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Functionalization of SBA-15 with CeO$_2$ nanoparticles for adsorptive desulfurization: Matters of template P123

Yu Yin and Zhi-Hao Wen
Jiangsu University of Science and Technology, P. R. China

Xiao-Qin Liu
Nanjing Tech University, P. R. China

Ai-Hua Yuan
Jiangsu University of Science and Technology, P. R. China

Lei Shi
Chinese Academy of Sciences, P. R. China

Abstract
Adsorption is one of the most promising methods for desulfurization of transportation fuels, due to the strategy which enables removal of organic sulfur compounds to be conducted at ambient conditions with high efficiency. Adsorbent is the key to the adsorptive performance. Both $\pi$ complexation and direct sulfur metal bonds are efficient methods for adsorptive desulfurization. For construction of these bonds, it is necessary to introduce active metal species on the support. In this work, Ce(NO$_3$)$_2$ was directly introduced into the as-synthesized SBA-15, and high dispersion of CeO$_2$ nanoparticles was obtained. With the loading content of 12–46 wt%, the particle sizes of the CeO$_2$ NPs are in the range of 4.4–6.3 nm. The good dispersion status of CeO$_2$ nanoparticles is contributed to the template P123 preserved in as-synthesized SBA-15, which provides a confined space for the dispersion of CeO$_2$ nanoparticles. However, the large CeO$_2$ particles (7.0 nm) are formed for the sample originated from template-free SBA-15. We also demonstrate that the adsorptive performance of SBA-15 is enhanced with the modification of CeO$_2$ nanoparticles. Besides, the performances of CeO$_2$ nanoparticle-modified samples stay in step with the dispersion status of the CeO$_2$ nanoparticles.

Keywords
CeO$_2$ nanoparticles, mesoporous silica, desulfurization, confined space, adsorption

Corresponding author:
Yu Yin, Jiangsu University of Science and Technology, 2 Mengxi Road, Jingkou District, Zhenjiang, Jiangsu 212003, China.
Email: season_july@just.edu.cn

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Introduction

Deep desulfurization from transportation fuels has been of great urgency due to more stringent environmental regulations worldwide (Cao et al., 2008; Sitamraju et al., 2015; Wang et al., 2012). Besides, fuel cell technologies call for the hydrogen resource with nearly zero sulfur content (Kannan and Kumar, 2016; Speder et al., 2016). Nowadays, refineries mainly rely on the hydro-desulfurization (HDS) process to remove sulfur compounds in industry. HDS technology is operated at harsh conditions, including super-high temperatures of 300–350°C and ultrahigh hydrogen pressures of 2–10 MPa (Shang et al., 2004; Singh and Kunzru, 2016; Sun and Prins, 2008; Vit et al., 2015). The HDS technology is efficient in removing inorganic sulfur compounds, including thiols and sulfides. However, it is less effective to remove organic sulfur compounds, including thiophene and its derivatives (Dai et al., 2006; Yang et al., 2003). It is highly desirable to further decline the sulfur concentration. Removal of organic sulfur compounds has been researched by various methods, including extraction, oxidation, and biological strategy (Moghadam et al., 2017; Xu et al., 2017). It is fortunate that these methods show positive effects on the removal of organic sulfur compounds. However, they inevitably show some shortcomings referring to consuming energy, producing byproducts, and generating slow biodegradation. There is thereby an urgent need but it is still a significant challenge to achieve deep desulfurization levels. Among the alternatives, one of the most important future directions of desulfurization is adsorption. There is great potential in using adsorbents for deep desulfurization, because organic sulfur molecules can be captured at ambient conditions with high efficiency (Song et al., 2014; Vilarrasa-Garcia et al., 2011b; Xiong et al., 2010). It is commonly known that both π complexation and direct sulfur metal (S–M) bonds can work for adsorptive desulfurization (Danmaliki and Saleh, 2017; Khan et al., 2017; Shi et al., 2017; Song et al., 2013). Thus, active species, such as Cu₂O (Jiang et al., 2013; Wang et al., 2009b), CeO₂ (Song et al., 2016; Xiao et al., 2013a), etc. are always incorporated into the porous materials for fabrication of π complexation or direct S–M sites. It is known that the porous materials with high surface areas are highly desirable for loading active species (Li et al., 2016; Xiao et al., 2013b; Yin et al., 2016). In addition, it is demonstrated in a number of studies that key to the adsorption performance of the adsorbent is the status of supported active species (Hernández-Maldonado and Yang, 2004b; Song et al., 2011).

Since the M41-typed mesoporous materials were first synthesized in 1992, a large number of mesoporous materials have been synthesized by use of the surfactant template method (Feng et al., 2012; Liu et al., 2002; Stein, 2003; Thomas, 2010). Among the mesoporous materials, mesoporous silica shows high surface areas and modest pore sizes and is very suitable for application as the support (Cruz et al., 2016; Eedugurala et al., 2015; Gaudin et al., 2016; Sun et al., 2015; Zhang et al., 2008). In general, mesoporous silica is a promising host for preparation of the selective adsorbent (Anbia and Mohammadi, 2008; Tian et al., 2010; Wang et al., 2006; Yin et al., 2014). Normally, the as-synthesized mesoporous silica is first to calcine, which leads to generate template-free mesoporous silica with open pores. The precursor is then incorporated into the open pores, with the second calcination to convert the precursor to active species (Cheng et al., 2015; Shao et al., 2012; Vilarrasa-Garcia et al.,
2011b). This conventional method requires repeated calcination, which is low efficiency and energy consuming. According to the previous reports of Zhu and Liu’s groups, there is a special confined space between template P123 and silica walls in as-synthesized mesoporous silica (Yin et al., 2012; Yue et al., 2008). By direct introduction of the precursor into the as-synthesized SBA-15 (ASS), high dispersion of active species is achieved by use of the extraordinary confined space.

Herein, we report for a new strategy for functionalization of mesoporous silica SBA-15 with CeO$_2$ nanoparticles (NPs) in order to prepare adsorbents for desulfurization. Before removal of the template P123, Ce(NO$_3$)$_2$ was directly introduced into ASS via solid-state grinding. Followed with calcination in air, the resultant adsorbents were obtained. We denoted the adsorbents as CeO$_2$-ASS. For contrast, Ce(NO$_3$)$_2$ was introduced into template-free SBA-15 (TFS) as well for preparation of the CeO$_2$-TFS sample. The results show that by use of ASS as the support, the CeO$_2$ NPs are controlled in the size of 4.4–6.3 nm. The confined space between template P123 and silica walls in ASS plays an important role on the high dispersion of CeO$_2$ NPs. For the sample based on TFS, however, the large CeO$_2$ NPs (7.0 nm) are formed and give rise to partly disordered and blocked pores of SBA-15. We also demonstrate that the CeO$_2$ NP-modified materials show better performances than pure SBA-15 on adsorptive desulfurization. This is contributed to the formation of S–M bonds between CeO$_2$ and thiophene. It is important to highlight that the CeO$_2$-ASS samples show much better adsorptive desulfurization performances than CeO$_2$-TFS.

### Experimental

#### Materials synthesis

**ASS and TFS.** Mesoporous silica SBA-15 was synthesized following the literature method, which was first reported by Zhao et al. (1998). Two gram of pluronic EO$_{20}$PO$_{70}$EO$_{20}$ (P123) was first added to 75 g of HCl aqueous solution (1.6 m). The mixture was stirred for half an hour. After dissolving, 4.25 g of silica source tetraethylorthosilicate was added. Then, stirring was conducted once again at 40°C for 24 h. The mixture was then transferred to the teflon-lined autoclave for hydrothermal treatment at 100°C for 24 h. After cooling to room temperature, the powder was collected by filtration. ASS was obtained after the powder was dried at room temperature. TFS was obtained by removal of template P123, which was conducted by calcination at 550°C for 5 h in flowing air.

**xCeO$_2$-ASS.** The precursor Ce(NO$_3$)$_3$$\cdot$6H$_2$O was introduced into ASS via solid-state grinding at room temperature for 30 min. The thoroughly mixed powder was calcined in flowing air at 500°C for 5 h to form active CeO$_2$ NPs, and template P123 was removed simultaneously. The obtained composites were denoted as $x$CeO$_2$-ASS, where $x$ represents the weight ratio of CeO$_2$ in the CeO$_2$-ASS samples.

**xCeO$_2$-TFS.** In a conventional process, $x$CeO$_2$-TFS samples were prepared by introduction of Ce(NO$_3$)$_3$$\cdot$6H$_2$O into TFS via solid-state grinding at room temperature for 30 min. The thoroughly mixed powder was calcined in flowing air at 500°C for 5 h to form active CeO$_2$ NPs. The obtained composites were denoted as $x$CeO$_2$-TFS, where $x$ represents the weight ratio of CeO$_2$ in the CeO$_2$-TFS samples.
**Characterization**

XRD spectra were collected with a Bruker D8 Advance diffractometer using Cu Ka radiation in the 2θ ranges from 0.7° to 6° (for low-angle patterns) and 5° to 70° (for wide-angle patterns) at 40 kV and 40 mA. High-resolution transmission electron microscopy (HRTEM) was performed on a Tecnai G2 F30 S-Twin electron microscope operated at 300 kV. The N2 isotherms were measured using a BELSorp-max system at 77 K. Prior to measurement, the samples were pretreated under vacuum at 200°C for 4 h. The Brunauer–Emmett–Teller surface areas were calculated according to the adsorption branch in the relative pressure of 0.04–0.20. The total pore volumes were evaluated at the relative pressure of 0.99. The pore size distributions were calculated by Barrett–Joyner–Halenda method according to the desorption branch. The ceria content of a sample was tested on J-A1100 inductively coupled plasma-optical emission spectrometry.

Fourier transform infrared (IR) spectra were recorded on a Nicolet Nexus 470 spectrometer with a spectral resolution of 2 cm⁻¹ using transparent KBr pellets. Thermogravimetric (TG) analysis was performed on a thermobalance (STA-499C, NETZSCH). About 10 mg of sample was heated from the room temperature to 800°C in a flow of air (25 ml min⁻¹).

**Adsorptive test**

The simulated fuel was prepared using thiophene as the representative of organic sulfur contaminants. By mixing thiophene with isoctane, the sulfur concentration was controlled to be 550 ppmw (parts per million by weight). The desulfurization performance of adsorbents was evaluated on the basis of breakthrough curves. Experiments were performed at room temperature in a vertical quartz column with 6 mm in diameter. Adsorbents (0.2 g) were filled into the vertical quartz column, and a quartz grid was supported. Prior to measurement, the adsorbents were activated in situ by calcination at 200°C for 2 h in air. After cooling to room temperature, the gas of air was switched to the simulated fuel, which was pumped up with a mini creep pump at a rate of 3.0 ml h⁻¹. Effluent solutions were collected at regular intervals until saturation was reached. The sulfur content in effluent solutions was determined with a Varian 3800 gas chromatograph (GC) equipped with a pulsed-flame photometric detector. A calibration curve was prepared to analyze the GC results. Breakthrough curves were generated by plotting the normalized sulfur concentration versus the cumulative fuel volume. The normalized concentration (c/c₀) was obtained from the detected content (c) divided by the initial content (c₀), and the cumulative fuel volume was normalized by the adsorbent weight. The adsorption capacity was calculated by integral calculus.

**Results and discussion**

**Status of supported CeO₂ NPs**

Figure 1(a) depicts the low-angle XRD patterns of SBA-15, CeO₂-ASS, and CeO₂-TFS samples. Mesoporous silica SBA-15 shows an intense diffraction line indexed as (100), and two weak lines indexed as (110) and (200) reflections. This indicates that SBA-15 contains a 2D p6mm hexagonal symmetry. All of the ceria-containing samples show the similar patterns with SBA-15. This indicates the ordered mesoporous structures are well maintained after the
The introduction of CeO₂. In addition, in comparison with SBA-15, the intensity of the (100) reflection of CeO₂-ASS and CeO₂-TFS samples declines. The weak intensity of diffraction peaks results from the decreased scatter contrast between silica walls and pore space, which is presumably due to the incorporation of CeO₂ into pores of SBA-15.

The wide-angle XRD patterns of the samples are shown in Figure 1(b). From the patterns of support SBA-15, a broad diffraction peak can be seen at 2θ of 23°, which is attributed to amorphous silica. For the samples of CeO₂-ASS and CeO₂-TFS, some new peaks at 2θ of 28.5°, 33.2°, 47.5°, and 56.3° derived from CeO₂ (JCPDS 81-0792) emerge on the pattern. This indicates that the CeO₂ species do exist in the samples. Besides, for the CeO₂-ASS samples, the CeO₂ peaks become intense with the increase of ceria content. It should be noted that the diffraction peaks of CeO₂ for the 36CeO₂-TFS sample are more intense than all of the CeO₂-ASS samples. The average particle sizes of CeO₂ NPs in the samples were calculated by the Scherrer formula based on full width at half maximum values from CeO₂ peaks at 2θ of 28.5°. Table 1 displays the results of particle sizes. The particle sizes of CeO₂ NPs in the CeO₂-ASS samples are in the range of 4.4–6.3 nm. While the CeO₂ NPs in the

**Table 1.** Physicochemical properties of SBA-15, CeO₂-ASS, and CeO₂-TFS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CeO₂ contenta (wt%)</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt; (m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;p&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt; g&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>D&lt;sub&gt;p&lt;/sub&gt; (nm)</th>
<th>d&lt;sub&gt;CeO₂&lt;/sub&gt;b (nm)</th>
<th>Adsorption capacity at saturation (mmol S g&lt;sup&gt;−1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>0</td>
<td>875</td>
<td>1.137</td>
<td>5.9</td>
<td>–</td>
<td>0.105</td>
</tr>
<tr>
<td>12CeO₂-ASS</td>
<td>12.3</td>
<td>830</td>
<td>1.049</td>
<td>6.3</td>
<td>3.6</td>
<td>0.131</td>
</tr>
<tr>
<td>22CeO₂-ASS</td>
<td>22.1</td>
<td>754</td>
<td>0.900</td>
<td>6.3</td>
<td>3.6</td>
<td>0.159</td>
</tr>
<tr>
<td>36CeO₂-ASS</td>
<td>36.2</td>
<td>573</td>
<td>0.711</td>
<td>6.3</td>
<td>3.6</td>
<td>0.165</td>
</tr>
<tr>
<td>46CeO₂-ASS</td>
<td>46.3</td>
<td>432</td>
<td>0.495</td>
<td>3.6</td>
<td>5.9</td>
<td>0.136</td>
</tr>
<tr>
<td>36CeO₂-TFS</td>
<td>36.3</td>
<td>484</td>
<td>0.579</td>
<td>3.7</td>
<td>7.0</td>
<td>0.115</td>
</tr>
</tbody>
</table>

aICP data.
bCeO₂ crystallite size calculated by the Scherrer formula.
36CeO$_2$-TFS sample show the particle size of 7.0 nm, which is remarkably larger than the 36CeO$_2$-ASS sample (5.1 nm).

Figure 2 shows the HRTEM images of CeO$_2$-ASS and CeO$_2$-TFS samples. The TEM image of pure SBA-15 is presented in Figure S1. The silica walls of SBA-15 appear as dark, and pore spaces appear as white. Thus, highly ordered pore structures of SBA-15 can be judged. After functionalization of SBA-15 with ceria, the TEM images have a slight change. For the 36CeO$_2$-ASS sample, the mesopores keep with a long-range order as well as SBA-15. In addition, some shadow areas appeared, which contributed to dispersed CeO$_2$ NPs on the SBA-15. As for the 36CeO$_2$-TFS sample, CeO$_2$ NPs with large sizes can be identified. Moreover, the channels of SBA-15 are found to be partly disordered and blocked by the CeO$_2$ NPs.
Figure 3(a) depicts the N\textsubscript{2} isotherms of the adsorbents. Figure 3(b) shows the pore size distribution curves calculated from the desorption branches of isotherms. Table 1 displays the surface areas, pore volumes, and pore sizes of the adsorbents. Support SBA-15 shows a type IV isotherm shape with an H1 hysteresis loop at the relative pressure ($p/p_0$) of 0.60–0.80. This is characteristic of materials with regular and cylindrical mesopores. In general, the isotherm shapes of 12CeO\textsubscript{2}-ASS, 22CeO\textsubscript{2}-ASS, and 36CeO\textsubscript{2}-ASS samples show great similarity to that of support SBA-15. There is difference on no more than closing point. For the 12CeO\textsubscript{2}-ASS, 22CeO\textsubscript{2}-ASS, and 32CeO\textsubscript{2}-ASS samples, the closing point of the hysteresis loop shifts to a slightly lower relative pressure of 0.45. This gives direct evidence of the introduction of oxides into the pores of SBA-15. For the 46CeO\textsubscript{2}-ASS sample, the closing point of the hysteresis loop is at the relative pressure of 0.45 as well. In addition, the desorption branch of the isotherm shows a serious delay, which gives rise to the two steps of desorption curves. This indicates that massive pore spaces should be occupied with the introduced oxides. The 36CeO\textsubscript{2}-TFS sample, derived from TFS, shows a great different isotherm curve with others. The hysteresis loop is parallel and horizontal at the relative pressure ($p/p_0$) of 0.40–0.75. This indicates that the sample contains slit pores. This result coincides with the partly disordered and blocked pores observed from the TEM image. When it comes to surface areas, SBA-15 shows the highest value of 875 m\textsuperscript{2} g\textsuperscript{-1}. The surface areas of the CeO\textsubscript{2}-ASS samples are in the range of 830–432 m\textsuperscript{2} g\textsuperscript{-1}. It is noteworthy that the 36CeO\textsubscript{2}-TFS sample shows the lower surface area and pore volume than 36CeO\textsubscript{2}-ASS, even if ceria content is identical. Further results show that the pore size of SBA-15 is 5.9 nm. For the 12CeO\textsubscript{2}-ASS, 22CeO\textsubscript{2}-ASS, and 36CeO\textsubscript{2}-ASS samples, the pore sizes are 6.3 nm in chief and 3.6 nm in minor. For the 46CeO\textsubscript{2}-ASS sample, the pore size is 3.6 nm in chief and 5.9 nm in minor. For the 36CeO\textsubscript{2}-TFS sample, the pore size is centered at 3.7 nm.

According to the XRD, TEM, and N\textsubscript{2} adsorption–desorption results, it is necessary to have a summary on the combination status of CeO\textsubscript{2} NPs and SBA-15. First, due to the similar low-angle XRD patterns with SBA-15, white dark contrast on the TEM images, and distinct hysteresis loop on the N\textsubscript{2} adsorption–desorption isotherms, it is safe to deduce that the mesoporous structures of SBA-15 are well preserved after the modification of CeO\textsubscript{2} NPs.
Second, on the basis of weaken intensity of (100) reflection on the low-angle XRD patterns, identified CeO$_2$ NPs on the TEM images, and movement of the closing point of the hysteresis loop on the N$_2$ adsorption–desorption isotherms, it is reasonable to believe that the CeO$_2$ NPs are introduced into the pores of SBA-15. Third, the CeO$_2$ NPs show various statuses with the diverse ceria content and synthetic methods. In detail, the sizes of CeO$_2$ NPs in the CeO$_2$-ASS samples derived from wide-angle XRD pattern are in the range of 4.4–6.3 nm. In comparison with 36CeO$_2$-ASS (5.1 nm), the size of the CeO$_2$ NPs in the 36CeO$_2$-TFS sample is larger (7.0 nm). Moreover, the 36CeO$_2$-ASS sample shows higher surface area, pore volume, and pore size than the 36CeO$_2$-TFS sample. These data are consistent with the notion that CeO$_2$ NPs in the CeO$_2$-ASS samples have better dispersion status than in CeO$_2$-TFS. In other words, the application of ASS as support is propitious to the high dispersion of CeO$_2$ NPs.

To further verify the location of the ceria, XPS analyses were carried out to study the surface properties of the samples. Figure S2 shows the results, and Table S1 summarizes the atomic concentration of Si, O, and Ce elements in the 36CeO$_2$-ASS and 36CeO$_2$-TFS samples. The theoretical value of the atomic concentration of Ce is 30.78. It is unusual that the value measured with XPS technique (1.03, 1.12) is much lower than the theoretical value (30.78). Take in mind that the XPS is the surface technique. The measured low atomic concentration of Ce is due to the formation of aggregated ceria on the surface of SBA-15. What needs to be emphasized is that the concentration is strongly low both in the 36CeO$_2$-ASS and 36CeO$_2$-TFS samples. Thus, it is safe to say that the location of most ceria is inside the mesopores of the porous silica rather than on the surface.

Proposed mechanism for high CeO$_2$ dispersion in CeO$_2$-ASS

IR spectra of the samples before and after calcination are presented in Figure 4. The bands in the range of 2850–3000 and 1350–1500 cm$^{-1}$ appearing on the spectrum of ASS are the
characteristics of template P123 (Figure 4(a)) (Tian et al., 2002). With calcination, ASS transforms to TFS, the bands of template P123 is absent, which is ascribed to massive decomposition of the template P123. The carbon content in ASS is 30.59 wt%, after calcination, the carbon content in SBA-15 goes down to 0.32 wt%. This indicates that there is little carbonaceous substance remaining after the removal of template P123. With introduction of Ce(NO_3)_2 into ASS, some new bands at 1380 cm\(^{-1}\) appeared in the 36CeO_2-ASS sample. The new bands are due to the asymmetric stretching vibration of N–O (Yin et al., 2012), which illustrates the existence of NO\(^{-}\). For the 36CeO_2-ASS sample after calcination, the bands belonging to both template P123 and NO\(^{-}\) are invisible. This indicates that both template removal and Ce(NO_3)_2 conversion can finish in a step of calcination. The conversion of Ce(NO_3)_2 in the CeO_2-TFS sample is also conscious by comparing the spectra before and after calcination.

As shown in Figure 5, the decomposition behaviors of the samples are investigated by the TG technique. In ASS, the removal of template P123 takes place from 155 to 270°C with a massive weight loss of 50%. In cooperation, there is a sharp DTG peak at 162°C. It is worthwhile to note that pure P123 decomposes at about 210°C (Zhao et al., 1998). In comparison, the decomposition temperature of P123 in ASS is lower than pure P123. There is the strong possibility that the silica frameworks in ASS catalyze the removal of the template P123. For the Ce(NO_3)_2-modified template-free SBA-15 sample (36CeO_2-TFS), the decomposition procedure due to evaporation of adsorbed water goes from room temperature to 80°C. The decomposition of Ce(NO_3)_2 in 36CeO_2-TFS proceeds from 80 to 450°C with a weight loss of 35.5%, which coincides with the calculated value of 35.7%. This indicates the massive conversion of Ce(NO_3)_2 to CeO_2. For the Ce(NO_3)_2-modified ASS, the curve of weight loss shows its own characteristics. In the 36CeO_2-ASS sample, the conversion of Ce(NO_3)_2 in ASS starts from 80 to 168°C. There is a weight loss of 25.2%, which is well consistent with the calculated value of 25.3%. This suggests the massive conversion of Ce(NO_3)_2 to CeO_2 as well. Subsequently, the removal of template P123 starts from 168 to 355°C, corresponding to a sharp DTG peak at 208°C.

**Figure 5.** (a) TG and (b) DTG curves of SBA-15, CeO_2-ASS, and CeO_2-TFS samples before calcination. DTG curves are plotted offset for clarity.

According to the aforementioned results, CeO\textsubscript{2} NPs in the CeO\textsubscript{2}-ASS samples show better dispersion status than in CeO\textsubscript{2}-TFS. Next, we explored the proposed reasons. For the CeO\textsubscript{2}-ASS samples, Ce(NO\textsubscript{3})\textsubscript{2} was directly introduced into the ASS with template P123. IR results prove that both template removal and Ce(NO\textsubscript{3})\textsubscript{2} conversion can be achieved in a step of calcination. TG results show that the removal of P123 in 36CeO\textsubscript{2}-ASS occurs at temperature of 216°C. This decomposition temperature is much higher than that in ASS (162°C) and almost the same as pure P123 (210°C). This word points that the Ce(NO\textsubscript{3})\textsubscript{2} is indeed incorporated into the confined space between template P123 and silica walls. Therefore, the catalysis of silica walls to the decomposition of the template P123 does not work. We have noticed that the conversion of Ce(NO\textsubscript{3})\textsubscript{2} in the 36CeO\textsubscript{2}-ASS sample completes before the decomposition of template P123. That is to say, the conversion of Ce(NO\textsubscript{3})\textsubscript{2} is carried through within the confined space. Hence, at current time, we have to demonstrate that the conversion order of precursor and template P123 is key to the dispersion status of CeO\textsubscript{2} NPs. If the conversion of precursor takes precedence over the removal of template P123, the confined space will give a boost for the high dispersion of CeO\textsubscript{2} NPs. Otherwise, the earlier decomposition of template P123 will result in the damage of the confined space. As for the 36CeO\textsubscript{2}-TFS sample, the template P123 decomposes before the introduction of Ce(NO\textsubscript{3})\textsubscript{2}. Therefore, the template P123 can no longer play a role on the dispersion status of CeO\textsubscript{2} NPs. To this end, we show that the better CeO\textsubscript{2} dispersion in CeO\textsubscript{2}-ASS results from the confined space in ASS.

**Performance on adsorptive desulfurization**

The adsorptive desulfurization performances of the samples are measured with the simulated fuels, which contain 550 ppmw of sulfur. The breakthrough curves are shown in Figure 6. The values of adsorption capacity were calculated according to the breakthrough curves at saturation, and results are listed in Table 1. The support SBA-15 is capable of 0.105 mmol g\textsuperscript{-1} of thiophene, which exhibits the worst performance among all the samples. After modification of SBA-15 with CeO\textsubscript{2} NPs, the desulfurization capacities evidently

![Figure 6](image-url)

**Figure 6.** Breakthrough curves of thiophene in a fixed-bed adsorber with SBA-15, CeO\textsubscript{2}-ASS, and CeO\textsubscript{2}-TFS samples.
improve. The adsorption capacities for the 12CeO₂-ASS, 22CeO₂-ASS, and 36CeO₂-ASS samples step up from 0.131 to 0.165 mmol g⁻¹ with the increase of ceria content. For the sample of 46CeO₂-ASS, the adsorption capacity is 0.136 mmol g⁻¹. The counterpart sample of 36CeO₂-TFS shows the worst performance among all the CeO₂ NP-modified samples. The uptake is as low as 0.115 mmol g⁻¹. Many adsorbents so far have been prepared for removal of organic sulfur compounds. For Ce(IV) exchanged Y zeolite, the adsorption capacity is 0.122 mmol g⁻¹ with 297 ppmw of sulfur in commercial diesel (Hernandez-Maldonado and Yang, 2004a). The Cu(I)/SBA-15 adsorbent is derived from modification of SBA-15 with CuCl. The sulfur capacity of this adsorbent is 0.123 mmol g⁻¹ with 760 ppmw of sulfur in aromatic oil (Dai et al., 2006). Metallic nickel NPs are supported on mesoporous silica for preparation of Ni/SBA-15. This adsorbent could capture 0.053 mmol g⁻¹ of sulfur with diesel containing 240 ppmw of sulfur (Park et al., 2008). These results indicate that the present 36CeO₂-ASS adsorbent is highly competitive for application in adsorptive desulfurization. Adsorption–desorption cycles for the 36CeO₂-ASS sample were tested according to a reported method (Oliveira et al., 2009; Rodrigues et al., 2014; Vilarrasa-Garcia et al., 2011a). Figure S3 shows the results that three cycles of adsorption and desorption could be achieved by use of this reported method.

We have noticed that with the introduction of CeO₂ in SBA-15, the sulfur capacities of the CeO₂-ASS and CeO₂-TFS samples are much higher than SBA-15. There are a number of studies which indicate that Ce(IV), with the valence electronic configuration 4f⁰5d⁰6s⁰, has high positive charge and polarizability. Sulfur compounds can be adsorbed over Ce(IV) by a direct S–M interaction (Wang et al., 2009a). The IR spectrum of the 36CeO₂-ASS sample adsorption with model fuel was recorded (Figure S4). After adsorption with model fuel, the new bands at ~3000 cm⁻¹ could contribute to the interaction between the 36CeO₂-ASS sample and sulfur via the direct S–M interaction. Thus, the enhanced performances of CeO₂-ASS and CeO₂-TFS over SBA-15 can contribute to the modified CeO₂ species, which form S–M bonds with thiophene. It should be further pointed out that the CeO₂-ASS samples show better desulfurization performances than CeO₂-TFS. The aforementioned results indicate that CeO₂ NPs in the CeO₂-ASS samples have better dispersion status than in CeO₂-TFS. Taken together, these results suggest that the desulfurization performances of the samples are consistent with the dispersion status of CeO₂ NPs. In other words, high dispersion of CeO₂ NPs is in favor of better performance on desulfurization.

Conclusions

In conclusion, with the introduction of Ce(NO₃)₂ into ASS, high dispersion of CeO₂ NPs can be obtained (CeO₂-ASS). The particle sizes of the CeO₂ NPs are in control of 4.4–6.3 nm in the CeO₂-ASS samples, with the CeO₂ content of 12–46 wt%. The high dispersion of CeO₂ NPs can be attributed to the ASS with template P123, which provides a confined space for the dispersion of CeO₂ NPs. However, the large CeO₂ NPs (7.0 nm) are formed for the sample originated from template-free SBA-15 (CeO₂-TFS). The high dispersion of CeO₂ NPs makes the CeO₂-ASS adsorbents better perform on desulfurization than CeO₂-TFS.

Declaration of Conflicting Interests

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Supplementary Material

The Supplementary material for this article is available on the Journal site.

References


Supplementary Information

Functionalization of SBA-15 with CeO$_2$ Nanoparticles for Adsorptive Desulfurization: Matters of Template P123

Yu Yin*,a, Zhi-Hao Wen a, Xiao-Qin Liu b, Ai-Hua Yuan a, and Lei Shi c

a School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China

b State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, P. R. China

c State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, P. R. China

Supplementary Experimental Details

Materials Characterization

TEM images were recorded on a JEM-200CX electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Physical Electronic PHI-550 spectrometer equipped with an Al Kα X-ray source (hv = 1486.6 eV) and was operated at 10 kV and 35 mA. Elemental analysis experiment was carried on Elementar Vario EL III instrument. Fourier transform infrared (IR) spectra were recorded on a Nicolet Nexus 470 spectrometer with a spectra resolution of 2 cm$^{-1}$ using transparent KBr pellets. For the measurement of IR spectrum after adsorption with model fuel, the sample was added to the model fuel and stirred for more than four hours. After drying, the IR spectrum were recorded.

Adsorption-desorption Experiment

The adsorption-desorption cycles were investigated. Simulated fuel (550 ppm w) was pumped into the adsorbent with a mini creep pump at a rate of 3.0 mL·h$^{-1}$ until near saturation. Then the feed was switched to pure isooctane in order to regeneration the column. When the effluent sulfur concentration descended to near zero, the feed was again switched to simulated fuel. Three desulfurization/regeneration cycles were performed.
Figure S1. TEM image of SBA-15.

Figure S2. XPS peak fitting of Ce 3d spectra of the samples.

Figure S3. Adsorption-desorption cycles in a fixed-bed adsorber with the 36CeO₂-ASS sample.
**Figure S4.** IR spectra of the 36CeO$_2$-ASS sample before and after adsorption with model fuel

**Table S1** Atomic concentration of elements in the 36CeO$_2$-ASS and 36CeO$_2$-TFS samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>O</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>2.56</td>
<td>66.67</td>
<td>30.78</td>
</tr>
<tr>
<td>36CeO$_2$-ASS</td>
<td>25.69</td>
<td>68.56</td>
<td>1.03</td>
</tr>
<tr>
<td>36CeO$_2$-TFS</td>
<td>24.85</td>
<td>69.85</td>
<td>1.12</td>
</tr>
</tbody>
</table>

**Table S2** Elemental analysis results of C and H weight ratio in the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as synthesized SBA-15</td>
<td>30.59</td>
<td>5.83</td>
</tr>
<tr>
<td>SBA-15</td>
<td>0.32</td>
<td>2.79</td>
</tr>
<tr>
<td>36CeO$_2$-ASS</td>
<td>0.10</td>
<td>2.03</td>
</tr>
<tr>
<td>36CeO$_2$-TFS</td>
<td>0.11</td>
<td>1.64</td>
</tr>
</tbody>
</table>