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Water soluble polymer stabilized iron(0) nanoclusters: A cost-effective and magnetically recoverable catalyst in hydrogen generation from the hydrolysis of sodium borohydride and ammonia borane

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Dedicated to Prof. Yuan Kou at Peking University on the occasion of his 65th birthday.

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ABSTRACT

Water soluble polymer stabilized iron(0) nanoclusters were prepared from the reduction of iron(III) chloride by sodium borohydride (SB) and ammonia borane (AB) mixture in the presence of polyethylene glycol (PEG) as stabilizer and ethylene glycol as solvent at 80 °C under nitrogen atmosphere. PEG stabilized iron(0) nanoclusters were isolated from the reaction solution by centrifugation and characterized by UV–Vis, TEM, HRTEM, XRD, ICP-OES and FT-IR methods. The particle size of PEG stabilized iron(0) nanoclusters ranges from 4.0 nm to 8.5 nm with a mean value of 6.3 nm. They are redispersible in water and yet highly active catalysts in hydrogen generation from the hydrolysis of SB and AB. They provide a turnover frequency of TOF = 6.2 and 6.4 min^{-1} for the hydrolysis of SB and AB at 25.0 ± 0.5 °C, respectively. The TOF values are the best ever reported for the iron catalysts and comparable to other non-noble metal catalyst systems in both hydrolysis reactions. Kinetics of hydrogen generation from the hydrolysis of AB in the presence of PEG stabilized iron(0) nanoclusters was also studied by varying the catalyst concentration, substrate concentration, and temperature. This is the first kinetic study on the hydrolysis of AB in the presence of an iron catalyst. Moreover, PEG stabilized iron(0) nanoclusters can be separated magnetically from the catalytic reaction solution using a magnet and show catalytic activity even after tenth run.

1. Introduction

Many efforts have been devoted to use hydrogen as an energy carrier in our daily life applications for a decade and many successful systems have been developed in recent years [1,2]. However, the development of an efficient and cost effective method for the hydrogen storage is still a key issue in hydrogen economy [3]. Chemical hydrides such as sodium borohydride ($NaBH_4$, SB) have been tested as solid state hydrogen storage materials because of their relatively high gravimetric hydrogen density and low molecular weights [4,5]. Recently, ammonia borane (H_3NBH_3, AB) has been attracting a great deal of attention as a hydrogen storage material due to its high hydrogen content (19.6 wt%) [6,7], stability and safety under fuel cell operating conditions [8]. Both SB and AB release hydrogen upon hydrolysis according to Eqs. (1) and (2), respectively, only in the presence of a suitable catalyst [9,10].

$$NaBH_4\ (aq) + 2H_2O\ (l) \xrightarrow{\text{catalyst}} NaBO_2\ (aq) + 4H_2\ (g) \qquad (1)$$

$$H_3NBH_3\ (aq) + 2H_2O\ (l) \xrightarrow{\text{catalyst}} (NH_4)BO_2\ (aq) + 3H_2\ (g) \qquad (2)$$

Many catalyst systems including transition metals and their alloys have been tested for hydrogen generation from the hydrolysis of AB [11], but only noble metal catalysts such as Pt, Rh and Ru [12,13] can provide rapid hydrogen generation. Due to the concerns over the practical use of such expensive metals as catalyst, the development of an effective and low-cost non-noble metal catalyst system to further improve the kinetic properties under moderate conditions is essential for the practical application of this system. In this regard, despite the fact that several nickel and cobalt catalysts have been reported in the hydrolysis of AB [14,15,11,16–18], to the best of our knowledge, there is only one study on the use of iron catalyst in the hydrolysis of AB [19], reporting that the amorphous iron nanoparticles generated in situ from the reduction of iron(II) sulfate by SB–AB mixture are active catalyst providing a turnover frequency of 3.1 min^{-1} in the hydrolysis of AB. Considering the fact that iron is the most ubiquitous of the transition metals, the development of more active and stable iron catalyst for the hydrolysis of AB is desired. One promising way of increasing activity is the use of transition metal(0) nanoclusters as catalysts because a large percentage of atoms lies on the surface of nanoclusters

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[20,21]. However, high reactivity of iron(0) nanoclusters towards agglomeration and oxidation restricts the application of oxygen free systems and requires the stabilization of nanoparticles [22]. Herein, we report the synthesis and characterization of iron(0) nanocluster catalysts stabilized by water soluble polymer and their use in hydrogen generation from the hydrolysis of SB and AB. Polymer stabilized iron(0) nanoclusters were prepared from the reduction of iron(III) chloride by a mixture of SB and AB in the presence of polyethylene glycol (PEG) in ethylene glycol (EG) solution at 80 °C. They are stable enough in solution to be isolated as solid material by centrifugation and characterized by UV–visible (UV–Vis) electronic absorption spectroscopy, transmission electron microscopy (TEM), high resolution-TEM (HRTEM), X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES) and FT-IR methods. PEG stabilized iron(0) nanoclusters are redispersible in water and yet show high catalytic activity in the hydrolysis of SB and AB. The hydrolysis of both substrates catalyzed by PEG stabilized iron(0) nanoclusters was followed by monitoring the volume of hydrogen generation versus time. Kinetics of catalytic hydrolysis of AB was studied depending on the catalyst concentration, substrate concentration, and temperature. This is the first kinetic study on the hydrolysis of AB in the presence of an iron catalyst. Moreover, PEG stabilized iron(0) nanoclusters can be recovered from the catalytic solution using a magnet and reused in the hydrolysis of AB at 25.0 ± 0.5 °C. Our approach for the preparation of polymer stabilized iron(0) nanoclusters is novel and provides the isolation of high quality iron(0) nanoparticles which can be redispersed and reused in subsequent catalytic runs without losing activity significantly.

2. Experimental

2.1. Materials

Iron(III) chloride hexahydrate (98%), sodium borohyride (98%), polyethylene glycol (average molecular weight = 2000 g mol^{-1}), ethylene glycol and borane ammonia complex (97%) were purchased from Aldrich®. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

2.2. Preparation of PEG stabilized iron(0) nanoclusters

PEG stabilized iron(0) nanoclusters were prepared from the reduction of iron(III) chloride by a mixture of SB and AB in the presence of PEG in ethylene glycol solution at 80 °C under continuous argon flow. In a 250 mL three-necked round bottom flask, 135 mg (0.5 mmol) of $FeCl_3{\cdot}6H_2O$ and 62 mg (1.0 mmol monomer unit) of PEG were dissolved in 15 ml of ethylene glycol (molar ratio of PEG to Fe is 2). The resultant mixture in ethylene glycol was refluxed under continuous stirring at 1000 rpm at 80 °C. Then, a mixture of 142.0 mg of SB and 32.0 mg AB dissolved in 1.0 mL water was quickly injected into the metal–polymer solution at 80 °C. The abrupt color change from pale yellow to black in less than 10 s indicates the completion of the reduction of iron(III) to iron(0) nanoclusters. The PEG stabilized iron(0) nanoclusters were separated from the solution by centrifugation at 6000 rpm for 10 min and dispersed in 10 mL water for catalytic application (see later).

2.3. Instrumentation

UV–Vis electronic absorption spectra of precursor metal salt and PEG stabilized iron(0) nanoclusters were recorded in aqueous solution on Varian-Carry 100 double beam instrument. Transmission electron microscope (TEM) images were obtained using a JEM-2100 (JEOL) instrument operating at 200 kV. The nanocluster solution prepared as described in Section 2.2 was centrifuged at 6000 rpm for 10 min. Then, the nanocluster sample was redispersed in 5 mL methanol. One drop of the diluted colloidal solution was deposited on the silicon oxide coated copper grid and evaporated under inert atmosphere. Samples were examined at magnifications between 100 and 800k. Particle size of the nanoclusters is calculated directly from the TEM image by counting non-touching particles. Size distributions are quoted as the mean diameter ± the standard deviation. X-ray diffraction (XRD) pattern was recorded on a Rigaku Miniflex diffractometer with CuKα (30 kV, 15 mA, $\lambda = 1.54051$ Å), over a 2θ range from 5° to 90° at room temperature. FT-IR spectra were recorded on a Bruker Vertex 70 spectrophotometer by an Attenuated Total Reflectance (ATR) module. The iron contents of the PEG stabilized iron(0) nanocluster samples after centrifugation were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Leeman-Direct Reading Echelle) after each sample was completely dissolved in the mixture of HNO_3/HCl (1/3 ratio).

2.4. Testing the catalytic activity of PEG stabilized iron(0) nanoclusters in the hydrolysis of SB and AB

The catalytic activity of PEG stabilized iron(0) nanoclusters was tested in the hydrolysis of SB or AB by measuring the rate of hydrogen generation. To determine the rate of hydrogen generation, a jacketed reaction flask (50.0 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer (Heidolph MR-301) and thermostated to 25.0 ± 0.5 °C by circulating water through its jacket from a constant temperature bath. Then, a graduated glass tube filled with water was connected to the reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction. Next, aliquot of nanoclusters in 10 mL water was transferred to the jacketed reaction flask. Firstly, PEG stabilized iron(0) nanoclusters were employed as catalysts in the hydrolysis of SB. In a typical experiment for the hydrolysis of SB, 76.0 mg (2.0 mmol) of $NaBH_4$ was dissolved in 1.0 mL water and injected into the nanocluster solution in the jacketed reaction flask at 25.0 ± 0.5 °C. After hydrogen generation from the hydrolysis of SB was completed in the presence of PEG stabilized iron(0) nanoclusters, 63.0 mg of AB dissolved in 1.0 mL water was injected into the reaction solution without any purification. The hydrogen generation from both hydrolyses in the presence of PEG stabilized iron(0) nanoclusters was measured every minute until no hydrogen gas evolution was observed.

2.5. Effect of PEG concentration on the catalytic activity of iron(0) nanoclusters in the hydrolysis of AB

In order to determine the effect of PEG concentration on the catalytic activity of iron(0) nanoclusters in the hydrolysis of AB (200 mM), catalytic activity tests were performed at 25.0 ± 0.5 °C starting with various PEG/Fe ratios in the range of 1–10 by keeping the initial concentrations of Fe, SB and AB constant at 0.5, 4.0 and 1.0 mmol, respectively. In all the experiments, the total volume of catalytic solution was kept constant at 10.0 mL and all experiments were performed following the same procedure as described in Section 2.2.

2.6. Kinetics of hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters

In order to determine the rate law for catalytic hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters, three different sets of experiments were performed as described in Section 2.2. Firstly, the AB concentration was kept constant at 200 mM and the Fe concentration was varied in the range of 5.0–30.0 mM at

25.0 ± 0.5 °C. Secondly, the iron concentration was kept constant at 25.0 mM and the AB concentration was varied in the range of 0.1–2.0 M. Finally, the catalytic hydrolysis reaction of AB in the presence of PEG stabilized iron(0) nanoclusters was performed at constant catalyst (25.0 mM) and constant AB (200 mM) concentration by varying the temperature in the range of 15.0–35.0 °C in order to obtain the activation energy.

2.7. Catalytic lifetime of PEG stabilized iron(0) nanoclusters in the hydrolysis of AB

In order to determine the catalytic lifetime of PEG stabilized iron(0) nanoclusters in the hydrolysis of AB, the total turnover number (TTON) was measured. Such an experiment was started with, 10.0 mL of aqueous solution containing PEG stabilized iron(0) nanoclusters catalyst (15.0 mM Fe) and 500 mM AB (160 mg) at 25.0 ± 0.5 °C. After the conversion of all AB present in the solution, checked by monitoring the stoichiometric H_2 gas evolution (3.0 mol H_2/mol H_3NBH_3), a new batch of 160.0 mg of AB was added and the reaction was continuing in this way until no hydrogen gas evolution was observed.

2.8. Reusability of PEG stabilized iron(0) catalyst in the hydrolysis of AB

A reusability test started with a 10.0 mL of aqueous solution containing PEG stabilized iron(0) catalyst (15.0 mM Fe) and 200.0 mM AB (62 mg) at 25.0 ± 0.5 °C. Next, PEG stabilized iron(0) nanoclusters were isolated from the reaction solution using a magnet when the hydrolysis was completed in each run. The magnetically recovered PEG stabilized iron(0) nanoclusters were redispersed in 10.0 mL water and a new catalytic run was started by the addition of a new batch of 62.0 mg AB as described in Section 2.2.

3. Results and discussion

3.1. Preparation and characterization of the PEG stabilized iron(0) nanoclusters

PEG stabilized iron(0) nanoclusters can be prepared from the reduction of iron(III) chloride by a mixture of SB and AB in the presence of polyethylene glycol (PEG) in ethylene glycol solution under inert atmosphere at 80 °C. PEG serves as stabilizer to prevent the agglomeration and oxidation of iron(0) nanoclusters in solution, which are highly reactive with respect to both agglomeration and oxidation. The mixture of SB and AB is used to reduce the metal precursor in the presence of PEG because the use of sole SB as a reducing agent results in the agglomeration of nanoparticles, a fact which has previously been observed by Xu et al. [19], and this agglomeration causes a decrease in catalytic activity (see later) [23]. The abrupt color change from pale yellow to black observed within 10 s after the addition of reducing agents into the solution of metal precursor indicates the reduction iron(III) to iron(0). The conversion of iron(III) chloride to iron(0) nanoclusters was nicely followed by taking UV–Vis electronic absorption spectra of the reaction solution during the preparation of PEG stabilized iron(0) nanoclusters (Fig. 1). Upon addition of the mixture of SB and AB into the solution, the absorption band of iron(III) ions at 240 nm [24] is replaced by the characteristic absorption continuum for iron(0) nanoclusters [25].

Iron(0) nanoclusters formed from the reduction of the precursor iron(III) chloride by SB–AB mixture in the presence of PEG stabilizer are stable in aqueous solution and no precipitation of bulk metal is observable in solution standing for weeks at room temperature in inert gas atmosphere. They can be isolated as solid material by centrifugation and characterized by TEM, SEM, EDX, XRD, ATR-IR, ICP-OES and UV–Vis electronic absorption spectroscopy. The iron content of nanocluster catalyst was determined by ICP-OES.

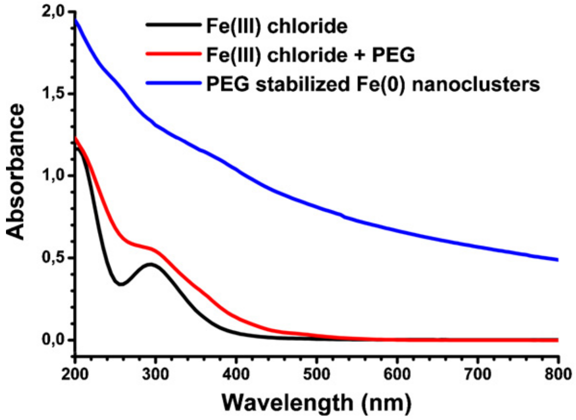

Fig. 1. UV–Vis electronic absorption spectra of iron(III) chloride in the presence of PEG before and after injection of sodium borohydride and AB mixture.

Fig. 2 shows the SEM image, the EDX spectroscopy elemental mapping image and the corresponding EDX spectrum of the PEG stabilized iron(0) nanoclusters. From the SEM image given in Fig. 2a it can be concluded that the iron(0) nanoclusters were embedded in the polymer matrix in powder form and it is impossible to see them from the low resolution SEM image due to their very small particle size. However, EDX elemental spectroscopy elemental mapping image given in Fig. 2b revealed that iron atoms are scattered almost homogenously inside the polymer matrix. In addition to SEM image, the elemental composition of the PEG stabilized iron(0) nanoclusters was determined by EDX elemental analysis. The EDX spectrum given in Fig. 2c revealed that PEG stabilized iron(0) nanoclusters consist of Fe, C, O and Cl atoms as expected. The Cl atoms originate from the metal precursor iron(III) chloride, C and O atoms come from the polymer matrix. No B peak was observed in the EDX spectrum indicating the removal of all boron residuals coming from the SB or AB.

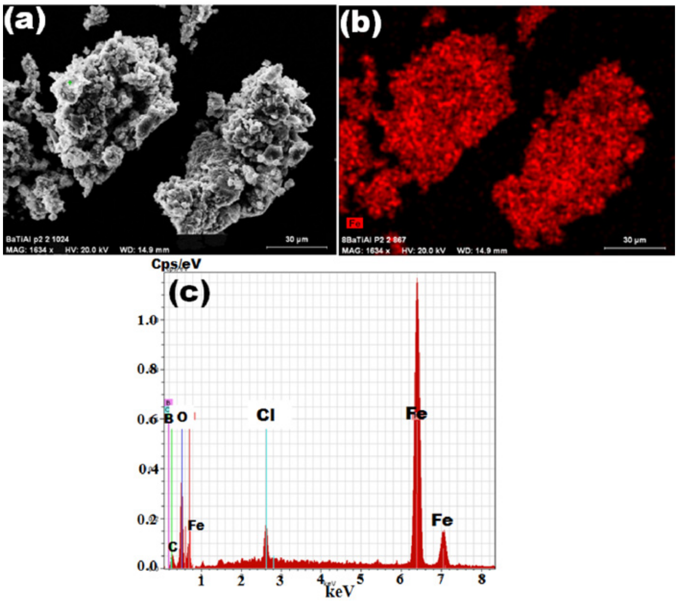

Fig. 2. (a) SEM image, (b) EDX spectroscopy elemental mapping image for Fe atoms and (c) corresponding EDX spectrum of the powder PEG stabilized iron(0) nanocluster samples.

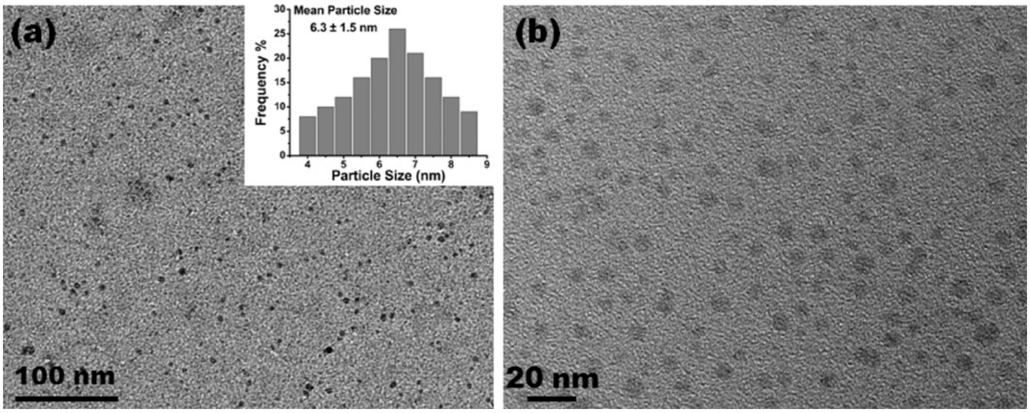

Fig. 3. (a) Low resolution TEM image with the inset showing the corresponding particle size histogram and (b) HRTEM image of PEG stabilized iron(0) nanoclusters.

The detailed morphology and particle size of the PEG stabilized iron(0) nanoclusters in solution were also studied by taking TEM and HR-TEM images (Fig. 3). In the TEM image, 100 untouching particles were counted for the construction of histogram. The particle size of PEG stabilized iron(0) nanoclusters ranges from 4.0 nm to 8.5 nm with a mean value of 6.3 nm (the inset in Fig. 3a).

As clearly seen from the HR-TEM image given in Fig. 3b, well-dispersed and nearly spherical nanoparticles were obtained without any agglomeration after the reduction of iron(III) chloride by SB–AB mixture in the presence of PEG. It is noteworthy that agglomeration of iron(0) nanoclusters is observed when SB is used as the sole reducing agent, which leads to the lower catalytic activity. Such an observation has also been reported by Xu et al. for the in situ generated iron nanoparticle catalysts in the hydrolysis of AB, whereby the rate of hydrogen generation and stability of the catalyst were increased by changing the reducing agent from the sole SB to the SB–AB mixture [19]. The powder XRD investigation has shown that the catalyst obtained using sole SB is composed of α-Fe crystallites whereas the latter exists in an amorphous phase. In the light of these results, we also investigated the crystallinity of two different catalysts by powder XRD. The PEG stabilized iron(0) nanoclusters prepared from the reduction of iron(III) chloride by SB–AB mixture are found to be amorphous (Fig. 4b), while the nanoclusters prepared using sole SB are composed of α-Fe crystallites with a larger particle size (Fig. 4a). Therefore, it can be concluded that the use of SB as a sole reducing agent for the preparation of iron(0) nanoparticles results in the crystalline catalyst with a larger particle size showing lower activity in the hydrolysis of AB, in line with the previous report [19]. To support the conclusion that an amorphous phase of iron was formed from the reduction of iron(III) chloride by SB–AB mixture, the amorphous PEG stabilized iron(0) nanocluster samples were annealed in an inert atmosphere [26]. The powder XRD pattern of the annealed sample showed that the amorphous phase of iron(0) nanoclusters changes into the crystalline counterpart.

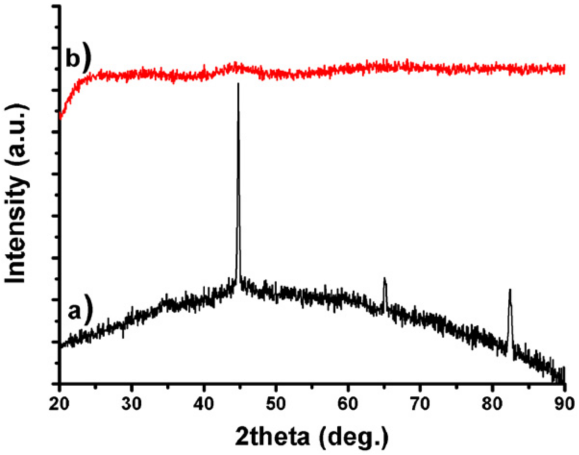

Fig. 4. X-ray diffraction patterns of PEG stabilized iron(0) nanoclusters prepared from the reduction of iron(III) chloride by (a) sodium borohydride and (b) a mixture of sodium borohydride and AB.

Fig. 5a shows the plots of volume of hydrogen versus time during the hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters at different PEG/Fe ratios. The inset in Fig. 5a shows the plot of the hydrogen generation rate versus the [PEG]/[Fe] ratio for the hydrolysis of AB at 25.0 ± 0.5 °C. As clearly seen from Fig. 5a, the hydrogen generation rate decreases with the increasing concentration of polymeric stabilizer after the ratio of 2 as expected [27]. The lower activity of iron(0) nanoclusters in the presence of one fold PEG was due to the agglomeration of the particles during the catalytic reaction. Additionally, TEM images of the PEG stabilized iron(0) nanoclusters at different PEG/Fe ratios of 2, 3, or 4 given in Fig. 5b, c and d, respectively, show that the increasing amount of PEG stabilizer results in the formation of larger particles embedded in the polymer matrix. Therefore, the activity of the iron(0) nanoclusters in the hydrolysis of AB decreases as a result of reduction of active surface area. The [PEG]/[Fe] ratio of 2 leads to the formation of small nanoparticles stabilized by polymer. By considering both the catalytic activity and the stability of the nanoclusters in the hydrolysis of AB, the [PEG]/[Fe] ratio of 2 was used for all the kinetic experiments.

The integrity of the PEG stabilizer was confirmed by comparing IR spectra of the PEG stabilized iron(0) nanoclusters and neat PEG, both taken using ATR cell (Fig. 6). The FT-IR spectra of neat PEG and PEG-stabilized iron(0) nanocluster samples essentially show no difference with the exception of C–O stretching bands. Only, a small lower energy shift is observed in the absorption band at around $1100\,\mathrm{cm}^{-1}$ for the C–O stretching of PEG molecule indicating that the PEG stabilizer coordinates to the iron(0) atoms on the nanoclusters surface through its O atoms. This shift in the C–O stretching band implies an interaction of electron density on the carbonyl oxygen atom with the partial positive charge on the surface of iron(0) nanoclusters, weakening the C–O bond due to the electron donation from the Lewis base oxygen to the Lewis acid, metal surface atoms.

3.2. Catalytic activity and kinetics of hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters

The well-characterized PEG stabilized iron(0) nanoclusters were employed as catalysts in the hydrolysis of SB and AB consecutively.

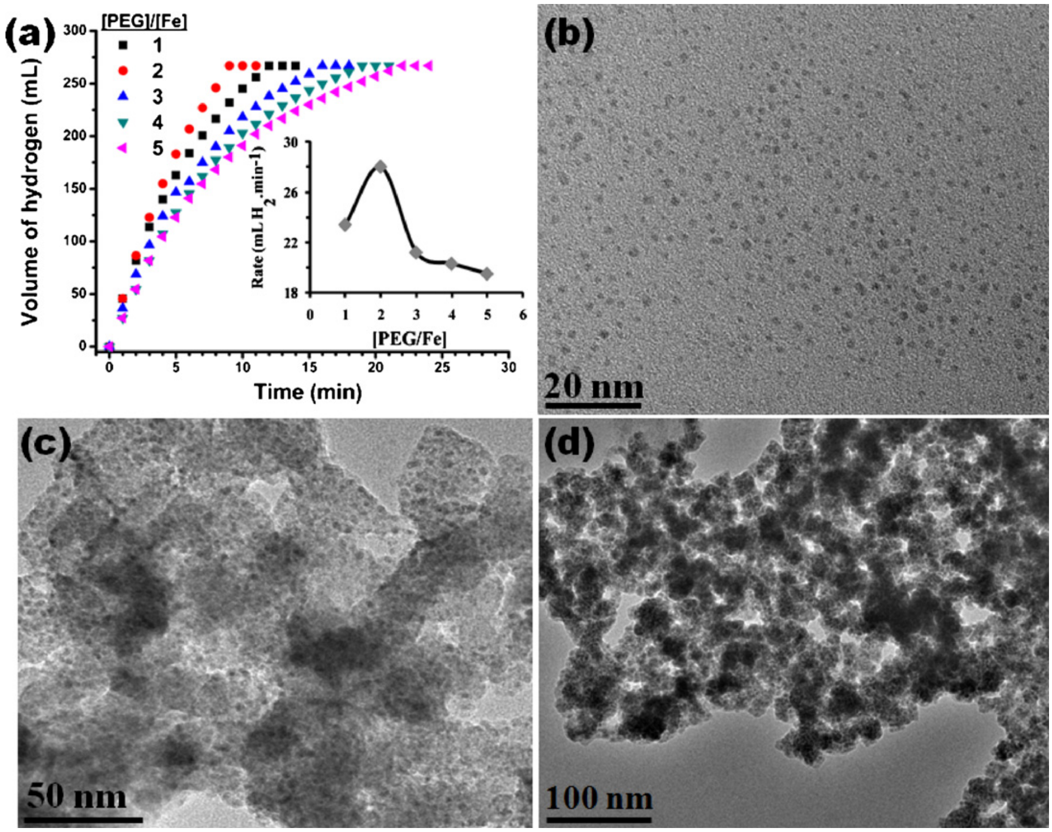

Fig. 5. (a) The plot of volume of hydrogen generated versus time during the hydrolysis of AB catalyzed by PEG stabilized Fe(0) nanoclusters at different PEGs to Fe ratio and TEM images of PEG stabilized Fe(0) nanoclusters at different [PEG]/[Fe] ratios, (b) [PEG]/[Fe] = 2, (c) [PEG]/[Fe] = 3 and (d) [PEG]/[Fe] = 4.

Fig. 7 shows the volume of hydrogen generation versus time during the consecutive hydrolyses of SB (150 mM) and AB (200 mM) in the presence of PEG stabilized iron(0) nanoclusters (25.0 mM Fe). The stoichiometric hydrogen gas generation (4 mol H_2/mol of SB and 3 mol H_2/mol of AB) was completed in less than 5 min for both hydrolysis reactions in the presence of PEG stabilized iron(0) nanoclusters corresponding to TOF values of 6.2 min^{-1} and 6.5 min^{-1} for the hydrolysis of SB and AB, respectively. The main achievement here is the preparation of nearly monodispersed iron(0) nanoclusters stabilized by a water soluble polymer, which are much more active and stable compared to the iron catalyst in situ generated without using any stabilizer [19]. Obviously, ammonia borane or its hydrolysis product does not provide enough stability for the iron(0) nanoparticles, therefore, only aggregates of 60 nm size have been observed in the absence of additional stabilizer [19].

After testing the activity of PEG stabilized iron(0) nanoclusters in the hydrolysis of both SB and AB, we performed a detailed kinetic study only on the hydrolysis of AB. Fig. 8a shows the plots the volume of hydrogen generated versus time during the catalytic hydrolysis of 200.0 mM AB solution in the presence of iron(0) nanoclusters starting with different catalyst concentrations

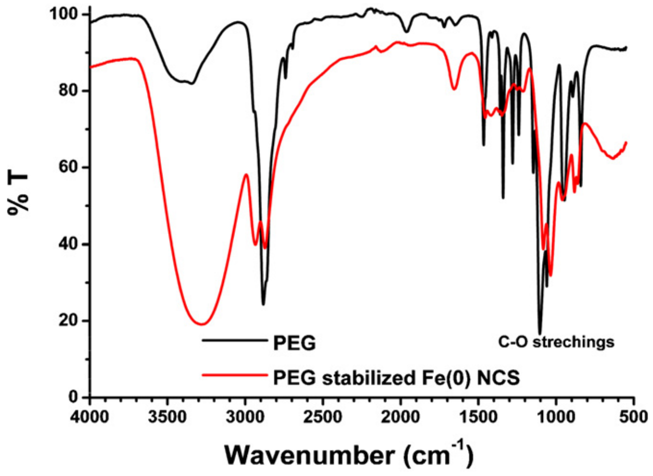

Fig. 6. IR spectra of PEG-stabilized iron(0) nanoclusters taken with ATR module.

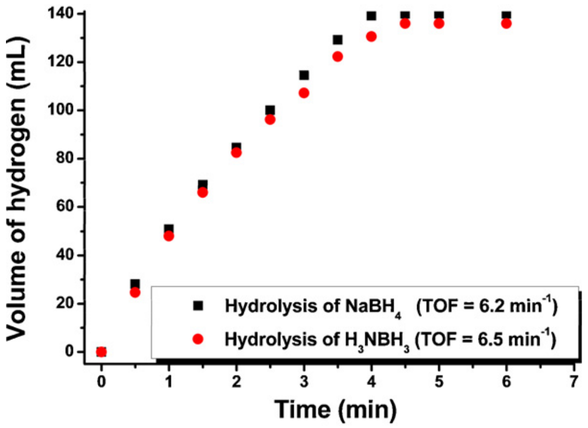

Fig. 7. Volume of hydrogen generation versus time plots for the hydrolysis of SB (150 mM) and then hydrolysis of AB (200 mM) in the presence of PEG stabilized iron(0) nanoclusters (25.0 mM Fe) at 25.0 ± 0.5 °C. AB was added to the solution after the complete hydrolysis of SB.

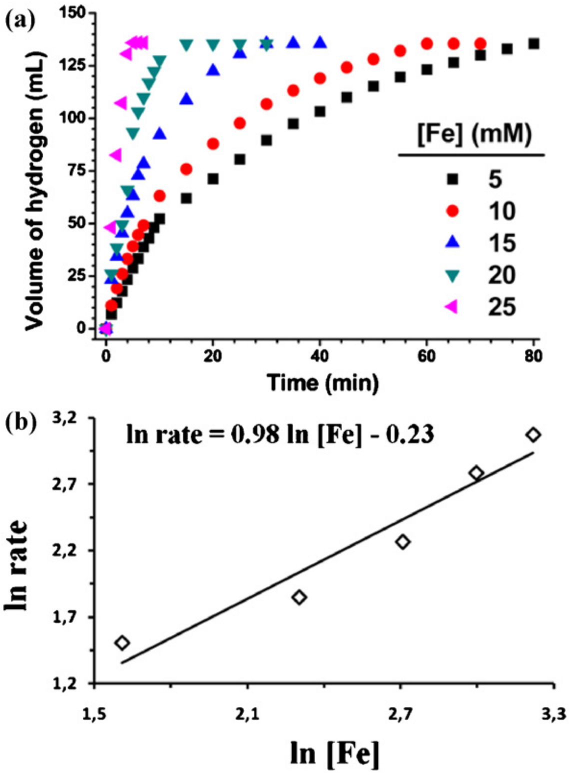

Fig. 8. (a) The volume of hydrogen versus time plots depending on metal concentration for PEG-stabilized iron(0) nanoclusters at 25.0 ± 0.5 °C. (b) The plot of hydrogen generation rate versus the concentration of metal (both in logarithmic scale).

at 25.0 ± 0.5 °C. The initial rate of hydrogen generation was determined from the initial, nearly linear portion of each plot for different catalyst concentrations. The hydrogen generation rate reached up to 36.4 mL H_2 min^{-1} for the hydrolysis of AB in the presence of iron(0) nanocluster catalyst (25.0 mM Fe) corresponding to a turnover frequency of 6.5 min^{-1}, which is the highest value ever reported for the hydrolysis of AB using iron catalyst. Fig. 8b shows the plot of hydrogen generation rate versus iron concentration, both in logarithmic scale. The line obtained has a slope of 0.98–1.00 indicating that the hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters is first order with respect to the catalyst concentration.

The effect of substrate concentration on the hydrogen generation rate was also studied by performing a series of experiments starting with different initial concentrations of AB while keeping the catalyst concentration constant at 25.0 mM Fe at 25.0 ± 0.5 °C (Fig. 9a). It is clearly seen from the slope of the rate versus concentration plot given in Fig. 8b that the hydrogen generation from the catalytic hydrolysis of AB in the presence of PEG stabilized iron(0) nanoclusters is a first order reaction with respect to the AB concentration in the range of 0.1–0.5 M AB. However, the deviation from the first order dependency is observed in the higher substrate concentration and the slope of the plot approaches to zero when the [AB]/[Fe] ratio is greater than 200, that is, the hydrogen generation from the catalytic hydrolysis of AB in the presence of PEG stabilized iron(0) nanoclusters becomes pseudo-zero order with respect to the AB concentration.

The hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters was carried out at various temperatures in the range of 15.0–35.0 °C starting with the initial substrate concentration of 200 mM AB and an initial catalyst concentration of 25.0 mM Fe. Fig. 10 shows the plot of volume of hydrogen generated versus time for the hydrolysis of AB in the presence of PEG stabilized iron(0) nanoclusters at five different temperatures. The values of rate constant k for the catalytic hydrolysis of AB were obtained from the slope of each plot in Fig. 10 and used to calculate the activation energy (Arrhenius plot is shown in the insets): $E_a = 37.0 \pm 2.0\ kJ\ mol^{-1}$.

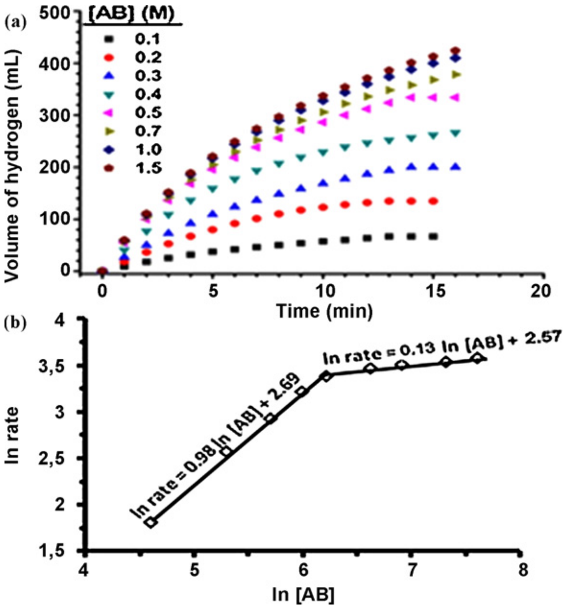

Fig. 9. (a) The volume of hydrogen versus time plots depending on the substrate concentrations at constant catalyst concentration for the hydrolysis of AB catalyzed by PEG stabilized Fe(0) nanoclusters (25.0 mM Fe) at 25.0 ± 0.5 °C. (b) The plot of hydrogen generation rate versus the concentration of the substrate (both in logarithmic scale).

A catalyst lifetime experiment was performed starting with PEG stabilized iron(0) nanoclusters (15.0 mM Fe) and 500 mM AB in 10.0 mL aqueous solution at 25.0 ± 0.5 °C. The PEG-stabilized iron(0) nanoclusters provide 1300 turnovers over 42 h before deactivation.

Fig. 11 shows the volume of hydrogen generation versus time during the reusability test of PEG stabilized iron(0) nanoclusters in the hydrolysis of AB at room temperature. During the reusability

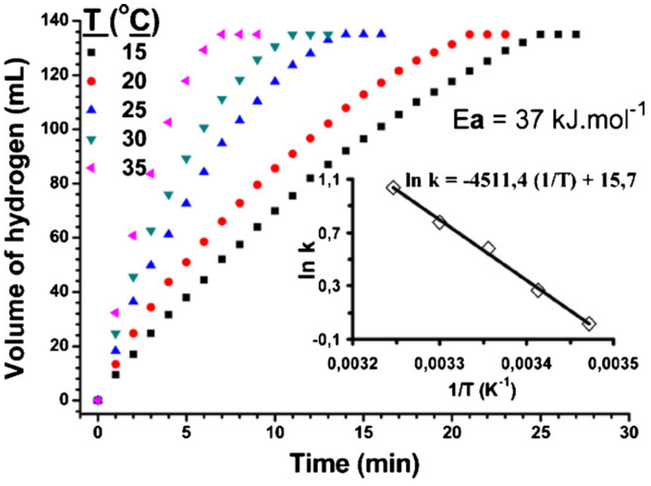

Fig. 10. The volume of hydrogen versus time plots at different temperatures for the hydrolysis of AB (200.0 mM) catalyzed by PEG-stabilized iron(0) nanoclusters (25.0 mM) in the temperature range 15.0–35.0 °C. The inset of the figure shows Arrhenius plot (ln k versus the reciprocal absolute temperature $1/T$ (K^{-1}).

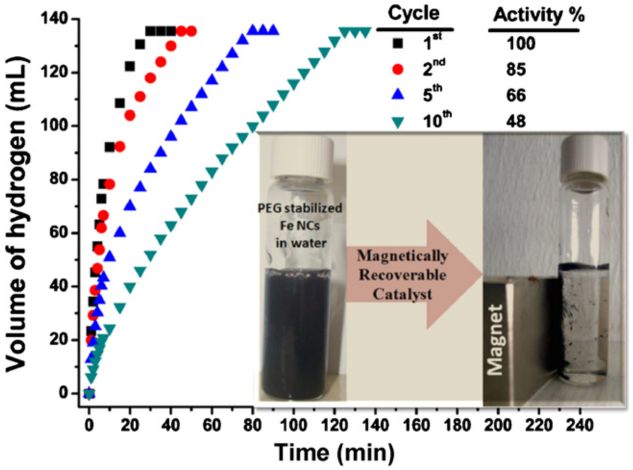

Fig. 11. Volume of hydrogen versus time plots for the hydrolysis of AB catalyzed by PEG stabilized iron(0) nanoclusters during the reusability test. The inset shows a photograph representing the magnetically recovery of PEG stabilized iron(0) nanoclusters after each catalytic run.

test, PEG stabilized iron(0) nanoclusters were recovered from the catalytic reaction solution after each catalytic run magnetically (Fig. 10). Magnetically recovery of nanoparticles has recently been demonstrated for hollow Co–B nanospindles in the hydrolysis of AB [29]. The reusability test shows that the PEG stabilized iron(0) nanoclusters retain 80% of its initial activity after 2nd run and 40% of its initial activity after 10th run.

4. Conclusions

To sum up, our study on the preparation and characterization of water soluble polymer stabilized iron(0) nanoclusters as catalysts in the hydrolysis of SB and AB leads to following conclusions and insights:

- Water dispersible iron(0) nanoclusters having average particle size of 6.3 ± 1.5 nm can be easily generated from the reduction of iron(II) chloride by SB and AB mixture in ethylene glycol at 80 °C.
- Our protocol yields nearly spherical iron(0) nanoclusters with uniform particle size distribution in water.
- PEG stabilized iron(0) nanoclusters were stable enough in solution to be isolated as solid material and characterized by TEM, SEM, EDX, XRD, ATR-IR, ICP-OES and UV–Vis electronic absorption spectroscopy.
- Powder XRD study reveals that PEG stabilized iron(0) nanoclusters prepared from the reduction of iron(III) chloride by sole SB exists in α-Fe crystalline structure which shows the lower stability and catalytic activity in the hydrolysis of AB than the amorphous ones obtained using SB–AB mixture.
- PEG stabilized iron(0) nanoclusters show high activity in hydrogen generation from the hydrolysis of both SB and AB at room temperature providing TOF values of 6.2 min^{-1} and 6.5 min^{-1}, respectively.
- The hydrogen generation from the hydrolysis of AB in the presence of PEG stabilized iron(0) nanoclusters is first order with respect to the catalyst concentration. However, it shows a variation at different substrate concentrations; first order in AB concentration in the range of 0.1–0.5 M and zero order in AB concentrations higher than 0.5 M.
- PEG stabilized iron(0) nanoclusters can be recovered from the catalytic reaction solution magnetically and retain 80% of their initial activity after 2nd and 40% after 10th run.

As a conclusion, easy preparation, cost-effectiveness, magnetically recoverability and high activity of PEG stabilized iron(0) nanoclusters make them promising candidate as catalyst in hydrogen generation from the boron based chemical compounds for proton exchange membrane fuel cells under ambient conditions.

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