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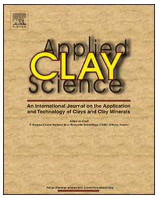

Research paper

Heterogeneous poly(ionic liquids) catalyst on nanofiber-like palygorskite supports for biodiesel production

Wen Zhang[a], Meisheng Li[a,*], Jie Wang[a], Yijiang Zhao[a,*], Shouyong Zhou[a], Weihong Xing[b]

[a] *School of Chemistry and Chemical Engineering, Huaiyin Normal University, Jiangsu Key Lab for Chemistry of Low-Dimensional Materials, Jiangsu Collaborative Innovation Center of Regional Modern Agriculture & Environmental Protection, No.111 West Changjiang Road, Huaian, 223300, Jiangsu Province, PR China*

[b] *State Key Laboratory of Materials-Oriented Chemical Engineering, School of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing, 210009, Jiangsu Province, PR China*

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ABSTRACT

New heterogeneous poly(ionic liquids) catalysts (PAL-PILs) were successfully prepared by grafting polymerization of acid ionic liquids (ILs) (1-butysulfonate-3-vinylimidazole hydrogen sulfate) onto nanofiber-like palygorskite (PAL) supports that had been, in advance, covalently modified by γ-methacryloxypropyl trimethoxy silane (OPAL). Using the ester yields and PILs grafting degrees as main indexes, the optimized immobilization conditions were that the mass ratio of OPAL to ILs monomer was 1:2, the immobilization temperature and time were 60 °C and 30 h, the initiator (2,2′-Azobis(2-methylpropionitrile) dosage was about 5 wt%, respectively. Then, the esterification between methanol and oleic acid was carried out to investigate the catalytic properties of PAL-PILs. For the homogeneous ILs catalyst, the yield of methyl oleate was about 85%. For the PAL-PILs, on which only about 41% of ILs used in homogeneous catalysis was immobilized, the yield could reach over 69% after reacting only 5 h at 75 °C at atmospheric pressure, when the molar ratio of methanol to oleic acid is adjusted to 12:1. More importantly, the yield of methyl oleate still maintained at about 22% after 6 recycling experiments. Moreover, the PAL-PILs catalysts exhibited efficient catalytic properties and could be recycled easily. These results offer great potential for the PAL-PILs in the biodiesel production for further research.

1. Introduction

The developing of renewable and environmental-friendly energy (Panwar et al., 2011) is desired and urgent for the sustainable development of human society. Biodiesel (Demirbas, 2006), whose main components are methyl esters, is a new kind of clean-burning and environmental-friendly diesel fuel. To reduce the cost of biodiesel production, different low cost raw materials (Shu et al., 2007; Bhatti et al., 2008; Biermann et al., 2011; Sankaranarayanan et al., 2012; Singh et al., 2014) such as microalgae, plant oil, recycled cooking oils, animal fats, or grease, are used as feedstock. Nowadays, biodiesel production has possessed a large energy market in Europe (Melero et al., 2009). Obviously, it will represent one of the most significant alternatives to conventional petrodiesel fuel in the future.

The processes to produce biodiesel include dilution, pyrolysis, micro-emulsification and transesterification (Fukuda et al., 2001). Among these technologies, transesterification or esterification has become the main process for biodiesel synthesis, e.g. the esterification (Souza et al., 2009) between free fatty acid with methanol or the transesterification (Russbueldt and Hoelderich, 2010) of triglycerides with methanol. Meanwhile, these processes need catalysts to speed up reaction velocities. The traditional catalysts are strong acid or alkali. Nevertheless, it is very difficult to remove and separate these catalysts after reaction, thereby producing large amount of wastes, causing equipment corrosion and environmental problems (Zhen et al., 2014). To overcome these drawbacks, designing novel catalysts is necessary.

Room temperature ionic liquids (ILs), as a kind of environmental-friendly liquids, have many unique properties, such as high thermal stability and negligible vapor pressure. Moreover, strong acid ILs can be used as catalysts in many transesterification or esterification reactions. Deng et al. (2001)) reported the esterification of carboxylic acids with alcohol in 1-butylpyridinium chloride-aluminum(III) chloride. The conversions could reach 65%–100% after reacting 2 h at 110 °C. Gui et al. (2004)) synthesized three acidic ILs and used them as catalysts for the esterification. In the esterification of ethanol with acetic acid, a conversion of 92.8% and a selectivity of 100% were gained for the 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate. In addition, Fan et al. (2013)) synthesized three basic catalysts for the transesterification of soybean oil with methanol. Choline hydroxide (ChOH) catalyst exhibited better performance compared with others. Biodiesel

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* Corresponding authors.
E-mail addresses: lms1108@hytc.edu.cn (M. Li), cyjzhao@yahoo.com (Y. Zhao).

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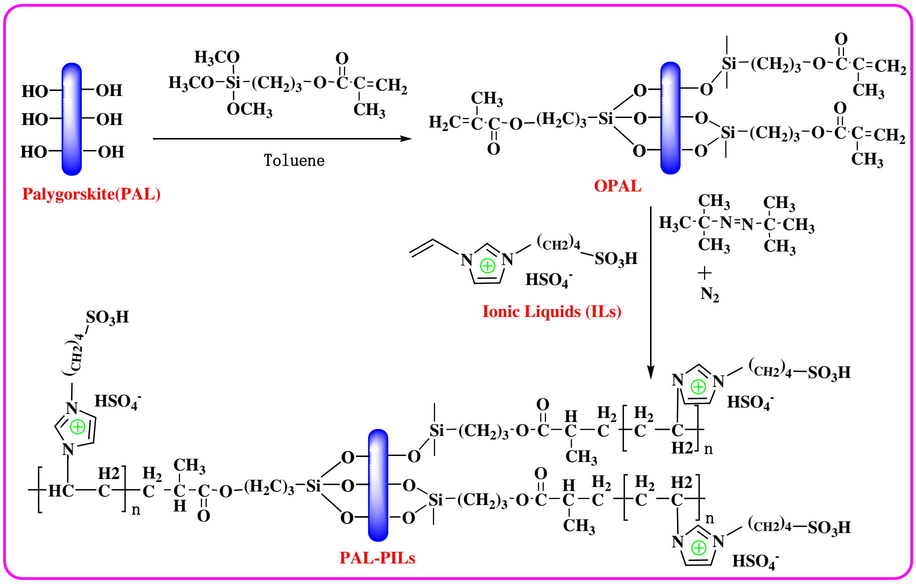

Scheme 1. The preparation procedure of OPAL and PAL-PILs.

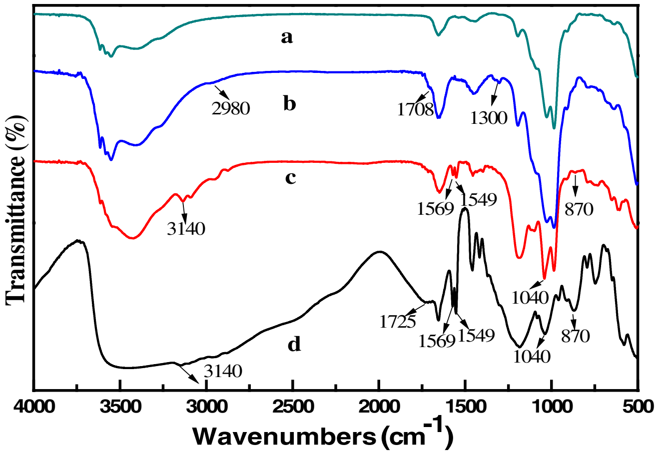

Fig. 1. FT-IR spectra of PAL (a), OPAL (b), PAL-PILs (c) and $[(CH_2)_4SO_3HVIm]HSO_4$ (d).

yield was about 95% under suitable conditions. In all, ILs used as catalysts for the synthesis of biodiesel have become a hot topic in recent years. However, the high synthesis cost of ILs, the high mass transfer resistance due to the high viscosity, and difficult to recycle after reaction limited their wide industrial application in the transesterification or esterification process. To reduce the using amount of ILs and recycle them conveniently, many efforts have been reported to immobilize ILs on solid supports to prepare heterogeneous solid catalysts (Li et al., 2012).

The drawback of the traditional immobilized ILs is that the acid sites covered on the support surface fell off easily from the surface (not stability), thereby decreasing the activities (Liang, 2013). To ensure the stability of grafting layer, Flavel et al. (2013)) considered that a high grafting density was one of the most important decisive factors. Thus, to obtain high stability and high activity of immobilized ILs, ILs should own both a high acidity and functional groups for the grafting reaction. Recently, polymerizable Brønsted acidic ILs have attracted great interest, because they combined the unique properties of ILs with the intrinsic polymer properties and presented the advantages of both ILs and polymers (Tong et al., 2011; Pourjavadi et al., 2012a,b, 2013). Importantly, there is a functional C═C double bond in the ILs monomer, which can be used for following immobilization reactions. Moreover, after graft polymerization, there is an acid active group in every monomer unit of polymeric ILs (PILs) chains, thereby making the acidity and the graft density extremely high.

For the supports, it should own large specific surface, high porosity, connected pore structure and enough hydroxyl groups for the anchorage of ILs. Up to now, various supports have been employed, such as silica (Qiao et al., 2006), zeolite (Liu et al., 2006), montmorillonite clay (Ratti et al., 2010) and polymer (Noshadi et al., 2014). Practical issue is that most of these supports need to be chemically synthesized. This additional step increases the cost of the overall ILs immobilization process considerably. Palygorskite (PAL) is a kind of natural nanofiber-like crystalline hydrated magnesium aluminum silicate mineral with a diameter of about 100–500 nm and a length of 1–2 μm, which makes PAL high specific surface, excellent thermal/mechanical stability and silanol-based chemistry of the surface (Xu et al., 2013). Importantly, the acid activated PAL owns large amounts of hydroxyl groups, thereby ensuring the next high graft density. Moreover, PAL is a kind of abundant natural resources in the world, especially rich in our city (Huaian, Jiangsu Province, China), holding about 44% of the world's proven reserves (Yang, 1995). Therefore, the natural PAL is a potential inorganic support for ILs.

Herein, the nanofiber-like PAL was selected as a solid support and activated in dilute hydrochloric acid to generate enough surface hydroxyl groups firstly. Then, heterogeneous poly(ionic liquids) catalysts (PAL-PILs) were prepared successfully by grafting polymerization of acid ILs (1-butysulfonate-3-vinylimidazole hydrogen sulfate) onto PAL supports that had been, in advance, covalently modified by γ-methacryloxypropyl trimethoxy silane (KH570). The PAL-PILs were used to catalyze the esterification between methanol with oleic acid. For comparison, the homogeneous ILs were also evaluated in esterification. Meanwhile, the recycling experiment was carried out to investigate the stability and reusing performances of the PAL-PILs.

2. Experimental

2.1. Materials

The pure PAL was supplied by Jiangsu Jiuchuan Nano-material Technology Co., Ltd. Methanol (≥ 99.5%) was purchased from Shanghai Shiyi Chemical reagent Co., Ltd., γ-methacryloxypropyl trimethoxy silane (KH-570) and oleic acid (AR) from Sinopharm Chemical Reagent Co., Ltd., 1-butysulfonate-3-vinylimidazole hydrogensulfate ($[(CH_2)_4SO_3HVIm]HSO_4$) as monomer from ShangHai Cheng Jie Chemical CO.,LTD and 2,2′-Azobis(2-methylpropionitrile) (AIBN) as initiator from Shanghai Chemical Co., Ltd. Oleic acid (CH_3