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Introduction

Metal-organic frameworks (MOFs),¹⁻⁸ including zeolitic imidazolate frameworks (ZIFs), are attractive porous materials with several outstanding properties.^{5,9–12} However, microporous ZIFs (pore size <2 nm) such as ZIF-8 may have a low diffusion rate for reactants with a large size (>2 nm).¹³ Thus, hierarchical porous ZIFs (HPZIFs) containing two different pore regimes (micropore-mesopore, or mesopore-macropore), may improve the low rate of diffusion of reactants and products leading to higher performance compared to microporous materials. Thus, several methods were reported for the synthesis of HPZIFs. Template molecules, such as surfactants,^{14,15} polystyrene,¹⁶ organic dyes,¹¹ and metal oxides,¹⁷ are usually required for the synthesis of extra pores. Some of these reagents are environmentally unfriendly and expensive. The synthesized materials require post-synthetic procedures to remove the template molecules.¹⁷⁻²⁴ Thus, extra efforts should be made to improve the synthesis procedure and make it simpler with a tunable pore structure without the need for post-synthetic treatment.

Hierarchical porous ZIF-8 for hydrogen production via the hydrolysis of sodium borohydride[†]

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Hydrides show good performance for hydrogen gas storage/release. However, hydrogen gas release from hydrides via hydrolysis is a slow process and thus requires a catalyst. Herein, terephthalic acid (TPA) is used for the synthesis of a hierarchical porous zeolitic imidazolate framework (HPZIF-8). A mechanistic study of materials synthesis involved an *in situ* synthesis of zinc hydroxide nitrate nanosheets with an interplanar distance of 0.97 nm. Terephthalic acid modulates the pH value of the synthesis solution leading to the formation of HPZIF-8 with the Brunauer-Emmett-Teller (BET) surface area, Langmuir surface area, and total pore size of 1442 m² g⁻¹, 1900 m² g⁻¹, and 0.69 cm³ g⁻¹, respectively. The formed phases during the synthesis undergo fast conversion to HPZIFs at room temperature. The application of the prepared materials in the hydrolysis of NaBH₄ is reported. Acidity plays an important role in the catalytic performance of the materials. ZIF-8 prepared using terephthalic acid shows high catalytic activity with a hydrogen rate of 2333 mL_{H₂} min⁻¹ g_{cat}^{-1} (8046 mL_{H₂} min⁻¹ g_{Zn}^{-1}). The material exhibits high catalytic activity without any deterioration of its performance for several uses during continuous NaBH₄ feeding. There are no changes in the material's structure after catalysis indicating the high recyclability of the materials

> Hydrogen (H_2) gas is a clean energy source (the combustion byproduct is water). It can be produced by using several methods including water splitting or phototrophic microorganisms.²⁵⁻²⁸ Other methods,^{29,30} such as hydrolysis of hydride (e.g. sodium borohydride, NaBH₄), are promising for applications in direct borohydride fuel cells.^{31,32} Hydrides offer onboard H₂ for applications^{33,34} in unmanned airplanes, fuel cells,³⁵ and proton exchange membrane fuel cells, and can be used for hydrogen storage³⁶ and heat storage.³⁷ The hydrolysis of one mole of NaBH₄ produces four moles of H₂ (two moles from NaBH₄ and two moles from water molecules). Furthermore, NaBH₄ is lightweight and produces highly pure hydrogen with good hydrogen storage capacity (10.8 wt%). However, the hydrolysis process is kinetically unfavorable. Thus, several materials, $CuO(a)C,^{38}$ including Co@ZIF-8,³⁹ CoB@ZIF-8,⁴⁰ Ru@ZIF-67,⁴¹ have been investigated as catalysts to increase the hydrolysis rate *i.e.* the hydrogen generation rate. However, these materials are still under active development.

> Herein, the synthesis of hierarchical porous ZIF-8 using terephthalic acid (TPA) is reported. Zn₅(OH)₈(NO₃)₂(H₂O)₂ nanosheets, with an interplanar distance of 0.97 nm, were observed during the synthesis. Terephthalic acid (TPA) causes a pH drop (from 6.4 to 5.2) of the reaction solution which was modulated to be pH 10.2 using an organic linker, 2-methylimidazole (Hmim). All observed phases, except for using a high concentration of terephthalic acid, can be used for the formation of HPZIF-8 with tunable pore size. The materials

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show high efficiency for hydrogen production *via* sodium borohydride at a rate of 2333 $mL_{H_2} min^{-1} g_{cat}^{-1}$. The acidity of the prepared materials plays an important role in their catalytic performance.

Experimental

Materials and methods

 $Zn(NO_3)_2 \cdot 6H_2O$, NaBH₄, 2-methylimidazole (Hmim), terephthalic acid, and NaOH, were purchased from Sigma Aldrich (Germany). The solution of terephthalic acid (1 mM) was prepared in dimethylformamide (DMF).

Synthesis of HPZIF-8

A white precipitate of zinc hydroxide nitrate nanosheets was observed after the addition of NaOH (0.1 mL, 0.1 mmol) to the solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.8 mL, 0.84 M). A Hmim solution (8 mL, 3.0 M) was added to the previous solution. Then, water was added to adjust the final volume to 17 mL. The solution was stirred at room temperature for 30 min. The material obtained (denoted as ZIF-8 (NaOH)) was separated using centrifugation (13 000 rpm, 20 min), and washed using ethanol (2 × 20 mL). The material was dried in an oven at 85 °C overnight.

The synthesis of ZIF-8 using terephthalic acid was performed using the same procedure as mentioned above, except that a solution of terephthalic acid (1–5 mmol) was added before adding the solution of Hmim (8 mL, 24 mmol). All materials were separated using centrifugation and washed using ethanol (2×20 mL).

Hydrolysis of NaBH₄

ZIF-8 (synthesized using the previous procedure¹¹), ZIF-8 (NaOH), and ZIF-8 (TPA) were tested for the hydrolysis of NaBH₄. One hundred milligrams (100 mg) of each material was added to a NaBH₄ solution (0.19 g, in 100 mL) in a 100 mL flask at ambient temperature. The progress in the reaction was monitored *via* measuring the water volume using the water displacement method.³⁸

The effect of the catalyst amount was investigated using 100, 50, and 10 mg of ZIF-8 (TPA) following the same procedure as mentioned above. The recyclability of the catalyst was tested using 10 mg of ZIF-8 (TPA). After the first cycle, the reaction flask was charged with 0.19 g of NaBH₄. Following the same procedure, the effect of the NaBH₄ amount was investigated using 0.19 g (0.05 M), 0.38 g (0.1 M), and 1.5 g (0.4 M) in 100 mL H₂O. The flask was charged with NaBH₄ of different amounts. The rate of hydrogen generation (mL_{H₂} g_{cat}⁻¹ min⁻¹) was calculated using the following equation:

The rate of hydrogen generation (mL_{H₂} g_{cat}⁻¹ min⁻¹)
=
$$V_{H_2O}(mL) \times t^{-1}(min) \times wt_{cat}^{-1}(g)$$

where $V_{\rm H_2O}$ (mL) represents the water volume (mL) displaced by hydrogen gas in time (*t*), and wt refers to the weight of the catalyst in grams.

Characterization instruments

Powder X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert Pro diffractometer (Cu Ka1 radiation, wavelength, 1.54 Å). Transmission electron microscopy (TEM) imaging was carried out using JEM-2100 (JEOL, Japan) with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) imaging was carried out using SEM-7000 (JEOL, Japan). Nitrogen (N₂), and carbon dioxide (CO₂) adsorption-desorption isotherms (25 °C) were obtained using a Micromeritics ASAP 2020 instrument (UK). Pore size distribution was measured using nonlocal density functional theory (the NLDFT method, using N2@77 on carbon slit pores). Fourier transform infrared (FT-IR) spectra for Zn₅(OH)₈(NO₃)₂(H₂O)₂ and Zn₅(OH)₈(NO₃)₂(H₂O)₂ after the addition of TPA and Hmim were recorded using Shimadzu-470 via a KBr disc technique. The reaction after the addition of Hmim was immediately stopped using an ice bath and fast frozen (-65 °C) before freeze-drying using a freeze dryer (Alpha 1-2 LDplus, Martin Christ Gefriertrocknungsa, Germany). The final product i.e. TPA@ZIF-8 was also obtained. The amount of TPA in the final product was quantified using gas-chromatography mass spectrometry (GC-MS, Thermo Scientific[™] ISQ[™] 7000 Single Quadrupole GC-MS). 2-Methylimidazole was dissolved in chloroform (CHCl₃, HPLC grade). TPA@ZIF-8 was digested in HCl (12 M) using a sonication bath. The digested material was extracted using CHCl₃. An internal standard method was also reported using the Hmim solution.

Results and discussion

The schematic representation of the synthesis of HPZIF-8 using terephthalic acid (TPA) is shown in Fig. 1. The synthesis procedure is a one-pot approach involving the successive addition of NaOH, TPA, and Hmim solutions (Fig. 1). The homogenous solution of zinc nitrate is converted to a white precipitate consisting of Zn₅(OH)₈(NO₃)₂(H₂O)₂ using a controlled amount of NaOH (Fig. 2a).¹⁷ The crystal structure of $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ reveals that the interplanar distance between the $Zn_5(OH)_8^{2+}$ layers is 0.97 nm (Fig. 1). The SEM (Fig. S1[†]), and TEM (Fig. 3a) images of $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ indicate a sheet-like morphology of the formed phases. The XRD pattern of the observed phases in the presence of TPA was recorded (Fig. 3a). The XRD peaks of TPA are the predominant peaks indicating the dissolution of the formed phases due to acidity (Fig. 2a). After the addition of the Hmim solution, the ZIF-8 crystal was observed only at a low concentration of TPA (1 mmol, Fig. S2[†]). No ZIF-8 crystal was observed at a high concentration of TPA (>1 mmol, Fig. S2[†]). The materials were formed only after 2 h (Fig. 2b). According to XRD (Fig. 2b), the $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ crystal was formed after 1 h before the conversion to ZIF-8.

The formation of HPZIF-8 was tracked *via* following the changes in the pH value of the reaction solution (Fig. 1 and 4). The $Zn(NO_3)_2$ solution is acidic (a pH value of 5.3–6). After the addition of NaOH, the pH value increases to 6.5 and a white



Fig. 1 Schematic representation of hierarchical porous ZIF-8 formation using NaOH and terephthalic acid.



Fig. 2 XRD for (a) the observed phases before and after the addition of TPA acid, and (b) the formation of ZIF-8 using TPA acid.

precipitate of $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ is observed (Fig. 2a). $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ is stable in the pH range of 5–9.⁴² After the addition of the terephthalic acid solution, the reaction solution becomes acidic with a pH value of 5.2–5.5 (Fig. 4). The addition of Hmim (Hmim: Zn ratio of ~35) increases the pH value of the reaction solution to 10.5 for NaOH and terephthalic acid (1 mmol), while the pH value upon addition of high concentration terephthalic acid (5 mmol) reaches 9.2. Terephthalic acid dissolves the formed phase of $Zn_5(OH)_8(NO_3)_2$ ·2H₂O, thus it takes a long reaction time for



Fig. 3 TEM images of (a) Zn₅(OH)₈(NO₃)₂(H₂O)₂, (b) ZIF-8 (NaOH), and (c) ZIF-8 (TPA).



Fig. 4 pH changes of the reaction solutions during the synthesis of ZIF-8 using NaOH, and terephthalic acid (TPA).

the formation of ZIF-8 (Fig. 3b). The reaction takes place in two steps, first the re-formation of $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$, and second, the conversion to HPZIF-8 (Fig. 1). There is no formation of HPZIF-8 when there is a high concentration of terephthalic acid (Fig. S2[†]). This may be due to the interaction between terephthalic acid and the Zn^{2+} ions which prevents coordination between the Zn^{2+} ions and Hmim (Fig. S2[†]).

The chemical bonds and the changes occurred during the formation of ZIF-8 were also monitored using FT-IR spectroscopy (Fig. S3 and S4[†]). The FT-IR spectrum of $Zn_5(OH)_8(NO_3)_2$ ·2H₂O shows peaks at 1621 cm⁻¹, 1372 cm⁻¹, and 448 cm⁻¹ corresponding to the δ -vibration of the interlayer

water molecules, NO₃⁻ vibrations, and Zn-O vibrations, respectively (Fig. S3[†]). The peaks in the range of $500-1350 \text{ cm}^{-1}$ and $1350-1500 \text{ cm}^{-1}$ correspond to the bending and stretching of the imidazolate ring, respectively.¹¹ The FT-IR spectrum of the freeze-dried sample of Zn₅(OH)₈(NO₃)₂·2H₂O with TPA and Hmim shows the signals corresponding to the N-H bending and the stretching vibrations of free Hmim at 1675 and 1596 cm⁻¹ (Fig. S4[†]). The peak at 420 cm⁻¹ corresponds to Zn-N indicating the successful coordination of Hmim and Zn i.e. formation of the ZIF-8 crystal (Fig. S4[†]). The Zn-N bond is observed even after a short time *i.e.* in the freeze-dried sample (Fig. S4[†]). The FT-IR spectrum of TPA@ZIF-8 also shows a peak at 448 cm⁻¹ (Zn-O) indicating that TPA interacts with the Zn node of the ZIF-8 crystal (Fig. S4[†]). The presence of TPA can be confirmed by the appearance of the IR peak at 1695 cm⁻¹ which corresponds to the carbonyl group (C=O) of the carboxylic group of TPA (Fig. S4[†]). The amount of TPA in TPA@ZIF-8 was determined using GC-MS (Fig. S5-S8[†]). The mass spectra of Hmim, and TPA@ZIF-8 after digestion confirm the observation of Hmim, and TPA at retention times (RT) of 7.26 and 30.24 min, respectively (Fig. S5-S8[†]). The GC-MS data reveal that the percentage of TPA in TPA@ZIF-8 is 7.3% (Fig. S5-S8†).

The porosity of the materials is characterized by using N_2 adsorption–desorption isotherms (Fig. 5 and Table 1). Data reveal the formation of HPZIF-8 with tunable pore size (Fig. 4 and Table 1). The surface area of the synthesized hierarchical porous ZIF-8 using TPA is higher than that of ZIF-8 synthesized using NaOH alone (Table 1).^{43,44} The pore size distribution measured using NLDFT reveals a wide pore width (15–65 nm, Fig. 5b). The TEM images confirm the formation of the mesoporous structure (Fig. 3b and c). The mesopores are formed in the crystal (*i.e.* interparticle) as shown in Fig. 3b



Fig. 5 (a) N_2 adsorption (closed symbols)-desorption (open symbols) isotherms for hierarchical porous ZIF-8 using NaOH and TPA, and (b) pore size distribution using NLDFT.

Table 1 Textural properties of the prepared materials

Materials	$\binom{S_{\mathrm{BET}}}{(\mathrm{m}^2\mathrm{g}^{-1})}$	S _{Lan}	$S_{\rm Ext}$	$(\mathrm{cm}^3\mathrm{g}^{-1})$	V _{Micro}	V _{Meso}
ZIF-8 (NaOH)	1300	1350	97	0.56	0.42	0.14
ZIF-8 (TPA)	1442	1900	50	0.69	0.64	0.05

 $S_{\rm BET}$, BET surface area; $S_{\rm Lan}$, Langmuir surface area; $S_{\rm Ext}$, external surface area; $V_{\rm Total}$, total volume at P/P_0 at 0.99; $V_{\rm Micro}$, micropore volume; $V_{\rm Meso}$, mesopore volume.

and c. According to SEM images, the particle size of HPZIF-8 (NaOH) and HPZIF-8 (TPA) is 50–200 nm and 1–4 μ m, respectively (Fig. 6). The basic properties of the ZIF-8 surface have been characterized using CO₂ sorption (adsorption–desorption) isotherms as shown in Fig. 7a. Based on the adsorbed

amount of CO_2 , ZIF-8 prepared using TPA has the lowest basic character (Fig. 7b).

Hydrolysis of NaBH₄

The products of the reaction of $NaBH_4$ and water *i.e.* hydrolysis are hydrogen gas and sodium metaborate salt ($NaBO_2$). Kinetically, the process is slow and unfavorable. Thus, a catalyst is highly required. It was reported that metal-based materials are more active catalysts for hydride hydrolysis and hydrogen generation.⁴⁵

Herein, hydrogen production from NaBH₄ hydrolysis with and without catalysts is investigated (Fig. 8a). The hydrolysis of NaBH₄ without a catalyst is a very slow process (Fig. 8a). ZIF-8 enhances the hydrolysis of NaBH₄. On the basis of their performance, the materials can be arranged as ZIF-8 (TPA) > ZIF-8 > ZIF-8 (NaOH) > no catalyst in terms of reaction time (Fig. 8a).



Fig. 6 SEM images of (a) ZIF-8 (NaOH), and (b-d) ZIF-8 (TPA) with different magnifications.



Fig. 7 (a) CO₂ adsorption (closed symbols)-desorption (open symbols) isotherms, and (b) the adsorbed amount of CO₂ for different modulator species.



Fig. 8 (a) NaBH₄ hydrolysis using the synthesised materials, and (b) catalyst loading using ZIF-8 (TPA), [NaBH₄] = 0.05 M, T = 30 °C, stirring 1000 rpm.

ZIF-8 (TPA) requires only 18 min to reach the maximum hydrogen volume which was a very short time compared to those required by other materials. This observation is mainly due to its acidity. As discussed in the previous section, CO_2 adsorption reveals that ZIF-8 (TPA) has a highly acidic surface (Fig. 7). The difference in the hydrogen generated rate can also be observed by the naked eye *via* hydrogen bubbles collected under water (see Movie 1, ESI[†]).

The effect of the catalyst amount using ZIF-8 (TPA) is investigated as shown in Fig. 8b. A high catalyst amount requires a short time (18 min) to reach the maximum hydrogen production, while low catalyst loading needs a longer time (120 min). However, the efficiency shows an insignificant decrease for a catalyst loading of 10 mg indicating the high performance of the synthesized materials even at low catalyst loading.

The effect of NaBH₄ concentration (0.05, 0.1, and 0.4 M) has been investigated (Fig. 9a). The concentration continuously increased after a certain period leading to an increase in the volume of generated hydrogen (Fig. 9a). Data analysis



Fig. 9 (a) The effect of NaBH₄ loading (ZIF-8 (TPA, 10 mg)), and (b) recyclability using ZIF-8 (TPA, 10 mg), [NaBH₄] = 0.05 M, T = 30 °C, stirring 1000 rpm.



Fig. 10 XRD of ZIF-8 (TPA) after catalysis.

reveals the rate of hydrogen generation of 400 mL_{H₂} min⁻¹ g_{cat}^{-1} , 600 mL_{H₂} min⁻¹ g_{cat}^{-1} , and 2333 mL_{H₂} min⁻¹ g_{cat}^{-1} for 0.05 M, 0.1 M, and 0.4 M of NaBH₄, respectively (Fig. 9a). This observation indicates that the rate of hydrogen generation increases with an increase in the concentration of NaBH₄. It also reveals that hydrogen can be generated continuously *via* direct addition of NaBH₄ without the need to separate or activate the catalyst (Movie 2, ESI[†]).

The material can be recycled several times (three times) without any significant deterioration of its catalytic performance (Fig. 9b and Movie 2†). The catalyst was not separated after each run indicating no deterioration of the material's catalytic performance. This observation indicates that the catalyst needs no activation or treatment after catalysis. The high catalytic performance of ZIF-8 (TPA) is due to the high surface area of the material and the acidic character of its surface. The material's crystalline structure after catalysis is also preserved (Fig. 10).

Several mechanistic studies have been proposed to explain the hydrolysis of NaBH₄.³⁸ According to the reaction, half of the generated hydrogen atoms come from the water molecule *via* O–H bond cleavage of H_2O . This is the rate-determining step according to the kinetic isotope effect experiment.⁴⁶ The concentration of water (55.5 M) in our case is high compared to the NaBH₄ concentration (0.05-0.4 M) which indicates that it is a pseudo-first-order reaction. There are two models to explain NaBH₄ hydrolysis, called Langmuir-Hinshelwood, and Michaelis–Menten.³⁸ The large surface area of ZIF-8 offers many active sites. It was reported that the water molecules are dissociative on the surface of ZIF-8 forming Zn-OH.47 The ZIF-8 crystals offer acido-basic sites including alkaline OH and N⁻, Brønsted acid sites (N-H), and Lewis acid sites (low-coordinated zinc). Thus, the two reactants *i.e.* BH₄⁻ and H₂O can be adsorbed on the solid catalyst. The reaction may obey the Langmuir-Hinshelwood (LH) model. After the adsorption of BH₄⁻ and H₂O on the surface of ZIF-8, the adsorbed molecules undergo a bimolecular reaction producing H₂ and BH₃(OH)⁻ molecules. This process is followed by Na⁺BH₃H⁻···HOH via hydrogen bonding between a hydridic hydrogen atom (BH₃H⁻), and an acidic hydrogen atom of H₂O. Three successive reactions are followed giving 4 H₂ molecules and NaBO₂.

ZIF-8 materials offer many advantages compared to other materials (Table 2). The materials can be simply synthesized without the need for a solvothermal reaction⁴⁰ *i.e.* at room temperature with the need for only stirring. The synthesis takes place *via* one step without the need for multiple steps, or expensive reagents.⁴⁰ The materials were synthesized within a short reaction time including the separation step (Table 2). The materials have high chemical stability because of the

Table 2	Summary of some materials used for NaBH ₄ hydrolysis
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Catalyst	Synthesis conditions	Catalysis conditions	Rate ^a	Time (min)	Ref.
Co@ZIF-8	Two steps; DP(H ₂ O, N ₂ , RT, 2 h), followed by <i>in situ</i> reduction using NaBH ₄ (N ₂ , RT, 30 min)	Cat, 6 mol%; NaBH ₄ , 0.75 mmol, 30 °C	2935	10	39
CoB@ZIF-8	Two steps; solvothermal (MeOH, 120 $^{\circ}$ C, 4 h), followed by reduction using NaBH ₄ (EtOH, 35 $^{\circ}$ C)	Cat, 10 mg; NaBH ₄ , 1.67 wt%; NaOH, 5 wt%	453.6	700	40
Co@C-derived Co- MOF-71	Two steps; solvothermal (DMF, 110 °C, 24 h), carbonization of Co-MOF-71 (700 °C, 8 h, N ₂)	Cat, 20 mg; NaBH ₄ , 10 wt%; NaOH, 6 wt%; 30 °C	1680	70	45
Zn1Co1-Co@NC	Two steps; solvothermal (MeOH, 120 °C, 4 h), carbonization (900 °C, 3 h, He gas)	Cat, 10 mg; NaOH, 0.8 g; NaBH ₄ , 100 mg	1807	43	51
ZIF-8 (TPA)	One step (RT, 2 h)	Cat, 10 mg; NaBH ₄ , 1.5 g; 30 °C	$2333 \\ 8046^{b}$	7.5	Here

^{*a*} mL min⁻¹ g⁻¹. ^{*b*} mL_{H₂} min⁻¹ g_{Zn}⁻¹; deposition-precipitation, DP; DMF, *N*,*N*-dimethylformamide.

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strong coordination bonds of M (metal)–N (ligand).^{48–50} The materials have a large surface area and acidic surface properties. ZIF-8 (TPA) shows superior catalytic activity for NaBH₄ hydrolysis at ambient temperature. The catalyst shows a high hydrogen generation rate of 2333 mL_{H₂} min⁻¹ g_{ZIF8}⁻¹ (8046 mL_{H₂} min⁻¹ g_{Zn}⁻¹) which is higher than those of several other catalysts (Table 2). The catalyst can be used for several cycles without any deterioration of their catalytic performance and any change in the material's crystalline structure (Table 2). It can also be used for continuous charging of NaBH₄ with high catalytic performance. The large surface area of ZIF-8 causes no deactivation of the catalyst due to the deposition of borate species on their surface.⁵¹

Conclusions

Terephthalic acid assists the synthesis of hierarchical porous ZIF-8. It modulates the intermediated phase that formed during the reaction. The synthesis process produces a tunable mesopore structure with a high reactant diffusion rate. ZIF-8 synthesized using terephthalic acid shows high catalytic performance for NaBH₄ hydrolysis. The material provides a high hydrogen generation rate at room temperature in a short time. The catalysts are recyclable several times without any deterioration in their performance and any change in the material's crystalline structure. The reaction solution can be charged with a higher NaBH₄ amount in the presence of a catalyst without degrading the catalytic performance of the used catalyst. Our results offer several advantages which make the synthesis easier with outstanding catalytic performance.

Conflicts of interest

The authors declare no competing financial interests.

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