



The preparation and use of p(2-acrylamido-2-methyl-1-propanesulfonic acid)-tris(dioxa-3,6-heptyl)amine (p(AMPS)-TDA-1) ionic liquid microgel in hydrogen production

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Abstract

Microgels of polymeric ionic liquid (PIL) combine the advantages of the both ionic liquids and polymeric microgels. The microgel in this work was prepared from 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) treated with tris(dioxa-3,6-heptyl) amine (TDA-1) (p(AMPS)-TDA-1), synthesized in a water in oil microemulsion via photo-irradiation, with a wavelength of 420 nm, for 2 h. The synthesized p(AMPS)-TDA-1 PIL microgels were then characterized via microscope, scanning electron microscope, Fourier transform infrared spectrometer, thermogravimetric analyzer, and zeta potential measurements. Applications of these PIL microgels were also investigated by using p(AMPS)-TDA-1 PIL as a template for in situ Co and Ni metal nanoparticle preparation and as a catalyst in the hydrolysis of NaBH₄ for H₂ production. The potential for p(AMPS)-TDA-1 PIL microgels as metal-free catalyst in the methanolysis of NaBH₄ for H₂ generation was explored as well. It was found that the metal-free p(AMPS)-TDA-1 PIL microgel displayed superior catalytic activity in methanolysis of NaBH₄ reaction with a hydrogen generation rate (HGR) of 854 ± 51.6 mL H₂/(min g of catalyst) and very low activation energy (E_a), 14.3 kJ/mol E_a . Reusability tests on the p(AMPS)-TDA-1 PIL microgel as a metal-free catalysis showed promising results; At end of the 10th trail, no decrease in the 100% conversion was observed with only 14% decrease in activity.

Keywords Poly ionic liquid microgel/nanogel · Metal-free smart microgel catalyst, methanolysis · H₂ production · Green catalyst

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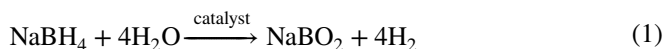
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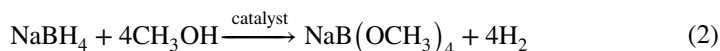
Introduction

At the end of eighteenth century and start of nineteenth century, research with ionic liquids had been started at different laboratories. One of the first known ionic liquids forms among all studies is ethyl ammonium nitrate $[\text{C}_2\text{H}_5\text{NH}_3]^+[\text{NO}_3]^-$ was synthesized by Paul Walden (1914) with a neutralization reaction of ethylamine and concentrated nitric acid [1]. Although this research did not garner notable interest at that time, Walden's research is now considered the original work in the field of ionic liquids. In general, ionic liquids (ILs) consist of cations and anions (i.e., salts) with a melting point at or below 100 °C [2]. Intriguing properties of ionic liquids, such as low vapor pressures, low flammability, high thermal stability, adjustable polarities, miscibility with other organic and inorganic compounds [3–5], give them many applications in the fields of energy and environmental science. ILs are also considered an ideal green solvent alternative to the organic solvents that are frequently used in separation science, the synthesis of specific compounds (drugs, etc.), and sensors [6–8]. Current industrial applications of ILs include catalysis [9], energy [10], organic and polymer chemistry [11], nanotechnology [12], electrochemistry [13], analytical chemistry [14], and biotechnology [15]. The polymerized forms of IL, also called poly(ionic liquid)s (PILs), are attractive area of research as they expand the applications of polymeric materials into the aforementioned fields [16].

Hydrogen (H_2) is a clean, eco-friendly, and green energy carrier from renewable sources and has great potential as a fuel source as it contains three times more energy than petroleum [17–20]. To overcome storage problems associated with H_2 gas, chemical hydrides, particularly NaBH_4 , have gained much attention in recent years as a precursor of pure H_2 due to its nonflammable, non-toxic and high theoretical hydrogen capacity [21, 22]. The total 10.8 wt% NaBH_4 is stored as H_2 can be released by hydrolysis reaction (Eq. 1) with the same amount of extra H_2 coming from water in the presence of catalyst with a controlled rates of hydrogen generation rates (HGRs) [21, 23, 24].



The hydrolysis of NaBH_4 in Eq. (1) is a pervasive method in H_2 generation; water is a readily available solvent, the reaction is eco-friendly, and NaBH_4 has high solubility in water compared to other solvents such as ethanol and methanol [25]. Complications arise due to the decrease in reaction rates between water and the by-product of Eq. (1), NaBO_2 , as well as unattainable reaction kinetics at low temperatures and have led researcher to seek new solvents and methods to utilize NaBH_4 [22, 26]. Alcoholysis studies using borohydrides have recently been reported [27–31] and offer a promising alternative to Eq. (1) with advantages such as elimination of freezing problems in hydrolysis reaction, fast HGRs, the elimination of the catalyst, and easy regeneration of reaction by-products via treatment with sodium hydride that regenerates sodium borohydride in a single step. Methanolysis of NaBH_4 proceeds from Eq. (2):



NaBH_4 is soluble in methanol (16.4 g NaBH_4 per 100 g CH_3OH) and reacts with the reaction medium, generating H_2 and sodium tetramethoxyborate. In addition to the common metal nanocatalyst for methanolysis reaction, metal-free catalyst can also be used in the generation of H_2 .

In this study, the synthesis of p(AMPS)-TDA-1 PIL microgels from the prepared AMPS-TDA-1 monomer was used in in situ metal nanoparticle preparation such as Co and Ni and employed as catalysts in hydrolysis and methanolysis reaction of NaBH_4 for H_2 production. Various parameters such as the amounts of catalyst and temperature in methanolysis of NaBH_4 were investigated as well as the sustainability of p(AMPS)-TDA-1 PIL microgels after multiple methanolysis of NaBH_4 reactions.

Experimental

Materials

The synthesis of the PIL microgel 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, 50% in water solution, Sigma-Aldrich) as the vinyl anionic monomer, tris(dioxa-3,6-heptyl)amine (TDA-1, 95%, Acros) as the ionic liquid cation, *N,N* methylene bisacrylamide (MBA, 98%, Sigma-Aldrich) as cross-linker, and 2,2 azobis (2-methyl-propionamide) dihydrochloride (AIBN, 97%, Aldrich) as a photo-initiator were used. To generate water in oil emulsion, Span 80 (viscosity 1000–2000 mPa s, Aldrich) was used as surfactant, and commercial gasoline (total, without lead, 98 octane) was used as oil medium. Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, >98%, Fluka) and nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, >98%, Acros) were used as metal sources, sodium borohydride (NaBH_4 , >98%, Merck) was used as reducing agent and hydrogen storage material in hydrolysis and methanolysis reactions. Methanol (>99%, Sigma-Aldrich) was used as a solvent for hydrogen production; acetone (technical grade, Kimetsan), ethanol (technical grade, Kimetsan), and double distilled (DD) water were used for the final washing of the microgels.

Synthesis of p(AMPS)-TDA-1 PIL microgels

The synthesis of PIL p(AMPS)-TDA-1 microgels was carried out by using reverse suspension polymerization technique in gasoline using Span 80 as an inverse suspension stabilizing agent. Initially, the monomer AMPS-TDA-1 was prepared prior to emulsification by the following literature [32]. TDA-1 was added dropwise to 5 mL of 50 wt% AMPS solution in DI water at 1:1 molar ratio while stirring in 1 h in an ice-bath and then stirred for another 1 h after the addition was complete. Next, 0.945 mL of this ionic liquid solution was mixed with 1.6 mL Span 80 and 10 mL gasoline. Prior to emulsification, the cross-linker, MBA, 10 mol% of used AMPS were added into the micro-emulsion solution, and the mixture was stirred at 1000 rpm for 5 min. After emulsification, 0.5 mL of freshly prepared initiator solution (AIB/AMPS in 1:10 molar ratio in DI water) was added to the mixture and stirred at 1000 rpm in a photoreactor (LZC-4, Luzchem, Canada, 420 nm) for

2 h. Finally, the synthesized p(AMPS)-TDA-1 PIL microgels were precipitated into excess acetone and centrifuged. The centrifugation was done using acetone–ethanol (50:50 v/v), ethanol, ethanol–water (50:50 v/v), and acetone, respectively, at 24,863g at 20 °C. The washed p(AMPS)-TDA-1 PIL microgels were dried with a heat gun and stored in closed tubes for further use. Under the same reaction condition, p(AMPS) microgels were synthesized in parallel as a control.

Characterization

For characterization of the p(AMPS)-TDA-1 PIL microgels, an optic microscope and scanning electron microscope (SEM) were used for size analysis, Fourier Transform Infrared (FT-IR) spectrometer for structural analysis, thermogravimetric analyzer (TGA) for thermal stability, and zeta potential measurements for the surface charge characterization.

SEM images of synthesized p(AMPS)-TDA-1 PIL microgels were acquired using an SEM (JEOL JSM-5600) with an operating voltage of 20 kV. For SEM characterization, the p(AMPS)-TDA-1 PIL microgels were placed onto carbon tape-attached aluminum SEM stubs at room temperature and coated with a gold film, a few nanometers in thicknesses, under vacuum.

The FT-IR spectrum of AMPS monomer, TDA-1 IL agent and p(AMPS)-TDA-1 PIL microgels was recorded by using FT-IR spectrometer (Thermo Nicolet iS10) equipped with attenuated total reflection (ATR) between 4000 and 650 cm^{-1} .

Thermal stabilities of AMPS, AMPS-TDA-1 and p(AMPS)-TDA-1 PIL microgels were compared via TG analysis (SII TG/DTA 6300, EXSTAR) under nitrogen atmosphere with a flow rate of 200 mL/min and heating rate of 10 °C/min from 90 to 900 °C.

Zeta potential of p(AMPS)-TDA-1 PIL microgels was measured by using a zeta potential analyzer (ZetaPlus, Brookhaven Inst. Corp., BIC) at 25 °C with the microgel suspension in DI water. The zeta potential values of p(AMPS)-TDA-1 PIL microgels were presented as an average of ten consecutive measurements.

Catalytic performances of p(AMPS)-TDA-1 microgels for hydrogen production from NaBH_4

In situ synthesis of metal nanoparticles within p(AMPS)-TDA-1 PIL microgels

To prepare the metal nanoparticle of Co and Ni, 0.15 g of p(AMPS)-TDA-1 PIL was placed into 300 ppm Co^{2+} and Ni^{2+} solutions in DI water to load these metal ions into the microgel networks. After loading the metal ions, the microgels were placed in 0.1 M NaBH_4 DI water solution and stirred at 250 rpm until no gas evolution was observed. The metal nanoparticle-containing microgel composites, p(AMPS)-TDA-1-M (M: Co, Ni) PIL, were then washed and dried in the above-mentioned manner and used for hydrogen production via hydrolysis of NaBH_4 . The metal ion content of p(AMPS)-TDA-1-M was determined by the atomic absorption spectroscopy from the metal ion solutions that were obtained via the treatment of

microgel composites with 5 M HCl, and the results of AAS measurements are given in Table 1. The amounts of metal nanoparticle content of p(AMPS)-TDA-1-M (M: Co and Ni) composites were found as 125.4 ± 5.1 and 131.7 ± 3.7 mg/g for Co and Ni, respectively.

Hydrolysis of NaBH_4

The synthesized p(AMPS)-TDA-1 PIL microgels and their Co and Ni metal-containing counterparts were used as catalysts in the hydrolysis NaBH_4 for H_2 production. Briefly, certain amount of p(AMPS)-TDA-1 PIL microgels and Co and Ni metal nanoparticle-containing microgel composites (0.05 g) were placed in 50-mL round bottom flask containing 20 mL DI water and 0.0965 g of NaBH_4 . This flask was connected to a 250-mL water-filled inverted cylinder that allows the measurements of produced H_2 from the reaction over time. The produced H_2 was accumulated in a 250-mL inverted graded cylinder filled with distilled (DI) water, and the generated H_2 from NaBH_4 reactions was recorded as a function of time by displacement of the DI water. The geodesic pressure of water in the measuring cylinder is not taken into account. The rate of hydrogen generation was compared repeated at least three times, and the average values were calculated and presented with the standard deviations.

Methanolysis of NaBH_4

Similar to the hydrolysis reaction, the methanolysis of NaBH_4 was carried out under the same conditions except substituting the reaction solvent of 20 mL DI water with 20 mL of methanol. The effect of the amount of catalysts, and the size of the microgel, the reaction temperature, and the sustainability of the catalyst was investigated. Different sizes of p(AMPS)-TDA-1 PIL microgels were obtained by separating the microgel suspension in methanol and centrifugation. The microgel suspension was centrifuged at 100, 500 and 1000 rpm at 18 °C, and the obtained particles were within a size range $> 5 \mu\text{m}$, $3\text{--}5 \mu\text{m}$, and $< 3 \mu\text{m}$. These particles with different size ranges were also used in the methanolysis of NaBH_4 .

Activation parameters

The activation parameters such as activation energy (E_a), enthalpy (ΔH), and the entropy (ΔS) for the methanolysis of NaBH_4 catalyzed by p(AMPS)-TDA-1PIL microgels were calculated from the reactions that were performed at different

Table 1 Metal nanoparticle content of p(AMPS)-TDA-1 PIL-M composites

Metal nanoparticle	Amount in p(AMPS)-TDA-1 PIL microgel (mg/g)
Co	125.4 ± 5.1
Ni	131.7 ± 3.7

temperatures, 0, 10, 25, 35, and 45 °C using Arrhenius (Eq. 3) and Eyring (Eq. 4) equations:

$$\ln(k) = \ln(A) - E_a/RT \quad (3)$$

$$\ln(k/t) = -(\Delta H/R)(1/T) + \ln(k_B/h) + \Delta S/R \quad (4)$$

where k is the reaction rate constant and was calculated according to a zero-order kinetic expression, E_a is the activation energy, T is the absolute temperature, k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), h is Planck's constant ($6.626 \times 10^{-34} \text{ J s}$), ΔH is the enthalpy, ΔS is the entropy and R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

Reuse of experiments

The reuse of metal-free p(AMPS)-TDA-1 PIL microgel catalyst in methanolysis of NaBH_4 reaction was carried out using 50 mg of catalyst, at 25 °C in 20 mL methanol containing 0.0965 g of NaBH_4 at 1000 rpm mixing rate. The same catalyst was used consecutively up to ten times in the methanolysis experiments by just adding 0.0965 g of NaBH_4 for each new experiment. The conversion is calculated based on Eq. (2), and the activation values were calculated by taking the ratio of initial 5 min hydrogen generation rates to each use of the catalyst.

Results and discussion

Synthesis and characterization of p(AMPS)-TDA-1 PIL microgels

There are two main pathways reported for the preparation of PIL microgels in the literature: (1) polymerization of ionic liquid monomers and (2) ion exchange reactions of polymerized materials [33–35]. Many PIL microgels have been converted to IL forms by using ion exchange mechanisms [36–38]. In this study, the prepared ionic liquid monomer was used in the polymerization and simultaneous cross-linking via photopolymerization reaction in water in oil micro-emulsion. Microgels of AMPS-TDA-1 were synthesized in a reverse suspension polymerization technique in gasoline using Span 80 as an inverse suspension stabilizing agent. The emulsifier/solvent volume ratio was varied to obtain different cross-linking densities for the microgel samples. The highest yield was obtained at a ratio of 1.6:10 (volume/volume). As presented in Fig. 1a, AMPS-TDA-1 monomer was prepared and used in the preparation of IL microgels using Span 80 as surfactant in gasoline, and MBA cross-linker as 10 mol% of the monomer in the presence of AIBN initiator.

This IL microgel precursor is irradiated at 420 nm under 1000 rpm mixing rate for 2 h, and the schematic presentation of PIL microgels synthesis scheme is shown in Fig. 1b. The optic microscope swollen in DI water and SEM images of the prepared p(AMPS)-TDA-1 microgels are given in Fig. 1c. It is clearly seen from optic microscope image that upon swelling in DI water, p(AMPS)-TDA-1 PIL microgel size increases up to a few tens of micrometers, and the SEM image also confirmed

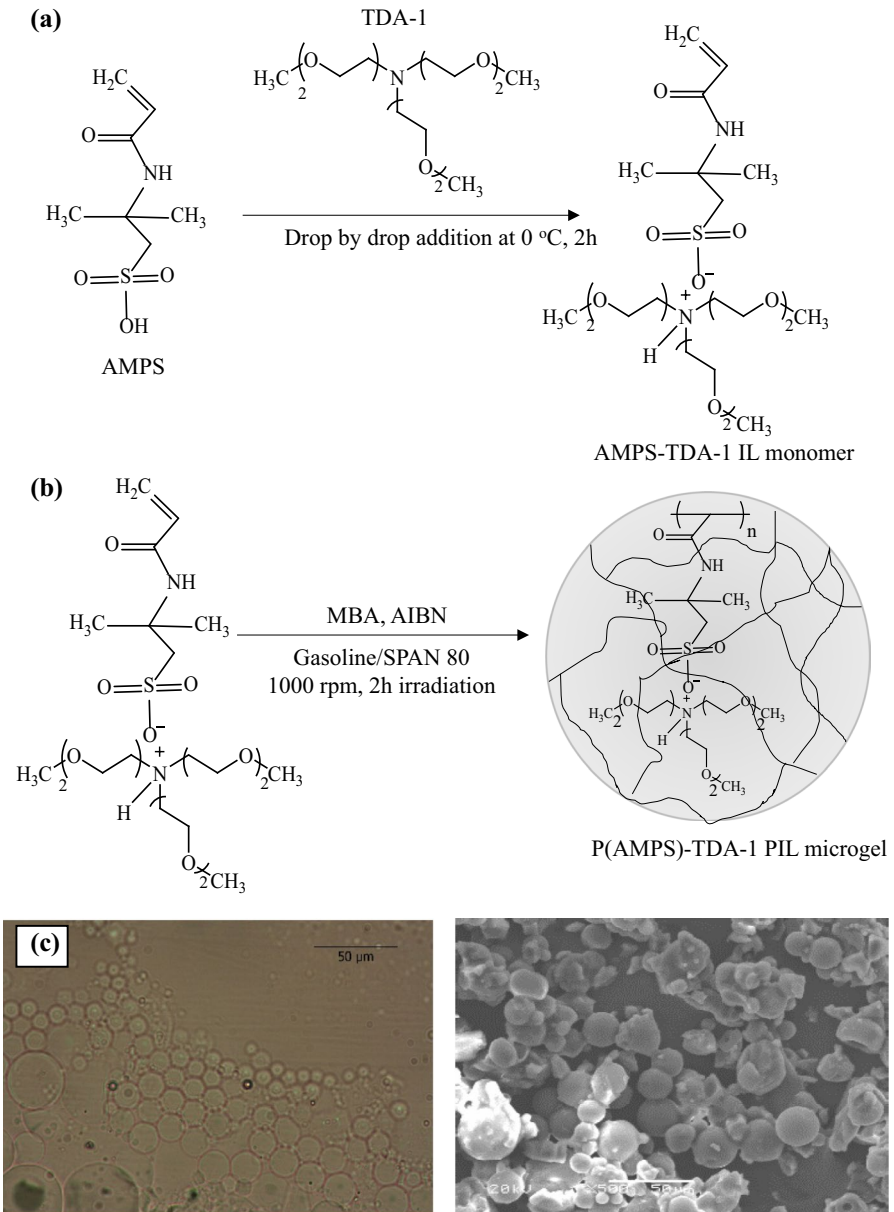


Fig. 1 The schematic presentation of **a** preparation of AMPS-TDA-1 IL monomer, **b** synthesis of p(AMPS)-TDA-1 PIL microgel, and **c** optic and SEM images of p(AMPS)-TDA-1 microgels

that the prepared p(AMPS)-TDA-1 PIL microgels are within a few μm (1–5 μm) in sizes in dried states.

The FT-IR spectra of TDA-1 agent, AMPS monomer, and p(AMPS)-TDA-1 PIL microgels were recorded and are illustrated in Fig. 2a. In the FT-IR spectrum

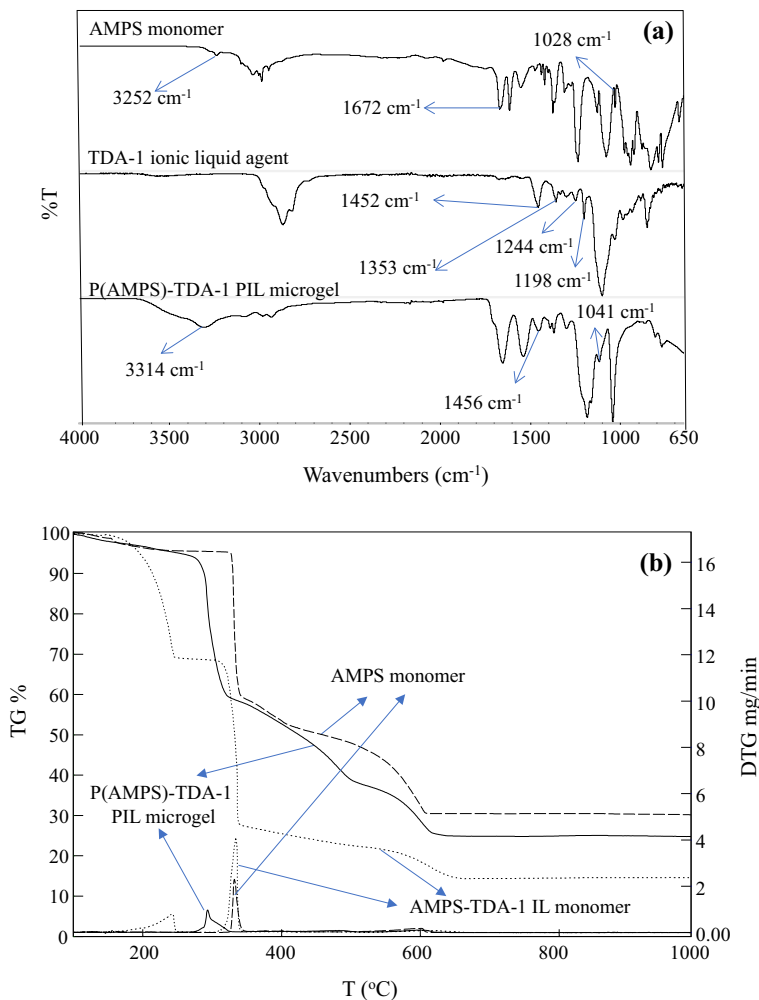


Fig. 2 **a** FT-IR spectra of AMPS, TDA-1, and p(AMPS)-TDA-1 and **b** TGA thermograms of AMPS, AMPS-TDA-1 IL monomer, and p(AMPS)-TDA-1 PIL microgels

of TDA-1, the C–H symmetric bending from O–CH₂ and O–CH₃ at 2868 and 2815 cm^{-1} , respectively, and C–H in-plane bending are observed at 1452 and 1353 cm^{-1} . Additionally, the C–C out-of-plane bending at 1097 and 771 cm^{-1} , C–N stretching at 1244 cm^{-1} , and C–N–C stretching vibrations at 1198 cm^{-1} were observed. The FT-IR spectrum of AMPS monomer also showed some characteristic peaks at 3252 cm^{-1} for N–H stretching and at 2981 and 2816 cm^{-1} for C–H stretching. The C=O stretching at 1672 cm^{-1} and S–O stretching at 1028 cm^{-1} are also present. The p(AMPS)-TDA-1 PIL microgels also show characteristic peaks from both AMPS monomer and TDA-1 ionic liquid agents. The N–H stretching peak shifted to 3314 cm^{-1} , C–H stretching peaks were observed at 2985 and 2824 cm^{-1} with small

shifts. The prominent peaks such as O–CH₂ peak were observed at 2868 cm⁻¹, in-plane bending of C–H at 1456 cm⁻¹, and the C–N–C stretching at 1186 cm⁻¹, and S–O stretching at 1041 cm⁻¹.

The thermal stabilities of AMPS monomer, AMPS-TDA-1 IL monomer, and p(AMPS)-TDA-1 PIL microgel were compared, and the corresponding thermograms are given in Fig. 2b. It is obvious from TGA thermogram of AMPS monomer that there are four main degradation steps: the first degradation was observed at 116 °C with 4.6% weight loss, the second one was observed up to 332 °C with 38.4% weight loss, the third one is at 408 °C with 47.6% weight loss, and the fourth at 602 °C with 69.5% weight loss. And almost complete degradation was occurred with 69.8% weight loss upon heating up to 900 °C. The degradation profile of prepared AMPS-TDA-1 IL monomer also displayed four steps: the first one was at 154 °C with 1% weight loss, and continued through temperatures up to 242, 335, 617 °C with 30, 71.4, and 85.5% weight losses for second, third and fourth degradation steps, respectively. The degradation of p(AMPS)-TDA-1 PIL microgels started at 184 °C with 5.6% weight loss, and 39.5% weight loss was observed at 293 °C in the second step, and the third step was observed at 482 °C with 61% weight loss, and the final step was seen at 604 °C with 74.6% weight loss. And upon heating up to 900 °C, the total of 75.1% weight loss was observed.

The surface charges of bare p(AMPS) and p(AMPS)-TDA-1 PIL microgels were also compared by suspending these microgels in 1 mM KCl solution and the average of 10 consecutive measurements are presented. It was found that the zeta potential of bare p(AMPS) microgel increased from -38.7 ± 1.3 to -24.2 ± 1.1 mV upon becoming p(AMPS)-TDA-1 PIL microgel. This is rational as the existence of amine groups of ionic liquid agents TDA-1 dissociation is much lower than the proton as in p(AMPS) microgels. Due to the neutralization of the protonated amine groups with sulfonic acid of IL agents (TDA-1), the increase in zeta potential p(AMPS)-TDA-1 PIL microgel is reasonable.

The sustainability of p(AMPS)-TDA-1-based PIL microgels as catalyst in H₂ production

Hydrolysis of NaBH₄

The hydrogen production from aqueous solution of NaBH₄ is called as hydrolysis. The p(AMPS)-TDA-1-M (M: Co, Ni) PIL microgel composites were used as catalysts in the hydrolysis of NaBH₄ using 0.0965 g of NaBH₄ containing 20 mL of DI water under 1000 rpm mixing rate at 25 °C, and corresponding generated H₂ versus time graph is given in Fig. 3a. No significance difference between self-hydrolysis (without catalyst) and bare p(AMPS)-TDA-1 PIL microgel (50 mg) as catalysts was observed, as the H₂ production was very slow, 82.5 ± 0.5 mL H₂ in 120 min and 105 ± 1.0 mL at 125 min, respectively. Comparatively, the Co and Ni metal nanoparticle containing p(AMPS)-TDA-1 microgel composites displayed superior catalytic activity than the bare p(AMPS)-TDA-1 PIL microgels. In the hydrolysis reactions, 10.6 mmol metal nanoparticle containing p(AMPS)-TDA-1-M

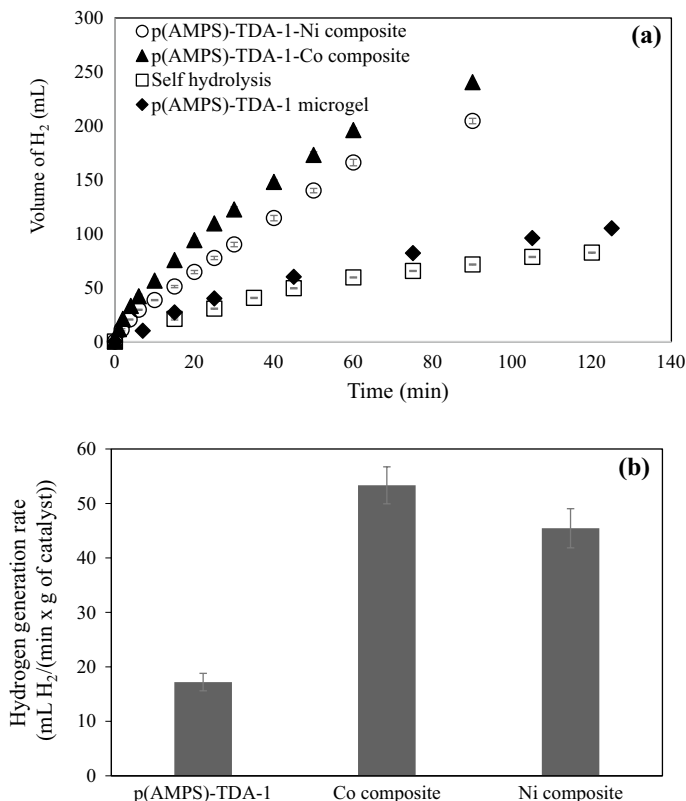


Fig. 3 **a** The hydrolysis of NaBH_4 reaction catalyzed by p(AMPS)-TDA-1-based PIL microgel and its Co and Ni metal nanoparticle-containing composites and **b** the comparison of their hydrogen generation rate (HGR) values [Reac. cond.: 50 mg of catalyst, 10.6 mol metal nanoparticle, 25 °C, 20 mL DD water, 0.0965 g of NaBH_4 , 1000 rpm mixing rate]

PIL microgel composites were used as catalyst in hydrolysis of NaBH_4 for H_2 production. The p(AMPS)-TDA-1-Co PIL microgel composite produced 251 ± 0.5 mL H_2 in 120 min, whereas p(AMPS)-TDA-1-Ni PIL microgel composite produced the same amount of H_2 (251 ± 0.5 mL H_2) in 210 min. The hydrogen generation rates (HGRs) for the hydrolysis reaction of NaBH_4 catalyzed by p(AMPS)-TDA-1-based PIL microgels were compared up to 200 mL H_2 production, given in Fig. 3b. It is clear that the p(AMPS)-TDA-1-Co PIL microgel composite resulted in better catalytic performance with 53 ± 3.4 mL H_2 /(min × g of catalyst) HGR, whereas p(AMPS)-TDA-1-Ni and p(AMPS)-TDA-1 PIL microgel composites HGR values were calculated as 45 ± 3.6 and 17 ± 1.6 mL H_2 /(min × g of catalyst), respectively. Upon the comparison of metal nanoparticles content of p(AMPS)-TDA-1 PIL microgels with unmodified p(AMPS) microgels reported in the literature [39], it was found that non-IL p(AMPS) microgels embedded lesser amounts of metal nanoparticles, e.g., 83.98 and 74.44 mg/g for Co and Ni metal nanoparticles versus 125.4 ± 5.1 and 131.7 ± 3.7 mg/g, respectively, for p(AMPS)-TDA-1 PIL microgels

composites. When comparing HGR, p(AMPS)-Co microgel composites were superior to p(AMPS)-TDA-1-Co composites, that is $88 \text{ mL H}_2/(\text{min} \times \text{g of catalyst})$ versus $53 \pm 3.4 \text{ mL H}_2/(\text{min} \times \text{g of catalyst})$, while HGR value of p(AMPS)-Ni composites was comparable with p(AMPS)-TDA-1-Ni composites with $47 \text{ mL H}_2/(\text{min} \times \text{g of catalyst})$ versus $45 \pm 3.6 \text{ mL H}_2/(\text{min} \times \text{g of catalyst})$ [39].

Methanolysis of NaBH_4

It was reported that PIL microgels can be used as free catalyst in methanolysis reaction of NaBH_4 [38, 40]. Our group reported very different polymer and materials that are modified with amine groups that can be used as IL materials as metal-free catalyst [41–44]. Based on these facts, the prepared p(AMPS)-TDA-1-based PIL microgels and composites were also tested as catalysts in methanolysis reaction of NaBH_4 for H_2 production. The graph of H_2 (mL) produced as a function of time (min) catalyzed by p(AMPS)-TDA-1 PIL microgels is illustrated in Fig. 4a. As can be seen, the self-methanolysis of NaBH_4 (without catalyst) was done using 0.0965 g of NaBH_4 containing 20 mL of methanol producing 250 mL H_2 at the end of 32.5 min. When comparing 50 mg of bare p(AMPS) versus p(AMPS)-TDA-1 PIL microgels, IL microgels-catalyzed methanolysis of NaBH_4 was better than bare p(AMPS) microgels as they both generate about 250 mL H_2 at 11 and 22 min, respectively. The Co and Ni metal nanoparticle composites of p(AMPS)-TDA-1 PIL microgels were also evaluated as catalysts in methanolysis of NaBH_4 , and it was observed that upon 10.6 mmol Co and Ni metal nanoparticle containing p(AMPS)-TDA-1-M microgels composites were used, almost similar catalytic activities were observed. And these are much lower than the catalytic activity of metal-free p(AMPS)-TDA-1 PIL microgels as their H_2 production capability were $218 \pm 2.5 \text{ mL H}_2$ and $200 \pm 3.5 \text{ mL H}_2$ at 20 min, respectively. Furthermore, as illustrated in Fig. 4b, the HGRs are also determined and compared and it is found that p(AMPS)-TDA-1 PIL microgel showed approximately fourfold better catalytic activity than its Co and Ni metal nanoparticle containing composites that are 854 ± 51.6 , 218 ± 15.2 , and $200 \pm 10.6 \text{ mL H}_2/(\text{min} \times \text{g of catalyst})$, respectively. The presence of metal nanoparticles in the PIL catalyst can reduce overall catalyst performance. This can be explained by means of competing effects of both catalysts for the same species as the mechanism of NaBH_4 methanolysis for metal nanoparticle is different than the functional groups on PIL as active sites [40]. The bare p(AMPS) on the other hand has HGR value of 684 ± 31.5 that is almost 1.25 times lesser than p(AMPS)-TDA-1 PIL microgel. Therefore, among all catalysts used in methanolysis reaction of NaBH_4 , metal-free p(AMPS)-TDA-1 PIL microgel showed better catalytic activities. Additionally, to determine the effect of p(AMPS)-TDA-1 PIL microgels size on H_2 production, microgels with different sizes such as $> 5 \mu\text{m}$, $3\text{--}5 \mu\text{m}$, and < 3 were separated by centrifugation as mention in Sect. 2.4.2 and used as catalyst in NaBH_4 methanolysis, and the corresponding H_2 versus time graph is shown Fig. 4c. It is apparent that there is no discernible size effect on H_2 generation. So that, the methanolysis of NaBH_4 catalyzed by p(AMPS)-TDA-1 PIL microgels was investigated in more detail without any filtration of the IL microgels.

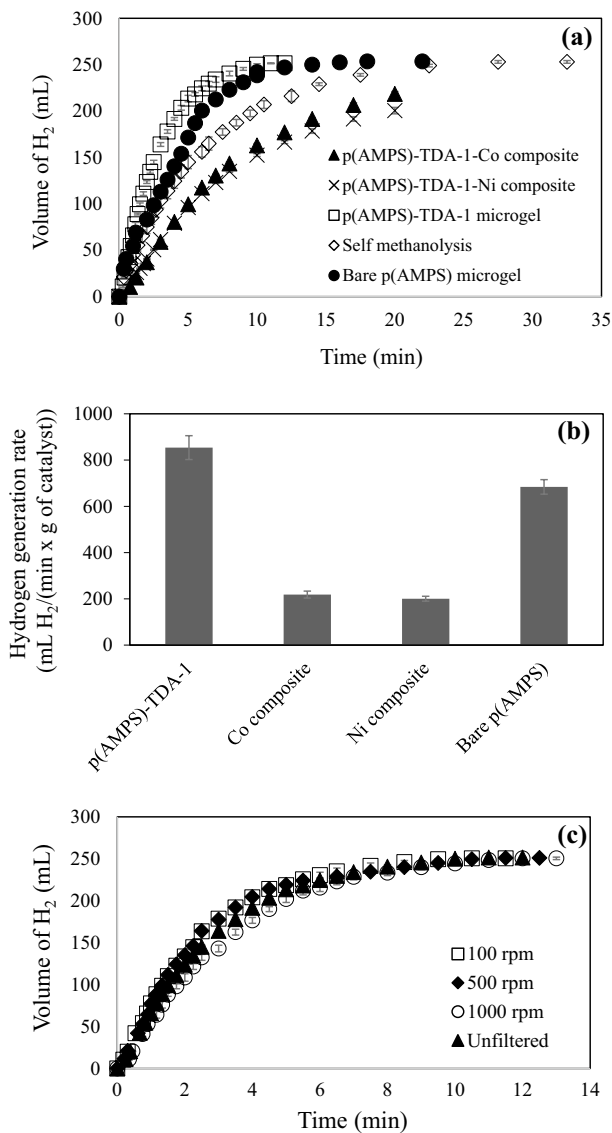


Fig. 4 **a** The methanolysis of NaBH₄ reaction catalyzed by p(AMPS)-TDA-1-based PIL microgel and its composites, **b** comparison of their HGR values and **c** the effect of p(AMPS)-TDA-1 microgel size on H₂ production. [Reac. cond.: 50 mg of catalyst, 10.6 mol metal nanoparticle, 25 °C, 20 mL methanol, 0.0965 g of NaBH₄, 1000 rpm mixing rate]

The effect of p(AMPS)-TDA-1 PIL catalyst amount in methanolysis of NaBH₄ To investigate the effect of catalyst amount in the methanolysis reaction of NaBH₄ for H₂ production, the methanolysis reaction was carried out with different amounts of catalyst, e.g., 10, 25, 50, 100, and 200 mg of p(AMPS)-TDA-1 PIL microgel catalysts. As demonstrated in Fig. 5a, there is no change in volume of the produced

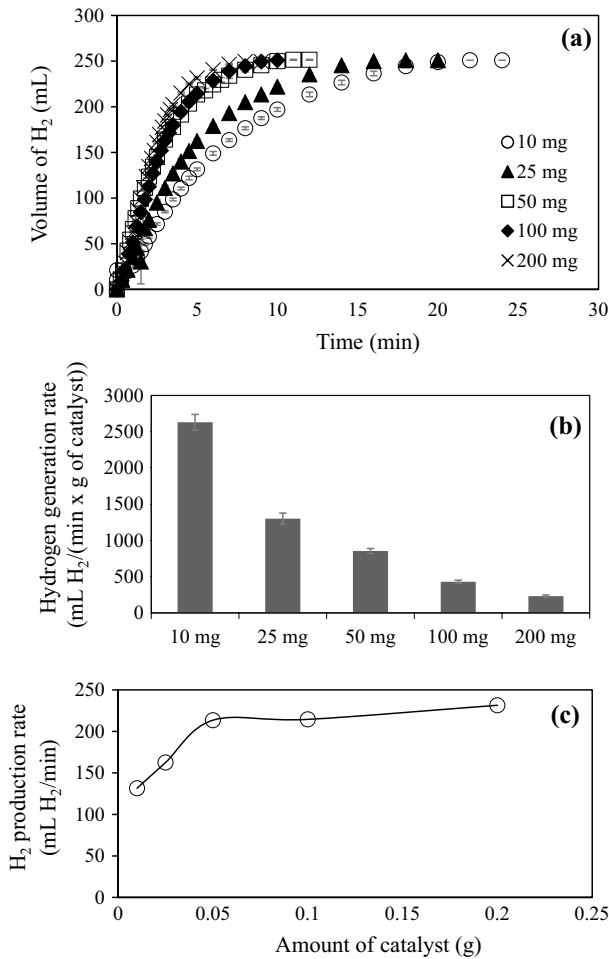


Fig. 5 a The effect of (AMPS)-TDA-1 PIL microgels catalyst amount on methanolysis of NaBH₄, b the comparison of their HGR values, and c the comparison of their reaction rates. [Reac. cond.: 25 °C, 20 mL methanol, 0.0965 g of NaBH₄, 1000 rpm mixing rate]

H₂ with the change in amount of catalysts. In other words, the produced amount of H₂ is the same at any given amounts of catalyst or independent from the amounts of catalyst as each amounts of catalysts provided 100% conversions. Alternatively, the time to produce the same amounts of H₂, for example 250 mL of H₂, was 24, 20, 12, 10, and 9 min by 10, 25, 50, 100, and 200 mg of p(AMPS)-TDA-1 PIL microgel catalysts, respectively. The HGR values were determined between the time zero and 5 min of H₂ production curves and are summarized in Fig. 5b. It can be clearly seen from the comparison of HGR values that the increase in the amounts of the catalyst leads to a decrease in HGR values for p(AMPS)-TDA-1 PIL microgel catalysts as HGR value are calculated as 2630 ± 108, 1300 ± 78, 854 ± 35, 429 ± 22, and 231 ± 15 mL H₂ / (min × g of catalyst) for 10, 25, 50, 100,

and 200 mg, respectively. On the other hand, as illustrated in Fig. 5c, the rate of hydrogen production (mL H₂/min) becomes almost linear after 50 mg catalyst. Therefore, in the determination of the effect of temperature in methanolysis reaction of NaBH₄ catalyzed by p(AMPS)-TDA-1 PIL microgels, 50 mg of catalyst is used to prevent wastefulness.

Effect of temperature on methanolysis of NaBH₄ The effect of temperature in the methanolysis of NaBH₄ reaction catalyzed by 50 mg of p(AMPS)-TDA-1 PIL microgels was investigated performing the reaction at different temperatures such as 0, 10, 25, 35, and 45 °C keeping the NaBH₄ concentration the same (4.825 mM or 0.0965 g) in methanol. The volume of produced H₂ as a function of time for these reactions is presented in Fig. 6a. The methanolysis reactions of NaBH₄ catalyzed by 50 mg of p(AMPS)-TDA-1 catalyst that all produced 250 mL H₂ were completed at 125, 33, 12, 10, and 8 min at 0, 10, 25, 35, and 45 °C, respectively. The initial HGR rates were calculated up to 5 min of reaction time for these temperatures range from 0 to 45 °C are 208 ± 21 to 434 ± 26, 854 ± 67, 918 ± 86, and 974 ± 76 mL H₂/(min × g of catalyst), respectively. It is obvious that the higher the reaction temperature, the bigger the HGRs; nevertheless even methanolysis reaction carried out at 0 °C, a reasonably good HGR is attained that is almost 1/5 of the methanolysis reaction that is carried out at 45 °C. Furthermore, the activation parameters such as E_a , ΔH , and ΔS were also calculated using well-known Arrhenius (Eq. 3) and Eyring (Eq. 4) equations, and corresponding graphs are demonstrated in Fig. 6b, c, respectively. The E_a for p(AMPS)-TDA-1 PIL microgels-catalyzed methanolysis reaction of NaBH₄ was computed as 14.3 kJ/mol. This value of E_a for p(AMPS)-TDA-1 PIL microgels in the H₂ production from methanolysis of NaBH₄ reaction is comparable with some of the lowest values reported in the literature. For example, this E_a value is significantly lower than the E_a values of metal-supported catalysts, Co/Al₂O₃ with 21.9 kJ/mol [22], Co-TiO₂ with 20.4 kJ/mol [24], Ni₂P/SiO₂ with 19.4 kJ/mol [45], CoCl₂ with 25 kJ/mol [30], and NiCl₂ with 26 kJ/mol [31]. Likewise, the E_a value of p(AMPS)-TDA-1 PIL microgels is also better than metal-free polymeric ionic liquid and other natural polymeric catalysts for methanolysis of NaBH₄ reaction reported in the literature, e.g., p(C₆VIImBr) with 34.3 kJ/mol [38], p(2-VP)⁺⁺C₆ with 20.4 kJ/mol [46], p(TAEA-co-GDE)-HCl with 30.4 J/mol [47], p-PEI microgels with 23.7 kJ/mol [41], Cell-EPC-DETA-HCl with 34.4 kJ/mol [44], HNT-NH₂-HCl with 30.4 kJ/mol [43], and H-PEI(750.000)-Hal nanotube with 16.4 kJ/mol [42]. Furthermore, the ΔH and ΔS values were also calculated from Eyring equation, illustrated in Fig. 6c, estimated as 23.9 kJ/mol and -184.2 J/mol K, respectively. As a result, these activation parameters in comparison with some of the similar studies reported in the literature suggest that p(AMPS)-TDA-1 PIL microgel catalysts has great potential in the methanolysis reaction of NaBH₄ for H₂ production as tangible and great potential in industrial applications.

The reusability studies of p(AMPS)-TDA-1 PIL microgel catalysts in methanolysis of NaBH₄ To determine potential industrial potential of a catalyst, the reusability

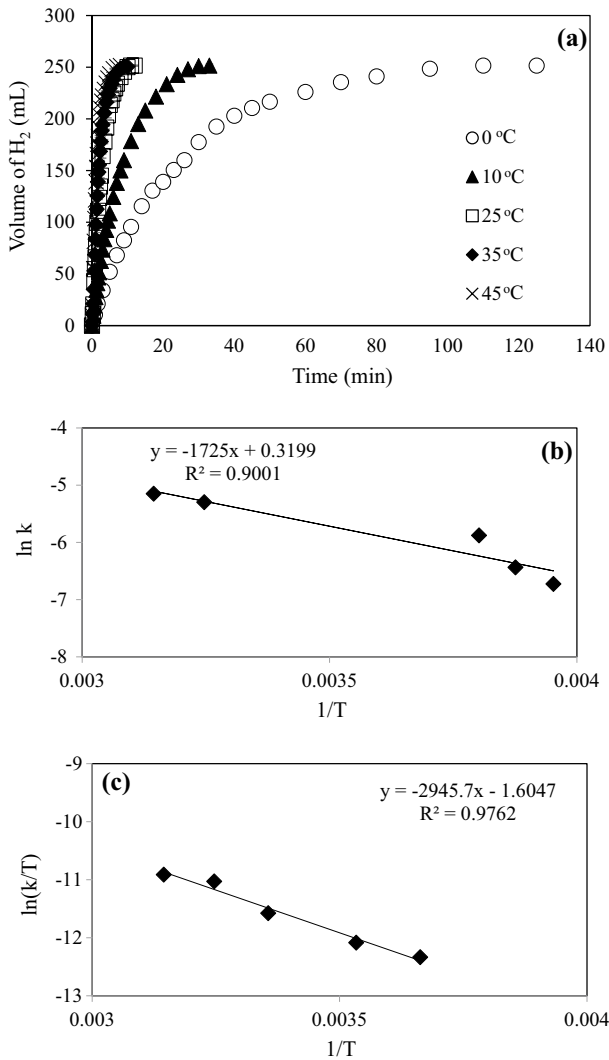


Fig. 6 **a** The effect of temperature on methanolysis of NaBH₄ reaction catalyzed by p(AMPS)-TDA-1 PIL microgels, **b** Arrhenius, and **c** Eyring graphs of p(AMPS)-TDA-1 PIL microgels-catalyzed methanolysis of NaBH₄. [Reac. cond.: 50 mg of catalyst, 20 mL methanol, 0.0965 g of NaBH₄, 1000 rpm mixing rate]

is as important as the catalytic performance, eco-friendliness, and the cost of the catalyst. Therefore, the catalytic performance of p(AMPS)-TDA-1 PIL microgel catalyst is tested in ten repetitive uses to determine the change in their conversion % and activities %. For this purpose, to 50 mg of p(AMPS)-TDA-1 PIL microgel catalyst in 20 mL methanol was added 0.0965 g of NaBH₄, and the H₂ production versus time is recorded at 25 °C. After this initial run, 0.0965 g of NaBH₄ was again added to the reaction media and the second use of p(AMPS)-TDA-1 PIL

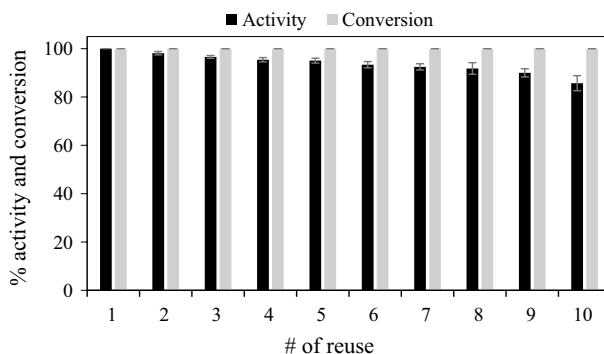


Fig. 7 The reusability of p(AMPS)-TDA-1 PIL microgel catalyst in methanolysis of NaBH_4 reaction. [Reac. cond.: 50 mg of catalyst, 25 °C, 20 mL methanol, 0.0965 g of NaBH_4 for each production, 1000 rpm mixing rate]

microgel catalytic performance is determined. The addition of NaBH_4 into reaction medium was repeated up to 10 times, and the change in the catalytic activity % and conversion % was calculated. As illustrated in Fig. 7, the methanolysis reaction of NaBH_4 catalyzed by p(AMPS)-TDA-1 PIL microgels was completed with 100% conversion for every reaction of 10 repetitive usages, and the catalytic activity value of $85.7 \pm 3.1\%$ after ten repetitive usages that is almost 14% reduction is calculated. Therefore, the reuse experiments of metal-free p(AMPS)-TDA-1 PIL microgels offers great opportunity as sustainable catalyst for the generation of green energy carrier such as H_2 . Similarly, another sustainable solvent, methanol that can be obtained from natural sources such as cellulose and/or plants, vegetable oil, CO_2 and so on can used in greener energy generation.

Conclusions

Here, the synthesis of ionic liquid p(AMPS)-TDA-1 microgels from AMPS-TDA-1 monomer using micro-emulsion polymerization method via photopolymerization was reported. The prepared p(AMPS)-TDA-1 PIL microgels were found to be in a few micrometer size range, and the zeta potential values were measured as -24.2 ± 1.1 mV in comparison with non-IL forms of p(AMPS) microgel that has -38.7 ± 1.3 mV. It was assumed that the addition of bulk amine group as a counterion in the structure of AMPS monomer induces the increase in zeta potential due to less separation of this bulky group in comparison with the proton of sulfonic acid groups of AMPS. Furthermore, the synthesized p(AMPS)-TDA-1 PIL microgels were used as a template for Co and Ni metal nanoparticles, and their amounts within microgel network were calculated and determined as 125.4 ± 5.1 and 131.7 ± 3.7 mg/g, respectively (measured by AAS). The usage of p(AMPS)-TDA-1-based PIL microgels and their metal nanoparticle-containing composites were used as catalyst in the hydrolysis and methanolysis of NaBH_4 . There is no

significant catalytic performance in H_2 production from hydrolysis of $NaBH_4$ that was observed in comparison with the similar studies [38]. The methanolysis of $NaBH_4$ catalyzed by p(AMPS)-TDA-1 PIL microgels on the other hand was found to be very effective. For example, the metal-free p(AMPS)-TDA-1 PIL microgels showed very high HGR, 854 ± 35 mL H_2 /(min \times g of catalyst), with a very low E_a value that is 14.3 kJ/mol that is better than most of metal-supported, metal-free and natural source catalysts [38–46]. Furthermore, the reusability of p(AMPS)-TDA-1 PIL microgel catalyst in the methanolysis reaction of $NaBH_4$ revealed that up to 10 repetitive use only 14% reduction in the catalytic activity no reduction in 100% conversions were observed. Therefore, the prepared metal-free p(AMPS)-TDA-1 PIL microgel catalysts reported here with lower E_a value and highly reusable properties provide significant advantages in comparison with the expensive and toxic metal nanoparticle-based catalyst and most of other metal-free catalyst reported in the literature qualifying these catalysts for real industrial applications.

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