic tetrahedron crystals, time of nucleation has been optimized up to 12 h. For maximum catalytic activity and uniform encapsulation of DTP, different loadings of DTP were studied. From which 18%-DTP@ZIF-8\_12 h was optimized for all reactions. Excess DTP leads to improper crystallization of ZIF-8 and it can be seen in SEM images. All the catalysts were fully characterized and tested against benzoic anhydride conversion to cinnamyl benzoate. Reaction parameters were studied and kinetic model developed. Reaction follows Eley-Rideal mechanism with activation energy 13.98 kcal/mol. Therefore the reaction is kinetically controlled.

# Acknowledgments

R. S. Malkar acknowledges University Grants Commission (UGC), India for the award of fellowship in Green Technology. G. D. Yadav acknowledges support from R. T. Mody Distinguished Professor Endowment and J. C. Bose National Fellowship of Department of Science and Technology, Government of India.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apcata.2018.04.038.

#### References

- K. Schlichte, T. Kratzke, S. Kaskel, Microporous Mesoporous Mater. 73 (2004) 81–88, http://dx.doi.org/10.1016/j.micromeso.2003.12.027.
- [2] K.-T. Li, C.-Y. Wang, Chem. Eng. Commun. 203 (2016) 1641–1647, http://dx.doi. org/10.1080/00986445.2016.1230101.
- [3] H. Yu, H. Fang, H. Zhang, B. Li, F. Deng, Catal. Commun. 10 (2009) 920–924, http://dx.doi.org/10.1016/j.catcom.2008.12.023.
- [4] J. Yang, F. Zhang, X. Wang, D. He, G. Wu, Q. Yang, X. Hong, Y. Wu, Y. Li, Angew. Chem. - Int. Ed. 55 (2016) 12854–12858, http://dx.doi.org/10.1002/anie. 201604315.
- [5] P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei, Y. Li, Angew. Chem. - Int. Ed. 55 (2016) 10800–10805, http://dx. doi.org/10.1002/anie.201604802.
- [6] C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu, Y. Li, J. Am. Chem. Soc. 139 (2017) 8078–8081, http://dx.doi.org/10.1021/jacs.7b02736.
- [7] H. Liu, L. Chang, L. Chen, Y. Li, J. Mater. Chem. A 3 (2015) 8028–8033, http://dx. doi.org/10.1039/C5TA00030K.
- [8] H. Ramezanalizadeh, F. Manteghi, Monatshefte Für Chem. Chem. Mon. 148 (2017) 347–355, http://dx.doi.org/10.1007/s00706-016-1776-9.
- [9] K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 10186–10191, http://dx.doi.org/10.1073/pnas.0602439103.
- [10] X.L. Yang, L.M. Qiao, W.L. Dai, Microporous Mesoporous Mater. 211 (2015) 73–81, http://dx.doi.org/10.1016/j.micromeso.2015.02.035.
- [11] M. Chen, J. Yan, Y. Tan, Y. Li, Z. Wu, L. Pan, Y. Liu, Ind. Eng. Chem. Res. 54 (2015) 11804–11813, http://dx.doi.org/10.1021/acs.iecr.5b02746.
- [12] M. Saikia, D. Bhuyan, L. Saikia, Appl. Catal. A Gen. 505 (2015) 501–506, http://dx. doi.org/10.1016/j.apcata.2015.05.021.
- [13] A.E.R.S. Khder, H.M.A. Hassan, M.S. El-Shall, Appl. Catal. A Gen. 487 (2014) 110–118, http://dx.doi.org/10.1016/j.apcata.2014.09.012.
- [14] J. Juan-Alcañiz, E.V. Ramos-Fernandez, U. Lafont, J. Gascon, F. Kapteijn, J. Catal. 269 (2010) 229–241, http://dx.doi.org/10.1016/j.jcat.2009.11.011.
- [15] X.-S. Wang, Y.-B. Huang, Z.-J. Lin, R. Cao, Dalt. Trans. 43 (2014) 11950–11958, http://dx.doi.org/10.1039/C4DT01043D.
- [16] L. Bromberg, X. Su, T.A. Hatton, ACS Appl. Mater. Interfaces 5 (2013) 5468–5477, http://dx.doi.org/10.1021/am400494y.
- [17] L.H. Wee, S.R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C.E. a Kirschhock, J. a Martens, Chem. Commun. (Camb.) 46 (2010) 8186–8188, http://dx.doi.org/10. 1039/c0cc01447h.
- [18] S.S. Nadar, V.K. Rathod, Int. J. Biol. Macromol. 95 (2017) 511–519, http://dx.doi. org/10.1016/j.ijbiomac.2016.11.084.
- [19] J. Liu, J. He, L. Wang, R. Li, P. Chen, X. Rao, L. Deng, L. Rong, J. Lei, Sci. Rep. 6 (2016) 1–11, http://dx.doi.org/10.1038/srep23667.
- [20] M. Ammar, S. Jiang, S. Ji, J. Solid State Chem. 233 (2016) 303–310, http://dx.doi. org/10.1016/j.jssc.2015.11.014.
- [21] K. Liang, R. Ricco, C.M. Doherty, M.J. Styles, S. Bell, N. Kirby, S. Mudie, D. Haylock, A.J. Hill, C.J. Doonan, P. Falcaro, Nat. Commun. 6 (2015) 4–11, http://dx.doi.org/ 10.1038/ncomms8240.
- [22] R.S. Malkar, G.D. Yadav, Ind. Eng. Chem. Res. 56 (2017) 8437–8447, http://dx.doi. org/10.1021/acs.iecr.7b01454.
- [23] M.S. Tiwari, A.B. Gawade, G.D. Yadav, Green. Chem. 19 (2017) 963–976, http://dx. doi.org/10.1039/C6GC02466A.
- [24] J. Molleti, M.S. Tiwari, G.D. Yadav, Chem. Eng. J. 334 (2018) 2488–2499, http:// dx.doi.org/10.1016/j.cej.2017.11.125.
- [25] A.F. Gross, E. Sherman, J.J. Vajo, Dalt. Trans. 41 (2012) 5458, http://dx.doi.org/ 10.1039/c2dt30174a.
- [26] M.S. Tiwari, G.D. Yadav, Chem. Eng. J. 266 (2015) 64–73, http://dx.doi.org/10. 1016/j.cej.2014.12.043.
- [27] S.R. Venna, J.B. Jasinski, M. a Carreon, J. Am. Chem. Soc. 132 (2010) 1–6, http:// dx.doi.org/10.1021/ja109268m.
- [28] S. Lazare, D. Bazer-bachi, F. Bonnier, E. Soyer, A. Quoineaud, N. Bats, J. Am. Chem. Soc. 132 (2010) 12365–12377, http://dx.doi.org/10.1021/ja103365s.
- [29] W. Dai, N. Tian, C. Liu, L. Yu, Q. Liu, N. Ma, Y. Zhao, (Zn, Ni, Cu) -BTC Functionalized With Phosphotungstic Acid for Adsorptive Desulfurization in the Presence of Benzene and Ketone, (2017), http://dx.doi.org/10.1021/acs. energyfuels.7b02851.
- [30] N.A.H. Md Nordin, S.M. Racha, T. Matsuura, N. Misdan, N.A. Abdullah Sani, A.F. Ismail, A. Mustafa, RSC Adv. 5 (2015) 43110–43120, http://dx.doi.org/10. 1039/C5RA02230D.
- [31] Y. Hu, H. Kazemian, S. Rohani, Y. Huang, Y. Song, Chem. Commun. 47 (2011) 12694, http://dx.doi.org/10.1039/c1cc15525c.
- [32] Y. Zhang, V. Degirmenci, C. Li, E.J.M. Hensen, ChemSusChem. 4 (2011) 59–64, http://dx.doi.org/10.1002/cssc.201000284.
- [33] M. Jian, B. Liu, R. Liu, J. Qu, H. Wang, X. Zhang, RSC Adv. 5 (2015) 48433–48441, http://dx.doi.org/10.1039/C5RA04033G.
- [34] S.H. Pang, C. Han, D.S. Sholl, C.W. Jones, R.P. Lively, Chem. Mater. 28 (2016) 6960–6967, http://dx.doi.org/10.1021/acs.chemmater.6b02643.
- [35] C.-Y. Sun, C. Qin, X.-L. Wang, G.-S. Yang, K.-Z. Shao, Y.-Q. Lan, Z.-M. Su, P. Huang,

C.-G. Wang, E.-B. Wang, Dalt. Trans. 41 (2012) 6906, http://dx.doi.org/10.1039/c2dt30357d.

- [36] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, The Properties of Gases and Liquids, 3rd ed., McGraw-Hill, New York, 1977.
- [37] H. Fogler, Elements of Chemical Reaction Engineering, 2nd ed., Prentice-Hall, New Delhi, 1995.
- [38] G.D. Yadav, N.S. Asthana, Appl. Catal. A: Gen. 244 (2003) 341–357, http://dx.doi. org/10.1016/S0926-860X(02)00605-1.
- [39] M.S. Tiwari, G.D. Yadav, RSC Adv. 6 (2016) 49091–49100, http://dx.doi.org/10. 1039/C6RA05379C.
- [40] P.R. Tambe, G.D. Yadav, J. Chem. Sci. 129 (2017) 1771–1779, http://dx.doi.org/ 10.1007/s12039-017-1395-y.