



Modified natural halloysite nanotube solely employed as an efficient and low-cost solid acid catalyst for alpha-arylstyrenes production via direct alkenylation

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ABSTRACT

Owing to unique mesoporous/macroporous hollow nanotubular structure, relatively high specific surface area, abundant surface hydroxyl groups, ecological and biocompatibility as well as low cost and large availability, the natural halloysite nanotube (HNT) has attracted great attention in drug delivery, catalysis, adsorption, energy storage, etc. HNT was generally used as support in catalysis, but rare report for HNT being solely used as catalyst. In this work, we firstly reported that HNTs were solely employed as a solid acid catalyst for alkenylation of diverse aromatics with phenylacetylene to their α -arylstyrenes. It was found that the HNT with a facile ion exchange and calcination pretreatment demonstrated outstanding catalytic performance in alkenylation of *p*-xylene with phenylacetylene, and 95.6% of phenylacetylene conversion with 95.8% of selectivity toward α -(2,5-dimethylphenyl) styrene was achieved. The HNT were characterized by N_2 physisorption, transmission electron microscopy (TEM), NH_3 temperature-programmed desorption (NH_3 -TPD), pyridine infrared spectroscopy (Py-IR), and Inductively coupled plasma (ICP), and thermogravimetric analysis (TGA) techniques. Correlated the nature of HNTs to reaction results, it was revealed that the catalytic performance of HNT was significantly dependent on their acidic properties and textural feature notably affected by ion exchange times (N_{IE}) and calcination temperature (T_C). Especially, besides acidic properties, the nature of the formed mesopores on the walls of HNTs strongly affects the catalytic activity, selectivity and coke-deposition behavior. The appropriate acidic sites and their accessibility are essential for obtaining satisfactory catalytic performance. The modified HNT catalyzed alkenylation can be extended to diverse substrates with good catalytic properties for diverse α -arylstyrenes production. The combination of excellent catalytic properties and the facile regeneration of deactivated HNT by calcination process allows it to be a promising candidate for, but limited to alkenylation of aromatics with phenylacetylene to their α -arylstyrenes.

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1. Introduction

Alkenylaromatics serve as industrially important organic intermediates for producing dyes, pigments, pharmaceuticals, flavors, agrochemicals, and natural products [1]. The alkenylation of aromatic compounds, also called as hydroarylation of alkynes, has attracted huge attention due to its versatile features of simple, environmentally benign, and atom economic for synthesizing alkenylaromatic compounds. The acid-catalyzed alkenylation of

aromatics has become a promising alternative for synthesizing alkenylaromatics because of its low cost and high activity [2–8].

Heterogeneous catalysis presents a promising approach for organic transformations because of its feature in terms of clean, easy-separation, catalyst reusability, and its applicability toward continuous production in a large scale. Recently, zeolite is being more and more regarded as an environmentally benign solid acid catalyst for Friedel–Crafts alkylation in academic and industrial fields [9–11]. However, not like the well-established Friedel–Crafts alkylation, the Friedel–Crafts alkenylation still remains a rigorous challenge to be resolved. The biggest issue is to eliminate the oligomerization and deep polymerization of alkynes efficiently owing to the less stability of alkenyl cation species than that of alkyl cation intermediate [12–16]. Till now, the rare report on

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alkenylation over solid acid catalysts can be found. Sartori had made some pioneering work on alkenylation of aromatics over HSZ-360 zeolite [17], unfortunately the results are not very satisfactory, and there exists an irreconcilable contradiction between the selectivity and the catalytic activity. The zeolites calcined at lower temperature exhibited high catalytic activity, but the considerable amount of acetophenone (5–20%) was detected; the higher calcination temperature could efficiently compress the formation of acetophenone, but led to remarkable decrease in the catalytic activity. Moreover, the low catalytic efficiency would be observed while the HY was used as catalyst for the alkenylation, ascribed to the reaction only taking place on the external surface of the catalyst because of its narrow pore channels within HY zeolite. Moreover, the improvement in the catalytic efficiency and enlargement in scope of substrates are desirable [14,18]. Recently, it was demonstrated that the Fe-containing mesoporous aluminosilicate exhibited very high activity for the Friedel–Crafts alkenylation of phenols with aryl-substituted alkynes under mild conditions [19]. However, the further increase in selectivity is indispensable.

In our advanced catalytic materials research group, the supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPA) catalysts on MCM-41 for alkenylation of diverse aromatics were developed [13]. However, the further improvement in catalytic activity, selectivity and the expansion in reactants scope is required. Moreover, the complex and high cost preparation process of mesoporous silica leads to the high cost for production of α -arylstyrenes via solid acid catalyzed alkenylation. The HPA/AC has been developed to overcome the high cost issue of the HPA/MCM-41 [15]. The efficient regeneration of deactivated catalyst by polar solvent washing method might require a large amount of evaporable solvent that consequently would produce environmental issue, besides the possible leaching of HPA led by polar solvent. In addition, we developed a novel and efficient $\text{SO}_4^{2-}/\text{meso-La}_2\text{O}_3\text{-ZrO}_2$ catalyst for alkenylation [16]. Although the catalyst could be regenerated by calcination treatment, the loss of active component is still a serious problem. Moreover, the further improvement in catalytic activity is required. In a word, the Friedel–Crafts alkenylation over solid acid catalysts are still scarcely reported, although this strategy could be a promising approach with easy separation, green and atom-economic features for the synthesis of 1,1-diaryllkenes. Therefore, the development of novel, low-cost, and robust solid acid catalysts for Friedel–Crafts alkenylation is highly desirable, but it still remains a challenge.

Halloysite nanotube (HNT), as a member of hydrated aluminosilicate of the kaolinite group, has a molecular formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ and possesses unique mesoporous/macroporous hollow nanotubular structure, relatively high specific surface area, abundant surface hydroxyl groups. Plus its ecological and biocompatibility as well as low cost and high availability, the HNT has attracted great attention in drug delivery, catalysis, adsorption, energy storage, etc [20–37]. As for its usage in heterogeneous catalysis, from references, HNT was generally used as catalyst support, but rare report for it being solely used as catalyst [29–37]. From the analysis on HNT structure and component, it has great potential to serve as solid acid catalyst for organic transformations now that the possible acidic sites on internal Al_2O_3 and at the interface of SiO_2 and Al_2O_3 . Moreover, the existence of a small amount of Fe_2O_3 can produce acidic sites. However, to the best of our knowledge, no report on HNT being solely used as solid acid catalysts can be found, although HNT as carrier for SO_3H -containing solid acid for one-pot conversion of cellulose to 5-hydroxymethylfurfural was reported [38,39].

In this work, we present the first example for HNT solely used as an efficient solid acid catalyst for alkenylation of diverse aromatics with phenylacetylene for clean production of α -arylstyrene. Besides the Al_2O_3 , SiO_2 , and H_2O , there are Na^+ , K^+ , etc., in HNT walls. The removal of Na and K might increase acidic sites on

the HNT. The calcination treatment can produce mesopores on the HNT walls due to dehydration during calcination process, besides it can adjust acidic properties. Therefore, we investigated the effect of ion exchange times (N_{IE}) and calcination temperature (T_{C}) on the textural feature and acidic properties of HNT as well as its catalytic performance in alkenylation of diverse aromatics with phenylacetylene to their corresponding α -arylstyrene. Various characterization techniques such as TEM, N_2 physisorption, Py-IR, NH_3 -TPD, ICP were employed to reveal the relationship between catalyst nature and catalytic performance. It was found that the catalytic performance of HNT was significantly dependent on their acidic properties and textural feature notably affected by N_{IE} and T_{C} . The combination of excellent catalytic properties and the facile regeneration of deactivated HNT by calcination process endows it to be a promising candidate for, but limited to alkenylation of aromatics with phenylacetylene to their α -arylstyrenes.

2. Experimental

2.1. Catalyst preparation

The natural halloysite nanotube (HNT) was purchased from Zhengzhou Jinyanguang Chinaware Co., Ltd., Henan, China. The obtained HNT was used without further purification. The content of halloysite in the mineral was measured by the previously reported method [40]. The result shows that the mineral is the halloysite-rich material, which contains 91% of halloysite and then 9% of kaolinite. Due to the existence of a certain amount of K and Na, the ion exchange treatment could improve acid sites by removing Na^+ and K^+ from its framework. The ion exchange process was performed as follows: 1 g halloysite nanotubes was added to 1 M aqueous solutions of NH_4NO_3 and then stirred vigorously under refluxing conditions. Then the mixture was filtered, dried overnight and subsequently calcined at 500°C to obtain the catalyst powder. HNT catalysts with diverse ion exchanging times ($N_{\text{IE}}=0\text{--}3$) were prepared by using the similar procedure as above but with different N_{IE} . Moreover, the diverse HNT catalysts with different calcination temperatures ($450, 500, 550, 600^\circ\text{C}$) were also prepared.

2.2. Catalyst characterization

TEM images were obtained with Tecnai F30HRTEM, the specimens were prepared by the following procedure: the HNT sample was dispersed in ethanol with ultrasonic and then a drop of sample suspension was dropped onto a carbon coated copper grid, which was left to stand for 10 min before transferred into the microscope. The amount of Na and K of the halloysite nanotubes catalyst was measured by the ICP technique on the ICP spectrometer (Optima 2000DV, PerkinElmer). Nitrogen physisorption experiments were carried out at -196°C on a Quantachrome Autosorb instrument. The specific surface area was calculated by the BET method, and the pore size distribution was calculated by BJH model from the adsorption branch of the isotherms. The coke amount deposited on spent catalysts was obtained by TGA analysis, which was conducted using a PerkinElmer STA 6000 with a heating rate of $10^\circ\text{C min}^{-1}$ from 30 to 800°C in an air stream. The XRD patterns were collected from 5 to 80° at a step width of 0.02° using Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a $\text{CuK}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$).

The acidic properties of the samples were measured by NH_3 -TPD and Py-IR. NH_3 -TPD measurements were performed to characterize the acidic properties of the samples. After pre-treatment of 50 mg samples in Ar (up to 450°C with a ramp rate of $10^\circ\text{C min}^{-1}$, then kept for 0.5 h, 30 ml min^{-1} Ar flow), the samples were saturated with ammonia (10% NH_3 -90% Ar) at 100°C via the pulse injec-

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