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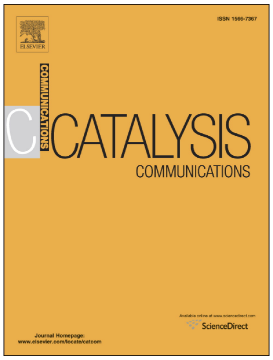

## The supported sulphated La2O3-ZrO2 on SBA-15 as a promising mesoporous solid superacid catalyst for alkenylation of p-xylene with phenylacetylene

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# The supported sulphated $La_2O_3$-$ZrO_2$ on SBA-15 as a promising mesoporous solid superacid catalyst for alkenylation of *p*-xylene with phenylacetylene

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## Abstract

The well-dispersed supported sulphated $La_2O_3$-$ZrO_2$ (SLZ) superacid catalysts on SBA-15 with loadings were prepared and applied in alkenylation of *p*-xylene with phenylacetylene. The amount of acidic sites increases with the enlarged loading, it reaches maximum at the loading of 25%, and then decreases while the loading is further increased. The increasing loading leads to a continuous decrease in specific surface area and pore volume. The optimized 25% SLZ/SBA-15 catalyst shows the outstanding catalytic performance, attributed to the more acidic sites and the not too low surface area and pore volume. The developed well-ordered mesoporous sulphated $La_2O_3$-$ZrO_2$ solid superacid catalyst may be extended to diverse transformations.

*Keywords*: Well-ordered mesoporous solid superacid, Supported type catalyst, Alkenylation, Heterogeneous catalysis, Clean synthesis

## 1. Introduction

The alkenylation of arenes with alkynes is a useful protocol for alkenyl aromatics production in organic synthesis. This is an alternative to the classical methods like the Heck-Mizoroki, Suzuki-Miyaura, Stille, and Negishi reactions for synthesizing alkenyl aromatics [1]. Compared with the traditional cross coupling methods, this approach avoids the use of prefunctionalized substrates, and thereby provides a facile and clean route for the preparation of the desired alkenyl aromatics that extensively applied in many fields such as pharmaceuticals, agrochemicals, natural products, flavors, and dyes [2-4]

Homogeneous metal complex catalysis demonstrated satisfactory activity and selectivity for alkenyl aromatics production [5-8]. However, owing to the existing disadvantage in terms of expensive, low recyclability, and purification of the desired products from traces of a metal contaminant, it is highly desirable for developing a cheap and clean method. Heterogeneous catalysis provides clean and economical alternative to homogeneous catalysis in terms of its clean, easy-separation, catalyst reusability [9-11]. Up to now, just a few reports on alkenylation over solid acid catalysts can be found, although extensive reports on alkylation can be found [12,13]. Sartori made a pioneering work on alkenylation of aromatics over HSZ-360 zeolite. Unfortunately, the catalytic results are not satisfactory, and an irreconcilable contradiction between the selectivity and the catalytic activity exists [14]. The low catalytic efficiency would be observed while HY was used as catalyst for the alkenylation. Therefore, the improvement in the catalytic efficieny is desirable [15,16]. Mesoporous solid acids have shown a great prospect for alkenylation of diverse aromatics.

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Haldar demonstrated that the Fe-containing mesoporous alluminosilicate exhibited very high activity for the Friedel-Crafts alkenylation of phenols with aryl-substituted alkynes under mild conditions [17], but the improvement in selectivity is still required. The $H_3PW_{12}O_{40}$/MCM-41 as a fascinating mesoporous solid acid catalyst for alkenylation of diverse aromatics was developed [18]. Unfortunately, the recovery of spent $H_3PW_{12}O_{40}$/MCM-41 catalyst requires the usage of a large amount of polar and evaporable solvent, which can lead to economic and environmental issues, besides the possible $H_3PW_{12}O_{40}$ leaching. Therefore, it is highly desirable for developing a more efficient and robust mesoporous solid acid catalyst for alkenylation.

Sulfonated $ZrO_2$ has been extensively employed as a solid superacid catalyst to catalyze diverse reactions [19,20]. However, rare report on alkenylation can be found. We developed a novel and efficient $SO_4^{2-}$/meso-$La_2O_3$-$ZrO_2$ catalyst for alkenylation [21,22]. Although the usage of volatile organic solvent can be avoided for regenerating spent catalyst, the preparation of a well-ordered mesoporous $La_2O_3$-$ZrO_2$ is required for accelerating mass transfer. But it still remains a challenge, besides the cost of La and Zr is relatively high. Therefore, the preparation of a highly-ordered mesoporous $La_2O_3$-$ZrO_2$ based superacid catalyst for alkenylation is highly desirable. Supported sulfonated $ZrO_2$ catalysts on SBA-15 have been prepared and used in some acid-catalyzed reactions but not in alkenylation [23-25]. From our previous report [22], the addition of La remarkably improved the acidic properties and alkenylation catalytic performance of sulfonated $ZrO_2$. Therefore, in this work, we prepared highly-ordered mesoporous SLZ/SBA-15 solid superacid catalysts by supporting different amount of $La_2O_3$-$ZrO_2$ with La/(La+Zr) molar fraction of 0.1 on SBA-15 by incipient wetness impregnation (IWI), which overcomes the challenge for synthesizing well-ordered mesoporous $La_2O_3$-$ZrO_2$ based solid superacids, besides the required amount of relatively high cost La and Zr becomes lowering. The 25% SLZ/SBA-15 with optimized SLZ loading shows outstanding catalytic performance in alkenylation. $N_2$ adsorption–desorption, X-ray diffraction (XRD and $NH_3$ temperature-programmed desorption ($NH_3$-TPD) characterization techniques were employed to reveal the relationship between the nature and catalytic properties of the developed highly-ordered mesoporous solid superacid catalyst.

## 2. Experimental

### *2.1. Catalyst Preparation*

The preparation of SBA-15 material was performed according to the procedure described by Zhao et al [26]. 4.0 g of P123 purchased from Sigma-Aldrich Co. was dissolved in the mixture of 30 g of de-ionized water and 120 g of 2 M HCl solution with stirring at 35 $^oC$. Then, 8.50 g of tetraethylorthosilicate (TEOS) was added into the above solution with stirring at 35 $^oC$ for 20 h. The resulting mixture was aged at 80 $^oC$ overnight. The obtained solid product was recovered, washed, and then dried at room temperature. The final product was obtained by calcination at 500 $^oC$ for 6 h.

The catalyst precursors $La_2O_3$-$ZrO_2$/SBA-15 with diverse $La_2O_3$-$ZrO_2$ loadings were prepared by IWI method (x% LZ/SBA-15, x=20, 25, 30) by using the mixed aqueous solution containing zirconium nitrate (Sinopharm Group, AR) and lanthanum nitrate (Tianjin Guangfu Institute, AR) with 0.1 of molar fraction of La/(La+Zr) as an impregnant with a subsequent calcination process at 550 °C for 6 h. The highly ordered mesoporous solid superacid x% SLZ/SBA-15 catalysts were prepared by a wetness impregnation in 1 M $H_2SO_4$ followed by drying at 105 $^oC$ and calcination process at 500 $^oC$. For comparison, the physically mixed mesoporous solid acid containing 20% mesoporous $SO_4^{2-}$/$La_2O_3$-$ZrO_2$ and 80% SBA-15 (20% SLZ/SBA-15 (PM)) was prepared. The traditional mesoporous $SO_4^{2-}$/$La_2O_3$-$ZrO_2$ solid superacid was prepared on the basis of references

[21,22]. Moreover, for comparison, the $H_2SO_4$-treated SBA-15 sample (SA-SBA-15) was also prepared by soaking SBA-15 into 1M $H_2SO_4$ solution with the same calcination process as above.

*2.2. Catalyst Characterization*

XRD patterns of the samples were recorded in the 2 Theta range of 20-80$^o$ with a step of 0.02$^o$ on a Rigaku D/max-2400 apparatus using Cu Kα radiation. Nitrogen adsorption experiments at -196 $^o$C were carried out on a Beishide 3H-2000PS1 instrument to measure the specific surface area and pore volume. The samples were degassed at 130 $^o$C for 6 h prior to $N_2$ 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 $^o$C (a ramp rate of 10 $^o$C min$^{-1}$) for 0.5 h, followed by cooling to room temperature. The pretreated sample was saturated with ammonia at 100 $^o$C via the pulse injection of $NH_3$. $NH_3$ desorption process was carried out from 100 to 600 $^o$C at a heating rate of 10 $^o$C min$^{-1}$ with an Ar flow of 30 ml min$^{-1}$.

*2.3. Catalytic Performance Measurement*

The catalytic performance test on the SLZ/SBA-15 catalysts for alkenylation of *p*-xylene with phenylacetylene was performed in a stainless steel fixed-bed flow reactor. 1.0 g of catalyst suppressed into tablets and sieved into 20-60 mesh was loaded into the reactor for all performance tests. The remaining space of the reactor was filled with 20–60 mesh quartz granules. Before the introduction of feedstock, the catalyst was in situ pre-activated for 1 h in $N_2$ flow at 30 ml min$^{–1}$. The liquid feed was introduced into the fixed-bed reactor by a syringe measuring pump. $N_2$ (99.999% purity) was used to maintain reaction system pressure to keep the liquid phase of reaction mixture. The reaction was performed at 140 $^o$C. Quantitative analysis of the effluent was performed on a

FULI 9790 II GC equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μm ) and a FID detector. The GC chromatogram of products can be found in our previous papers [21,22]. 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. The molecular structure of alpha-(2, 5-dimethylphenyl) styrene (I) was further identified by $^1$H NMR (Fig. S1). The catalyst stability and regeneration performance (calcination regeneration from previous report [21, 22]) were measured. No extra fresh catalyst was added for the regeneration performance test.

## 3. Results and discussion

It was previously demonstrated that the $ZrO_2$ loading has a significant influence on the properties of acidic sites on the supported $ZrO_2$/SBA-15 catalysts [23-25], and subsequently affects the catalytic performance of solid acid catalysts. Therefore, the effect of $La_2O_3$-$ZrO_2$ loading on the catalytic performance of x% SLZ/SBA-15 catalysts in Friedel-Crafts alkenylation of *p*-xylene with phenylacetylene has been investigated. Table 1 presents the reaction results, and 20 % SLZ/SBA-15 (PM) and SA-SBA-15 are included for comparison.

From Table 1, 20 % SLZ/SBA-15 catalyst shows ca. 3.5 times much higher conversion towards phenylacetylene than 20 % SLZ/SBA-15 (PM) although they containing the same amount of SLZ (in the physically mixed 20 % SLZ/SBA-15 (PM), the traditional mesoporous SLZ prepared by soft template method [21,22] was used), suggesting the promoting role of supporting SLZ on highly-ordered mesoporous SBA-15. SA-SBA-15 shows a very low catalytic activity and quite low selectivity (a large amount of oligomers on SA-SBA-15 can be observed), implying the activity of 20 % SLZ/SBA-15 originating from the well-dispersed SLZ. It was also found that the catalytic activity and selectivity of x% SLZ/SBA-15 catalysts for alkenylation are strongly dependent on the SLZ loading on SBA-15. The conversion rises along with the increase in SLZ loading from 20 to 25%, but a decreased conversion can be observed as the SLZ loading is further increased up to 30%. The 25% SLZ/SBA-15 catalyst shows the highest catalytic activity with medium selectivity among the three x% SLZ/SBA-15 solid superacid catalysts. The decreasing selectivity along with the increase in SLZ loading is originated from the increasing side-products with respect to acetophenone and oligomers (Table 1). 25% of the optimum SLZ loading is required for alkenylation. Furthermore, the supported SLZ catalyst with 25% loading shows much superior catalytic activity to the neat mesoporous SLZ, suggesting the significantly enhancing role of supporting. The structure-performance relationship of the as-prepared well-ordered SLZ/SBA-15 solid acid catalysts for alkenylation *p*-xylene with phenylacetylene was revealed by correlating the reaction results to the nature of catalysts obtained by $N_2$ adsorption-desorption, $NH_3$-TPD, and XRD characterizations.

Fig. 1 shows the $N_2$ adsorption-desorption isotherm and the pore-size distribution (inset). The specific surface area ($S_{\mathrm{BET}}$) and pore volume ($V_{\mathrm{total}}$) are also listed in Fig. 1. From Fig. 1, the characteristic of type IV with a clear H1 hysteresis loop for all samples can be observed, suggesting the well-ordered mesoporous structure of the samples can be maintained after they are suffered from loading $La_2O_3$-$ZrO_2$ and $H_2SO_4$ treatment [27-29]. However, the addition of $La_2O_3$-$ZrO_2$ leads to a remarkable decrease in both $S_{\mathrm{BET}}$ and $V_{\mathrm{total}}$. The continuously decreased $S_{\mathrm{BET}}$ and pore volume can be observed as the SLZ loading is increased from 20 to 30%. Especially, a significant decrease in $S_{\mathrm{BET}}$ and $V_{\mathrm{total}}$ takes place while the loading increases from 25 to 30%. The decrease in $S_{\mathrm{BET}}$ and $V_{\mathrm{total}}$ is unfavorable for the catalytic reaction.

$NH_3$-TPD technique was used to investigate the acidic properties of the as-prepared x % SLZ/SBA-15 catalysts with different x values and the 20 % SLZ/SBA-15 (PM) and SA-SBA-15. The $NH_3$-TPD profiles are presented in Fig. 2. Based on the previous reports [21-25], the $NH_3$-TPD profiles can be divided into three regions, which can be assigned as weak (150-300 $^oC$), medium (300-450 $^oC$), and strong (450-600 $^oC$) acid sites. From Fig. 2, the x % SLZ/SBA-15 catalysts show three types of acid sites with the peak center at around 216, 360, and 480 $^oC$. The 20 % SLZ/SBA-15 (PM) and SA-SBA-15 also show three types of acidic sites but with lower strength in comparison with x % SLZ/SBA-15. The x % SLZ/SBA-15 solid acids show much higher acidic sites than 20 % SLZ/SBA-15 (PM) and SA-SBA-15, which endows then with much higher catalytic activity that shown in Table 1. It is understandable that the x % SLZ/SBA-15 solid acids show much higher amount of acidic sites. However, it is interesting that 20 % SLZ/SBA-15 shows much higher amount of acidic sites than 20 % SLZ/SBA-15 (PM), although they have the same content of SLZ. In order to discover the origin, we performed the XRD experiments on the x % SLZ/SBA-15 and 20 % SLZ/SBA-15 (PM) samples, and the XRD patterns are presented in Fig. 3. From Fig. 3, the well-resolved XRD peaks corresponding to the tetragonal La-Zr-O composite can be observed on the 20 % SLZ/SBA-15 (PM) [21,22], but no peak on x % SLZ/SBA-15 samples can be observed. This suggests the high dispersion of SLZ on SBA-15 for x % SLZ/SBA-15 catalysts, which endows them with much more acidic sites in comparison with 20 % SLZ/SBA-15 (PM). From Fig. 2, with the increase in SLZ loading from 20 to 30%, the sum of weak and medium acidic sites increases, and reaches the maximum (989.0 $\mu$mol.g$^{-1}$) at 25% loading, and then decreases up to 974 $\mu$mol.g$^{-1}$. The 25 % SLZ/SBA-15 shows the highest amount of weak and medium acidic sites among the three x % SLZ/SBA-15 catalysts with diverse SLZ loadings, which endows it with highest catalytic activity.

The high amount of strong acidic sites of SA-SBA-15 leads to the formation of many oligomers. The amount of strong acidic sites increases from 18.4 to 180.4 μmol.g$^{-1}$ as the SLZ loading increases from 20% to 30%, which results in the increasing amount of oligomers (Table 1). In summary, the weak and medium strong acids are main active sites for alkenylation, but the strong acidic sites will promote the formation of oligomers, which is in consistent with the previous reports [21, 22].

From Fig. S2, no visible XRD peak at low angle can be well-resolved on the supported SLZ catalysts, suggesting that the mesopores are disordered after loading SLZ. From Fig. 1, the mesopores of the supported SLZ catalysts definitely appear. Table 1 shows that the supported SLZ catalysts, especially the 25% SLZ/SBA-15, exhibit outstanding catalytic performance, although the loading of SLZ deteriorates the degree of order of the mesopores. Therefore, we can safely say that the more weak and medium acidic sites and the mesopore of the developed solid acid catalysts allow them to show promising catalytic performance for production of alpha-arylstyrene through alkenylation of aromatics with phenylacetylene. The 25% of optimum SLZ loading is required for achieving superior catalytic performance.

As an industrially important catalytic reaction process, the stability and regeneration of solid acid catalyst is of great significance. Fig. 4 shows the catalytic performance vs. time on stream in alkenylation over fresh and regenerated 25% SLZ/SBA-15 solid superacid catalyst. No fresh catalyst was compensated for regeneration performance test. From Fig. 4, 72.1% conversion can be maintained for up to 480 min of time on stream on the 25% SLZ/SBA-15 solid superacid catalyst, while less than conversion over our previously reported catalyst $SO_4^{2-}$/*meso*-$La_{0.1}Zr_{0.9}O_\delta$ can be observed. Moreover, the spent 25% SLZ/SBA-15 solid superacid catalyst can be basically recovered by a facile calcinations process.

## 4. Conclusions

In summary, the highly-ordered mesoporous $SO_4^{2-}/La_2O_3-ZrO_2$/SBA-15 with diverse SLZ loadings were prepared and used in the production of alpha-arylstyrene through Friedel-Crafts alkenylation. The catalytic performance of x% SLZ/SBA-15 solid superacid catalysts are remarkably dependent on the acidic and textural properties that strongly affected by SLZ loading. The 25% SLZ/SBA-15 solid superacid catalyst shows outstanding catalytic performance and good regeneration behavior in alkenylation. Owing to the much superior acidic properties and ordered mesoporous structures, the SLZ/SBA-15 solid superacid could be considered as a promising solid acid catalyst for clean synthesis of many fine chemicals through diverse catalytic transformations.

## Acknowledgements

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2016.xx.xxx.

## B. Supplementary material

## Supplementary Figures

## References

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**List of Figure Captions:**

**Fig. 1.** Nitrogen adsorption-desorption isotherms and pore size distributions from adsorption branch of the SLZ/SBA-15 catalysts with different SLZ loadings. SA-SBA-15 is included for comparison.

**Fig. 2**.$NH_3$-TPD profiles of the SLZ/SBA-15 catalysts prepared by IWI with different SLZ loadings. (a) 20 %, (b) 25 %, (c) 30 %. The 20% SLZ/SBA-15 (PM) (d) and SA-SBA-15 (e) are included for comparison.

**Fig. 3.** XRD patterns of the SLZ/SBA-15 catalysts with diverse SLZ loadings. The 20% SLZ/SBA-15 (PM) is included for comparison.

**Fig. 4.** The catalytic stability and regeneration performance of the developed supported sulphated $La_2O_3$-$ZrO_2$ on SBA-15 (25% SLZ/SBA-15) for the alkenylation of *p*-xylene with phenylacetylene.

**Tables:**

**Table 1.**

Reaction results for the alkenylation of *p*-xylene with phenylacetylene over SLZ-based solid superacid catalysts with diverse preparation methods and SLZ loadings.

| Catalyst | Conversion (%) | Product distribution (%) | | | | |
|---|---|---|---|---|---|---|
| | | Ⅰ | Ⅱ | Ⅲ | Ⅳ | Ⅴ |
| 20% SLZ/SBA-15 (PM) | 22.6 | 90.3 | 3.1 | 0.5 | 2.3 | 3.9 |
| 20% SLZ/SBA-15 | 78.5 | 91.4 | 0.6 | 0.1 | 3.8 | 4.1 |
| SA-SBA-15 | 11.2 | 82.2 | 0.9 | 0.0 | 4.7 | 12.2 |
| $SO_4^{2-}/La_2O_3-ZrO_2$ | 89.6 | 90.5 | 0 | 0.1 | 5.1 | 3.3 |
| 25% SLZ/SBA-15 | 99.5 | 90.0 | 0.7 | 0.4 | 3.6 | 5.3 |
| 30% SLZ/SBA-15 | 92.3 | 89.8 | 1.1 | 0.0 | 3.0 | 6.1 |

Reaction conditions: $m$ (cat.)= 1.0 g, $n_{\text{p-xylene/Phen}}$= 25:1, $T_r$= 140 $^{o}$C, $P_s$ = 1.0 MPa, $TOS$ = 4 h, VHSV = 6 ml g$^{-1}$ h$^{-1}$ cat.

**Figures:**

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Graphical Abstract

Highlights

- Well-ordered mesoporous $SO_4^{2-}/La_2O_3\text{-}ZrO_2$/SBA-15 solid superacid is prepared.
- $SO_4^{2-}/La_2O_3\text{-}ZrO_2$/SBA-15 shows outstanding catalytic performance in alkenylation.
- The catalytic performance is strongly dependent on acidic and textural properties.
- The acidic and textural properties are notably affected by $La_2O_3\text{-}ZrO_2$ Loading.
- The developed mesoporous solid superacid has a great prospect in clean synthesis.