Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Fabrication of hydrophobic and oleophilic polyurethane foam sponge modified with hydrophobic Al_2O_3 for oil/water separation

Liying Kong[a], Yang Li[a], Fengxian Qiu[a,*], Tao Zhang[a], Qing Guo[a], Xiaoying Zhang[a], Dongya Yang[a], Jicheng Xu[a,b], Mengwei Xue[c]

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, China
[b] Institute of Chemical and Materials Engineering, Zhenjiang College, Zhenjiang 212003, China
[c] School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171, China

ARTICLE INFO

Article history:
Received 27 August 2016
Received in revised form 23 July 2017
Accepted 28 September 2017
Available online xxx

Keywords:
Polyurethane
Hydrophobic Al_2O_3
Foam sponge
Oil absorption

ABSTRACT

In current work, hydrophobic and oleophilic polyurethane (Al_2O_3/PUF) foam sponge was prepared by foaming technology. The material was characterized by XRD, TEM, BET, SEM and water contact angles (CA). The Al_2O_3/PUF was applied to removal of oil or organic solvent from oil/water system. Water contact angle of Al_2O_3/PUF could exceed 140°. The absorption capacity of Al_2O_3/PUF could be obtained 37 g/g and found to be reusable up to 10 cycles while maintaining its high absorption capacity. The result indicated that prepared foam sponge has good potential application in oil–water separation.

Introduction

Crude oil spills, the petrochemical and metallurgical industries, pharmaceutical factories and toxic organic solvents have caused serious environmental pollution on a global scale [1]. It is extremely urgent and important to develop effective and inexpensive materials that can remove oils or organic solvents from water [2,3]. Some cleanup techniques for oil spills and organic solvents including in situ burning, chemical dispersion, oil skimming and physical absorption can be found in the previous works [4,5]. Due to the simplicity and efficacy of physical absorption, it becomes a widely appreciated method to remove oil spills and organic solvents. Oil and solvents absorption requires cheap, reliable, environmentally friendly absorbents with high oil absorption capacity, oil/water selectivity and reusability [6,7].

Recently, several efforts have been made to develop synthetic organic sorbents with low cost, high oil absorption capacity and good oil–water selectiveness, such as organic polymer [8], inorganic nanowire membranes [9], macroporous nanocomposites [10], carbon nanotubes [11], Iranian activated bentonite [12], inorganic metal oxide [13–15], biological structure carbon [16] and silica particles (such as nanosilica, microsphere silica, graphene oxide–silica, nanostructured porous silicon and so on) [17]. Polyurethane (PU) in the form of foam possessed a large specific area and enough space for absorption. Davis et al. demonstrated a method to reduce the surface roughness of a spray-casted polyurethane/silica/fluoroacrylic superhydrophobic nanocomposite coating. By changing the main slurry carrier fluid, fluoropolymer medium, surface pretreatment, and spray parameters, the arithmetic surface roughness values of 8.7, 2.7, and 1.6 μm on three test surfaces were achieved. All the superhydrophobic surfaces showed lower ice adhesion than that of the polished aluminum surface [18]. Steele et al. investigated substrate adhesion for superhydrophobic coatings fabricated from Moisture-cured polyurethanes (MCPUs) modified with waterborne perfluoroalkyl methacrylic copolymer (PMC) and a fatty amine/amino-silane surface modified montmorillonite clay nanofiller (organoclay) [19]. Polyurethane foam (PUF) is an efficient absorbent for oil or organic molecule, which exhibits a range of valuable application properties such as low apparent density, good mechanical properties, high weather ability and low thermal conductivity [20]. Li et al. reported that PU cubes were modified by grafting polymerization with oleophilic monomer lauryl methacrilate (LMA) in solvent and coating with LMA microspheres [21]. Calcagnile et al. presented a novel composite material based on commercially available polyurethane foams (PUF) functionalized with colloidal superparamagnetic iron oxide nanoparticles and submicrometer polytetrafluoroethylene (PTFE) particles, which can efficiently separate oil from water. Untreated foam surfaces are

* Corresponding author.
E-mail address: fxqiuchem@163.com (F. Qiu).

https://doi.org/10.1016/j.jiec.2017.09.050
1226-086X/

inherently hydrophobic and oleophobic, but they can be rendered water-repellent and oil-absorbing by a solvent-free, electrostatic polytetrafluoroethylene particle deposition technique. It was found that combined functionalization of the PTFE-treated foam surfaces with colloidal iron oxide nanoparticles significantly increases the speed of oil absorption [22]. Moreover, the PUF is a porous and a hydrophilic polymer with the characteristics of low cost, high absorption ability, good elasticity and easy large scale fabrication [23]. Therefore, polyurethane foam composites have been intensively explored as a promising oil–water separation absorbent with a remarkable absorption capability resulting from their pores structure, excellent elasticity and mechanical stabilities, and diverse chemical modification of surface [24–26].

Hollow micro and nanospheres with well-defined structure and shape, low density, high specific surface area, large void fraction, low thermal expansion and refractive index, make them useful as adsorption, catalysis, electrochemistry and sensors due to high specific surface area, high porosity and excellent physical–chemical properties, moreover aluminum oxides itself are low toxicity and cost [27–29]. Due to this well dispersion of the hollow Al_2O_3 in the polymer matrix and the interfacial interaction between the inorganic and organic phases, the Al_2O_3 composites has been significantly improved in the thermal stability and mechanical properties. In this work, hollow Al_2O_3 spheres were prepared by one-pot hydrothermal synthetic routes and thermal treatment. Then the hydrophobic Al_2O_3 was obtained using hollow Al_2O_3 spheres modified with γ-methacryloxypropyltrimethoxysilane (KH-570). A hydrophobic and oleophilic polyurethane (Al_2O_3/PUF) foam sponge was prepared with polyether polyol (NJ-330), hydrophobic Al_2O_3, sodium bicarbonate, silicone oil, dibutyltin dilaurate (as catalyst, DBLT) and isophorone diisocyanate (IPDI) as raw materials by foam technology. This Al_2O_3/PUF foam sponge could cover all the reticulated network of the foams. The unmodified foams exhibit inherent hydro- and oleophobicity, whereas when they get modified, they become hydrophobic and oleophilic, exhibiting water-repellent and oil-absorbing behavior [30]. The products were characterized with X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), water contact angles (WCA) and fourier transform infrared spectroscopy (FT-IR). Furthermore, the process of oil absorption was investigated by numerous kinds of oils and organic solvents. To our knowledge, this study is the first report about the preparation of Al_2O_3/PUF foam sponge and its application on the oils and organic solvents absorption.

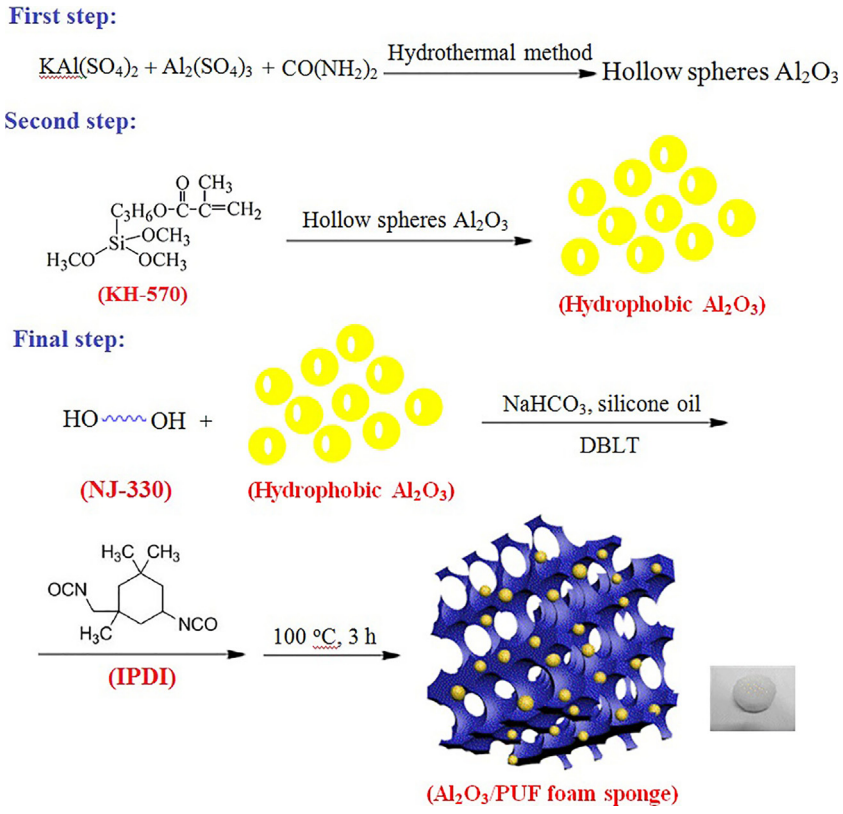
Experimental

Materials

Polyether polyol (NJ-330, M = 3000 g/mol) was obtained from Ningwu Chemical Co., in Jurong, Jiangsu, China. Isophorone diisocyanate (IPDI, purity ≥ 99.5% and -NCO content ≥ 37.5%) was supplied by Rongrong Chemical Co., in Shanghai, China. Dibutyltin dilaurate (DBLT), silicone oil ($[-Si(CH_3)_2O-]_n$), and sodium bicarbonate ($NaHCO_3$), aluminium potassium sulfate ($KAl(SO_4)_2{\cdot}2H_2O$), urea ($CO(NH_2)_2$), γ-methacryloxypropyl trimethoxysilane (KH570), aluminium sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$), and Sudan III were purchased from Sinopharm Chemical Reagent Co., Ltd., in Shanghai, China. Diesel oil was brought from Sinopec, in Zhenjiang, Jiangsu, China. Bean oil was produced by Nanjing Baoyang Trade CO., in Nanjing, Jiangsu, China.

Preparation of hydrophobic and oleophilic foam polyurethane sponge (Al_2O_3/PUF)

The hydrophobic and oleophilic polyurethane foam sponge was prepared by three steps.



Scheme 1. The synthetic route of hydrophobic and oleophilic polyurethane (Al_2O_3/PUF) foam sponge.

Please cite this article in press as: L. Kong, et al., Fabrication of hydrophobic and oleophilic polyurethane foam sponge modified with hydrophobic Al_2O_3 for oil/water separation, J. Ind. Eng. Chem. (2017), https://doi.org/10.1016/j.jiec.2017.09.050