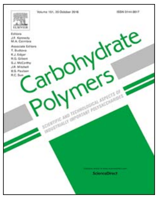
Carbohydrate Polymers 186 (2018) 25–34

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Pd@HNTs-CDNS-g-C_3N_4: A novel heterogeneous catalyst for promoting ligand and copper-free Sonogashira and Heck coupling reactions, benefits from halloysite and cyclodextrin chemistry and g-C_3N_4 contribution to suppress Pd leaching

Samahe Sadjadi[a,*], Majid M. Heravi[b,*], Masoumeh Malmir[b]

[a] *Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemicals Institute, PO Box 14975-112, Tehran, Iran*
[b] *Department of Chemistry, School of Science, Alzahra University, PO Box 1993891176, Vanak, Tehran, Iran*

ARTICLE INFO

Keywords:
Halloysite nanoclay
Cyclodextrin nanosponges
g-C_3N_4
Pd(0)Nanoparticles
C—C coupling reaction

ABSTRACT

For the first time, a ternary hybrid system composed of halloysite nanotubes, HNTs, cyclodextrin nanosponges, CDNS, and g-C_3N_4 is prepared and used for immobilization of Pd(0) nanoparticles and development of a heterogeneous catalyst, Pd@HNTs-CDNS-g-C_3N_4 for promoting ligand and copper-free Sonogashira and Heck coupling reactions in aqueous media. HNT as a porous tubular clay with outstanding thermal, mechanical and textural properties can act as a support for immobilizing Pd nanoparticles. The role of CDNS can be explained on the base of its capability to form inclusion complexe with substrates and bringing them in the vicinity of the catalytic active sites. Regarding the role of g-C_3N_4 in catalysis, it is proved that its presence can suppress the Pd leaching dramatically. The contribution of each component as well as synergistic effect between them results in high catalytic activity and recyclability (up to 10 reaction runs) of the catalyst.

1. Introduction

Halloysite nanoclay (HNTs) is a tubular clay ($Al_2(OH)_4Si_2O_5{\cdot}2H_2O$) composed of tetrahedral siloxane on outer surface and aluminol groups on inner surface. The water molecules in the structure of HNTs are located between the interlayer spaces (Pasbakhsh & Churchman, 2015; Szczepanik & Słomkiewicz, 2016; Yuan, Thill, & Bergaya, 2016). The properties of HNT are very similar to those of Kaolin. However, the porous morphology of HNTs as well as some other features of this clay (Zhang, Tang, Yang, & Ouyang, 2016) such as inert entity, bio-compatibility and high mechanical and chemical stability and surface area (Tully, Yendluri, & Lvov, 2016), make this clay a unique candidate for various applications such as drug delivery purposes (Kumar-Krishnan et al., 2016; Zhai et al., 2010), separation, catalysis (Zhang, He, Ouyang, & Yang, 2013) and energy storage. Mostly, this naturally occurring clay is modified through surface functionalization (Massaro, Colletti et al., 2017; Massaro, Lazzara, Milioto, Noto, & Riela, 2017; Yuan et al., 2008). To date, various functional groups have been introduced for tuning the surface chemistry of HNTs. This topic has been recently, reviewed (Massaro, Lazzara et al., 2017). Notably, functionalized HNTs can be potentially used for immobilizing various chemicals including, catalytically active species (Battistoni, Dimonte, Ubaldi, Lvov, & Erokhin, 2017; Sadjadi, Heravi, Malmir, 2017; Sadjadi, Hosseinnejad, Malmir, Heravi, 2017; Vinokurov et al., 2017; Yuan et al., 2016; Yang et al., 2015; Zhang, He et al., 2013; Zhang, Ouyang, & Yang, 2014; Massaro et al., 2016) and developing heterogeneous catalysts with low leaching.

β-Cyclodextrin, β-CD, belong to the class of cyclic oligosaccharide with seven glucopyranoside moieties. The unique conical scaffold of β-CD is designed in such a way that forms a hydrophobic inner space as well as a hydrophilic outer one (Manivannan & Ramaraj, 2012). The cavity of CD is a good candidate for accommodating diverse range of chemicals with appropriate physical and chemical properties through host-guest interactions. The ability of formation of inclusion complex has expanded the applications of CD in various fields including, drug delivery, food, synthesis of nanoparticles (Noël, Léger, Ponchel, Philippot et al., 2014), aqueous biphasic catalysis, etc. (Bai et al., 2013; Gogoi & Sarma, 2017; Menuel, Léger, Addad, Monflier, & Hapiot, 2016; Noël, Légera, Ponchel, Hapiot, & Monflier, 2014). In the latter case, CD can serve as a molecular transfer shuttle and facilitate their conversion at the aqueous/organic interface (Hapiot, Bricout, Menuel, Tilloy, & Monflier, 2014; Hapiot & Monflier, 2017).

Cyclodextrin nanosponges, mostly known as CDNS, belong to the carbohydrate hyper-cross linked polymers that can be synthesized

---

[*] Corresponding authors.
E-mail addresses: s.sadjadi@ippi.ac.ir (S. Sadjadi), m.heravi@alzahra.ac.ir (M.M. Heravi).

https://doi.org/10.1016/j.carbpol.2018.01.023
Received 17 November 2017; Received in revised form 6 January 2018; Accepted 8 January 2018

facilely from reaction of a cross linker and cyclodextrins, CDs, as monomers. Various kinds of CDs, mostly β-CD, and cross linking agents, such as carbonyl diimidazole, diisocianates and diarylcarbonates (Trotta, 2011; Tejashri, Amrita, & Darshana, 2013) can be employed for the synthesis of CDNS. The cross linking reaction can proceed under ultrasonic or microwave irradiation or readily occurs in solvent or *via* melting procedure. Compared with CDs, CDNS benefits from various advantageous including, insolubility in classic solvents, high thermal and pH stability (Shende, Deshmukh, Trotta, & Caldera, 2013; Shringirishi et al., 2014; Trotta, 2011; Torne, Darandale, Vavia, Trotta, & Cavalli, 2013). CDNS can encapsulate diverse range of hydrophobic and hydrophilic guest molecules due to its nanoporous structure and the existence of native cyclodextrins cavities (Olteanu, Arama, Bleotu, Monciu, & Lupuleasa, 2015; Swaminathan et al., 2010; Trotta et al., 2011). Although, CDNS is mainly considered as a promising candidates for encapsulation of diverse range of drugs and acting as drug carrier (Anandam & Selvamuthukumar, 2014; Cavalli, Trotta, & Tumiatti, 2006), its cavities can be exploited for encapsulation of other active molecules such as catalytic species (Boscolo, Trotta, & Ghibaudi, 2010; Cintas, Cravotto, Gaudino, Orio, & Boffa, 2012; Cravotto, Calcio Gaudino, Tagliapietra, Carnaroglio, & Procopio, 2012; Di Nardo et al., 2009;), gases, pollutants etc. (Arkas, Allabashi, Tsiourvas, Mattausch, & Perfle, 2006; Trotta, 2011).

Graphitic carbon nitride, referred as g-C_3N_4, is an emerging class of metal-free polymeric semiconductor materials (Li et al., 2010; Mamba and Mishra, 2016; Wen, Xie, Chen, & Li, 2017; Zhang, Xie et al., 2013), which can be synthesized through poly condensation of simple organic raw materials such as urea, melamine and cyanamides and formation of covalent bonds between N and C atoms, (Martin et al., 2014; Su, Antoniettia, & Wang, 2012; Ye, Cui, Qiu, & Wang, 2014; Zhang, Hu, & Jiang, 2014). These materials exhibit outstanding optical, electronic and morphological, properties and can be considered as promising candidates for development of various (photo) catalysts (Li et al., 2010; Mamba & Mishra, 2016; Molla, Iqubal, Ghosh, & Kamaluddin Islam, 2015; Molla, Iqubal, Ghosh, & Islam, 2016; Nadagouda, Nasir Baig, Varma, & Verma, 2016; Ong, Tan, Ng, Yong, & Chai, 2016; Su, Vinu, Aldeyab, & Zhong, 2015; Wen et al., 2017; Zhang, Xie et al., 2013;). Recently, development of novel hybrid systems composed of g-C_3N_4 and inorganic materials has gained increasing attention (Kumar et al., 2014; Molla et al., 2016; Nadagouda et al., 2016; Zhu et al., 2016).

Sonogashira and Heck C—C coupling reactions are key Pd-catalyzed organic transformations, which can be used for the synthesis of more complex chemicals, drugs and natural products (Lin, Huang, Wu, Mou, & Tsai, 2010). In most of methodologies developed for these coupling reactions, use of copper co-catalysts and phosphine ligands were imperative (Hajipour, Shirdashtzade, & Azizi, 2014). Moreover, Pd catalysts used for promoting these chemical transformations were mostly homogeneous and in some protocol use of costly or toxic solvents and bases was inevitable. Hence, development of an eco-friendly, efficient and cost-effective procedure for C—C coupling reactions has received growing attention. In this line, disclosing of heterogeneous catalysts and development of ligand and copper-free methods in aqueous media were focused (Bakherad, 2013; Bakherad, Doosti, Mirzaee, & Jadidi, 2017; Esmaeilpour, Sardarian, & Javidi, 2016; Gholap et al., 2005; Hajipour et al., 2014; Nasrollahzadeh, Khalaj, & Ehsani, 2014; Nasrollahzadeh, Maham, & Tohidi, 2014; Nasrollahzadeh, Sajadi, Maham, & Ehsani, 2015; Roya et al., 2014; Rathod & Jadhav, 2017; Shunmughanathan, Puthiaraj, & Pitchumani, 2015; Thorwirth, Stolle, & Ondruschka, 2010; Zhou et al., 2014;).

In continuation of our studies on heterogeneous catalysts (Sadjad, Heravi, Zadsirjan, & Farzaneh, 2017; Sadjadi, Malmir, Heravi, 2017), we have recently focused on the utility of CDNS (Sadjadi, Heravi, Daraie, 2017b; Sadjadi, Heravi, Daraie, 2017a) and HNTs (Sadjadi, Heravib, Malmir, & Masoumi, 2016; Sadjadi & Bahri-Laleh, 2017; Sadjadi, Heravi, Malmir, 2017; Sadjadi, Hosseinnejad, Malmir, Heravi, 2017) for immobilization of catalytic active species. Considering the unique properties of CDNS and HNTs as catalyst supports, herein, we report a novel ternary hybrid system composed of HNTs, CDNS and g-C_3N_4 as an efficient support for immobilizing Pd(0) nanoparticles. The resulting hybrid system, Pd@HNTs-CDNS-g-C_3N_4 was used as an efficient and heterogeneous catalyst for promoting ligand and copper-free Sonogashira and Heck coupling reactions in aqueous media under mild reaction condition, (Schemes 1 and 2 in supporting information). It was postulated that the hybrid system not only took advantage of excellent features of HNTs, the presence of CDNS, which could form inclusion complexes with substrates and bring them close to the catalytic active sites could accelerate the reaction rate. g-C_3N_4 on the other hand, could suppress the Pd leaching dramatically. To verify this assumption and investigate the presence of synergistic effect between the components of the hybrid system, recyclability of the catalyst and leaching of Pd were examined and compared with some control samples.

2. Experimental

2.1. Materials and instruments

The chemicals used for the synthesis of the catalyst included urea, halloysite clay, (3-chloropropyl) trimethoxysilan, (3-Aminopropyl) triethoxysilane (APTES), toluene, β-cyclodextrin, diphenyl carbonate, $Pd(OAc)_2$, $NaBH_4$, all purchased from Sigma-Aldrich and used without any purification.

The reagents applied for accomplishing Sonogashira and Mizoroki-Heck coupling reactions included acetylenes, styrene, halobenzene, distilled water, K_2CO_3, and distilled water. All were analytical grade and purchased from Merck.

The progress of the C—C coupling reactions was monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. All the organic products were known and their identification was performed by comparing their melting points, determined in open capillaries using an Electrothermal 9100, and FTIR spectra with authentic samples. For some selected products ^{13}CNMR and ^{1}HNMR spectroscopy were also accomplished to verify their formation.

The ultrasonic apparatus used for homogenizing HNTs was Bandelin HD 3200 with output power of 150 W and tip TT13.

The structure of Pd@HNTs-CDNS-g-C_3N_4 was confirmed by using SEM/EDS, TEM, TGA, FTIR, BET, XRD, and ICP-AES. Room temperature powder X-ray diffraction patterns of the catalyst and pure HNTs were recorded by employing a Siemens, D5000. CuKα radiation from a sealed tube. To record transmission electron microscope (TEM) images of the catalyst, CM30300Kv field emission transmission electron microscope was used. The N_2 adsorption-desorption isotherm of Pd@HNTs-CDNS-g-C_3N_4 and study of textural properties of the catalyst and the control samples (vide infra) were achieved by using BELSORP Mini II instrument. Notably, the samples were degassed prior to the analysis by heating the samples at 423 K for 3 h. SEM/EDS images of the hybrid catalyst as well as its components were recorded by using a Tescan apparatus, using Au-coated samples and acceleration voltage of 20 kV. To record the FTIR spectra of the catalyst and its components, PERKIN-ELMER- Spectrum 65 instrument was used. To perform thermo gravimetric analyses (TGA) and determine the content of the each component in the hybrid catalyst, a METTLER TOLEDO thermo gravimetric analysis apparatus was employed. The heating rate of the apparatus was 10 °C min^{-1} and the scan was performed in the range of 50–650 °C under inert (N_2) atmosphere.

2.2. Synthesis of CDNS

CDNS was synthesized according to the literature (Cavalli et al., 2006; Swaminathan et al., 2010; Trotta et al., 2011). Briefly, β-cyclodextrin (1 mmol) was slowly added into the melted diphenyl carbonate (8 mmol). Upon introduction of β-cyclodextrin, a white solid was