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Catalytic performance of strong acid catalyst: Methyl modified SBA-15 loaded perfluorinated sulfonic acid obtained by the waste perfluorinated sulfonic acid ion exchange membrane

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ABSTRACT

Mesoporous molecular sieve (SBA-15) was modified using the trimethylchlorosilane as functional agent and the silylation SBA-15 mesoporous material was prepared in this work. The alcohol solution of perfluorinated sulfonic acid dissolved from the waste perfluorinated sulfonic acid ion exchange membrane (PFSIEM) was loaded onto the resulting mesoporous material by the impregnation method and their physicochemical properties were characterized by FT-IR, N_2-physisorption, XRD, TG-DSC and TEM. The catalytic activities of these synthesized solid acid catalysts were evaluated by alkylation of phenol with *tert*-butyl alcohol. The influence of reaction temperature, weight hour space velocity (WHSV) and reaction time on the phenol conversion and product selectivity were assessed by means of a series of experiments. The results showed that with the increase of the active component of the catalyst, these catalysts still remained good mesoporous structure, but the mesoporous ordering decreased to some extent. These catalysts exhibited good catalytic performance for the alkylation of phenol with *tert*-butanol. The maximum phenol conversion of 89.3% with 70.9% selectivity to 4-t-butyl phenol (4-TBP) was achieved at 120 °C and the WHSV is 4 h^{-1}. The methyl group was loaded on the surface of the catalyst by trimethylchlorosilane. This is beneficial to retard the deactivation of the catalyst.

1. Introduction

Tert-butylated phenols could be produced by the alkylation of *tert*-butanol with phenol under acidic catalyst, which have been widely used for the synthesis of phenol resins, surfactants, lubricants and antioxidants, *etc.* [1–4]. Conventionally, the liquid acid and the ion exchange resins were mainly used as catalysts to produce *tert*-butylated in industry. The liquid acid catalysts have some disadvantages such as corrosiveness of reaction apparatus, low product selectivity, environmental non-friendliness, and discharging large quantities of wastewater [5–8]. The ion exchange resin catalysts could react under mild condition and have non-corrosive action, but they are prone to inactivation limiting its application [9]. Therefore, the research and development of highly selective, environmentally friendly, inexpensive, and recyclable solid acid catalysts have been widespread concerned. Currently, the solid acid catalysts of alkylation of phenol including traditional zeolite such as Hβ, HY, HM, HZSM-5 [1,10–12], acid-functional mesoporous materials [13] and metal oxide [14] were studied.

The waste perfluorinated sulfonic acid ion exchange membrane (PFSIEM) which was the composite membrane consisting of polytetrafluoroethylene fiber, perfluorinated sulfonic acid and perfluorinated carboxylic acid resin was achieved from chlor-alkali plants [15]. The alcohol solution of perfluorinated sulfonic acid could be made of PFSIEM under a certain temperature and pressure [16]. Among perfluorinated sulfonic acid resin exhibits good performance such as high thermal stability (< 280 °C), chemical inertness and strong acidity ($H_0 = -12$), but they generally showed a dense non-porous, low surface area (< 0.02 m^2/g), so that a large number of acid sites are buried and they were limited in practical application. In order to enhance catalytic activity of the catalyst, various catalysts using the mesoporous molecular sieve as support for alkylation, acylation, isomerization, esterification, ketalization, etherification, *etc.* have been reported [17–22]. Zhu et al. [23] reported that catalytic activities of the supported Nafion-CTAB/MCM-41 synthesized by hydrothermal method is better than CTAB for brominating reaction of 1, 7-heptanediol. It was found that Nafion-CTAB/MCM-41 has both phase-transfer and strong acidity function. Morales et al. [24] reported that Nafion/SBA-15 made by a post-synthetic impregnation method is a good hybrid material for the Friedel-Crafts acylation of anisole. However, the surface of SBA-15

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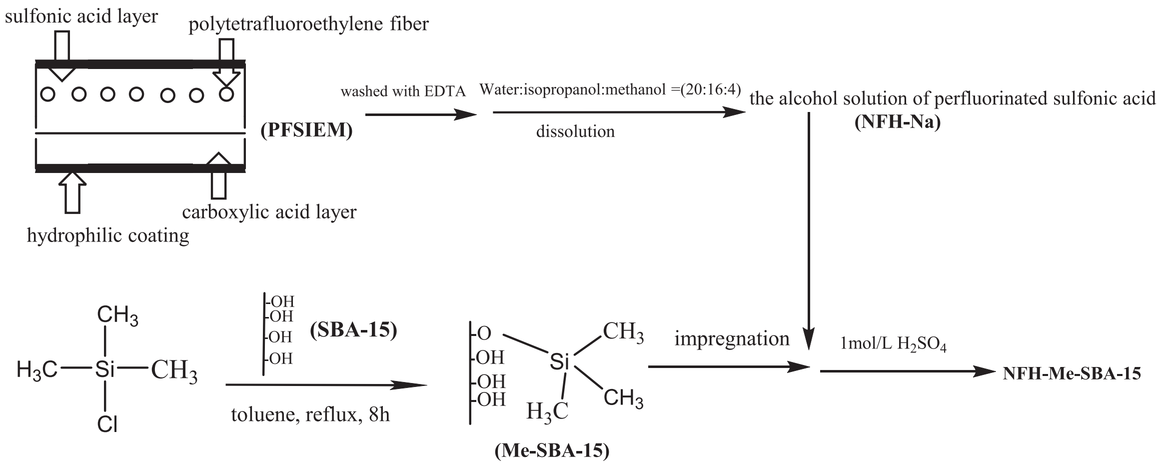
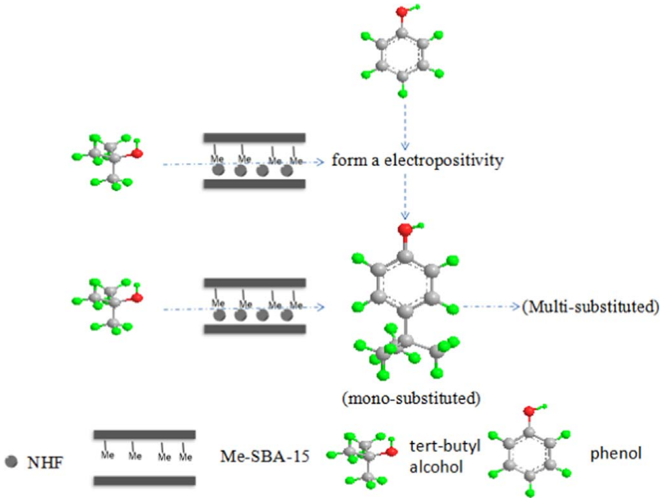


Scheme 1. Synthetic route of NFH-Me-SBA-15 catalyst.



Scheme 2. A possible reaction mechanism over NFH-Me-SBA-15 catalyst.

mesoporous material has a lot of silicon hydroxyls, leading to that SBA-15 mesoporous material has the hydrophily. This is unfavourable for the application of filling lipophilic matter as support. Therefore, it is significance to investigate the grafting functional groups on the surface of SBA-15 mesoporous material, *viz.* conducting the hydrophobicity modification of SBA-15 in application of nanomaterials. The methyl, hydrophobic group, was introduced into the SBA-15 mesoporous materials resulting in change in physicochemical property of the resulting catalyst, making for desorption of product molecules and effectively inhibiting the inactivation of catalyst [25].

In this work, trimethylchlorosilane was used to modify the surface of SBA-15 mesoporous molecular sieve. The alcohol solution of perfluorinated sulfonic acid (denoted as NFH) was prepared by the waste perfluorinated sulfonic acid ion exchange membrane (PFSIEM). A series of modified SBA-15 samples were functionalized by the impregration method with the alcohol solution of perfluorinated sulfonic acid, and the catalysts with different acid densities were obtained. Furthermore, their catalytic activities were also evaluated by the alkylation of phenol with *tert*-butyl alcohol. Particularly, the influence of the amount of support, reaction temperature, WHVS and reaction time were discussed. The results show that silylation catalyst exhibited much higher catalytic activity in the alkylation of phenol with *tert*-butyl alcohol as compared with the results reported in the Ref. [26].

2. Experimental

2.1. Materials

The waste perfluorinated sulfonic acid ion exchange membrane (PFSIEM) was achieved from chlor-alkali plants (Zhenjiang, China). Tetraethyl orthosilicate (TEOS, 99%) and Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (Pluronic P123) were used as sources for silicon and the structure-directing agent, respectively. Moreover, trimethylchlorosilane, concentrated hydrochloric acid (HCl), concentratured sulfuric acid (H_2SO_4), ethylenediamine tetraacetic acid disodium salt (EDTA), methanol and isopropanol were also used in the experiment. All the reagents were analytical grade and were purchased from Shanghai Chemical Reagent Co., Ltd.

2.2. Catalyst preparation

2.2.1. Preparation of the alcohol solution of perfluorinated sulfonic acid resin [16]

The waste perfluorinated sulfonic acid ion exchange membrane (PFSIEM) was washed with EDTA solution and diluted hydrochloric acid, respectively. Then, the polytetrafluoroethylene networks were stripped from the sodium form or the acid form of perfluorinated sulfonic acid ion exchange membrane. Water, isopropanol, methanol (20:16:4, volume ratio) and 2 g of the sodium form of membrane was added into a 100 mL Teflon-lined stainless steel autoclave and crystallized at 230 °C for 6 h. After cooling to ambient temperature, 5 mL of the clear solution was dried at 110 °C to obtain a thin film. The clear solution concentration was calculated (the concentration required to achieve of the experiment was 0.05 g/mL), denoted as NFH-Na.

2.2.2. Preparation of mesoporous SBA-15 [27]

4.0 g of P123 and 20 mL of HCl (37 wt%) was dissolved into 120 mL of deionized water until the solution became clear. Then, 9 mL of tetraethyl orthosilicate was added to the solution. After being stirred at 35 °C for 24 h, the mixture was aged under static conditions and constant pressure at 100 °C for 48 h. After cooling to ambient temperature, the solid product was filtered, washed with distilled water, dried overnight in an oven. The template agent was removed by calcination at 550 °C for 5 h.

2.2.3. Silylation of SBA-15 [28]

1 g of SBA-15 was dried under vacuum at 110 °C for 12 h before adding 1.5 g of trimethylchl orosilane and 30 mL toluene under the nitrogen protection. The mixture was refluxed for 6 h at 80 °C. After cooling to room temperature, the reaction mixture was washed respectively with toluene and ethanol, and dried under vacuum at