

Research Article

Hydrogen Sorption onto Hypercrosslinked Polymer Decorated with Metal-Organic Framework

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Metal-organic framework decorated styrene-maleic acid (SMA) co-polymer beads were synthesized by slow diffusion of TEA. The obtained materials were characterized by FTIR, scanning electron microscopy, and thermogravimetric analysis. The different dicarboxylic acid linkers influenced the crystal morphologies and hydrogen-storage behavior of the polymer beads. Hydrogen-storage measurements revealed slow micropore opening mechanism involved in adsorption of hydrogen.

1. Introduction

Hydrogen is considered as an interesting energy vector particularly for vehicular applications due to its attractive properties such as nontoxicity, clean combustion, and high energy density [1]. Hydrogen binds to surfaces by weak dispersive interactions (physisorption) or through stronger chemical associations (chemisorption). Physisorption correlates with surface area, high surface area favours higher gas uptake. Thus, materials with large surface areas and low densities are attractive candidates for hydrogen-storage applications [2]. The physisorption method of hydrogen storage required sorbent with a large surface area such as activated carbons and carbon nanostructures [3], zeolites [4], porous polymers [5], and metal-organic frameworks (MOFs) [6]. Due to weak sorbent-sorbate interaction, physisorption-based hydrogen-storage systems show fast kinetics with a charging time of minutes. However, the same weak interaction results in less than 2 wt% gravimetric hydrogen uptake at ambient temperature and applicable pressure [7]. However, a number of significant technological hurdles need to be overcome for realizing these applications which include safe, compact, and high capacity hydrogen-storage systems [8]. Low-density microporous solids have garnered considerable scientific attention due to their potential practical applications including emerging energy challenges, catalysis,

hydrogen and methane storage, and chemical separations [9]. Hypercrosslinked polymers (HCPs) represent a class of predominantly microporous organic materials that exhibit high surface areas, “Davankov-type” resins being the most studied hypercrosslinked materials [10]. Due to light elemental compositions, additional functionalities can be introduced to the porous organic polymers through large number of synthesis routes; chemical and thermal stability and scalable technology possess potential advantage for gas sorption [11]. Porous metal-organic frameworks (MOFs) have been emerging as one type of the most promising materials for hydrogen storage because of their amenability to design and extraordinary permanent porosity [12]. Potential reaction sites on the organic ligands in MOFs render postsynthetic modification possible, leading to the introduction of additional active sites for stronger hydrogen binding. All these characteristics of MOFs make them one of the most promising sorbent materials for hydrogen storage [13].

The structural versatility of MOFs has given new insights for rational design and assembly of materials possessing novel topologies and exceptional host-guest properties. Synthesis of polymer materials and exploring specific properties of polymer confinement are achievable via nanochannels of MOFs. Polymer encapsulation is also achievable through tailored pore size optimization which has opened new dimensions for

material based MOF-polymer hybridization [14]. Rodrigues et al. [15] have revealed the association of metallic core with organic linkers to yield a variety of arrangements and have demonstrated that change in the organic linker aids in control of bonded water to the central metal at molecular level in absence of any hydroxo or aquo ligands which acts as a precatalyst for polymerization of isoprene.

In the present work, hypercrosslinked polymers decorated with metal-organic frameworks were developed as materials for hydrogen storage. The effect of varying organic ligands in MOF formation was studied. Hypercrosslinked polymer was chosen for this study due to its high surface area, microporous network structure, and easy synthesis method. The MOFs were synthesized by slow diffusion of TEA. The formation of metal-organic frameworks with carboxylic acid units of polymer and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was also studied to examine the effect of formation of additional network in the polymer. These materials were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TG), and Fourier Transform Infrared (FTIR) spectroscopy. The hydrogen-storage capacity was measured at 300 K by gas sorption analyzer. The preliminary results indicate that such MOF decorated hypercrosslinked polymers can be considered for hydrogen storage.

2. Materials and Methods

2.1. Materials. Styrene (S, Merck India) and divinylbenzene (DVB, Fluka, India) were purified by washing with 1N NaOH. Maleic anhydride (MAN, Merck, India) and AIBN were recrystallised from chloroform prior to use. NaOH, methylisobutylketone (MIBK), NaCl, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1,4-benzenedicarboxylic acid (H_2BDC), 1,6-naphthalenedicarboxylic acid (H_2NDC), biphenyldicarboxylic acid (H_2BPDC), N,N dimethylformamide (DMF), and TEA were of analytical reagent grade from commercial sources and were used without further purification.

2.2. Synthesis

2.2.1. Synthesis of Hypercrosslinked SMA Beads. Hypercrosslinked styrene-maleic acid (SMA) copolymer beads were synthesized by suspension polymerization technique using free radical initiator as reported in our previous communication [16]. Briefly, homogeneous solution of monomers (styrene and MAN), crosslinker (DVB) in MIBK was added to aqueous salt solution with in situ formed magnesium hydroxide. The mixture was stirred at 800 rpm to obtain uniform sized (200 μm –400 μm diameter) spherical beads of crosslinked styrene-maleic anhydride which were further hydrolyzed to produce crosslinked styrene-maleic acid (SMA) copolymer beads. The beads were then water soxhlated and finally acetone soxhlated and dried under vacuum at 50°C to constant weight.

2.2.2. Synthesis of Metal-Organic Framework Decorated SMA Beads. Metal-organic frameworks were synthesized by slight modification from the literature following the method of slow

diffusion of TEA [17]. Solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and dicarboxylic acid in DMF was diluted with toluene. Requisite amounts of SMA beads were allowed to swell in this solution. The mixture was placed under reduced pressure for 5 hr to ensure complete filling up of pores with solutions. The supernatant liquid was decanted and slow vapor diffusion of triethylamine (TEA) in toluene was allowed. The system was sealed and kept undisturbed for 2 days at room temperature. These SMA beads were then washed with DMF and dried under vacuum at 50°C to constant weight.

2.3. Characterization. The SMA beads and SMA beads decorated with MOFs were characterized using Fourier Transform Infrared (FTIR) spectroscopy (Model FTIR-8400, Shimadzu, Japan). Each sample was grounded thoroughly with KBr to form pellet which was then analyzed in the wavelength region 4000 to 400 cm^{-1} . The morphologies of the materials were observed on a JEOL ASM 6360A scanning electron microscope. TG analysis was carried out in nitrogen with a heating rate of 10 degree ($^\circ$)/min.

2.4. Hydrogen Adsorption. Hydrogen gas adsorption studies were carried out in a Sorptomatic 1990 instrument of Thermo Finnigan, Italy that records the fall of pressure and automatically converts the same into amount of gas adsorbed as per ASTM standards. The instrument was standardized with hydrogen and nitrogen to determine the dead volume. As per the recommended standards, 1.0 gm of beads was evacuated (10^{-6} torr) at 70°C for 2 hr in a previously evacuated glass sample holder to ensure cleanliness of surface and availability of clean pores for adsorption. A typical measurement for sample was continued for about 24 hr at room temperature (300 K).

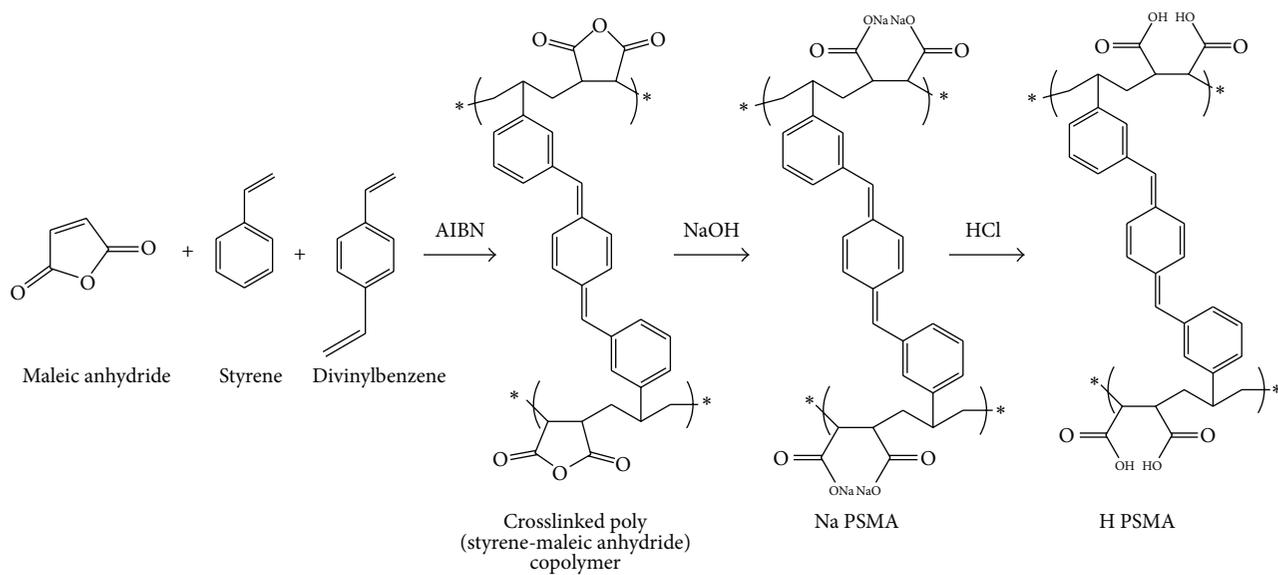
3. Results and Discussion

Hypercrosslinked SMA beads with rigid porous network structures were synthesized under optimized reaction conditions with S: MANh mole ratio of 1:1.6 and 30 mol% DVB content at 80°C under continuous agitation at 800 rpm [16]. Figure 1(a) shows the schematic representation of the formation of SMA copolymer beads. The number average molecular weight between the crosslink (M_c) and the effective crosslink mole fraction (F_c) in the polymer was calculated using Flory-Rehner equation [18] and was found to be 438.179 and 0.114%, respectively,

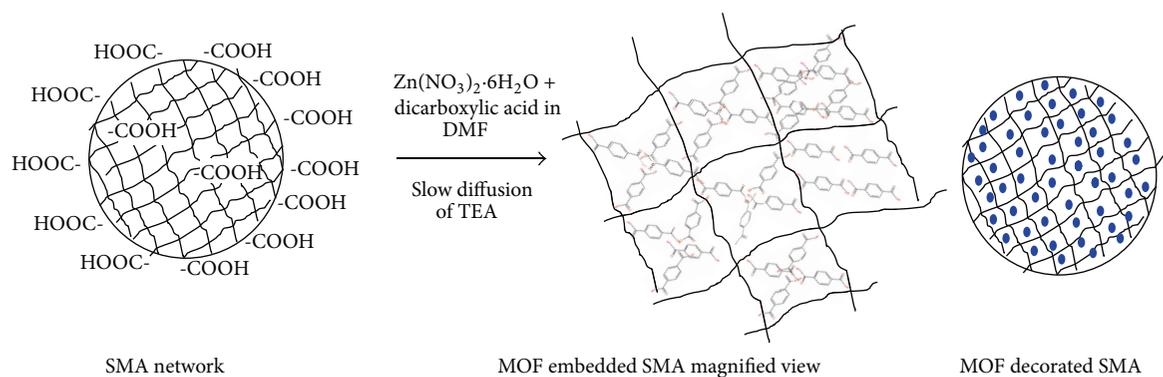
$$\ln(1 - \nu_2) + \nu_2 + \chi \nu_2^2 + \left(\frac{V_1 \rho_2}{M_c} \right) \times \left(\nu_2^{1/3} \nu_{2r}^{2/3} - \frac{\nu_2}{2} \right) = 0, \quad (1)$$

$$F_c = \frac{1}{2M_c},$$

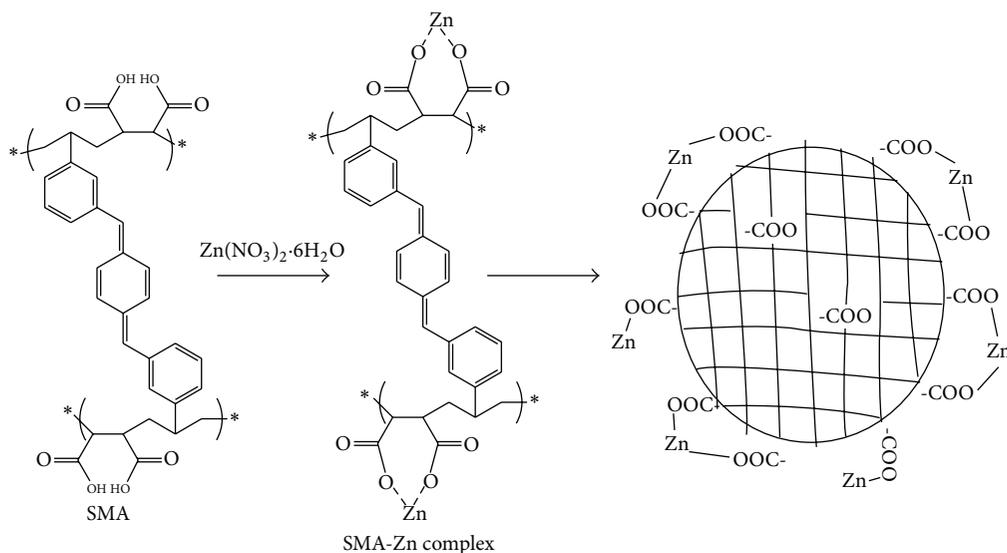
where χ is the Flory polymer solvent interaction parameter taken as 0.5, ρ_2 is the polymer density, ν_{2r} is polymer volume fraction in reference state, and ν_2 is polymer volume fraction in swollen state.



(a)



(b)



(c)

FIGURE 1: (a) Schematic presentation of SMA bead formation, (b) MOF decorated SMA beads, and (c) SMA-Zn complex formation.

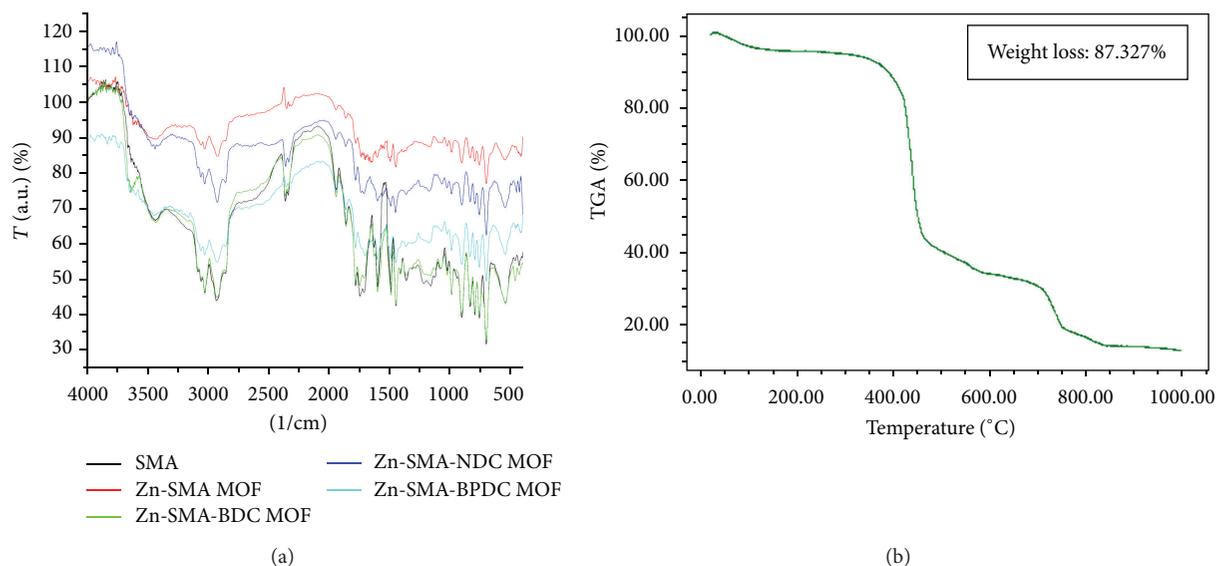


FIGURE 2: (a) FTIR and (b) TGA.

The SMA decorated with MOFs was also synthesized using under optimized reaction conditions at 300 K with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: dicarboxylic acid ratio 1:2 wt%. It was observed that highly oriented crystal structures were formed in the hypercrosslinked SMA beads with reaction time of 48 hr indicating that the slow diffusion of TEA was essential for formation of MOF. No significant change in the density of the polymer was noted on formation of MOF in polymer matrix. The schematic presentation of MOF decorated SMA beads is shown in Figure 1(b). The formation polymer metal complex was observed without addition of dicarboxylic acid [19] which is schematically shown in Figure 1(c). The formations of such complexes are known to induce additional network in the polymer matrix.

The FTIR spectra of hydrolyzed SMA beads, beads containing MOF and SMA-Zn complex are shown in Figure 2(a). The adsorption peaks around 3500 cm^{-1} and 1710 cm^{-1} (shoulder peak) correspond to the free acid formed after hydrolysis of anhydride groups of copolymer. Broad band peak around 3000 cm^{-1} indicates the presence of high concentration of $-\text{COOH}$ groups, indicating the presence of high maleic acid content. Characteristic $>\text{C}=\text{C}<$ aromatic peak also appears at 795 cm^{-1} and 850 cm^{-1} . The peak at 1600 cm^{-1} and 1410 cm^{-1} corresponds to the carboxylate anion. The IR spectrum of in situ formed MOF in porous SMA polymer shows no specific change in the peak position, confirming the formation of MOF with only slight decrease in the intensity of the 1710 cm^{-1} peak revealing the formation of polymer metal complex which is predominantly observed in the SMA-Zn beads.

Thermogravimetric analysis revealed that the decomposition of the polymer starts at 400°C (Figure 2(b)). The initial short dip in the curve presents the decomposition of the maleic acid to maleic anhydride and the sharp decomposition curve of styrene at 400°C . The residual weight was found to be

12.7% which increased on formation of Zn-polymer complex and MOF embedded in polymer which is due to Zn content in the material.

The presence of Zn in the Zn-SMA complex beads and MOF decorated SMA beads was confirmed from the EDX spectrum. The magnified surface SEM image of hypercrosslinked SMA beads revealed porous dense network structure with presence of micropores, voids, fissure, and well-developed flow line indicating capillary action being induced in the polymer matrix (Figure 3(a)). The SEM image of polymer-Zn complex formation shows uniform distribution of the Zn complex clusters in the size range $0.2\text{--}2\text{ }\mu\text{m}$ (Figure 3(b)). The result indicates that complex formation tends to occur at region with carboxyl content. The dense polymer network aids in close proximity of carboxylic groups of the polymer which results in complex formation with the metal ion being attached to the functional group of both chains [19]. The SEM images of SMA-(Zn-BDC) indicated the formation of well defined flower like crystal growth of the Zn-BDC MOFs in the polymer matrix (Figure 3(c)). The average size of these crystals was found to be around $5\text{ }\mu\text{m}$. Such flower shaped crystal of Zn-BDC MOFs known as MOF-5(γ) [20, 21] or MOF 69 [22, 23] is in well agreement with the literature. Changing the dicarboxylic acid showed a drastic change in the morphology of the MOF formed. It was observed that, with 1,6-naphthalene dicarboxylic acid linkers, the fine pellet shaped MOFs (Figure 3(d)) with average diameter of $2\text{--}3\text{ }\mu\text{m}$ were developed while globular structures (Figure 3(e)) of varying diameters were formed with 1,8-biphenyldicarboxylic acid. Such varied morphologies in the development of metal-organic frameworks were observed only with change in the dicarboxylic acid under similar reaction condition. With 1,4-benzenedicarboxylic acid the crystal growth was well defined with definite orientation of individual layer to form flower-like arrangement. Increasing

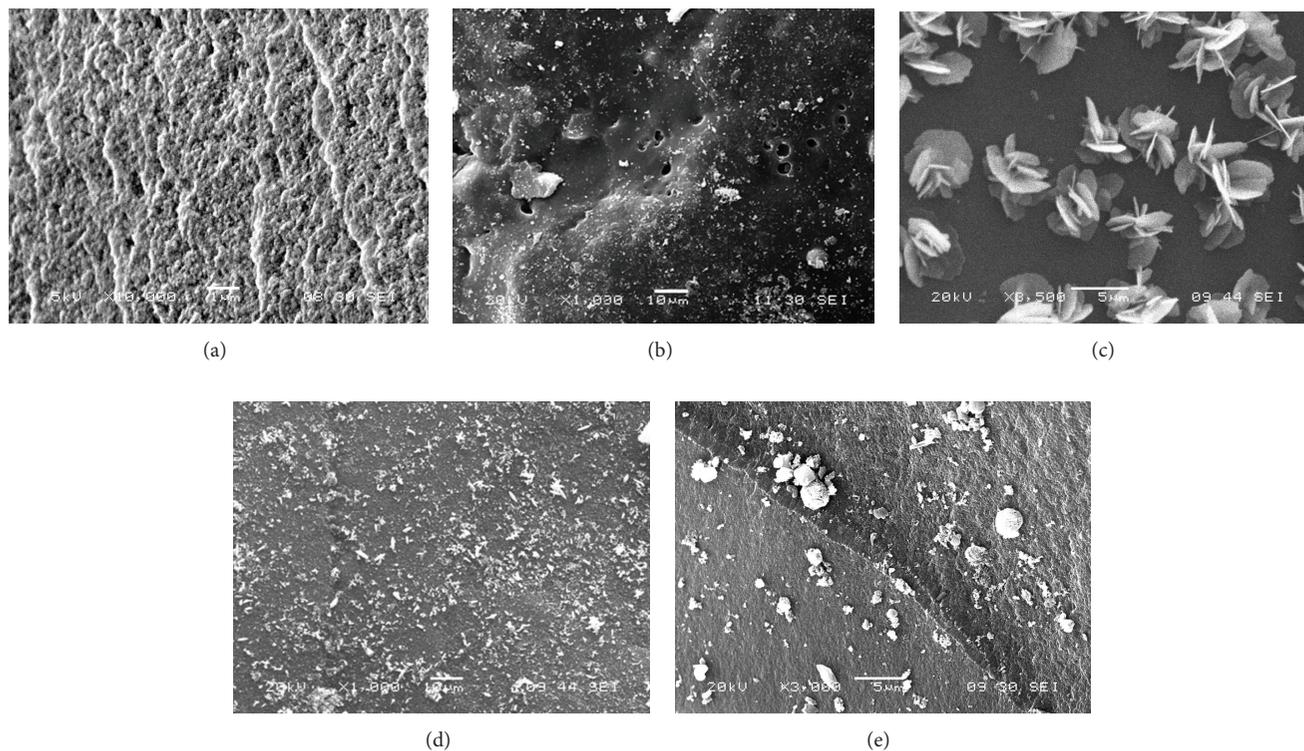


FIGURE 3: Magnified SEM images of (a) SMA surface, (b) SMA-Zn complex, (c) SMA-Zn-BDC, (d) SMA-Zn-NDC, and (e) SMA-Zn-BPDC.

the size of the dicarboxylic acid by using 1,6-NDC introduces steric strain in the structure which results in the formation of individual pellets structures and the pore diameter of the polymer restricts/hinders the further growth of the crystals. The globular ball shaped crystal structures originating due to the use of 1,8-BPDC are also a result of restricted pore diameter of the polymer and the increased size of dicarboxylic acid which introduces steric strain. Thus, the MOF morphology is found to be highly influenced by the steric interference between neighbouring ligands on the surface and orientation of the ligands in 3-dimensional network in the confined region/space of the pore.

These MOFs were found to be adhering to the inner pore surface with minimum contact, which can be clearly observed from the SEM micrographs. This finding supports the possibility of Zn forming complex with the polymer carboxylic group at specific sites in the pores which acts as nucleus to aid in further development of MOF crystals. Such MOFs can also be thought of having independent existence in the pores. The MOFs seem to be dispersed in the pores and are clustered on the pore surface at random spots. This is expected as the reacting constituents are mixed together and allowed to diffuse into the beads.

Porous polymers are well known for low adsorption of hydrogen at ambient temperatures and high pressures (~ 0.5 wt%) whereas MOFs can adsorb up to 7.5 wt% at 77 K [24] and about 1 wt% at room temperatures and 20 atmosphere [25]. Recently, 0.06 wt% hydrogen sorption at 32°C and 60 bar has been demonstrated on functionalized PEEK containing chlorosulphonated groups [26]. The H_2

storage capacity of microporous organic polymer HCP-PTMP-PVBC- 2 wt% Pt via spillover (0.21 wt%) was found to be enhanced by a factor of 1.75 as compared to 1 wt% Pt at 298.15 K and 19 bar [27]. MOF-5 synthesized by slow diffusion of TEA exhibited 2.63 wt% hydrogen adsorption at 1.74 MPa and 77 K [28].

Hydrogen adsorption in the hypercrosslinked SMA beads, SMA-Zn complex beads, and SMA beads decorated with MOFs was studied by allowing the beads to be in contact with the gas in discreet pressure ranges within 0–1 bar. The analysis was carried out by maintaining the equilibrium time of 1 min and equilibrium pressure deviation of 0.5 torr. All the measurements were carried out at room temperatures (300 K). The SMA polymers are known to adsorb hydrogen without attaining saturation limits [19, 29]. The slow micropore opening mechanism being predicted for the nonattainment of saturation. The hydrogen gets filled into large pores present on the surface; the pressure created in the pores allows the opening of micropores connected to these bigger pores through capillary action. Hydrogen thus diffuses into these pores. The same phenomenon was observed even with the SMA-Zn complex beads and MOF decorated SMA beads (Figure 4(a)). Instantaneous hydrogen adsorption on these beads for 25 hr revealed that hydrogen-storage capacity of the hypercrosslinked polymer beads (0.67 wt%) decreases slightly due to formation of metal complex and entrapment of MOFs in the pores. These findings can be attributed to the blockage of pores by the complex formation and MOF decoration. The hydrogen-storage capacities are presented in

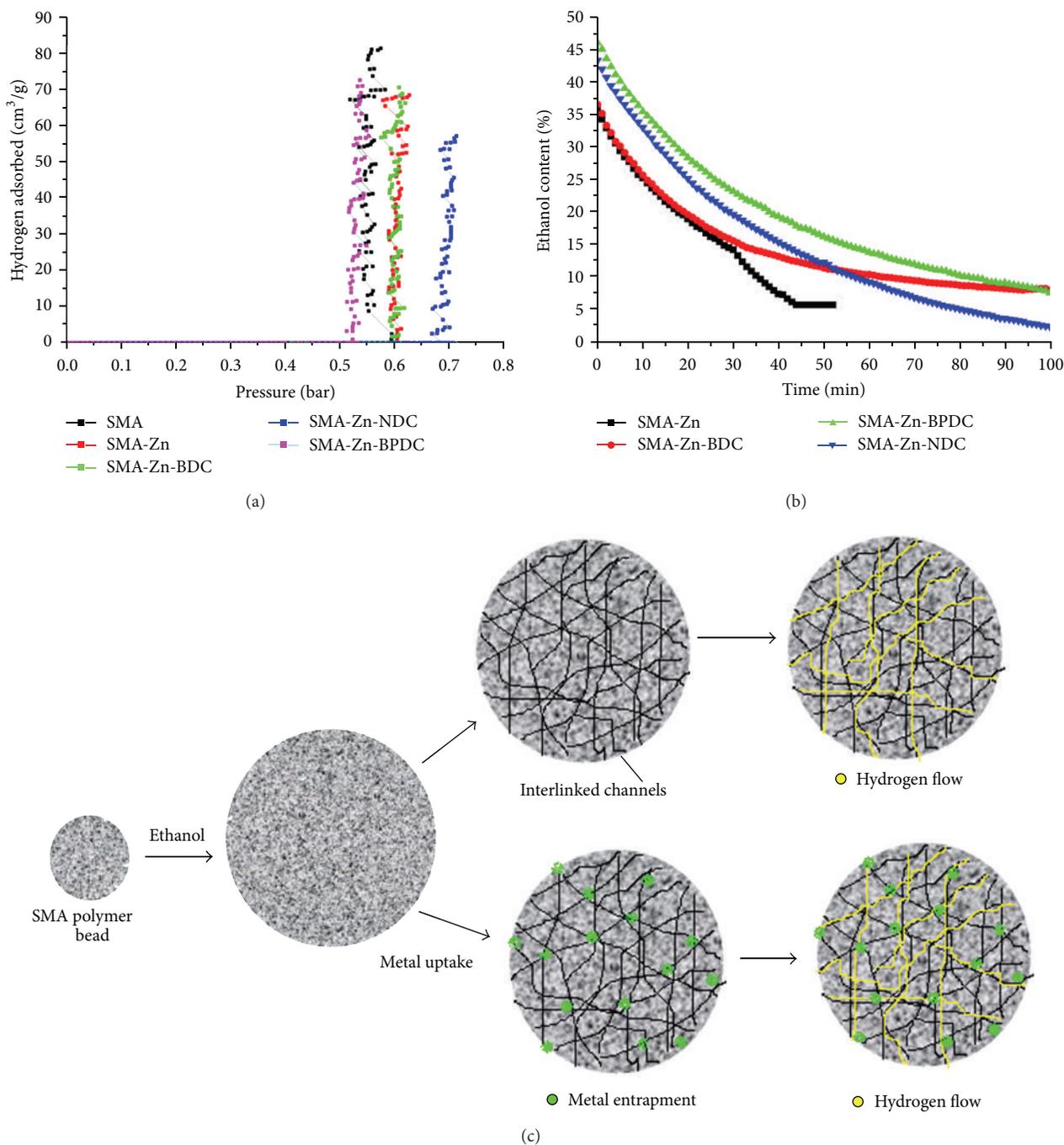


FIGURE 4: (a) Hydrogen adsorption, (b) ethanol retention plots, and (c) schematic presentation of hydrogen flow.

Table 1. Though the metal complex clusters and MOFs acts as sink for hydrogen storage, they serve as barriers during the process of micropore opening. This effect was found to diminish with long exposure time of 3 days where similar hydrogen adsorption capacity (~ 0.8 wt%) was noted for all types of beads.

To test the liquid hydrogen-storage capacity, the degree of swelling and solvent content in the MOF decorated SMA beads were noted with ethanol at 300 K and atmospheric

pressure (Table 2). It was observed that these beads swell rapidly up to 3 times their original volume. The maximum swelling and solvent retention was observed with SMA beads decorated with Zn-BPDC MOFs, with solvent retention capacity of 46.37% (Figure 4(b)). The residual solvent could be easily removed by exposing the beads to 50°C for 5 hr. It was also observed that these SMA beads were able to adsorb Zn(II) ions from aqueous solution and exhibited maximum adsorption of 143 mg/g.

TABLE 1: Hydrogen-storage capacity of the SMA decorated beads.

Material	Pressure (bar)	Hydrogen-storage capacity (wt%)
SMA beads	0.55	0.67
SMA-Zn complex beads	0.61	0.57
SMA-Zn-BDC beads	0.60	0.59
SMA-Zn-NDC beads	0.69	0.61
SMA-Zn-BPDC beads	0.53	0.47

TABLE 2: Degree of swelling and solvent content in SMA decorated beads.

	Ethanol	
	Sw (%)	W_Q
SMA-Zn	66	35.95
SMA-Zn-BDC	58	36.82
SMA-Zn-BPDC	86	46.37
SMA-Zn-NDC	77	43.66

4. Conclusions

Hypercrosslinked SMA beads decorated with MOFs were synthesized by the slow diffusion of TEA. The dicarboxylic acid significantly influenced the morphology of the MOFs formed inside the polymer matrix and hydrogen-storage capacity. The optimized reaction conditions yielded crystalline MOF. SMA decorated MOFs samples exhibit hydrogen-storage capacities: 0.59 wt%, 0.61 wt%, and 0.47 wt% at 300 K and 0.60 bar, 0.69 bar, and 0.53 bar for SMA-MOF-5, SMA-Zn-NDC, and SMA-Zn-BPDC, respectively, in 24 hr. The adsorption of Zn(II) ions from aqueous solutions by SMA beads suggests the recovery of Zn(II) from industrial effluents. Such Zn-SMA complexes can also be explored for hydrogen storage which exhibits hydrogen-storage capacity of 0.57 wt% at 300 K and 0.61 bar. The ethanol adsorption and retention in these decorated beads can be explored for storage of liquid hydrogen in fuel cells. The use of these polymer beads in fuel cell can render advantages of low cost, light weight, embedded catalyst activity, effective solvent and simultaneous hydrogen storage, and operation at higher temperatures, thus providing a solution to most of the shortcomings faced by the present fuel cells.

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