

Catalytic Liquid-phase Oxidation of Phenol under Mild Condition over Pt/CeO₂-ZrO₂-SnO₂/SBA-16: Loading Optimization and Kinetic Analysis

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Abstract

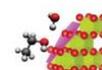
Phenol removal through catalytic liquid-phase oxidation using oxygen gas is a green and efficient method. This study reports a systematic investigation of Pt catalysts supported on CeO₂-ZrO₂-SnO₂/SBA-16, focusing on the effect of SnO₂ doping as well as CeO₂-ZrO₂-SnO₂ and Pt loading as a comprehensive strategy to tune catalytic performance under mild conditions. This approach offers a more integrated optimization of catalyst structure and composition, leading to enhanced activity and new mechanistic insights into phenol removal over multicomponent oxide-supported Pt catalysts. XRD and H₂-TPR analyses confirmed that 15 mol% Sn (Ce_{0.68}Zr_{0.17}Sn_{0.15}O₂) provided optimal redox behavior, while higher Sn content led to phase separation. Catalytic tests at 80 °C and atmospheric pressure showed that 7 wt% Pt/ 16 wt% Ce_{0.68}Zr_{0.17}Sn_{0.15}O₂/SBA-16 achieved the highest phenol removal (91%). Increasing CeO₂-ZrO₂-SnO₂ loading up to 16 wt% improved activity, though further increase reduced surface area and performance. Meanwhile, Pt loading was optimal at 7 wt%. Kinetic analysis revealed the reaction followed pseudo-first-order kinetics with a rate constant of 0.39 h⁻¹. The activation energy, derived from Arrhenius plots, was 57.7 kJ·mol⁻¹. These findings demonstrate that optimized CeO₂-ZrO₂-SnO₂ and Pt loadings significantly enhance phenol oxidation under mild conditions, offering a promising route for effective wastewater treatment.

Keywords: Catalytic phenol oxidation, CeO₂-ZrO₂-SnO₂, Kinetic analysis, Loading optimization

1 Introduction

Growing environmental concerns play a crucial role in promoting sustainable development within the industrial sector, which often generates hazardous byproducts and excess raw materials. A significant number of organic pollutants originating from industrial activities are released into wastewater streams. Among these, phenol is a particularly prevalent contaminant due to its extensive use as a precursor in the manufacturing of various chemicals such as phenolic resins, bisphenol A, salicylic acid, and caprolactam [1-3]. Unfortunately, phenol poses serious health risks to humans, potentially affecting the heart, central nervous system, and kidneys [4-5]. It is also known to be extremely toxic to aquatic organisms [6-8]. Consequently, developing an effective and practical method for phenol removal is essential.

Liquid phase oxidation using heterogeneous catalysts is a phenol removal method that offers many benefits, such as an easy recovering procedure and environmentally friendly [9-12]. However, many recent methods rely on additional oxidants like H₂O₂ [13] or peroxymonosulfate [14], which complicate real-world applications. In contrast, catalytic wet air oxidation (CWAO) using molecular oxygen is safer and more practical. For this purpose, platinum catalyst supported on CeO₂-ZrO₂ solid solution has attracted significant attentions, because the catalyst exhibited good catalytic performance in phenol oxidation [10-12]. CeO₂-ZrO₂ solid solution has high oxygen storage capacity as well as good thermal and chemical stability with cubic fluorite-type structure [15-17]. In this catalyst, CeO₂-ZrO₂ functions as an oxygen promoter for platinum, attributed to the facile and reversible



redox behavior of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple ion [18]. Nevertheless, the catalyst still requires arduous reaction condition to remove the phenol, such as elevated temperatures (around 160 °C) and high partial pressure oxygen gas (up to 2 MPa) [10-12]. Therefore, there is still a need to develop an efficient catalytic system capable of removing phenol at moderate temperatures (<100 °C) and at ambient pressure.

To improve catalytic performance under milder conditions, our previous study doped SnO_2 into the $\text{CeO}_2\text{-ZrO}_2$ support system [19,20]. The resulting $\text{Pt/CeO}_2\text{-ZrO}_2\text{-SnO}_2/\text{SBA-16}$ catalyst showed better performance for phenol removal compared to $\text{Pt/CeO}_2\text{-ZrO}_2/\text{SBA-16}$, highlighting the beneficial role of SnO_2 in enhancing redox behavior and oxygen mobility [21]. In this system, SBA-16 was employed as a mesoporous silica support due to its high surface area and three-dimensional pore structure, which facilitate uniform dispersion of active components and improve mass transport.

However, despite these promising results, several key questions remain unaddressed. Previous studies often explored catalyst compositions in a limited or empirical manner, without systematically investigating the effect of SnO_2 doping levels, the optimal loading of multicomponent oxide supports, or the influence of Pt content on both structural and catalytic properties. Furthermore, the reaction kinetics by using the catalyst also remains insufficiently understood. These gaps hinder the rational design of more efficient catalysts for phenol oxidation and similar liquid-phase oxidation reactions. Building upon our earlier findings, the present study aims to address these shortcomings through a comprehensive optimization of the $\text{Pt/CeO}_2\text{-ZrO}_2\text{-SnO}_2/\text{SBA-16}$ catalyst. Specifically, we examine the effects of SnO_2 content, $\text{CeO}_2\text{-ZrO}_2\text{-SnO}_2$ support loading, and Pt loading on catalytic activity under moderate reaction conditions. In addition, we conduct kinetic analysis to quantify the reaction rate and the activation energy. This approach offers new perspective into the design of effective catalysts for sustainable wastewater treatment.

2 Method

2.1 Catalyst preparation

The mesoporous silica support, SBA-16, was synthesized via a modified hydrothermal approach based on previously reported methods [22,23]. Initially, 1.6 g of Pluronic F-127 was dissolved in 90 mL of 0.2 mol L⁻¹ hydrochloric acid. After

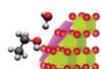
complete dissolution, 1.1 mL of 1,3,5-trimethylbenzene was introduced into the solution, followed by stirring at 35 °C for 3 hours to facilitate micelle formation. Subsequently, 7.1 mL of tetraethyl orthosilicate (TEOS) was added, and the mixture was stirred continuously for 20 hours. The resulting gel was poured into a Teflon-lined autoclave and underwent hydrothermal processing at 140 °C for 24 hours. The result was filtrated to obtain a solid product and then dried at ambient temperature followed by calcination at 400 °C for 4 hours in air (flow rate: 20 mL min⁻¹) to remove the template and obtain the final SBA-16 material.

A $\text{CeO}_2\text{-ZrO}_2\text{-SnO}_2$ solid was loaded onto SBA-16 using a co-precipitation method to obtain a composite with various doping amount of SnO_2 and loading amount of $\text{CeO}_2\text{-ZrO}_2\text{-SnO}_2$ by mixing certain amount of precursors of 1.0 mol L⁻¹ $\text{Ce}(\text{NO}_3)_3$, 0.1 mol L⁻¹ $\text{ZrO}(\text{NO}_3)_2$, and SnC_2O_4 powder to form x wt% $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2/\text{SBA-16}$ composites (see Table S1 and S2). This solution was stirred at room temperature for 30 minutes to ensure homogeneity before adding SBA-16 powder. After the addition, the suspension was stirred for another 30 minutes. The pH was gradually adjusted to 11 using a 5.6% aqueous ammonia solution, followed by continuous stirring for 12 hours. The resulting solid was separated by filtration and calcined at 900 °C for 1 hour. Hereafter, these x wt% $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2/\text{SBA-16}$ composites are denoted as CZSn_axSBA .

Platinum was introduced into the composite by an impregnation technique using a Pt precursor stabilized in ethanol with polyvinylpyrrolidone (Pt-PVP, Pt: 4.0 wt%). The Pt precursor was mixed added to the dispersed x wt% $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2/\text{SBA-16}$ composite in water to form y wt% Pt/x wt% $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2/\text{SBA-16}$ ($y = 0, 1, 3, 7, 10$). The mixture was stirred for 6 hours at room temperature to ensure uniform distribution of Pt, followed by solvent evaporation at 180 °C. The resulting material was then calcined at 500 °C for 4 hours to obtain the final catalyst. Hereafter, y wt% Pt/ x wt% $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2/\text{SBA-16}$ catalyst are denoted as $\text{PtyCZSn}_a\text{xSBA}$.

2.2 Catalyst characterization

The prepared catalysts were measured by X-ray diffraction (XRD; SmartLab, Rigaku) with Cu-K α radiation in the 2θ range 10–70°. Elemental compositions were analyzed by X-ray fluorescence spectroscopy (XRF, Supermini 200,



Rigaku) to verify the actual loading of Ce, Zr, Sn, and Pt in the catalysts. The specific surface area was evaluated by nitrogen adsorption–desorption measurements at $-196\text{ }^\circ\text{C}$ using a Tristar 3000 surface analyzer (Shimadzu) and the Brunauer–Emmett–Teller (BET) method was used to determine surface area. To assess the redox properties of the catalysts, temperature-programmed reduction (TPR) analysis was conducted under a 5 vol% H_2/Ar gas mixture (flow rate: 50 mL min^{-1}) with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$, using a Belcat-B instrument (MicrotracBel).

2.3 Catalytic test

The oxidation reaction of phenol was carried out in the oil bath using a 300 cm^3 three necked flask equipped with an opened condenser at $80\text{ }^\circ\text{C}$ in atmospheric pressure and magnetically stirred (500 rpm). An aqueous solution of phenol 1000 ppm (10 mL) and the catalyst (0.4 g) were mixed in the flask. After the preset reaction time, the aliquot was collected through the centrifugation process (Allegra 64R centrifuge, Beckman Coulter). The samples were then mixed with naphthalene solution in methanol (1000 ppm) for gas chromatography-mass spectrometry (GC-MS; GCMS-QP2010 Plus, Shimadzu) measurement to evaluate the phenol removal percentage and investigate the presence of intermediate compounds. The phenol removal percentage was calculated using Eq. 1.

$$\text{Phenol removal percentage} = \frac{C_0 - C}{C_0} \times 100\% \quad (\text{Equation 1})$$

where, C_0 and C are phenol initial concentration and phenol concentration after reaction, respectively.

Additionally, the rate constant (k) and activation energy of catalysts were also investigated by plotting the $-\ln[C/C_0]$ vs. the reaction time (t) and using the Arrhenius equation, respectively. The rate constant (k) was calculated following pseudo-first-order reaction and continued to investigate the activation energy (E_a) using the following Eq. 2 and Eq. 3.

$$\frac{dC}{dt} = kC_0 \quad (\text{Equation 2})$$

$$k = A e^{-E_a/RT} \quad (\text{Equation 3})$$

where A , R , and T are the pre-exponential factor, the gas constant, and the reaction temperature, respectively.

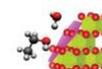
3 Result and Discussion

3.1 The effect of SnO_2 doping amount on the performance of catalyst

To examine the effect of SnO_2 content on the catalyst structure, a series of Pt-supported catalysts were synthesized with SnO_2 molar ratios of 0.05, 0.10, 0.15, 0.20, and 0.25 relative to the total metal oxides. Here, the Pt and $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2$ loading amount were fixed to be 7 wt% and 16 wt%, respectively. The composition of the prepared catalysts was in good agreement with the feed composition that confirmed by the XRF measurement as shown in Table 1. Fig. 1 presents the XRD patterns of the Pt7CZSn_a16SBA series. For the catalysts with $a \leq 0.20$, the diffraction patterns exhibit reflections corresponding only to the SBA-16 mesostructure, the cubic fluorite-type phase typical of $\text{CeO}_2\text{-ZrO}_2$, and metallic Pt. Notably, no obvious peaks attributable to SnO_2 are detected, suggesting that Sn^{4+} ions were successfully incorporated into the $\text{CeO}_2\text{-ZrO}_2$ lattice without forming a separate crystalline phase. Moreover, a subtle shift in the cubic fluorite-type diffraction peaks is observed with increasing SnO_2 content up to $a = 0.15$, particularly evident in the magnified XRD region between $2\theta = 25\text{-}35^\circ$. This shift can be attributed to the partial substitution of Ce^{4+} (ionic radius = 0.111 nm) and Zr^{4+} (0.098 nm) by the slightly smaller Sn^{4+} ion (0.095 nm) [24], which causes lattice contraction and confirms the successful doping of Sn^{4+} into the fluorite lattice. Further shift was not observed for $a = 0.20$ compared with $a = 0.15$, meaning that $a = 20$ may contain an impurity such as amorphous tin dioxide.

Table 1 The measured composition of the prepared 7.0wt%Pt/16.0wt% $\text{Ce}_{0.8(1-a)}\text{Zr}_{0.2(1-a)}\text{Sn}_a\text{O}_2/\text{SBA-16}$ (Pt7CZSn_a16SBA) catalysts with different a

| a | Measured composition |
|------|---|
| 0.05 | 7.3wt%Pt/16.8wt% $\text{Ce}_{0.75}\text{Zr}_{0.18}\text{Sn}_{0.07}\text{O}_2/\text{SBA-16}$ |
| 0.10 | 7.2wt%Pt/17.1wt% $\text{Ce}_{0.71}\text{Zr}_{0.17}\text{Sn}_{0.12}\text{O}_2/\text{SBA-16}$ |
| 0.15 | 6.8wt%Pt/16.4wt% $\text{Ce}_{0.69}\text{Zr}_{0.17}\text{Sn}_{0.14}\text{O}_2/\text{SBA-16}$ |
| 0.20 | 7.2wt%Pt/15.4wt% $\text{Ce}_{0.65}\text{Zr}_{0.16}\text{Sn}_{0.19}\text{O}_2/\text{SBA-16}$ |
| 0.25 | 7wt%Pt/16wt% $\text{Ce}_{0.6}\text{Zr}_{0.15}\text{Sn}_{0.25}\text{O}_2/\text{SBA-16}$ |



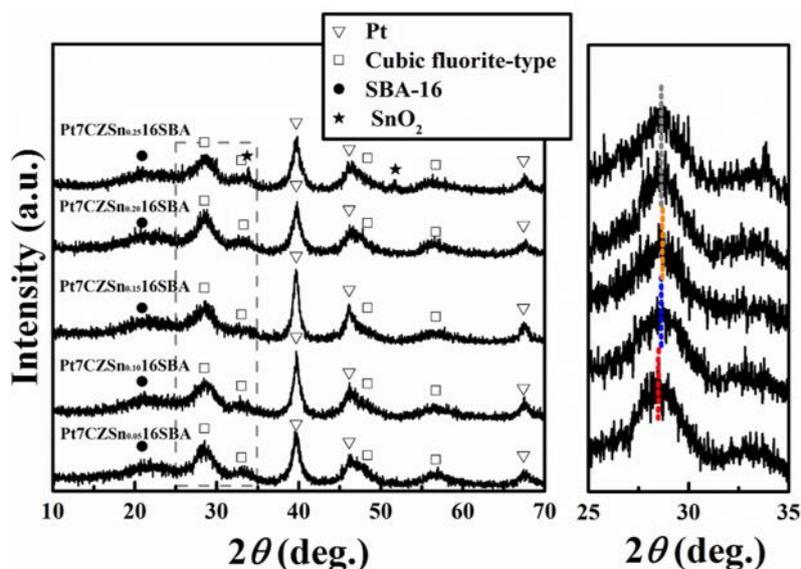


Figure 1 XRD patterns of Pt7Ce_{0.8(1-a)}Zr_{0.2(1-a)}Sn_aO₂/16SBA catalysts

In contrast, the XRD patterns of the catalyst with higher SnO₂ doping ($a = 0.25$) show additional peaks corresponding to crystalline SnO₂. This indicates that while some Sn⁴⁺ ions were still incorporated into the CeO₂–ZrO₂ lattice (as evidenced by the continued peak shift), excess SnO₂ began to segregate and form a distinct crystalline phase at higher loading levels. These results suggest a solubility limit for Sn⁴⁺ in the CeO₂–ZrO₂ solid solution under the present synthesis conditions.

The H₂-temperature programmed reduction (H₂-TPR) profiles of CZSn_{0.05}/16SBA, CZSn_{0.1}/16SBA, CZSn_{0.15}/16SBA, and CZSn_{0.2}/16SBA are presented in Fig. 2. Meanwhile, CZSn_{0.25}/16SBA was excluded from further analysis because the impurity phase of crystalline SnO₂ was unambiguously observed. There are two peaks identified as the surface and bulk reductions at lower and higher temperatures, respectively. As the SnO₂ doping level increased from a mole ratio of 0.05 to 0.15, a progressive shift of the reduction peaks toward lower temperatures was observed. This trend indicates enhanced redox behavior, attributable to improved reducibility of Ce⁴⁺ to Ce³⁺ facilitated by the presence of Sn⁴⁺. The incorporation of SnO₂ into the CeO₂–ZrO₂ lattice likely promotes the formation of oxygen vacancies associated with both the Ce⁴⁺/Ce³⁺ and Sn⁴⁺/Sn²⁺ redox pairs and the simultaneous reduction of Ce⁴⁺ and Sn⁴⁺ in the CeO₂–ZrO₂–SnO₂, which together enhance the material's ability to store and release oxygen during catalytic cycles [19, 25–28]. In the case of CZSn_{0.2}/16SBA, an increase in surface reduction

temperature was observed compared to CZSn_{0.15}/16SBA. This phenomenon may be attributed to the amorphous tin dioxide impurity.

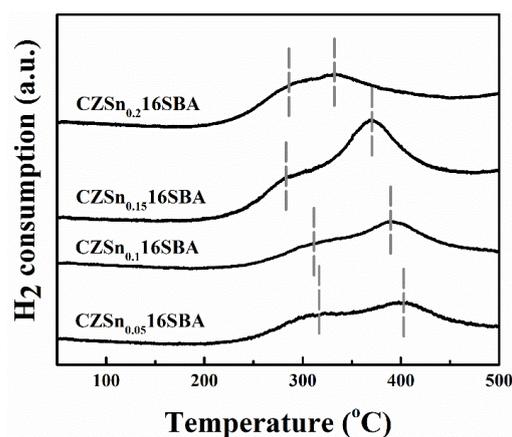


Figure 2 H₂-TPR profiles of CZSn_a/16SBA

Fig. 3 presents the phenol removal performance of Pt7CZSn_a/16SBA catalysts ($x = 0.05, 0.10, 0.15, 0.20$) after 6 hours of reaction at 80 °C under atmospheric pressure. The catalytic activity increased with the SnO₂ doping level, reaching a maximum at a Sn mole ratio of 0.15. At this optimal composition (Pt7CZSn_{0.15}/16SBA), the phenol removal percentage reached approximately 91%, as previously reported [21]. This improvement is consistent with the H₂-TPR results (**Fig. 2**), where Pt7CZSn_{0.15}/16SBA exhibited the lowest surface reduction temperature, signifying the most favorable redox properties. Enhanced redox behavior facilitates more efficient oxygen activation and transfer, which is critical for catalytic oxidation. However,



further increasing the SnO₂ content to a mole ratio of 0.20 led to a decline in phenol removal efficiency.

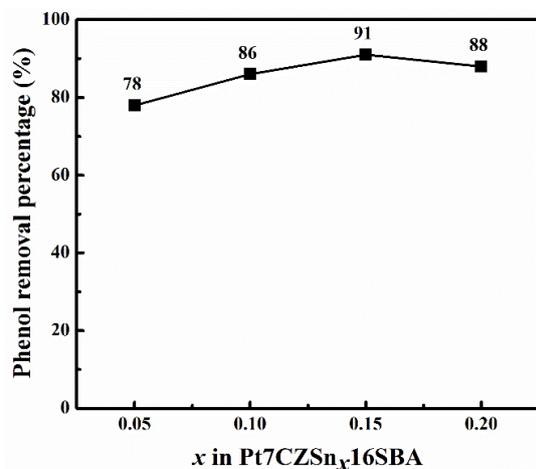


Figure 3 Phenol removal percentage after reaction using Pt7CZSn_x16SBA catalysts

3.2 The effect of CeO₂-ZrO₂-SnO₂ loading amount on the performance of catalyst

Following the optimization of SnO₂ doping within the CeO₂-ZrO₂-SnO₂ lattice, further investigation was conducted by varying the overall loading amount of the CZSn_{0.15} composite oxide onto SBA-16 that showed the higher catalytic performance having a molar Ce:Zr:Sn ratio of 0.68:0.17:0.15. Catalysts were synthesized with different CZSn_{0.15} loading amounts and a constant platinum content of 7 wt%, denoted as Pt7CZSn_{0.15x}SBA, where *x* indicates the weight percentage of CZSn_{0.15}.

The elemental composition and BET surface area are listed in **Table 2**. It was confirmed that increasing the CZSn_{0.15} content led to a progressive decrease in surface area. This reduction suggests successful dispersion and incorporation of CZSn_{0.15} into the SBA-16 framework. At higher loading amounts, CZSn likely filled the mesopores and partially covered the external surface of SBA-16, which reduced the available surface area [29,30].

XRD patterns of the Pt7CZSn_{0.15x}SBA catalysts are shown in **Fig. 4**. All samples displayed characteristic peaks associated with the mesoporous SBA-16, the cubic fluorite-type CeO₂-ZrO₂-SnO₂ phase, and metallic Pt. Notably, as the CZSn_{0.15} loading increased, the intensity of the fluorite-type diffraction peaks also increased, indicating the presence of a more crystalline CZSn_{0.15} phase.

Table 2 The measured composition and surface area of the prepared 7.0wt% Pt/ *x*wt% Ce_{0.68}Zr_{0.17}Sn_{0.15}O₂/ SBA-16 (Pt7CZSn_{0.15x}SBA) catalysts with different *x*

| <i>x</i> | Measured composition | Surface area (m ² ·g ⁻¹) |
|----------|---|---|
| 10 | 7.1wt%Pt/9.8wt%Ce _{0.67} Zr _{0.18} Sn _{0.15} O ₂ /SBA-16 | 290 |
| 16 | 6.8wt%Pt/16.4wt%Ce _{0.69} Zr _{0.17} Sn _{0.14} O ₂ /SBA-16 | 283 |
| 20 | 7wt%Pt/20.1wt%Ce _{0.68} Zr _{0.18} Sn _{0.14} O ₂ /SBA-16 | 216 |
| 25 | 6.9wt%Pt/24.8wt%Ce _{0.69} Zr _{0.18} Sn _{0.13} O ₂ /SBA-16 | 198 |

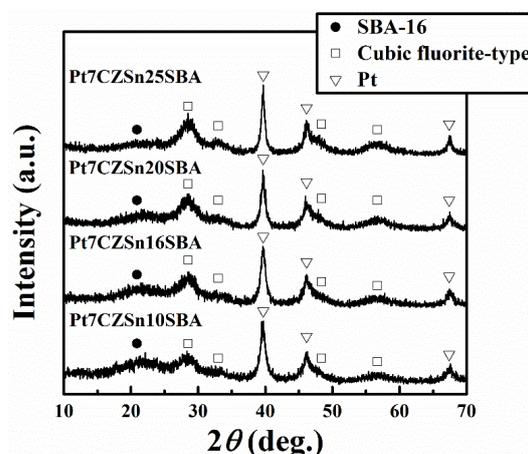
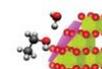


Figure 4 XRD patterns of Pt7CZSn_{0.15x}SBA catalysts

The Pt7SBA catalyst, without CZSn_{0.15}, shows some phenol removal activity due to the ability of Pt to activate molecular oxygen and subsequently oxidize the phenol. Interestingly, the incorporation of CZSn_{0.15} as an oxygen promoter significantly enhanced phenol conversion and suppressed the accumulation of benzoquinone, which is a common intermediate in phenol oxidation [31-32], as shown in **Fig. 5**. This facilitates a more efficient oxidation process, as the CZSn_{0.15} actively participates in oxygen transfer to Pt, leading to improved phenol conversion. As the CZSn content increased up to 16 wt%, catalytic activity improved, attributed to the greater availability of lattice oxygen, which facilitated the oxidation process. However, further increases in CZSn loading beyond 16 wt% led to a decline in catalytic performance. This reduction is likely due to excessive pore blockage and surface coverage of SBA-16 by the dense CZSn phase, resulting in a decreased surface area and limited accessibility to active sites. Catalysts with higher CZSn content also produced lower amounts



of benzoquinone intermediate, suggesting that CZSn enabled deeper oxidation toward final products such as CO₂ or other smaller molecules.

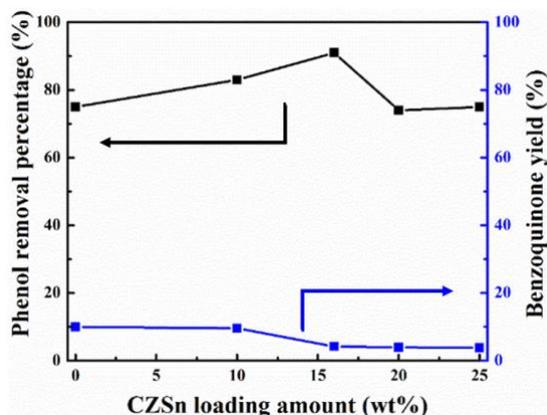


Figure 5 Performance Pt7CZSn_{0.15}xSBA catalysts with a reference of Pt7SBA ($x = \text{CZSn}_{0.15}$ loading amount)

3.3 The effect of Pt loading amount on the performance of catalyst

Following the naming convention used above, the catalysts with y wt% Pt loaded onto 16 wt% Ce_{0.68}Zr_{0.17}Sn_{0.15}O₂/SBA-16 are referred to as PtyCZSn_{0.15}16SBA. The XRD patterns of CZSn_{0.15}16SBA and PtyCZSn_{0.15}16SBA catalysts are presented in Fig. 6. No impurity phases were detected, indicating the high purity and successful incorporation of all components. As the Pt loading increased, the diffraction peaks corresponding to metallic Pt became more prominent, indicating improved crystallinity and higher Pt content. This trend also suggests the growth of Pt crystallite size with increasing loading, as evidenced by the sharpening and intensity enhancement of Pt-related peaks.

Table 3 summarizes the actual metal compositions and surface areas of the PtyCZSn16SBA catalysts. The elemental analysis confirmed that the measured compositions closely matched the nominal feed ratios, demonstrating good control over the synthesis. The surface area of the catalysts tended to decrease gradually with increasing Pt content, likely due to partial pore blockage or coverage of SBA-16 by Pt nanoparticles, which may reduce the accessible surface area for reactants [29,30].

The Pt loading effect on the catalytic performance of PtyCZSn_{0.15}16SBA ($y = 0, 1, 3, 7, 10$) was evaluated and the results are shown in Fig. 7. The introduction of Pt significantly enhanced the catalytic activity compared to the Pt-free CZSn16SBA, confirming the vital role of Pt as an

active site for oxidation. Phenol removal efficiency increased with increasing Pt loading up to 7 wt%, which is attributed to the higher number of available active Pt sites that facilitate the activation of oxygen species for phenol oxidation. However, further increase of Pt loading to 10 wt% led to a decline in catalytic activity. This drop can be correlated with the reduction in surface area, as observed in Table 3, likely due to pore blockage or particle agglomeration at higher Pt concentrations. These results indicate that 7 wt% is the optimal Pt loading, offering the best balance between active site availability and surface area for efficient phenol oxidation.

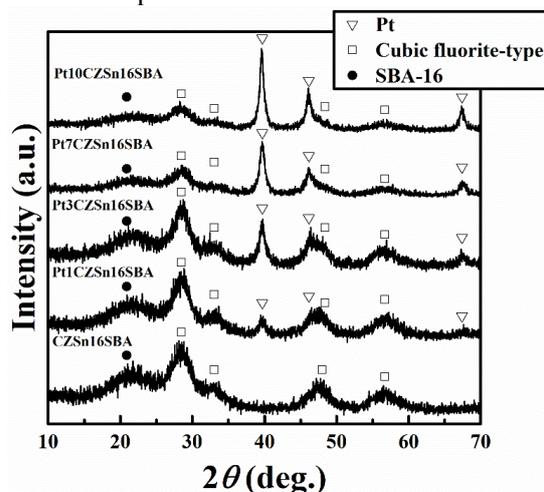


Figure 6 XRD patterns of y wt% Pt/ 16wt% Ce_{0.68}Zr_{0.17}Sn_{0.15}O₂/ SBA-16 (PtyCZSn_{0.15}16SBA) catalysts

Table 3 The measured composition and surface area of the prepared PtyCZSn_{0.15}16SBA catalysts

| y | Measured composition | Surface area (m ² ·g ⁻¹) |
|-----|---|---|
| 1 | 1.2wt%Pt/18.0wt%Ce _{0.69} Zr _{0.16} Sn _{0.15} O ₂ /SBA-16 | 290 |
| 3 | 3.2wt%Pt/15.3wt%Ce _{0.65} Zr _{0.18} Sn _{0.17} O _{2.0} /SBA-16 | 285 |
| 7 | 6.8wt%Pt/16.4wt%Ce _{0.69} Zr _{0.17} Sn _{0.14} O _{2.0} /SBA-16 | 283 |
| 10 | 9.8wt%Pt/16.3wt%Ce _{0.67} Zr _{0.18} Sn _{0.15} O _{2.0} /SBA-16 | 252 |

3.4 Kinetic Study of Phenol Oxidation over Pt7CZSn16SBA Catalyst

The reaction temperature effect on the catalytic activity of Pt7CZSn_{0.15}16SBA was examined at 60, 70, and 80 °C, under atmospheric pressure for 2-8 hours. As shown in Fig. 8, the catalytic performance improved significantly with



increasing temperature, indicating enhanced reaction kinetics at higher thermal energy.

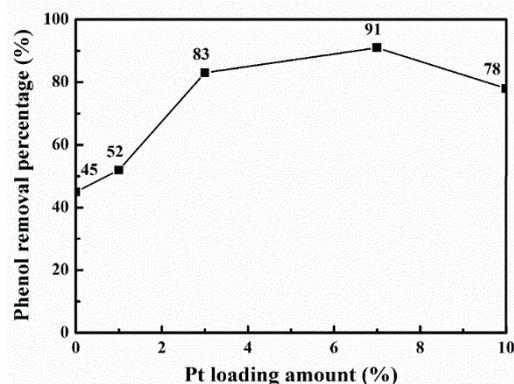


Figure 7 Performance of Pt/CZSn_{0.15}/16SBA catalysts with reference of CZSn/16SBA ($y = \text{Pt loading amount}$)

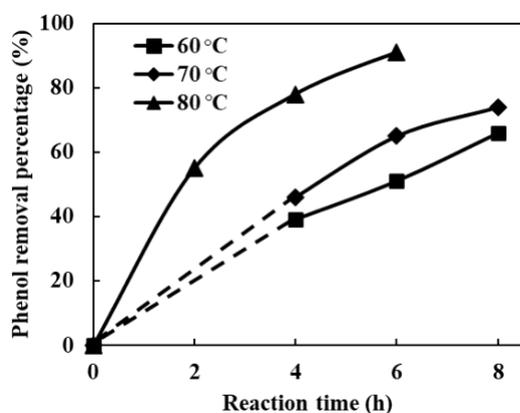


Figure 8 Phenol removal percentage after reaction using Pt7CZSn_{0.15}/16SBA catalyst at 60, 70, and 80 °C

To further evaluate the reaction kinetics, the concentration–time data were fitted to a pseudo-first-order kinetic model. **Fig. 9** presents the plots of $-\ln(C/C_0)$ versus reaction time at each temperature. The linearity of the plots suggests that phenol oxidation over Pt7CZSn_{0.15}/16SBA proceeds via pseudo-first-order kinetics, consistent with previous studies on similar systems [14].

Using the slope of each linear plot, the apparent rate constants were calculated based on the first-order rate law. The rate constants for phenol oxidation were determined to be 0,13 h⁻¹, 0,17 h⁻¹, and 0.39 h⁻¹ at 60°C, 70°C, and 80°C, respectively. Furthermore, the activation energy (E_a) was estimated from the Arrhenius equation using the rate constants at different temperatures. The corresponding Arrhenius plot (**Fig. 10**) exhibits good linearity, indicating reliable kinetic

behavior. The activation energy for phenol oxidation over Pt7CZSn_{0.15}/16SBA was calculated to be 57.7 kJ·mol⁻¹. This value is lower than the activation energy of cobalt catalyst loaded on various support (59.7–75.5 kJ mol⁻¹) and RuO₂ (61.4 kJ mol⁻¹) or CuO (72.6 kJ mol⁻¹) loaded on activated carbon for phenol removal [33–37]. These findings confirm that the catalyst demonstrates efficient oxidation activity under mild conditions and follows well-defined reaction kinetics.

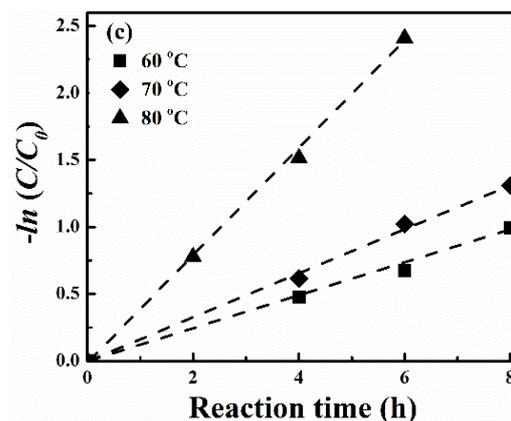


Figure 9 Reaction rate constant of phenol oxidation reaction using Pt7CZSn_{0.15}/16SBA catalyst

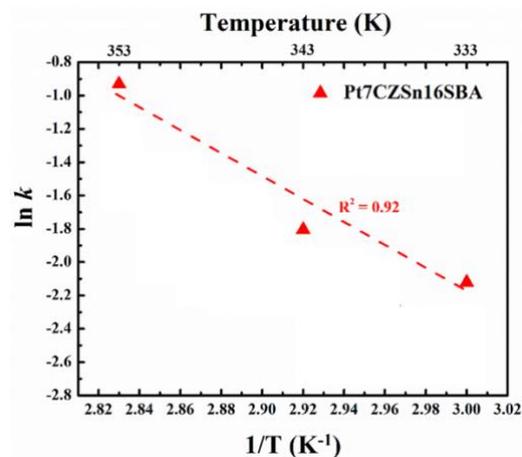
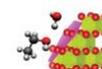


Figure 10 Arrhenius plot phenol oxidation using Pt7CZSn_{0.15}/16SBA catalyst

4 Conclusion

This study successfully demonstrated the optimization of Pt/CeO₂–ZrO₂–SnO₂/SBA-16 catalysts for phenol oxidation under mild reaction conditions. The optimum SnO₂ content in the CeO₂–ZrO₂–SnO₂ (CZSn) oxygen promoter was found at a molar ratio of 0.15, providing the highest redox activity and phenol removal efficiency. Further, the ideal loading amount of the



CZSn promoter on SBA-16 was determined to be 16 wt%, balancing sufficient oxygen storage capacity and surface area. The optimal platinum loading was 7 wt%, which maximized catalytic activity without excessively blocking the support's porosity. Kinetic studies confirmed that the reaction follows pseudo-first-order kinetics, with a rate constant of 0.39 h^{-1} at $80 \text{ }^\circ\text{C}$ and an apparent activation energy of $57.7 \text{ kJ}\cdot\text{mol}^{-1}$. These findings indicate that Pt7CZSn_{0.15}16SBA is a highly effective catalyst for phenol removal via catalytic wet air oxidation, offering promising performance at lower temperature and atmospheric pressure.

Acknowledgement

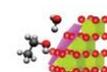
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