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Novel mesoporous composites based on natural rubber and hexagonal mesoporous silica: Synthesis and characterization

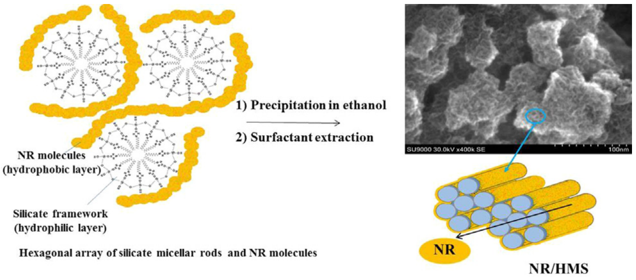
Sakdinun Nuntang [a], Sirilux Poompradub [a], Suchada Butnark [b], Toshiyuki Yokoi [c], Takashi Tatsumi [c], Chawalit Ngamcharussrivichai [a,d,*]

[a] Fuels Research Center, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand
[b] PTT Research and Technology Institute, PTT Public Company Limited, Wangnoi, Ayutthaya 13170, Thailand
[c] Division of Catalytic Chemistry, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[d] Center of Excellence on Petrochemical and Materials Technology (PETROMAT), Chulalongkorn University, Patumwan, Bangkok 10330, Thailand

HIGHLIGHTS

- NR molecules were incorporated into hexagonal meso-structure of HMS.
- NR/HMS composites exhibited an expanded unit cell and channel wall thickness.
- Nanosized NR/HMS composites with a lower particle size range were obtained.
- NR/HMS had high surface area, large pore volume and narrow pore size distribution.
- NR/HMS composites displayed an enhanced hydrophobicity.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study is the first report on the synthesis and characterization of mesoporous composites based on natural rubber (NR) and hexagonal mesoporous silica (HMS). A series of NR/HMS composites were prepared in tetrahydrofuran via an *in situ* sol–gel process using tetraethylorthosilicate as the silica precursor. The physicochemical properties of the composites were characterized by various techniques. The effects of the gel composition on the structural and textural properties of the NR/HMS composites were investigated. The Fourier-transform infrared spectroscopy (FTIR) and ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) results revealed that the surface silanol groups of NR/HMS composites were covered with NR molecules. The powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) data indicated an expansion of the hexagonal unit cell and channel wall thickness due to the incorporation of NR molecules into the mesoporous structure. NR/HMS composites also possessed nanosized particles (~ 79.4 nm) as confirmed by scanning electron microscopy (SEM) and particle size distribution analysis. From N_2 adsorption–desorption measurement, the NR/HMS composites possessed a high BET surface area, large pore volume and narrow pore size distribution. Further, they were enhanced hydrophobicity confirmed by H_2O adsorption–desorption measurement. In addition, the mechanistic pathway of the NR/HMS composite formation was proposed.

1. Introduction

In the past decade, the successful synthesis of hexagonal mesoporous silica (HMS) with wormhole-like or sponge-like

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[*] Corresponding author. Fuels Research Center, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand. Tel.: +66 2218 7528; fax: +66 2255 5831.
E-mail addresses: Chawalit.Ng@Chula.ac.th, n_chawalit@hotmail.com (C. Ngamcharussrivichai).

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framework structures, a large surface area, and a narrow pore size distribution, by a neutral assembly pathway between a neutral primary amine surfactant and a neutral inorganic precursor under mild conditions, has been reported [1–6]. Comparing HMS with other kinds of mesoporous silica materials that have hexagonal framework structures reveals the smaller particle sizes of HMS together with the random channel packing of silica molecular sieves that results in a high textural mesoporosity and better transport channels for chemical substances [1]. In addition, HMS exhibits a thicker silica framework that encourages a high thermal stability. Moreover, the amine surfactants used as templates are cheaper, and can be simply removed by extraction using a solvent, such as acidified water [2] and ethanol [3]. These advantages make HMS attractive for many applications.

Chemical modifications to, and the physical coating of, the HMS surface have been demonstrated to be a very useful method to prepare materials with unique surface properties for adsorption [7–11] and catalysis [6,12,13]. There are two general procedures to chemically modify the surface characteristics of siliceous mesoporous materials, which are (i) the co-condensation of the silica precursor with organosilane around a self-assembly amine template and (ii) the post-grafting of the surface via reaction of the silanol groups with organosilane. The co-condensation method is a one-step procedure and allows a better control of the loading and distribution of organo-functional groups [14], but it often produces materials with less ordered mesoporous structures. The post-grafting method can be used to prepare well-ordered functionalized mesoporous materials, but it often results in non-uniformly distributed organic moieties due to congregation of the organosilane on the channel pore mouth and on the exterior surface of the mesoporous materials [15,16]. In addition, the materials functionalized by these modification methods suffer a loss of surface area, pore size and pore volume [17].

In the past decade, polymer/silica composites have been extensively studied to prepare a new class of materials by combining the advantages of silica (e.g., porosity, surface area and thermal stability) and organic polymers (e.g., pH stability, hydrophobicity and chemical functionality) [18–22]. For example, silica-supported Nafion (SAC-13) was developed and evaluated for its catalytic performance in several acid-catalyzed reactions [23–25]. Silica-polyamine composites (SPC), made from silanized amorphous nano-porous silica gel and poly(allylamine), have been used as adsorbents for removing molybdenum and tungsten oxyanions in wastewater [26,27]. However, the polymers are entrapped within the porous silica network, which results in low textural properties, an uncontrollable pore size distribution and a decreased number of active functional groups.

Natural rubber (NR) is a hydrophobic polymer of *cis* 1,4-isoprene monomers. There have been many attempts to modify the properties of NR through various techniques, such as hydrogenation [28], functionalization [29] and adding nanofillers [30]. Of the nanofillers, the incorporation of silica fillers into the rubbery polymer has become of special interest since it imparts many interesting and useful properties to the resultant particle-filled composites obtained, such as enhanced mechanical properties and thermal stability [30–34]. The *in situ* silica filling in rubbers in particular has been focused on since it can be performed by a simple sol–gel reaction and results in a controlled size of silica particles with a high level of dispersion (low level of aggregation) in the rubber matrix. Generally, the generation of *in situ* silica within the rubbery polymer is undertaken in the presence of tetraethoxysilane (TEOS) as the silica precursor [35]. The base-catalyzed sol–gel reaction takes place in two steps. TEOS swelling in the polymer is hydrolyzed by water, followed by condensation of silicate species to form silica particles [36]. The important parameters affecting the rates of the sol–gel reaction are the types of polymer [37–39], solvent, silica precursor and base, the water: silica precursor molar ratio, the temperature, and the mixture pH [40,41].

In this work, we report the synthesis and characterization of novel composite materials with a high mesoporosity based on NR and HMS, prepared via an *in situ* sol–gel process. Unlike the conventional procedure for HMS synthesis, in this work tetrahydrofuran (THF) was used as synthesis media instead of ethanol to thoroughly dissolve the NR in the synthesis mixture and to obtain a high dispersion level of the NR in the silica framework. Using dodecylamine (DDA) as the organic template, the effects of molar composition of TEOS:H_2O:DDA on the physicochemical properties of the NR/HMS composites obtained were investigated. The composites obtained possessed a highly ordered hexagonal mesostructure and textural properties in accord with their enhanced hydrophobicity, which are attractive for using as adsorbents or catalyst supports.

2. Experimental

2.1. Preparation of mesoporous silica and composites with NR

2.1.1. Materials and reagents

TEOS and DDA (AR grade, 98%) were purchased from Sigma–Aldrich. NR (commercial grade) was supplied by the Thai Hua Chumporn Natural Rubber Co., Ltd. (Thailand). THF (AR, grade, 99.5%) was purchased from QREC Chemicals Co., Ltd. Absolute ethyl alcohol (C_2H_5OH) (AR grade, 99.5%) was purchased from Macron Chemicals Ltd. Sulfuric acid (H_2SO_4) (AR grade, >95%) was purchased from Sigma–Aldrich. All of the materials and reagents were used without further purification.

2.1.2. Pure silica HMSs

HMS was prepared using DDA as the organic template and TEOS as the silica source according to the procedure reported by Yin et al. [42]. Typically, DDA was dissolved in a solution of ethanol and deionized water under stirring to which TEOS was added dropwise. The molar composition of the synthesis mixture was 0.10 TEOS:0.03 DDA:2.94 H_2O:0.85 ethanol. The mixture was vigorously stirred for 0.5 h at 40 °C and then aged for 18 h at ambient temperature in order to obtain the HMS. Subsequently, the white solid product was recovered by filtration, thoroughly washed with deionized water, and dried at 100 °C overnight. Template removal was achieved by extraction with 0.05 M H_2SO_4/ethanol at 70 °C for 8 h. The HMS synthesized in ethanol was designated as HMS-E.

The preparation of HMS in THF as the synthesis media was also studied. The molar composition of the synthesis mixture was 0.10 TEOS:0.03 DDA:2.94 H_2O:0.37 THF. The synthesis procedure was otherwise similar to that of HMS-E, and the mesoporous material obtained was denoted as HMS-T.

2.1.3. NR/HMS composites

The NR/HMS composites were prepared via a sol–gel method adapted from the procedure described by Chaichua et al. [35]. Typically, 1 g of NR sheet with thickness of 1 mm was swollen in TEOS at room temperature for 16 h and then dissolved in THF to obtain a homogeneous solution. To this NR solution, DDA and additional TEOS were added drop by drop under constant stirring. After 1 h, deionized water was slowly added into the mixture and stirring was maintained at 40 °C for 0.5 h. The molar compositions of the synthesis mixtures are summarized in Table 1. The gel attained was aged at 40 °C for 3 days after which it was precipitated in 100 mL of ethanol. The solid product was then filtered and vacuum dried at 60 °C for 2 h. Finally, the mesoporous silica template in the composite was removed by extraction with 0.05 M H_2SO_4/ethanol