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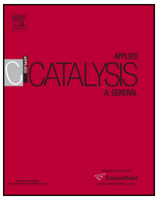

Supported phosphotungstic acid catalyst on modified activated carbon for Friedel–Crafts alkenylation of diverse aromatics to their corresponding α-arylstyrenes

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ABSTRACT

The supported phosphotungstic acid catalysts on modified activated carbon (PTA/AC) prepared by a facile wet impregnation method were employed for Friedel–Crafts alkenylation of diverse aromatics with phenylacetylene to synthesize their corresponding α-arylstyrenes. Reaction results demonstrate that the fabricated PTA/AC catalyst with 30 wt.% PTA loading exhibits outstanding catalytic performance. The 100% conversion of phenylacetylene with 95.7% selectivity towards α-(2,5-dimethylphenyl) styrene can be achieved over the developed 30 wt.% PTA/AC catalyst under optimized reaction conditions, and no visible loss in catalytic performance can be observed after it suffers from several times recycling. The various characterization techniques including X-ray diffraction, N_2 adsorption–desorption, Fourier transform infrared spectroscopy, and NH_3 temperature-programmed desorption were employed to reveal the relationship between the catalysts nature and catalytic properties. Moreover, the results on the scope of aromatics for the Friedel–Crafts alkenylation illustrate that the developed PTA/AC alkenylation catalyst can be efficiently catalyze the diverse aromatics and even for the electron deficient chlorobenzene. The developed PTA/AC catalyst, using the modified low-cost and sustainable AC as support, may be a robust and promising candidate for highly-efficient and clean α-arylstyrenes production through Friedel–Crafts alkenylation of diverse aromatics including electron-donating and electron-withdrawing groups substituted benzene derivatives as well as heterocyclic and polypolycyclic arenes with phenylacetylene.

1. Introduction

Alkenylaromatics, serve as industrially important intermediates for producing pharmaceuticals, agrochemicals, natural products, flavors and dyes, can be synthesized by the alkenylation of aromatics with alkynes, also known as hydroarylation of alkynes. Alkenylation has attracted considerable attention owing to the continuously growing demand for alkenylaromatics in chemical industry [1–4].

The heterogeneous catalysis provides an efficient approach for organic transformations in terms of clean, easy separation, reusability, and high selectivity. Recently, zeolite is being more and more regarded as an environmentally benign solid acid catalyst for Friedel–Crafts alkylation, and the acidity and pore size decisively affect the catalytic activation, selectivity and coke-resistance [5–7]. 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 efficiently eliminate the oligomerization of alkynes owing to the poor stability of alkenyl cation species [8–11]. However, the rare reports on alkenylation over solid acid catalysts can be found. Sartori had made some pioneering work on alkenylation of aromatics over HSZ-360 zeolite [12], 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 could 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 the HY zeolite, as well as the improvement in the catalytic efficieny and enlarge-

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ment in scope of substrates are deirable [11,13]. Recently, it was demonstrated that the Fe-containing mesoporous alluminosilicate exhibited vey high activity for the Friedel–Crafts alkenylation of phenols with aryl-substituted alkynes under mild conditions [14]. However, the further increase in selectivity is indispensable. Till now, the Friedel–Crafts alkenylations 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-diarylalkenes. Therefore, the development of novel and robust solid acid catalysts for Friedel–Crafts alkenylation is highly desirable, but it still remains a challenge.

It was demonstrated that heteropolyacid (HPA) can act as an efficient catalyst for the alkylation, due to its strong acidity and the Brønsted type fundamentally, which are comparable to those of HF and H_2SO_4. Among them, the phosphotungstic acid (PTA) is usually employed as the good catalyst for its high acidic strength and relatively high thermal stability [15]. But its lower surface area (about 5–8 m^2 g) is a serious drawback as the heterogeneous catalyst. The immobilization of HPA was considered as a sophisticated approach to increase PTA surface area. The supported PTA catalysts on diverse supports have demonstrated outstanding catalytic properties for various organic transformations [16–20], however, rare report on supported PTA catalyst promoted alkenylation can be found. We previously demonstrated that the supported PTA catalyst on MCM-41 under optimized conditions exhibited good catalytic performance in alkenylation. It was found that supported PTA catalyst could be a promising catalyst for the clean production of α-arylstyrenes [10]. However, further improvement in catalytic activity, selectivity and the expansion in reactants scope are 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. Therefore, searching a low cost and efficient support for PTA is desirable.

Activated carbon (AC) has been widely used as support for many kinds of catalysts [21–26]. The AC production from agricultural waste, lignocellulosics and plant origin could be considered as a simple protocol to obtain high-added value products from low cost raw materials and even wastes, as well as to resolve environmentally pollution problems in some degree. Moreover, AC supports show the visible advantages compared to oxide supports such as high surface area, high stability in acidic and basic media and at the same time the ability for facile recovery of the active metals by burning off the support [22,23]. With oxidation treatment, AC can gain more surface oxygen-containing groups, which can act as nucleation centers for the generation of well dispersed active components [26–28], which benefits the improvement in the catalytic performance of supported-type catalysts on AC.

In this work, the modified AC by oxidation pretreatment was employed as a carrier for preparing the supported PTA catalysts. It was found that the supported PTA catalyst on modified AC (PTA/AC) with appropriate PTA loading exhibited excellent catalytic performance in Friedel–Crafts alkenylation reactions of diverse aromatics, and even for the electron withdrawing groups substituted aromatics like nitrobenzene and chlorobenzene. Correlated catalytic performance with catalyst characteristics, it was illustrated that the catalytic performance of PTA/AC catalysts for Friedel–Crafts alkenylation was strongly dependent on the acidic properties, PTA dispersion, surface area and pore volume significantly affected by PTA loadings. Owing to the high activity and selectivity, good recyclability, the wide scope of aromatics, as well as the inherent sustainable and low cost feature of AC, the developed PTA/AC may be a robust and promising solid acid catalyst for the production of α-arylstyrenes via Friedel–Crafts alkenylation of aromatics with alkynes.

2. Experimental

2.1. Catalysts preparation

A commercially available AC derived from coconut shells (Aladdin, China) was used as support. The as-received AC was ground and sieved into final particles (less than 125 μm) for use. The AC surface modification process via H_2O_2 oxidation pretreatment was performed as follows: a certain amount of AC was immersed into a 35 wt.% H_2O_2 aqueous solution (5 ml g^{-1}AC) in a water–ice bath with continuously stirring for 6 h. The sample was filtered, washed with deionized water, and followed by drying at 105 °C overnight, and then the modified AC supports were obtained. The PTA/AC catalysts with diverse PTA loadings (10, 20, 30, and 40 wt.%) were prepared by wet impregnation method. The typical wet impregnation process is as follows: 0.23 g PTA (analytical reagent, AR, bought from China National Medicines Corp. Ltd.) was dissolved into 10 ml deionized water to obtain PTA impregant. 0.5 g treated AC was dispersed into the above PTA solution. The mixture was stirred and then stood for 24 h. The PTA impregnated catalysts were dried at 105 °C in air overnight, followed by calcinations in air at 300 °C for 3 h. Then the series of PTA/AC catalysts were obtained.

2.2. Catalysts characterization

XRD patterns of the samples were recorded using a Rigaku D/max-2400 apparatus using Cu Kα radiation. The diffractograms were recorded in the 2θ range 10–80° with a 2θ step size of 0.02° and a step time of 0.12 s at each point. The FT-IR spectra of the samples were collected on a Nexus Euro infrared spectrometer using the KBr pallet method, and the same collection conditions for all samples are used. Nitrogen adsorption experiments at −196 °C were carried out on a Beishide 3H-2000PS1instrument to measure the surface area and pore volume, and the samples were degassed at 200 °C for 6 h prior to the N_2 adsorption experiment. NH_3-TPD measurements were performed on an in-house constructed system equipped with a thermal conductivity detector (TCD) to measure the desorbed NH_3. 50 mg sample was loaded in quartz reactor between two quartz wool plugs, and then was pretreated in Ar at 300 °C (a ramp rate of 10 °C min^{-1}) for 0.5 h, followed by cooling to room temperature. The pretreated sample was saturated with ammonia at 100 °C via the pulse injection of ammonia. The desorption process was carried out from 100 °C to 700 °C at a heating rate of 10 °C min^{-1} with an Ar flow of 30 ml min^{-1}.

2.3. Catalytic performance measurement

The experiments of the alkenylation of aromatics with phenylacetylene were performed in the stainless steel autoclave reactor. Firstly, 15 g reactant mixture containing aromatics and phenylacetylene with desired molar ratio of aromatics to phenylacetylene was added into autoclave reactor, and then the desired amount of catalyst was added. After that, the autoclave was purged three times with N_2, and then the reactor was pre-filled with N_2 to 0.7–0.75 MPa (it reaches 1.0 MPa at reaction temperatures). After stirring 30 min at room temperature to make the reaction mixture homogeneous, the mixture was heated up to the desired reaction temperature, and then start to count the reaction time. After the reaction, the mixture was quickly cooled down to room temperature and then was filtered for catalyst separation. The 96–98% of carbon balance was obtained by external standard method. The carbon loss can be resulted from the possible adsorption and/or coke on catalyst. Quantitative analysis of the collected products was performed on a FULI 9790 II GC equipped with HP-5 column, 30 m × 0.32 mm × 0.25 μm, and FID detector. The GC/MS

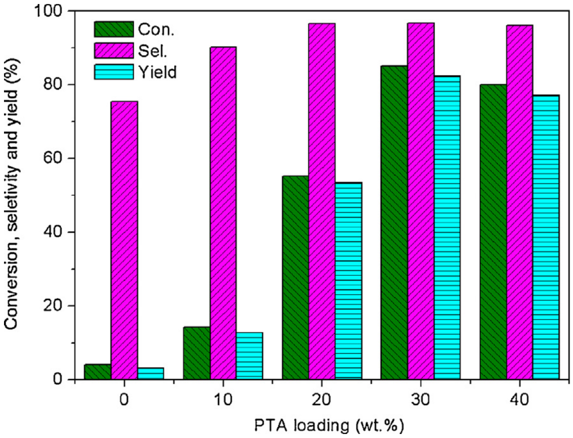


Fig. 1. Reaction results of the alkenylation of *p*-xylene with phenylacetylene over PTA/AC catalysts with diverse PTA loadings. Reaction conditions: W_{cat} 2.67 wt.%; $n_{Ar/Phen}$ 10; T 150 °C; P 1.0 MPa; t 5 h.

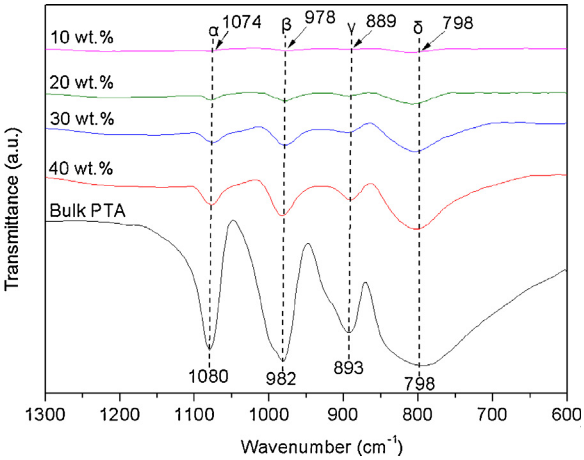


Fig. 2. FT-IR spectra of PTA/AC samples with diverse PTA loadings and bulk PTA is included for comparison.

and ^{1}HNMR were performed for the structure identification of samples (qualitative analysis, see supporting information). From our previous report, the alkenylation is a complex competition process. Based on the GC–MS data (Fig. S1–6) and the related references [22–24,29], it can be seen that, besides the main product (α-arylstyrene), a series of byproducts like acetophenone, α-(2,5-dimethylphenyl) ethylbenzene, β-(2,5-dimethylphenyl) styrene and oligomers can be detected. As the evaluation index of the alkenylation reaction, the phenylacetylene conversion was calculated by weight percent of the consumed phenylacetylene in the total phenylacetylene amount in the reaction mixture; the selectivity to α-arylstyrene was calculated by weight percent of desired α-arylstyrene in total products. The yield corresponding α-arylstyrene was the GC yield, which was calculated based on the conversion of phenylacetylene and the selectivity of the desired products.

3. Results and discussion

3.1. Effect of PTA loading

It was previously demonstrated that the PTA loading has a significant influence on the type and amount of the acidic sites on the supported PTA catalysts [30], and subsequently affects the catalytic performance of solid acid catalysts. Therefore, the effect of PTA loading on the catalytic performance of PTA/AC catalysts with diverse PTA loadings (10, 20, 30, 40 wt.%) in Firedel–Crafts alkenylation of *p*-xylene with phenylacetylene has been investigated firstly. The reaction results are presented in Fig. 1 and Table S1, and the pure AC was also included for comparison.

From Fig. 1, pure AC is almost inert for the alkenylation, owing to its lack of acid sites, only 4.1% of conversion with 75.4% of selectivity towards α-arylstyrene can be obtained, which is similar to the noncatalytic process (3.4% conversion with 55.9% selectivity). As for the supported PTA catalysts, the conversion increases with the rise of PTA loadings, and reaches the maximum (85.1%) while the PTA loading increases up to 30%. The further increased PTA loading leads to a decrease in conversion. The 30 wt.% PTA loading is appropriate for obtaining higher conversion of phenylacetylene and higher selectivity, and the 82.4% of maximum yield can be obtained over the 30 wt.% PTA/AC catalyst. The polymerization of phenylacetylene is a bottle-neck problem for solid acid catalyzed alkenylation. From Table S1, for the pure AC and the PTA/AC catalyst with 10 wt.% of low PTA loading, 23.9% and 9.1% of oligomers in product distribution can be observed (0.98 and 1.29% of oligomers were produced on AC and 10 wt.% PTA/AC). The much higher oligomers percentage in comparison with the other three samples is caused by the lower conversion. For blank experiment (entry 1 in Table S2), 0.955% of oligomers can be produced by thermal oligomerization. That is to say, the oligomers in the reaction mixtures over pure AC and 10 wt.% PTA/AC samples are mainly resulted from the thermal oligomerization under the reaction conditions. The amount of oligomers increases as the PTA loading rises (Table S1). The 82.3% of maximum yield for desired product with highest conversion and selectivity as well as medium oligomerization can be obtained on the 30 wt.% PTA/AC catalyst. Then the structure-performance relationship of the as-synthesized PTA/AC catalysts with diverse PTA loadings in alkenylation of *p*-xylene was investigated by correlating the reaction results to the nature of catalysts.

FT-IR is a good tool to investigate the structural characterization of supported PTA on AC. The FT-IR spectra of the PTA/AC samples with diverse PTA loadings are presented in Fig. 2, and the bulk PTA was also included for comparison. From Fig. 2, four characteristic peaks corresponding to P–O (α-peak, at around 1080 cm^{-1}), W=O (β-peak, at around 982 cm^{-1}), and W—O—W (γ- and δ-peaks, at around 893–798 cm^{-2}) appear on all of the samples, suggesting that the typical Keggin structure can be remained after being supported on AC [10,20]. The continuously intensified adsorption peaks with the increased PTA loadings are not surprised. By carefully comparing the peak positions on the diverse samples, the shift to lower wave number can be observed as the PTA loading decreases from 40 wt.% to 10 wt.%, might be ascribed to the possible interaction between PTA and AC. It looks like the high PTA dispersion at low loading may strengthen this kind of interaction. All in all, the Keggin structure of PTA still can be maintained although PTA suffers from impregnating and calcining for preparation of PTA/AC catalysts.

The acidic properties decisively affect the catalytic performance of solid acid catalysts. The NH_3-TPD technique was employed to reveal the acidic sites nature and catalytic performance of PTA/AC catalysts with diverse PTA loadings for Friedel–Crafts Alkenylation of *p*-xylene. Fig. 3 gives the NH_3-TPD profiles. From Fig. 3, both the amount and the strength of acidic sites for the PTA/AC catalysts monotonically increase as the PTA rises from 10 wt.% to 40 wt.%. Moreover, we cannot see any medium acid sites on the as-synthesized PTA/AC catalysts. However, the medium acidic sites on PTA/MCM-41 were definitely observed even if the 10 wt.% of low PTA loading [10]. Then why do the acid site strengths increase with larger PTA crystallite sizes? In fact, similar conclusion was drawn in many papers. But the reason can hardly be mentioned. The nature of acid sites is significantly dependent on PTA structure and support type [16–20]. From the XRD results, the dispersion becomes poor

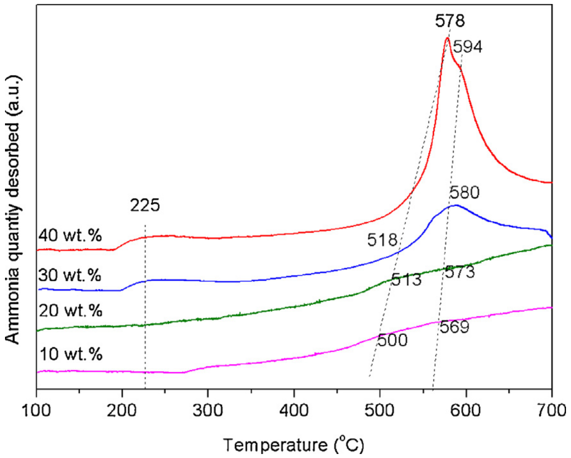


Fig. 3. NH_3-TPD profiles of PTA/AC samples with different PTA loadings. (a) 10 wt.%; (b) 20 wt.%; (c) 30 wt.%; (d) 40 wt.%.

as the PTA loading increases, and the low loading results in good PTA dispersion. The good dispersion may strengthen the interaction of PTA and support, which can be identified by the shift of IR peaks towards PTA on support in comparison of the bulk PTA. The smaller the PTA loading is, the more the shift is. The strong interaction leads to different acid species in comparison with the bulk PTA. From the reference [31], the supported PTA exhibits much weaker acid strength than the bulk PTA, which supports our above proposal.

Also only a few weak acidic sites on the samples can be observed. Correlated to reaction results, the higher concentration of acidic sites benefits the alkenylation, however the strong acidic sites also promotes oligomerization to produce oligomers and also leads to the deep polymerization for coke formation. The former can lead to the decrease in selectivity, and the latter can lead to deactivation of catalysts owing to the covering of acidic sites by coke. Therefore, the appropriate acidic properties are required for alkenylation, which is consistent with the previously reported results.

The PTA dispersion of the supported PTA catalysts can notably affect the acidic properties. Herein, the XRD technique was employed to investigate the PTA dispersity for the PTA/AC catalysts diverse PTA loadings, and the XRD patterns are presented in Fig S7. From Fig. S7, the characteristic peaks towards PTA crystalline phases become sharper and stronger as the PTA loading is increased from 20 wt.% to 40 wt.%, suggesting that the increased PTA loading can lead to larger PTA crystalline size owing to the agglomeration of PTA, which is consistent with the reported result [10]. This may cause the formation of much stronger acid sites, and also lead to the decrease in specific surface areas and pore volume those identified by the NH_3-TPD and N_2 adsorption–desorption experiments, which is consistent with the reported results. As a result, the too high PTA loading leads to the decrease in conversion and leads to the increase in formed oligomers.

The texture feature of the as-synthesized PTA/AC catalysts with diverse PTA loadings (10 wt.%, 20 wt.%, 30 wt.% and 40 wt.%) and the pure AC support were characterized by N_2 adsorption–desorption experiments. Fig. 4 presents the N_2 adsorption–desorption as well as the specific surface area and total pore volume for micropores of the samples by t-plot method. From Fig. 4, the sharp increase in adsorbed N_2 at initial period for increasing P/P_0 can be clearly observed, but no hysteresis can be seen. This shows that the presence of micropores but absence of mesopores on the samples [32–34]. Furthermore, the continuous decreased surface area and pore volume for micropores can be seen as the PTA loading rises. High loading can produces acidic sites, but it also leads to the decreased microporous surface area and pore volume, which may contribute the decrease in conversion and the increase in oligomers, besides the increased strong acid sites and their strength. Therefore, too high PTA loading is inappropriate for alkenylation over PTA/AC catalyst.

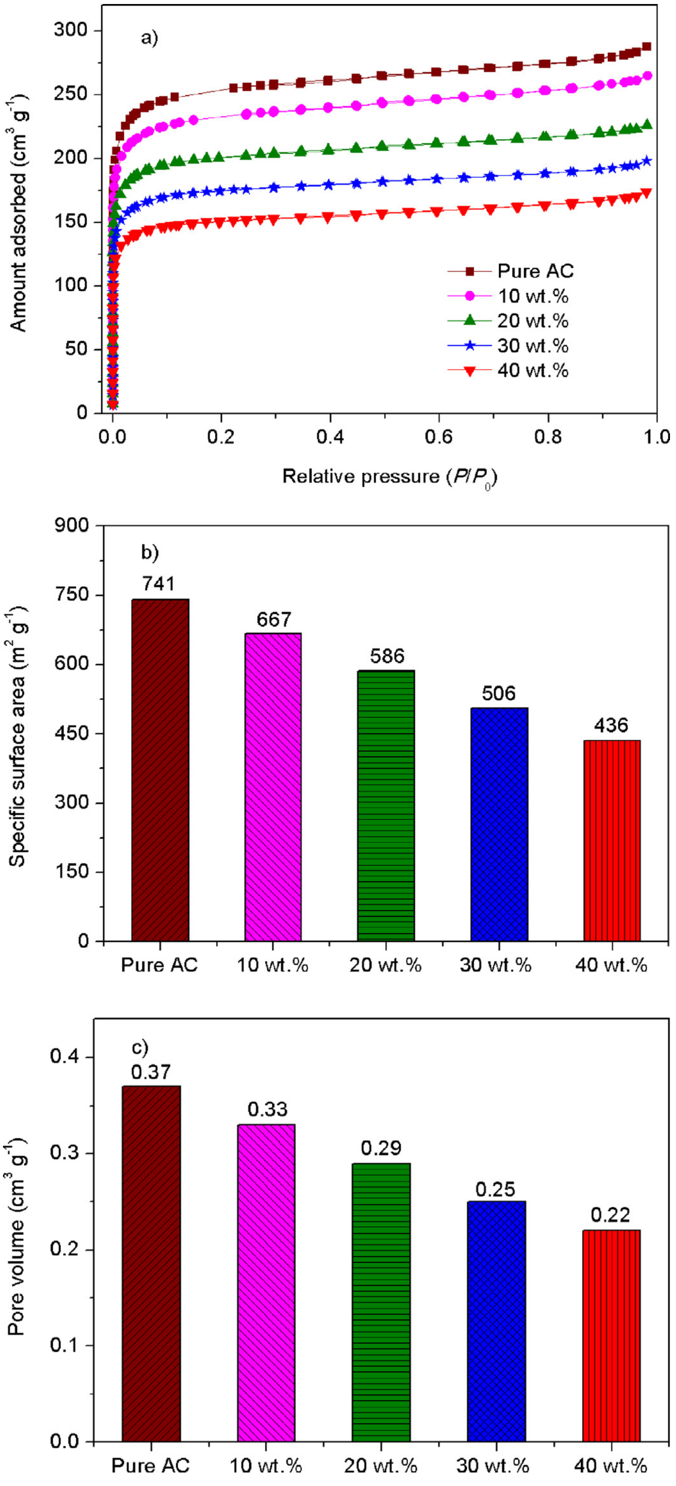


Fig. 4. N_2 adsorption–desorption isotherms (a), specific surface area for microproes by t-plot method (b), and pore volume for micropores by t-plot method (c) of the as-synthesized PTA/AC catalysts with diverse PTA loadings and the pure AC support.

From the above, the catalytic performance of PTA/AC catalysts is significantly dependent on their acidic properties, PTA dispersion, surface area, and pore volume, which is strongly affected by the PTA loading. The 30 wt.% PTA/AC sample can be chosen as a promising solid acid catalyst for α-arylstyrenes production via the

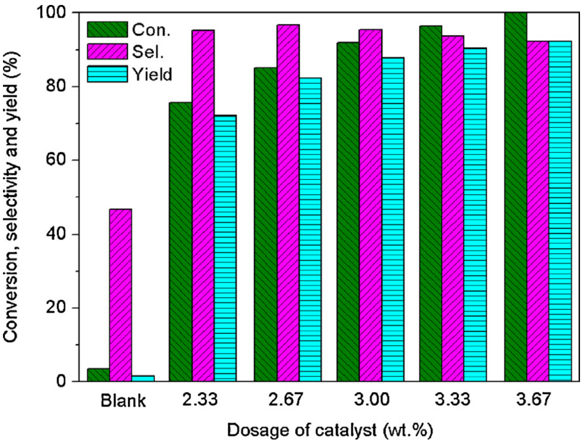


Fig. 5. Reaction results of the alkenylation of *p*-xylene with phenylacetylene over 30 wt.% PTA/AC catalyst with diverse catalyst dosages. Reaction conditions: $n_{\mathrm{Ar/Phen}}$ 10; *T* 150 °C; *P* 1.0 MPa; *t* 5 h.

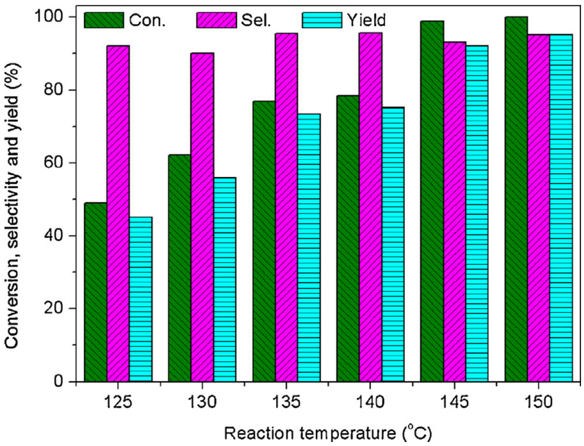


Fig. 7. Reaction results of the alkenylation of *p*-xylene with phenylacetylene over 30 wt.% PTA/AC catalysts at different reaction temperature. Reaction conditions: W_{cat} 3.33 wt.%; $n_{\mathrm{Ar/Phen}}$ 12; *P* 1.0 MPa; *t* 5 h.

Friedel–Crafts alkenylation of aromatics with alkynes. In order to further improve the reaction properties, the effect of reaction conditions including the dosage of catalyst, molar ratio of *p*-xylene to phenylacetylene, reaction temperature, and reaction time on catalytic performance in Friedel–Crafts alkenylation of *p*-xylene with phenylacetylene over the 30 wt.% PTA/AC has been investigated.

3.2. *Effect of reaction conditions*

3.2.1. *Effect of catalyst dosage*

Effect of dosage of 30 wt.% PTA/AC catalyst on the Friedel–Crafts alkenylation of *p*-xylene with phenylacetylene was investigated by changing the catalyst dosage from 2.33% to 3.67%. The dosage of catalyst (W_{cat}) is defined as the mass concentration of PTA/AC catalyst in the reaction mixture. The reaction results are presented in Fig. 5 and Table S2. From Fig. 5, the W_{cat} has significant effect on the conversion and selectivity. The continuous increase in conversion of phenylacetylene can be observed as the W_{cat} increase from 2.33% to 3.67%, and the reaction can hardly take place in the absence of catalyst. More than 90% (90.8%) of high yield with 94.2% selectivity can be obtained while the 3.33% of W_{cat} is used, and the further increase in W_{cat} up to 3.67% can lead to the decrease in selectivity. Moreover, the higher W_{cat} can lead to obvious polymerization (Table S2), which may in turn lead to deactivation of catalyst by coke formation, as well as can produce more oligomers. Thus, the optimum W_{cat} is 3.33%.

3.2.2. *Effect of molar ratio of* p*-xylene to phenylacetylene*

Fig. 5 provides the effect of molar ratio of *p*-xylene to phenylacetylene ($n_{p\text{-xylene/Phen}}$) on the alkenylation in the presence of 3.33% W_{cat} of the developed 30 wt.% PTA/AC catalyst. From Fig. 5, the uninterrupted increase in conversion can be obtained as the $n_{p\text{-xylene/Phen}}$ rises from 6:1 to 12:1, ascribed to enhanced collision probability of alkenyl cations with aromatic rings. The 100% of conversion with 95.1% of maximum selectivity can be obtained while the 12:1 of $n_{p\text{-xylene/Phen}}$ is used. The solvent effect of *p*-xylene can efficiently inhibit the self-polymerization of the alkyne. As a result, the increase in $n_{p\text{-xylene/Phen}}$ leads to the increase in percentage of the desired product, as well as compress the formation of oligomers (Table S3). The 12:1 of $n_{p\text{-xylene/Phen}}$ is essential for obtaining excellent reaction results.

3.2.3. *Effect of reaction temperature*

Fig. 6 illustrates the alkenylation results with different reaction temperatures, and the product distribution is presented in Table S4. From Fig. 6, the increase in reaction temperature results in a continuous increase in conversion, and the 100% conversion of phenylacetylene with 95.1% selectivity are obtained at 150 °C. Moreover, from Table S4, the increased reaction temperature can

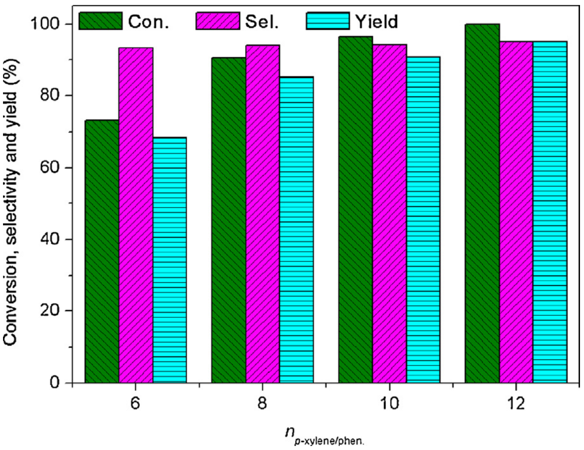


Fig. 6. Reaction results of the alkenylation of *p*-xylene with phenylacetylene over 30 wt.% PTA/AC catalysts at different $n_{p\text{-xy./Phen}}$ reaction conditions: W_{cat} 3.33 wt.%; *T* 150 °C; *P* 1.0 MPa; *t* 5 h.

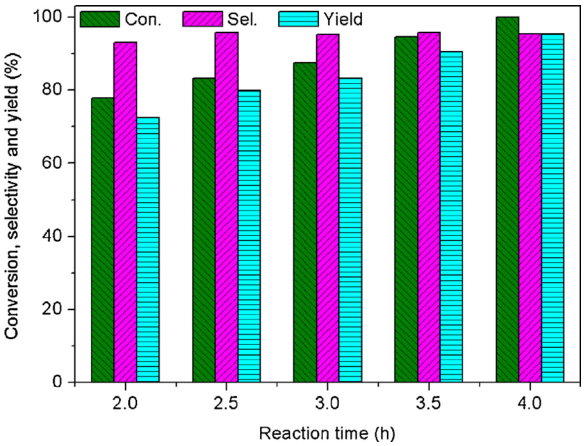


Fig. 8. Reaction results of the alkenylation of *p*-xylene with phenylacetylene over 30 wt.% PTA/AC catalysts for different reaction times. Reaction conditions: W_{cat} 3.33 wt.%; $n_{\mathrm{Ar/Phen}}$ 12; *T* 150 °C; *P* 1.0 MPa.

Table 1
Reaction results of the alkenylation of different aromatics with phenylacetylene over 30 wt.% PTA/AC catalyst.

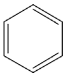
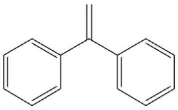
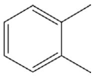
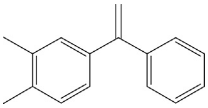
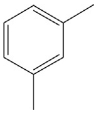
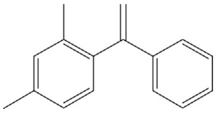
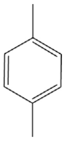
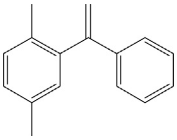
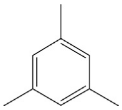
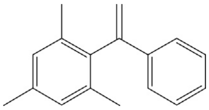
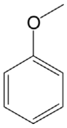
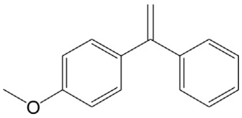
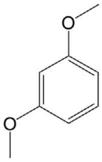
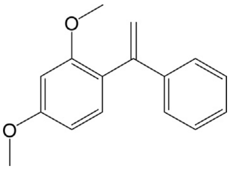
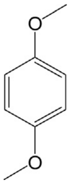
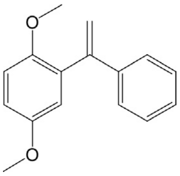
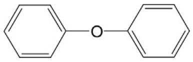
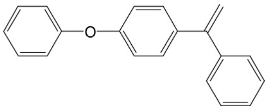
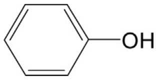
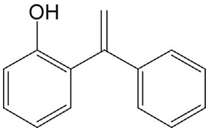
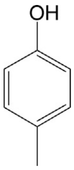
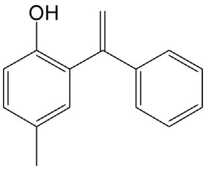
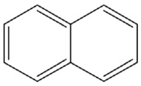
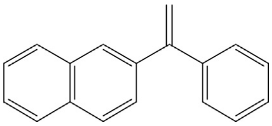
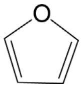
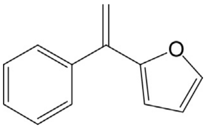
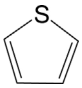
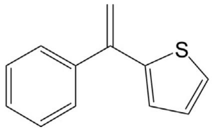
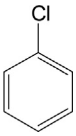
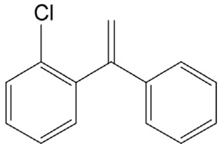
Entry	Aromatics	Products	Conversion (%)	Selectivity (%)	Yield (%)
1			70.6	81.6	57.6
2			100	90.2	90.2
3			100	91.3	91.3
4			100	95.1	95.1
5			100	96.1	96.1
6			94.6	90.6	85.7
7			96.8	83.1	80.4
8			98.2	93.4	91.7
9			95.3	93.9	89.5
10			98.3	82.1	80.7
11			100	83.6	83.6
12			99.0	91.2	90.3
13			98.3	90.3	88.8

Table 1 (*Continued*)

Entry	Aromatics	Products	Conversion (%)	Selectivity (%)	Yield (%)
14			99.0	93.5	92.6
15			92.6	93.1	86.2

Reaction conditions: W_{cat} 3.33 wt.%; $n_{Ar/Phen}$ 12; T 150 °C; P 1.0 MPa; t 4 h.

reduce the formation of acetophenone. Among the investigated temperature range, the higher reaction temperature doesn't lead to a decrease in oligomers. From above, the 150 °C is an appropriate reaction temperature.

3.2.4. *Effect of reaction time*

From Fig. 7 and Table S5, the increase in reaction time can lead to an increased conversion and selectivity but does not lead to the by-products formation. The 4 h is enough, and 100% conversion with 95.1% selectivity can be obtained. Moreover, from, Fig. 8, the 80% conversion has been achieved in 2 h, but further carrying out the reaction to get 20% more conversion to achieve 100% at the end of 4 h indicates that the reaction is slowed down. The decrease in rates with the extension of reaction time from 2 h to 4 h can be due to the continuously decreased concentration of the active intermediate alkenyl cation with the consumption of alkyne along with increased reaction times. The possible product inhibition cannot be excluded. Since the catalyst can be reused without visible loss in activity, the catalyst deactivation can be excluded.

3.3. *Recyclability of the as-synthesized catalyst*

In an industrialized production process, the recyclability of catalyst is definitely significant in heterogeneous catalysis. Therefore, the recyclability of the developed 30 wt.% PTA/AC catalyst for alkenylation was preliminarily investigated (a few fresh catalyst was recruited to reach the required 3.33% of W_{cat}). Results show that the developed catalyst can be reused 4 times without visible loss in catalytic performance, suggesting the large potential for the application in α-arylstyrenes via solid acid catalyzed Friedel–Crafts type of alkenylation reaction.

3.4. *Scope of aromatics*

From the above, the PTA/AC solid acid catalyst has a good performance on the direct alkenyaltion of *p*-xylene with phenylacetylene. 100% conversion and 95.1% selectivity can be obtained. Herein, the scope of the developed 30 wt.% PTA/AC catalyst was investigated by employing diverse aromatics as substrates, and the reaction results are listed in Table 1. The products molecular structures are identified by HNMR (Fig. S8–22). From Table 1, the developed supported PTA catalyst on AC exhibits outstanding catalytic performance in alkenylation of diverse aromatics including electron-donating groups substituted benzenes, polycyclic arenes, and heterocyclic aromatics. More interestingly, even if the electron-withdrawing group substituted chlorobenzene is used as substrate, the 92.6% of conversion with 93.1% of selectivity has still been obtained. Combing the higher catalytic efficiency (only 3.33% of catalyst dosage is used) with the excellent catalytic performance in the alkenylation of extensive substrates and the use of inherent low-cost and sustainable AC as support, the developed PTA/AC catalyst can be considered as a promising catalyst for clean and atomic economic synthesis of α-arylstyrenes via solid acid catalyzed Friedel–Crafts type of alkenylation reaction.

4. Conclusions

In this work, the supported PTA catalysts on low-cost and sustainable oxidation-modified AC carrier with diverse PTA loadings have been prepared. The catalytic performance of PTA/AC catalysts for Friedel–Crafts alkenylation is significantly dependent on their acidic properties, PTA dispersion, surface area, and pore volume, which strongly affected by the PTA loading. The 30 wt.% PTA/AC sample can be chosen as a promising solid acid catalyst for α-arylstyrenes production via the Friedel–Crafts alkenylation. The developed approach can be applied to various aromatics including electron-donating groups substituted benzenes, polycyclic arenes, heterocyclic aromatics, and even the electron-withdrawing group substituted chlorobenzene for the production of their corresponding α-arylstyrenes. On the basis of the excellent catalytic performance, wide scope of substrates, good recyclability of used catalyst, as well as the use of low cost and sustainable AC as support, the developed 30 wt./% PTA/AC catalyst can be considered as a promising candidate for the synthesis of diverse α-arylstyrenes through the acid catalyzed Friedel–Crafts alkenylation reaction.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.07.007

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