Journal of Solid State Chemistry 222 (2015) 7–11

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Highly porous organic polymers bearing tertiary amine group and their exceptionally high CO_2 uptake capacities

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ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form
20 October 2014
Accepted 26 October 2014
Available online 5 November 2014

Keywords:
CO_2 storage materials
Porous organic polymers
Amine functionalization
BET surface area
Surface basicity

ABSTRACT

We report a very simple and unique strategy for synthesis of a tertiary amine functionalized high surface area porous organic polymer (POP) PDVTA-1 through the *co*-polymerization of monomers divinylbenzene (DVB) and triallylamine (TAA) under solvothermal reaction conditions. Two different PDVTA-1 samples have been synthesized by varying the molar ratio of the monomers. The porous polymeric materials have been thoroughly characterized by solid state ^{13}C CP MAS-NMR, FT-IR and UV–vis spectroscopy, N_2 sorption, HR TEM and FE SEM to understand its chemical environment, nanostructure, bonding, morphology and related surface properties. PDVTA-1 with higher amine content (DVB/TAA=4.0) showed exceptionally high CO_2 uptake capacity of 85.8 wt% (19.5 mmol g^{-1}) at 273 K and 43.69 wt% (9.93 mmol g^{-1}) at 298 K under 3 bar pressure, whereas relatively low amine loaded material (DVB/TAA=7.0) shows uptake capacity of 59.2 wt% (13.45 mmol g^{-1}) at 273 K and 34.36 wt% (7.81 mmol g^{-1}) at 298 K. Highly porous nanostructure together with very high surface area and basicity at the surface due to the presence of abundant basic tertiary amine N-sites in the framework of PDVTA-1 could be responsible for very high CO_2 adsorption.

1. Introduction

Carbon dioxide considered as the primary anthropogenic greenhouse gas accumulated through the human activities, is responsible for global warming and climate change, which are major threats to the mankind in near future. The level of CO_2 in the atmosphere is increasing everyday through the combustion of fossil fuels and wastes, and also via several chemical reactions used in the industrial processes [1–3]. Thus, in order to decrease the CO_2 level in atmosphere, its removal from flue-gas streams via adsorption or sequestration is very important. Although, commercial carbon dioxide capture systems are known but their capture quantity/capacity is much smaller than that of the demand. Hence, research on the design and synthesis of high CO_2 adsorbent material for carbon capture and sequestration (CCS) is an emerging and first growing area of research [4–6]. In this context, CO_2 responsive porous polymers [7], various functionalized microporous and mesoporous materials [8–13], zeolitic imidazole frameworks (ZIF) [14–16], porous organic polymers (POP) [17–22], cation exchanged zeolites [23], porous carbons [24–27], metal organic frameworks (MOF) [28–31] having high CO_2 storage capacity utilizing the physical adsorption pathway have been reported in the recent times. Among these materials POPs are gaining further interest as suitable support for loading active metal ions to form highly reactive heterogeneous catalysts, which can catalyze a wide range of liquid phase chemical transformations [32,33].

Among these, porous organic polymers bearing electron donor nitrogen atoms such as 1°/2°/3° amine, imidazole, pyridine, etc. are particularly interesting as the lone electron pair of N atom can interact with the Lewis acidic CO_2 molecules [34–37]. Sayari et al. have shown that amine loading and surface alkyl chains can significantly affect the CO_2 adsorption amount among the amine functionalized porous materials [38,39]. On the other hand, for porous materials having high surface area and pore volume, the CO_2 uptake is increased several times compared to their non-porous analogue as the adsorbate gas molecule can be efficiently trapped inside the micro- and mesopores of the large surface area material and suitable dipolar interaction could occur with the nitrogen-donor sites located at the surface as well as inside the pore.

Herein, we report a simple strategy for the synthesis of very high surface area porous organic polymers (designated as PDVTA-1) bearing tertiary amine fraction via radical polymerization of different concentrations of two monomers divinylbenzene and triallylamine in the network under non-aqueous synthesis conditions. PDVTA-1 has been characterized by solid state MAS-NMR, Fourier transform infrared spectra (FT-IR), UV–vis spectroscopy, high resolution transmission electron microscopy (HR TEM), field emission scanning electron microscopy (FE SEM), nitrogen sorption and CHN analysis. High

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http://dx.doi.org/10.1016/j.jssc.2014.10.032
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surface area and basic nitrogen sites of the polymeric framework have been explored in CO_2 adsorption. It is found that higher amine loading is responsible for larger CO_2 uptake under identical conditions.

2. Experimental section

2.1. Materials

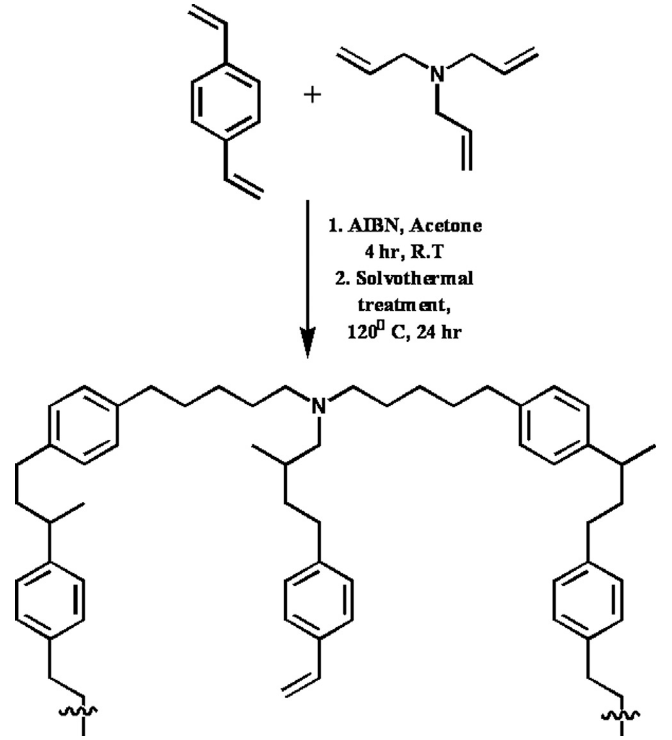
Divinylbenzene (DVB, monomer) and triallylamine (TAA, monomer) were obtained from Sigma Aldrich. Azobisisobutyronitrile (AIBN, radical initiator) was obtained from SRL and it was recrystallized from hot ethanol prior to use. All other chemicals used in the experiments were of analytical grade produced by E-Merk.

2.2. Instrumentation

Quantachrome Autosorb 1-C was used to record the N_2 adsorption/desorption isotherms of the porous organic polymers at 77 K. CO_2 adsorption isotherm of the porous polymer was recorded by using a Bel Japan Inc. Belsorp-HP at 273 K. The sample was degassed at 373 K for 8 h under high vacuum condition prior to both of the above mentioned measurement. ^{13}C CP MAS NMR spectrum of the sample was obtained on a Bruker Advance 500 MHz NMR spectrometer using a 4 nm MAS probe under static condition (spinning rate 5000 Hz, with side band suppression). Nicolet MAGMA-FT IR 750 Spectrometer Series II was used to record the FT IR spectra of the sample. The UV–vis diffuse reflectance spectra of the sample was recorded in a UV 2401PC with an integrating sphere attachment. $BaSO_4$ was used as the background standard. High resolution transmission electron microscopy (HR TEM) images of the mesoporous material were recorded using a JEOL 2010 TEM operated at 200 kV. Morphology and particle size of the samples was analyzed by using a Jeol JEM 6700 field emission scanning electron microscope (FE SEM). Elemental analyses of the materials were carried out using a Perkin Elmer 2400 Series II CHN analyzer.

2.3. Synthesis of porous polymer PDVTA-1

PDVTA-1 materials were synthesized via non-aqueous polymerization of a mixture of divinylbenzene and triallylamine under solvothermal condition using AIBN as a radical initiator [40]. The synthetic procedure for preparation of the porous polymer has been illustrated in Scheme 1. In a typical synthesis for PDVTA-1, 781 mg divinylbenzene (6 mmol) and 206 mg triallylamine (1.5 mmol) were taken in 15 ml acetone in a round bottom flask and the mixture was continuously stirred for 15 min. The flask was purged with nitrogen gas and 25 mg AIBN (0.15 mmol) was added to the mixture and resulting slurry was stirred for 4 h under nitrogen atmosphere at room temperature. Then the resultant mixture was autoclaved at 393 K for 24 h without stirring. The final product was washed thoroughly with acetone and dried in air. Five different PDVTA-1 samples were prepared by varying the molar ratio of divinylbenzene and triallylamine. With increasing the percentage of triallylamine from 0% to 20% gradually increase the surface area of the polymer, while the polymer remains hydrophobic in nature as that of pure divinylbenzene polymer. But further increase in the percentage of triallylamine (beyond 20%) leads to a decrease in the surface area and the polymer turns hydrophilic. The polymer PDVTA-1(1), with highest surface area and another polymer PDVTA-1(2) (molar ratio of divinylbenzene and triallylamine in the synthesis mixtures 80:20 and 87.5:12.5, respectively) were further characterized and their CO_2 adsorption behaviors were studied. It is pertinent to mention that there is not much difference between the materials PDVTA-1(1) and (2), as far as molecular structure is concerned (Scheme 1). Only they differ in the molar composition of monomer units in the framework, former being rich in triallyl amine moieties.



Scheme 1. Copolymerisation of divinylbenzene and triallylamine to obtain porous polymer PDVTA-1.

2.4. Acid–base titration for surface basicity of the polymers

The surface basicity of the polymers PDVTA-1(1) and PDVTA-1(2) were estimated by acid–base titration using (M/100) oxalic acid and standardized (M/100) NaOH solutions. The materials were dispersed in oxalic acid solutions and stirred for 2 h. After filtration, the concentrations of the solutions were measured by titrating with NaOH and the basicity of the materials were calculated from the change in acidity of the oxalic acid solutions over that in absence of PDVTA-1(1) and PDVTA-1(2). The estimated basicity for the polymers PDVTA-1(1) and PDVTA-1(2) were 1.625 mmol g^{-1} and 0.989 mmol g^{-1}, respectively.

3. Results and discussion

3.1. Solid state NMR and chemical environments at different C atoms

The chemical environment of different C atom in the polymeric network of PDVTA-1 and the presence of various organic functional groups have been confirmed by ^{13}C MAS NMR experiment. The ^{13}C CP MAS NMR spectrum for the porous polymer PDVTA-1 (1) is shown in Fig. 1a, which exhibit strong signals at 28.5, 41, 48, 126.9, 137 and 144 ppm due to different aliphatic and aromatic C atoms present in the polymer network as shown in the structure of Fig. 1. The weak signal at 111 ppm indicates the presence of little amount of unreacted double bonds of the substrates. Further, the weak signal at 15 ppm resembles the the aliphatic sp3 C atom as shown in the framework structure of PDVTA-1 in Fig. 1. The ^{13}C CP MAS NMR spectrum of PDVTA-1(2) (Fig. 1b), also exhibits similar chemical shifts of these carbon atoms as that of PDVTA-1(1). Thus, this ^{13}C CP MAS NMR analysis confirms the almost complete *co*-polymerization of divinylbenzene and triallylamine in PDVTA-1.