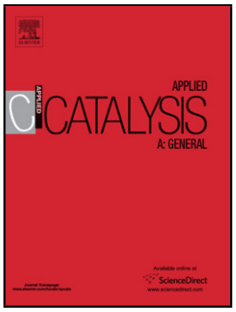

Title: Sulphated mesoporous La_2O_3-ZrO_2 composite oxide as an efficient and reusable solid acid catalyst for alkenylation of p-xylene with phenylacetylene

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Sulphated mesoporous La_2O_3-ZrO_2 composite oxide as an efficient and reusable solid acid catalyst for alkenylation of p-xylene with phenylacetylene

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- SO_4^{2-}/meso-La_2O_3-ZrO_2 is an efficient solid acid catalyst for direct alkenylation.
- Developed catalyst shows high selectivity and easily regeneration behavior.
- La incorporation into ZrO_2 significantly improves catalytic performance.
- Catalytic property strongly depends on catalyst nature affected by La addition.
- This work presents a robust catalyst for producing α-arylstyrenes via alkenylation.

Sulphated mesoporous La_2O_3-ZrO_2 composite oxide as an efficient and reusable solid acid catalyst for alkenylation of aromatics with phenylacetylene

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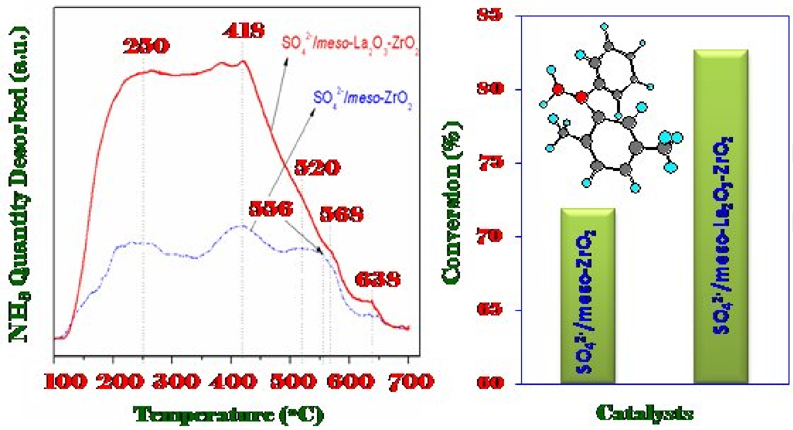

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ABSTRACT

Sulphated mesoporous La_2O_3-ZrO_2 composite oxides (SO_4^{2-}/*meso*-La_2O_3-ZrO_2) were firstly prepared by a surfactant-assisted co-precipitation/hydrothermal crystallization with subsequent impregnation method (SACPHC-IM). The prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst was employed as solid acid to catalyze direct alkenylation of *p*-xylene with phenylacetylene for clean production of *α*-arylstyrene. Various characterization techniques such as N_2 adsorption-desorption, X-ray diffraction (XRD), FT-IR, NH_3 temperature-programmed desorption (NH_3-TPD) were employed to reveal the relationship between catalyst nature and catalytic performance. The as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst shows much superior catalytic activity and similar selectivity to SO_4^{2-}/*meso*-ZrO_2, ascribed to increasing acid properties, enlarging specific surface area and increasing pore volume, reducing average crystalline size resulting from the promoting effect of adding La into ZrO_2 matrix. Furthermore, the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst was optimized by varying the atomic ratio of La/(La+Zr) from 0.05 to 0.2. The SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst with the 0.1 of optimum La/(La+Zr) atomic ratio exhibited excellent catalytic performance, ascribed to the increase in amount acid sites. The results for stability test demonstrated that close to 100% of maximum conversion can be achieved, and more than 80% of conversion can be maintained with the time on stream up to 780 min. Through simple calcination treatment, the spent catalyst can be almost complete recovered. The developed SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst could be a potential candidate for α-arylstyrene production via acid catalyzed direct alkenylation of aromatics with phenylacetylene.

Keywords: Mesoporous materials; SO_4^{2-}/ZrO_2 solid acid; La modification; Alkenylation; Heterogeneous catalysis

1. Introduction

The alkenylation of aromatic compounds, also called as hydroarylation of alkynes, presents a simple and atom economic approach for alkenylaromatic compounds, which are extensively used in diverse fine chemical fields like dyes, pigments, pharmaceuticals, flavors, agrochemicals, and natural products [1]. Recently, new and practical acid-catalyzed route through the formation of vinyl cations from alkynyl group for alkenylation reaction of aromatic compounds has been considered as a promising alternative to the classical precious metal and transition metal complexes catalyzed route through the formation of σ-aryl metal complexes between metal complex and aromatic ring [2-4].

Although the acid-catalyzed Friedel-Crafts alkylation is a very mature and extensively industrially used technique, some problems like more easily oligomerization of alkynes due to worse stability of vinyl cation than that of alkyl one, dissatisfactory selectivity, and narrow substrate scope remain to be resolved. Many efforts were continuously made on the acid catalyzed alkenylation reaction [5-7]. The traditional alkylation Lewis acid catalyst such as $AlCl_3$ could successfully catalyze alkenylation, but only 6% of extremely low yield with heavy pollution was obtained [8]. By employing the metal triflates $M(OTf)_x$, a breakthrough has been made, and a good yield for alkenylated products was achieved . Moreover, the $FeCl_3$ [4], HSO_3F, CF_3SO_3H [9], $[BMIM][Sb_2F_{11}]$ [10], etc. were also employed to catalyze this reaction, but there still exist the separation and equipment corrosion issues.

Heterogeneous catalysis provides a new and practical alternative to homogeneous catalysis in terms of its clean, easy-separation, catalyst reusability, and its applicability towards continuous production in a large scale. Solid acid catalysts, especially H-type zeolites, have been extensively used in Friedel-Crafts alkylation [11-15], but rare reports on Friedel-Crafts alkenylation can be found. Sartori and his colleagues had made some pioneering work on solid acid catalyzed alkenylation of aromatics over a Y-type HSZ-360 zeolite, unfortunately the results are not satisfactory, and there exits 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 resulted in remarkable decrease in the catalytic activity. Moreover, the low catalytic efficiency (1.0 g catalyst just for 1.0 g phenylacetylene) is another issue while this Y-type zeolite was used for the alkenylation, ascribed to the reaction only taking place on the external surface of the catalyst owing to its narrow pore channels within zeolite [16]. Although 95% of high alkenylated yield can be achieved on HUSY zeolite (superior to Nafion SAC-13), it only can be used in the intermolecular alkenylation of special substrates [17]. Therefore, the development of novel, highly-efficient and robust solid acid catalysts for alkenylation with wide substrate scopes is highly desirable.

In our NCES research group, we previously presented that the mesoporous supported phosphotungstic acid catalyst on MCM-41 demonstrated much superior catalytic activity, selectivity and stability to HY zeolite for the alkenylation of aromatic compounds with phenylacetylene, and good reaction results can be obtained while the diverse substrates were used [18]. However, there still exist many issues to be resolved. The catalytic stability is a seirous problem, as well as the selectivity is to be improved. Moreover, the facile calcination process cannot be used in the regeneration of the spent catalyst owing to the resuting decomposition of phosphotungstic acid at calcining coke process. To wash the spent catalyst by nonsolar solvent doesn't work on its recovery. Although the washing by polar solvent i.e acetone can eilminate the deposited coke from catalyst, the inevitable phosphotungstic acid leaching in polar solvent requires adding extra phosphotungstic acid to maintain the cataytic activity. Therefore, for one thing, we would fabricate new structured supported phosphotungstic acid catalysts to significantly improve the catalytic stability; for another thing, to develop the robust mesoporous solid acids that can bear high temperature for calcination regeneration process of coke-deposited catalyst, as well as they would demonstrate inproved catalytic activity, selectivity, stability. Recently, the mesoporous Fe-Al-MCM-41 was demonstarted to show high catalytic activity in direct alkenylation of phenols with phenylacetylene [19], however, the selectivity is still to be improved.

In this work, we aimed to develop a robust mesoporous solid acid catalyst for alkenylation, and the used solid acid catalyst may be regenerated by a facile calcination process. The sulphated mesoporous solid superacids were previously reported to efficiently catalyze diverse reactions [20-22], but no report on solid superacids catalyzed alkenylation can be seen. Moreover, rare earth metals especially La has been found to efficiently improve the catalytic performance of diverse solid acids like zeolite, sulfated zirconia [23-25]. From above, we proposed that sulphated mesoporous La_2O_3-ZrO_2 can be an efficient and robust catalyst for alkenylation. Herein, the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 were firstly prepared by a SACPHC-IM method and employed as solid acid to catalyze direct alkenylation of *p*-xylene with phenylacetylene for clean production of α-arylstyrene. The sulphated mesoporous SO_4^{2-}/*meso*-ZrO_2 catalyst was also prepared by using ACPHC-IM method and was used in this reaction. Various characterization techniques such as N_2 adsorption-desorption, XRD, FT-IR, NH_3-TPD were employed to reveal the relationship between catalyst nature and catalytic performance. It was found that the sulfonated soid superacid exhibited promising catalytic performance in alkenylation, and the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst shows much superior catalytic activity and similar selectivity to SO_4^{2-}/*meso*-ZrO_2. Furthermore, the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst was optimized by varying the atomic ratio of La/(La+Zr) from 0.05 to 0.2. The results for stability test demonstrated that close to 100% of maximum conversion can be achieved, and more than 80% of conversion can be maintained with the time on stream up to 780 min. Through simple calcination treatment, the spent catalyst can be almost complete recovered. The developed SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst could be a potential candidate for α-arylstyrene production via acid catalyzed direct alkenylation of aromatics with phenylacetylene.

2. Experimental

2.1. Catalyst preparation

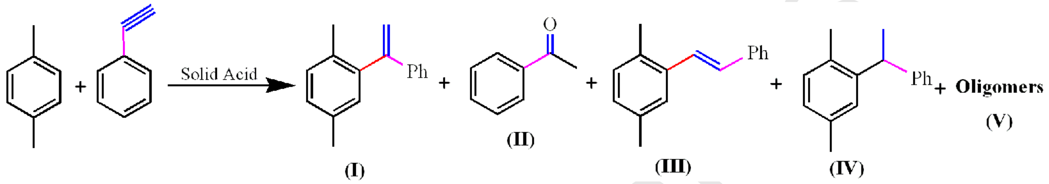
The mesoporous La_2O_3-ZrO_2 composite oxides with diverse atomic ratio of La to La and Zr (nLa/$_{(La+Zr)}$) and mesoporous ZrO_2 were synthesized by SACPHC method. Typically, 16.2 mmol zirconium nitrate (Sinopharm Group, AR) and 1.8 mmol of lanthanum nitrate (Tianjin Guangfu Institute, AR) were dissolved in deionizied water. A certain amount of CTAB (Kermel, AR) was added to 25 ml of deionized water to give a clear homogeneous solution. Then, the two solutions were mixed under continuously stirring for 2 h. Afterward, pre-determined amount of ammonium solution (25%) was added drop by drop under vigorous stirring, leading to a final pH value of 11. After precipitation, the gelatinous pale yellow mixture was stirred for further 4 h and subsequently transferred to Teflon autoclaves, which were kept at 105-120 °C for 60 h. The solid product was filtered, washed with deionized water and ethanol, subsequently dried at 105 ◦C overnight, and then calcined in a muffle furnace in air at 550 °C for 6 h. The La_2O_3-ZrO_2 composite oxides with diverse $n_{La/(La+Zr)}$ and mesoporous ZrO_2 were prepared by using the similar procedure as above but different $n_{La/(La+Zr)}$ or only neat Zr. The SO_4^{2-}/*meso*-La_2O_3-ZrO_2 with diverse $n_{La/(La+Zr)}$ and SO_4^{2-}/*meso*-ZrO_2 catalysts were prepared by impregnation method using 1M H_2SO_4 as impregnating reagent and the subsequently dried at 105 ◦C for 2 h and then calcined at 500 °C for 3 h.

2.2. Catalyst characterization

Nitrogen adsorption experiments at -196 °C were carried out 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. XRD patterns of the samples were recorded from 0 to 10 ° and 10 to 80 ° with a step width of 0.02 ° using a Rigaku D/max-2400 apparatus using Cu Kα radiation. FT-IR spectra were collected in the wavenumber range of 4000-400 cm^{-1} on EQUINOX-55 Fourier Transform Infrared Spectrometer (BRUKER). NH_3-TPD measurements were performed to characterize the acidity of the samples. After pre-treatment of 50 mg samples in Ar (up to 300 °C with a ramp rate of 10 °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 ^oC via the pulse injection of pure ammonia in a Ar stream. Finally, the NH_3 desorption step was performed from 100 and 700 ^oC at a ramp rate of 10 ^oC min^{-1} with 30 ml min^{-1} of Ar flow. The NH_3-TPD profiles were obtained via monitoring the desorbed ammonia with a thermal conductivity detector.

2.3. Catalytic performance test

The experiments on the alkenylation of *p*-xylene with phenylacetylene were performed in a stainless steel fixed-bed continuous-flow reactor. 1.0 g of catalyst suppressed into tablets and sieved into 20-60 mesh was loaded into the reactor for all the reaction tests, and the remaining space of the reactor tube was filled with 20-60 mesh quartz granules. Before the introduction of feedstock, the catalyst was in situ preactivated for 1 h in N_2 flow at 30 ml min^{-1}. The liquid stream was introduced into the fixed-bed reactor by a syringe pump. N_2 (99.999% purity) was used to maintain system pressure. Quantitative analysis of the collected reaction mixture from the fixed-bed reactor was performed on a FULI 9790 II GC equipped with an HP-5 column, 30 m×0.32 mm × 0.25 lm, and an FID detector. As an evaluation standard of alkenylation reaction, the phenylacetylene conversion was calculated by weight percentage of the transformed phenylacetylene in the total amount of introduced phenylacetylene in the feed. Based on the GC-MS data and our previous work [10], besides the main product α-arylstyrene (I), a series of byproducts like acetophenone (II), β-(*2,5*-dimethylphenyl) styrene (III) α-(*2,5*-dimethylphenyl) ethylbenzene (IV), and oligomers (V) can be detected, indicating the alkenylation reaction of p-xylene with phenylacetylene is a quite complex competition process. Besides the alkenylation, many sidereactions like hydration of phenylacetylene, hydrogenation of α-arylstyrene, the thermodynamic control alkenylation and the oligomerization reactions take place simultaneously (Scheme 1). In the end, the catalyst stability and regeneration performance were measured. The used catalyst was recovered by calcination process, and no extra fresh catalyst was added for the regeneration performance test.



Scheme 1 The alkenylation reaction process of *p*-xylene with phenylacetylene over the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid catalyst.

3. Results and discussion

3.1 The effect of La-doping

It was previously established that mesoporous solid acid exhibited much superior catalytic performance in alkenylation reaction containing activity, selectivity, and stability [10]. But the catalytic stability and regeneration performance are definitely required to be improved. Therefore, to develop a novel solid acid with improved catalytic stability and regeneration performance besides catalytic activity and selectivity is highly desirable. Sulfonated ZrO_2 has been employed to catalyze diverse reactions [26-30], but no report on alkenylation can be found. It was previously reported that the catalytic performance of solid acids can be efficient improved by introduction of rare earth metals, especially by La [31-35].

Therefore, in this work, we firstly investigated the catalytic properties of La-modified and unmodified SO_4^{2-}/*meso*-ZrO_2 on the alkenylation of *p*-xylene with phenylacetylene, and the reaction results are depicted in the Table 1.

From Table 1, in comparison of SO_4^{2-}/*meso*-ZrO_2, the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst exhibits higher catalytic activity with similar main product (I) percentage, and 82.7% of phenylacetylene conversion can be obtained. Moreover, more oligomers but less β-(*2,5*-dimethylphenyl) styrene isomer (III) over SO_4^{2-}/*meso*-ZrO_2 than that over SO_4^{2-}/*meso*-La_2O_3-ZrO_2 can be observed. In contrast to well-established alkylation, solid acid catalyzed alkenylation remains huge challenge to be resolved, and biggest difficulty is to efficiently inhibit the oligomerization of alkynes. Besides the high activity and main product percentage, the compressed oligomerization by adding La allows the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid to become a promising catalyst for alkenylation. Then various characterization techniques such as FT-IR, NH_3-TPD, nitrogen adsorption-desorption, XRD, and were employed to reveal the relationship between catalyst nature and catalytic properties.

The acidic properties play a decisive role in the catalytic performance of solid acid catalyst. The introduction of SO_4^{2-} group on the surface ZrO_2 can form surface acid sites. Fig. 1 shows the FT-IR spectra of *meso*-La_2O_3-ZrO_2 before and after sulfated. Comparing with the pristine *meso*-La_2O_3-ZrO_2 composite oxide, four new bands at 1225, 1137, 1043, and 995 cm^{-1} on the FT-IR of SO_4^{2-}/*meso*-La_2O_3-ZrO_2 sample assigned to characteristics of a bidentate SO_4^{2-} coordinated to Zr^{4+} can be observed. Such a chelating bidentate SO_4^{2-} structure could strongly withdraw electrons from its neighboring metal cations, resulting in a number of electronic deficient metal centres on the metal cations that act as strong Lewis acid sites [36], and partial Lewis acid site converts to the Bronsted acid site when it absorbs water [37]. Both B and L acid sites can catalyze the alkenylation reaction. The introduction of La into ZrO_2 lattice can affects the electronic structure, and therefore hopefully changes the surface acidic properties. NH_3-TPD experiments were performed on the La-modified and unmodified SO_4^{2-}/*meso*-ZrO_2 to reveal the effect of La addition into ZrO_2 on the catalytic properties. The NH_3-TPD profiles are presented in Figure 2.

From Fig. 2, the NH_3-TPD profiles can be divided into four regions. The low temperature region in the range of 150-350 ^{o}C (centred at 250 ^{o}C) is believed to be caused by weak acidic sites, and second region between 350 to 450 ^{o}C can be assigned to medium strong acidic sites, as well as the region of 450 to 600 ^{o}C can be appointed as strong acidic sites. Moreover, the last peak appearing at 638 ^{o}C should be superacid sites. In comparison of unmodified SO_4^{2-}/*meso*-ZrO_2, the modified SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid demonstrates much more weak and medium acid sites owing to the change in electronic features of ZrO_2 led by the La addition [38], which are active sites for alkenylation [18]. Therefore, SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid catalyst exhibits superior catalytic activity to the unmodified SO_4^{2-}/*meso*-ZrO_2. Moreover, the more strong acid sites on SO_4^{2-}/*meso*-ZrO_2 leads to more oligomers [13], the further polymerization of these oligomers can lead to coke formation, which further results in deactivation of catalyst.

Furthermore, nitrogen adsorption-desorption and XRD measurements were performed to reveal the effect of La addition on the catalyst textural feature, structure, and catalytic performance. Fig. 3 presents nitrogen adsorption-desorption isotherms and pore size distributions from adsorption branch. From Fig. 3, according to the IUPAC classification, the isotherms with type IV is the typical feature of mesoporous materials [39], indicating the existence of mesoporous structure in the two solid acids. The mesoporous SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acids have been successfully fabricated by SACPHC-IM method. Furthermore, we can see that adding La can lead to an obvious increase in pore volume from 0.23 to 0.28 ml g^{-1} and in specific surface area from 31.8 to 62.4 m^2 g^{-1}, which may result in more acid sites that improves catalytic activity. Moreover, the introduction of La into ZrO_2 can result in narrower pore distribution, which may be favorable for alkenylation reaction.

The effect of adding La on the catalyst structure was furthermore investigated by XRD experiments. The XRD patterns of as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts are presented in Fig. 4. From the low-angle XRD patterns of the two catalysts presented in Fig. 4a, the resolved diffraction peaks in the low-angle XRD pattern of SO_4^{2-}/*meso*-La_2O_3-ZrO_2 can be observed, indicating the ordered mesopores in this material, while no well-resolved diffraction peaks in the low-angle XRD pattern of SO_4^{2-}/*meso*-ZrO_2, suggesting its disordered mesoporous structure. The wide-angle XRD patterns of the La-modified and unmodified SO_4^{2-}/*meso*-ZrO_2 are shown in Fig. 4b. For the unmodified SO_4^{2-}/*meso*-ZrO_2, the well-resolved diffraction peaks assigned to tetragonal (JCPDS: 050-1089) and monoclinic (JCPDS: 037-1484) phases of ZrO_2 can be observed [35]. However, only five well-resolved diffraction peaks at 30.1, 34.7, 50.1, 59.5, and 73.7 ^{o} corresponding to the (011), (110), (112), (121), and (123) planes of tetragonal phase of ZrO_2 can be observed, suggesting the addition of La can efficiently induce the formation of tetragonal structure rather than monoclinic phase, which is in good agreement with the results in the reference [41]. The diffraction peaks of ZrO_2 become weaker and wider as the La is introduced, which indicates the decrease in average crystalline sizes resulted from the introduction of La. Moreover, no diffraction peak corresponding to La_2O_3 on the XRD pattern of SO_4^{2-}/*meso*-La_2O_3-ZrO_2 can be observed although the 0.1 of higher $n_{La/(La+Zr)}$ is used, suggesting the possible insertion of La into ZrO_2 matrix, consisting with the reported results [42]. Moreover, the shift of diffraction peaks corresponding to ZrO_2 phase to smaller angle can be observed in the presence of La, indicating an enlargement in ZrO_2 unit cell. The expansion of ZrO_2 lattice appears owing to the replacement of Zr^{4+} (0.84 Å) in the tetragonal phase structure by the La^{3+} (1.06 Å) with a larger ion radius. This result further confirms the La insertion into ZrO_2 matrix, which can strengthen the La-Zr interaction.

Correlated the diverse characterization results and reaction results, it can be found that the unique structural characteristic of La modified SO_4^{2-}/*meso*-ZrO_2 may be responsible for its higher specific surface area, larger pore volume, strengthened La-Zr interaction, and their resulting more weak and medium acid sites, which can remarkably affect the catalytic performance of solid acid catalyst for alkenylation reaction of *p*-xylene with phenylacetylene. Now that the addition of La can significantly improve the catalytic properties of SO_4^{2-}/*meso*-ZrO_2 for alkenylation, hopefully the catalytic performance can be further improved by varying the atomic ratio of La to La and Zr in the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst. Therefore, the followings we investigated the effect of La/(La + Zr) atomic ratio.

3.2 Effect of La/(La + Zr) atomic ratio

As is shown as above, the catalytic performance of mesoporous SO_4^{2-}/ZrO_2 for alkenylation of *p*-xylene is significantly dependent on the acidic properties, surface area, pore volume, pore size distribution, catalyst structure affected by the addition of La. Herein, we prepared a series of SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acids with diverse $n_{La/(La+Zr)}$ (0.05, 0.10, 0.15, 0.20), and measured their catalytic performance for alkenylation of *p*-xylene. Table 2 presents the reaction results. From Table 2, the phenylacetylene conversion increases with the rise of $n_{La/(La+Zr)}$. It reaches a maximum value (82.7%) as the $n_{La/(La+Zr)}$ increases up to 0.10, and then decreases with the further increase in $n_{La/(La+Zr)}$. Moreover, it can be found that the increase in $n_{La/(La+Zr)}$ results in a continuously decrease in the percentage of main product I, but an increase in the percentage of both sideproduct III and V. Especially, while the $n_{La/(La+Zr)}$ was increased from 0.15 to 0.20, significantly increase in percentage of both sideproduct III and V can be observed. From the reaction results, the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid with 0.10 of $n_{La/(La+Zr)}$ can be established for alkenylation reaction.

The catalytic performance of solid acids is remarkably dependent on their acid properties, and therefore, the NH_3-TPD techniques direct corresponding to acid properties were employed to reveal the relationship between catalytic properties and catalytic performance of the as-prepared series of SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acids with different molar ratios of La to La and Zr. The NH_3-TPD profiles are shown in Fig. 5.

From Fig. 5, the acid properties are significantly affected by $n_{La/(La+Zr)}$, and the amount of weak and medium strong acid sites increases with the increase of $n_{La/(La+Zr)}$, and reaches the maximum as the $n_{La/(La+Zr)}$ is 0.10. The further increase in $n_{La/(La+Zr)}$ leads to a decrease in the amount of weak and medium strong acid sites. Correlated to the acid nature to the reaction results of alkenylation, it can be concluded that the weak and medium strong acid sites are responsible for the alkenylation reaction. Furthermore, the continuously strengthened super acid sites lead by the increasing $n_{\mathrm{La/(La+Zr)}}$ can be observed, which can promote the oligomerization of phenylacetylene and the thermaldynamic controlled alkenylation [13]. Therefore, the increase in $n_{\mathrm{La/(La+Zr)}}$ results in the increased percentage of both β-(*2,5*-dimethylphenyl) styrene (III) and oligomers (V). The increase in oligomers may further lead to heavy coke deposition which contributes to deactivation of solid acid catalyst. The future work would be focused on compressing the super acids on the new mesoporous solid acid catalysts.

3.3. Effect of reaction parameters

Based on previously reported results for the effect of eaction conditions on the alkenylation of *p*-xylene over HPA/MCM-41 catalyst, herein we investigated the effect of reaction temperature (T_r) and volume hourly space velocity (*VHSV*) on the alkenylation reaction over the developed SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid catalyst. The reaction results are listed in Table 3 and 4, respectively.

From Table 3, the conversion of phenylacetylene increases with the rise of T_r up to 170 °C and reaches 98.4% of maximum at 170°C. The further increased reaction temperature results in a decrease in conversion, ascribed to the rapid deactivation at higher temperatures [43]. The change in T_r only leads to slight vibration in the percentage in sideproducts. 170 °C is the optimum T_r for the alkenylation reaction over SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid catalyst.

VHSV plays a significant role in the continuous-flow fixed bed reaction. As is shown in

Table 4, the conversion is enhanced with the increase of *VHSV*, and reaches 98.4 as *VHSV* rises up to 6 ml h^{-1} g^{-1}cat, but further increase in *VHSV* lead to a decrease in conversion. The lower *VHSV* means a longer time that the reactant and product molecules stay in the catalyst layer, which more easily leads to more serious oligomerizaiton and even the generation of high polymers for coke deposition. In addition, the long-time stay of the reactant is more favorable to the production of isomer which rises from 5.0% to 11.0% while the VHSV decreases from 6 to 4 ml h^{-1} g^{-1}cat. On the other hand, too high *VHSV* stands for a large number of reactants flowing through the catalyst layer in the unit time. The catalyst cannot provide adequate active sites for so many reaction substrates. In addition, it can also be speculated that at high VHSV part of the reactants did not have enough time to access the acid sites inside the pores [44]. From above, a *VHSV* of 6 ml h^{-1} g^{-1}cat is appropriate.

3.4. Catalytic stability and regeneration performance

The catalytic stability and regeneration behavior are crucial for a solid acid catalyst in practical application. Therefore, we investigated the stability and recovery performance of the developed SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid in alkenylation reaction. Fig. 6 presents the conversion and selectivity as a function of time on stream for the alkenylation of *p*-xylene with phenylacetylene over the fresh and calcining regenerated SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid catalysts.

As illustrated in Fig. 6, more than 80% conversion can be maintained for up to 780 min of time on stream. In comparison with our previously reported HPA/MCM-41 catalyst, the developed SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst in this work demonstrates higher catalytic stability, and about 70% conversion can be maintained for up to 1500 min of time on stream over SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst, while less than 40% conversion over HPA/MCM-41 catalyst can be observed. Furthermore, from Fig. 6, the catalytic performance of the spent SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst can be almost complete recovered by a facile and low cost calcination process without an extra addition of fresh catalyst, which allows it to be promising catalyst for α-arylstyrene production. The almost complete recovery of the used solid acid also demonstrated that the deactivation can be ascribed to coke deposition but not the leaching of SO_4^{2-}, now that the extra fresh catalyst is not required. In comparison with our previously result [10], although the developed catalyst demonstrates a little lower activity, the higher selectivity and easier regeneration of spent catalyst by facile calcination process allows it to be a promising solid acid catalyst for alkenylation reactions.

4. Conclusions

In summary, we developed a novel and efficient SO_4^{2-}/*meso*-La_2O_3-ZrO_2 catalyst for alkenylation through a SACPHC-IM method. The catalyst demonstrates excellent catalytic performance, and 98.4% conversion with 92.5% selectivity can be obtained under optimized reaction conditions. Especially the used catalyst can be easily but complete recovered by a facile and low-cost calcination process, in which neither organic solvent nor extra addition of fresh catalyst is required. The SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid should be a promising catalyst for alkenylation, of course the catalytic activity, selectivity and stability are required to be further improved. Moreover, it was found that the catalytic performance of SO_4^{2-}/*meso*-La_2O_3-ZrO_2 strongly depends on the acid properties, texture and structure nature affected by insertion of La with optimum amount.

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Figure Captions

Fig. 1. FT-IR spectra of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts.

Fig. 2. NH_3-TPD profiles of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts.

Fig. 3. Nitrogen adsorption-desorption isotherms of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts. Insets: Barrett-Joyner-Halenda (BJH) pore diameter distribution of the two samples from adsorption branch.

Fig. 4. a) Small-angle and (b) wide-angle XRD patterns of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts.

Fig. 5. NH_3-TPD profiles of the as-prepared SO_4^{2-}/ *meso*-La_2O_3-ZrO_2 solid acid catalysts with diverse $n_{La/(La+Zr).}$

Fig. 6. The catalytic stability and regeneration performance of the developed SO_4^{2-}/meso-$La_{0.1}Zr_{0.9}O_2$ catalyst for the alkenylation of *p*-xylene with phenylacetylene.

Tables:

Table 1

Effect of La-doping on the catalytic performance of SO_4^{2-}/ZrO_2 solid acid catalysts for the alkenylation of *p*-xylene with phenylacetylene.[a]

Catalyst	*Con.* (%)	Product distribution (%)				
		I	II	III	IV	V
SO_4^{2-}/ *meso*-ZrO_2	71.9	93.9	0.4	1.7	0.1	3.8
SO_4^{2-}/*meso*-La_2O_3-ZrO_2	82.7	93.6	0.2	4.6	0.1	1.5

[a] Reaction conditions: catalyst 1.0 g, $n_{Ar/Phen.}$ 25:1, T_r 150 °C, P_s 1.0 MPa, *VHSV* 6 ml h^{-1} g^{-1} cat, *TOS* 8 h.

Table 2

Catalytic performance in alkenylation of *p*-xylene with phenylacetylene over the as-prepared SO_4^{2-}/ *meso*-La_2O_3-ZrO_2 solid acid catalysts with diverse $n_{La/(La+Zr)}$.[a]

$n_{La/(La+Zr)}$	*Con.* (%)	Product distribution (%)				
		I	II	III	IV	V

0.05	73.5	95.9	0.4	2.3	0.1	1.3
0.10	82.7	93.6	0.4	4.6	0.1	1.5
0.15	78.8	93.2	0.2	4.5	0.1	1.9
0.20	71.0	88.3	0.3	6.5	0.3	4.3

[a] Reaction conditions: catalyst 1.0 g, $n_{\mathrm{Ar/Phen.}}$ 25:1, T_r 150 °C, P_s 1.0 MPa, *VHSV* 6 ml h^{-1} g^{-1} cat, TOS 8 h.

Table 3

Effect of T_r on the alkenylation of p-xylene with phenylacetylene over the developed SO_4^{2-}/meso-La_2O_3-ZrO_2 solid acid catalyst with 0.10 of the $n_{\mathrm{La/(La+Zr)}}$.[a]

T_r (°C)	*Con.* (%)	Product distribution (%)				
		I	II	III	IV	V

150	82.7	93.6	0.2	4.6	0.1	1.5
160	90.4	93.2	0.3	3.8	0.1	2.6
170	98.4	92.5	0.3	5.0	0.3	1.9
180	89.0	93.9	0.4	3.4	0.1	2.1
190	85.8	91.8	0.8	4.7	0.2	2.5

[a] Reaction conditions: catalyst 1.0 g, $n_{\mathrm{Ar/Phen.}}$ 25:1, P_s 1.0 MPa, *VHSV* 6 ml h^{-1} g^{-1} cat, *TOS* 8 h.

Table 4

Effect of *VHSV* on the alkenylation of p-xylene with phenylacetylene over the SO_4^{2-}/meso-$La_{0.1}Zr_{0.9}O_2$ solid acid catalyst.[a]

VHSV (ml $h^{-1}g^{-1}$cat)	*Con.* (%)	Product distribution (%)				
		I	II	III	IV	V

4	93.9	86.5	0.1	11.0	0.1	2.4
6	98.4	92.5	0.3	5.0	0.3	1.9
8	74.5	91.9	0.2	5.3	0.1	2.4

Figures:

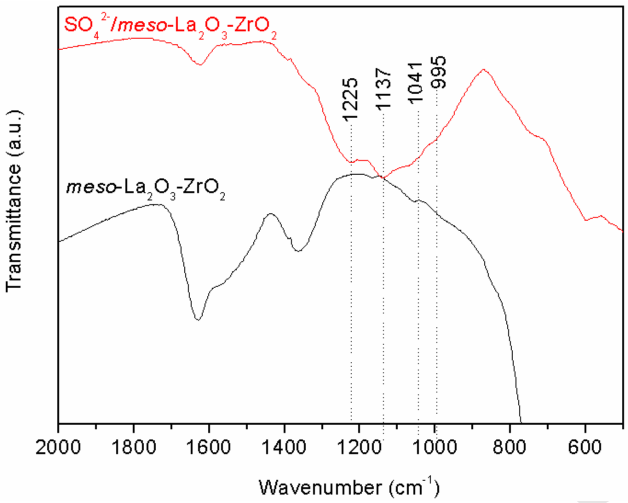


Fig. 1. FT-IR spectra of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts.

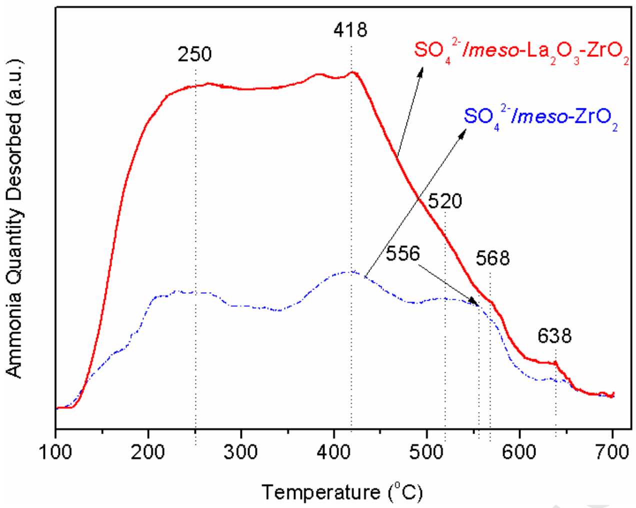


Fig. 2. NH_3 TPD profiles of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts.

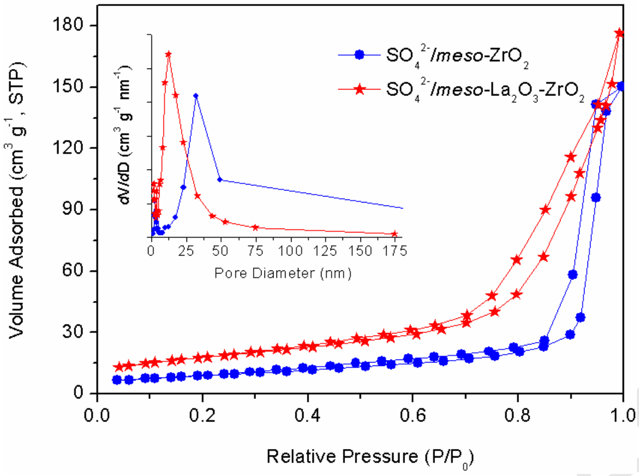


Fig. 3. Nitrogen adsorption-desorption isotherms of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts. Insets: Barrett-Joyner-Halenda (BJH) pore diameter distribution of the two samples from adsorption branch.

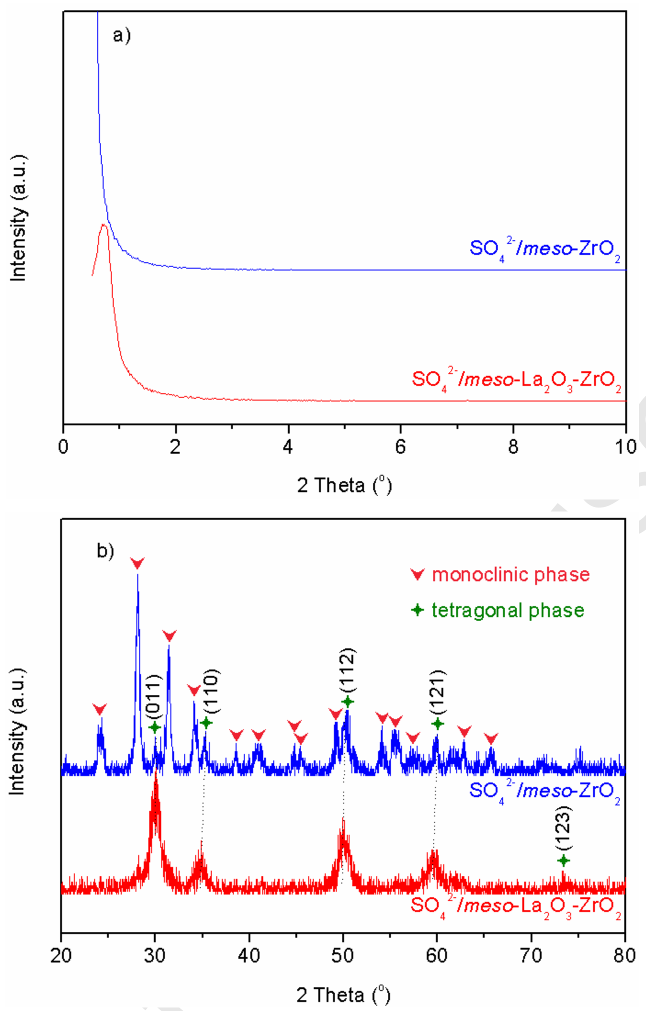


Fig. 4. a) Small-angle and (b) wide-angle XRD patterns of the as-prepared SO_4^{2-}/*meso*-La_2O_3-ZrO_2 and SO_4^{2-}/*meso*-ZrO_2 solid acid catalysts.

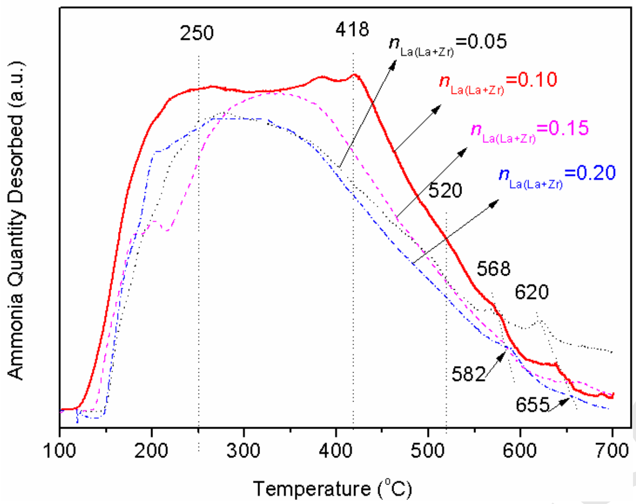


Fig. 5. NH_3-TPD profiles of the as-prepared SO_4^{2-}/ *meso*-La_2O_3-ZrO_2 solid acid catalysts with diverse $n_{La/(La+Zr)}$.

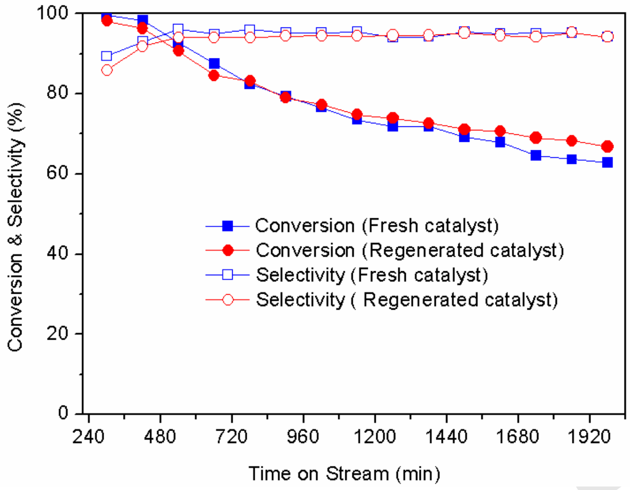
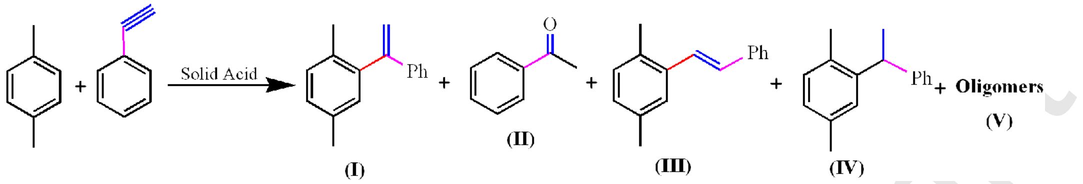


Fig. 6. The catalytic stability and regeneration performance of the developed SO_4^{2-}/meso-$La_{0.1}Zr_{0.9}O_2$ catalyst for the alkenylation of *p*-xylene with phenylacetylene.

Schemes:



Scheme 1 The reaction equation for the alkenylation of p-xylene with phenylacetylene over the SO_4^{2-}/*meso*-La_2O_3-ZrO_2 solid acid catalyst.