Controlled synthesis of $\alpha$-Al$_2$O$_3$ supported Ag particles with tuning catalytic performance

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ABSTRACT

Herein, $\alpha$-Al$_2$O$_3$ supported Ag particles with controllable size distribution are prepared successfully by tuning of the calcination conditions through an impregnation method. The size of Ag particles could be adjusted by changing the calcination time and temperature. The catalyst samples were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and other characterization methods under different calcination conditions, and the performance differences of their catalytic reduction of p-nitrophenol (4-NP) were investigated by UV-Vis spectroscopy. The results show that the Ag particles with increased particle size can be obtained on the surface of $\alpha$-Al$_2$O$_3$ support by increasing the calcination time or calcination temperature. The catalytic performance of the samples obtained by increasing the calcination time decreased, while the catalytic performance of the samples obtained by increasing the calcination temperature increased. This may be due to the interaction between Ag particles and the support, which changes the valence state of Ag species. Also the particle size effect acts on the catalyst and affects its catalytic performance together with the change of valence.

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1. Introduction

As the basis of the chemical industry, catalysts play a key role in modern industrial production. Supported metal catalysts have the advantages of high selectivity, high stability, low corrosiveness, and easy reusability, which have become one of the most widely used catalysts [1,2]. Catalysts are mainly composed of support and metal compounds, and their catalytic performance and composition are directly related to their structure. Therefore, structural modulation of catalysts is an important way to optimize their performance. Among many factors, the size of the metal particles plays a dominant role in determining
catalytic performance. Changes in the size of metal particles lead to changes in their electronic and geometric structures, which affect the catalytic performance of the catalyst, the so-called particle size effect [3,4]. It is generally believed that the finer the metal particles are dispersed on the support surface, the higher their catalytic activity [5,6]. Therefore, regulating the size of metal particles in catalysts is beneficial to achieve more efficient catalytic processes [7,8].

Many studies have been done on particle size regulation of supported metal catalysts. Pei et al. [9] adjusted the concentration of palladium salt solution and successfully prepared a series of palladium nanocatalysts with controllable size by calcining composite microspheres. Eskandari et al. [10] found that the addition of salt to the impregnation solution could control the size of metal particles in the catalyst samples. A series of platinum catalysts with particle size controlled by doping sodium chloride was synthesized. However, adjusting the average particle size of nanoparticles by this method would result in a final size distribution that would be wide. Therefore, they further explored the growth mechanism of nanoparticles with salt addition and sought to make more controlled particles with a concentrated size distribution [11]. Liu et al. [12] developed a preparation method to achieve the size and dispersion control of gold-based catalysts. In addition, the catalysts prepared by this method have higher activity compared to those prepared by conventional methods. It is evident from previous investigations that the catalyst preparation process has an important influence on the catalyst performance. The study of catalyst preparation conditions can help to improve the catalyst performance.

Among various types of supported metal catalysts, silver-based catalysts have special reactivity, selectivity, and stability in many catalytic systems, combined with the advantages of low price [13] and environmental friendliness [14], and thus have gained wide applications in many fields [15,16]. Many researchers have studied the size regulation for different synthesis methods of silver catalysts. Cheng et al. [17] successfully prepared silver nanoparticles of 10-30 nm by using the synergistic reduction effect of tannic acid and trisodium citrate. Smaller size silver nanoparticles could be obtained by increasing the concentration of tannic acid. Under the conditions of ethylene glycol as the reducing agent and PVP as the protecting agent, Liu et al. [18] prepared quasi-spherical silver nanoparticles with particle sizes of 25, 35, 45, 60, and 70 nm by varying the reaction temperature. Zhang et al. [19] used the crystal seed method to prepare silver nanoparticles with adjustable sizes. The size tuning was carried out by the following three points: First, the local surface plasmon resonance of the solution was detected during the reaction process, and the reaction was stopped when the resonance peak reached a specific position. Second, the number of crystalline species was varied when the amount of precursor AgNO3 was fixed. Third, the number of precursor AgNO3 was varied when the amount of crystalline species was fixed.

However, it has to be considered that silver-based catalysts occupy an essential position in industrial applications as catalytic materials for ethylene epoxidation reactions. Silver-based catalysts for industrial use usually consist of large silver nanoparticles (100–200 nm) supported by α-Al2O3 with a relatively low surface area [20,21]. In addition, to scale up and save cost, the industrial preparation of supported silver catalysts is usually done by the impregnation method. The support is impregnated with impregnating solution and then dried and calcined to modify the surface structure and surface properties. However, it is not easy to control the size of metal particles in this method. When the impregnation conditions are controlled, it can end up with homogeneous and highly dispersed metal particles. During calcination, the precursor salt is thermally decomposed and generates an active phase on the surface of the support. The factors such as calcination temperature
and time can often modulate the catalyst particle size and improve the catalytic activity. Therefore, in this study, the particle size of \( \alpha \)-Al\(_2\)O\(_3\)-supported silver catalysts was regulated by changing the calcination time and temperature based on the impregnation method, and the variation pattern was investigated.

Precious metal catalysts (e.g., gold, silver, and palladium) show excellent performance in the reduction of p-nitrophenol (4-NP) to p-aminophenol (4-AP) \([22,23]\), so this reaction has been widely used for the evaluation of precious metal catalysts \([24,25]\). The 4-NP reduction catalyzed by Ag nanoparticles has been thoroughly studied \([26,27]\). In this study, the reduction of 4-NP was used as a model reaction to examine the performance of Ag-based catalysts.

In this study, Ag/\( \alpha \)-Al\(_2\)O\(_3\) particles with controllable particle size distribution were successfully prepared by changing the calcination conditions of the conventional impregnation method. During the catalyst preparation, the calcination time and calcination temperature were varied in a small range to adjust the catalyst particle size, while keeping the carrier type as well as the metal loading constant. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) were used to analyze the compositional structure of the catalyst materials. X-ray photoelectron spectroscopy (XPS) was used to determine the physicochemical properties of the materials. Ultraviolet-visible spectroscopy (UV-Vis) was used to evaluate the reaction rate of catalytic 4-NP reduction. In the experimental interval, the particle size of Ag/\( \alpha \)-Al\(_2\)O\(_3\) increased with the increase of calcination time and calcination temperature. The catalytic performance of the samples with prolonged calcination time was weakened, while the catalytic performance of the samples with increased calcination temperature was enhanced. Based on the analysis of the comparative tests and characterization results, insights were provided on the possible reasons for the increase in particle size and catalytic performance of the samples obtained by increasing the calcination temperature.

2. Experimental

2.1. Materials

Alpha-aluminum oxide (\( \alpha \)-Al\(_2\)O\(_3\)) was obtained from Lanzhou Petrochemical Research Center, PetroChina, with specific surface area of 1.2 m\(^2\)/g, pore volume of 0.53 mL/g, and average pore diameter of 1757 nm. Absolute ethanol (99.5%) was obtained from Beijing Chemical Works. Silver nitrate (AgNO\(_3\), \( \geq 99.0\% \)), sodium borohydride (NaBH\(_4\)), and absolute oxalic acid (H\(_2\)C\(_2\)O\(_4\)) were obtained from Sigma-Aldrich. 4-Nitrophenol (4-C\(_6\)H\(_5\)NO\(_3\), 4-NP) and ethylenediamine (C\(_2\)H\(_8\)N\(_2\), EDA) were obtained from Macklin. Water was purified using a Milli-Q system (Millipore).

2.2. Synthesis of Ag precursor

Silver oxalate (Ag\(_2\)C\(_2\)O\(_4\)) as Ag precursor was prepared as follows. H\(_2\)C\(_2\)O\(_4\) and AgNO\(_3\) with a molar ratio of 2:5 were dissolved in deionized water and stirred at a constant speed for 2 h. Then, the solid-liquid mixture was separated by filtration. The separated solid product was washed alternately by deionized water and absolute ethanol several times until the pH of the residual liquid stabled at 7. The sediment was dried by vacuum drying oven 12 h with no light to prevent the further decomposition of Ag\(_2\)C\(_2\)O\(_4\).
2.3. Preparation of Ag/α-Al₂O₃

The Ag/α-Al₂O₃ catalysts were prepared by the excess impregnation method. Typically, the as-prepared Ag₂C₂O₄ and EDA were calculated based on a pre-designed loading (3:1 molar ratio of EDA to Ag₂C₂O₄). The impregnation solution containing Ag₂C₂O₄ was added to the support, and the sample was placed for 1 h to ensure adequate impregnation (3:1 mass ratio of impregnation solution to support). The samples were then filtered and dried 12 h in a vacuum oven. To obtain Ag particles with different sizes, we used a method of varying calcination conditions, including calcination time (group 1, denoted as G1) and calcination temperature (group 2, denoted as G2). The calcination process was carried out in a tube furnace. All samples (including G1 and G2) had a common calcination condition: a constant temperature rise rate of 5 K/min, an end calcination temperature of 250°C, and calcination in Argon gas atmosphere. The base calcination time for all samples in G1 was 2 h, to which calcination times of 0 h, 12 h, 24 h, 48 h, and 60 h were added for different samples, respectively. That is, the total calcination time for each sample in G1 was 2 h, 14 h, 26 h, 50 h, and 62 h, respectively. The calcination time for G2 samples was 2 h, and the calcination temperatures were 270°C, 290°C, and 310°C, respectively.

2.4. Catalytic reduction of 4-NP

The reduction of 4-NP by the Ag/α-Al₂O₃ catalyst in the presence of an excess amount of NaBH₄ was studied in a standard quartz cuvette and monitored by a UV-Vis spectroscopy to examine the catalytic activity at room temperature. The principle of this method for the determination of 4-NP concentration in solution is the Lambert-Beer law, which describes the relationship between the absorbance of the solution and the concentration of the light-absorbing substance. That is, the absorbance of the solution is proportional to the concentration of the light-absorbing substance under the premise of a constant optical path. The reaction procedures was as follows. 5 mg of to-be-tested samples were diluted to be a 1 mL solution with ultrasonic (referred to be sample solution in the following). 2.0 mL Milli Q water, 10 μL 5 mM 4-NP was slowly added into the quartz cuvette, and then, 100 μL 0.2 M NaBH₄ was added. The mixture solution turned from white to yellow after the addition of NaBH₄ standard solution. Immediately after the addition of 20 μL of the sample solution, UV-Vis spectra of the solution were recorded every 1 min in the scanning range of 200–500 nm. The initially obtained data can be seen as the spectra without the catalytic reaction with the sample solution, t = 0. The rate constant of the reduction proceeds was determined by measuring the change in absorption in 400 nm as a function time. The bright yellow solution gradually changed to white with the addition of sample solution [28].

2.5. Characterization

The morphologies and sizes of the as-prepared samples were characterized by HITACHI SU3500 scanning electron microscope (SEM) and HITACHI-600 transmission electron microscope (TEM). High-resolution TEM (HRTEM) images were collected on a JEOL JEM-2100 instrument. The powder X-ray diffraction (XRD) were examined on a Bruker D8 Advance diffractometer using Cu-Kα radiation (wavelength λ = 0.15406 nm) in the 2θ range 20°–80°. The X-ray photoelectron spectroscopy (XPS) was measured on Thermo ESCALAB 250XI. The actual loading weight of Ag was examined by AGILENT ICP-OES.
3. Results and discussion

In order to eliminate the effect of differences in the loading amounts of each catalyst in the experiments for catalytic performance testing, ICP-OES tests were first performed. All catalyst samples were weighed 0.06–0.1 mg, dissolved, and diluted with hydrogen nitrate and MilliQ water to a solution concentration of about 5 mg/L. The Ag loading was calculated based on the ratio of the measured Ag content to the sample weight (see Table S1 and Table S2 in the supporting material for details). In the experimental group with the change of calcination time, the actual loading of Ag was stabilized at about 25 wt%. The actual loading of Ag was stabilized at about 20 wt% in the experimental group that varied the calcination temperature. The results show that the loading of Ag on the support is the same in each group of catalysts, which provides a reasonable premise for the subsequent comparison of the size change effect and the valence change effect.

The morphology of obtained Ag/α-Al2O3 catalyst was analyzed by SEM and TEM. Figure 1(a) shows the SEM image of the sample at the calcination time of 12 h. As can be seen in the figure, the large flat regions are the crystal plates of α-Al2O3 support. Smaller white particles, i.e. the loaded Ag particles, are attached to the surface of the support. Although no surfactant was added to help dispersion, the Ag particles were evenly distributed on the carrier, which indicates a better exposure of the active site of Ag and facilitates the reaction process of reducing 4-NP to 4-AP. Figure 1(b) shows the TEM image of the sample with a calcination temperature of 290°C. The black dots in it are Ag particles and the light gray area is the α-Al2O3 support. This image also shows that the Ag particles are uniformly distributed on the support. Figure 1(c) shows the EDS mapping of the Ag/α-Al2O3 catalyst, which indicates the spatial distribution of each element. The images with different colors indicate the enriched areas of Ag, Al and O of the sample, respectively. The results show the presence of elements Ag, Al and O on the surface of the sample, suggesting that Ag was successfully attached to the α-Al2O3 surface. In this study, we adjusted the Ag particle size by varying the calcination temperature and calcination time in a small range. According to the SEM image analysis (see Figures S1 and S2 in the supporting material), the average particle size of Ag particles increased significantly with the increase of calcination time and the increase of calcination temperature in the experimental interval. As shown in Figure 1(d,e), with the increase of calcination time from 0 h to 60 h based on 2 h, the average particle size of Ag particles increased from 0.28 to 0.39 μm. With the increase of calcination temperature from 270 to 310 °C, the variation of the average particle size of Ag particles ranged from 0.12 to 0.15 μm. This result indicates that, within the experimental interval, the increase of calcination time and calcination temperature caused the Ag particles to agglomerate and increase the particle size.

The physical phases and structures of the catalysts were tested by XRD. Figure 2 shows the XRD patterns of two sets of Ag catalysts loaded on α-Al2O3 support under different calcination conditions. The peaks marked in the figure represent Ag(111), Ag(100) and Ag(110), respectively. The other peaks represent α-Al2O3 supports (PDF#46-1212). In the figure, the largest peak is Ag(111), while Ag(100) and Ag(110) peaks are smaller than Ag(111) peak, and Ag is stable in the form of Ag(111). The lattice fringe spacing from HRTEM image also shows that the crystal plane of the particles are mainly Ag (111) (see Figure S3 in the supporting material). With the change of calcination time as well as calcination temperature, the relative relationship of all three peaks did not change.
significantly and no new peaks appeared. This indicates that changing the calcination conditions in the small range of the experimental interval is not sufficient to cause the phase transition of Ag, or the change is too small to be observed.

The catalytic activity of the catalyst sample was evaluated by reducing 4-nitrophenol with NaBH₄, in order to investigate the practical effect of the variation of catalyst calcination conditions on the catalytic performance. The conversion of 4-nitrophenol to 4-aminophenol could be tracked by UV-Vis spectroscopy. The aqueous solution of 4-NP shows an absorption peak at 317 nm. After the addition of NaBH₄, the -OH group in 4-NP was deprotonated to form the 4-nitrophenol salt anion under alkaline conditions, and the absorption peak was shifted from 317 to 400 nm [29]. At the same time, the color of the solution changed from light yellow to bright yellow (see Figure S4 in supporting material).

As the concentration of 4-NP decreases during the reaction, the absorbance at 400 nm
also decreases. According to the Lamber-Beer law, the rate constant of this reaction process can be determined by measuring the absorption peak at 400 nm with the change of time. Therefore, the performance differences of catalyst samples prepared under different treatment conditions can be reflected by the different changes of absorbance with time during the catalytic 4-NP reduction reaction. According to the Langmuir-Hinshelwood model, considering the excess of NaBH₄ used compared with 4-NP, whose concentration can be considered to remain constant throughout the reaction process, the reaction kinetics is considered to follow a pseudo-first-order law and follows the following kinetic equation [30]:

\[
\ln \left( \frac{C_t}{C_0} \right) = \ln \left( \frac{A_t}{A_0} \right) = -k_{app} \times t
\]

where \( k \) is the quasi-level kinetic rate constant, \( A_0, C_0, A_t, \) and \( C_t \) represent the absorbance and concentration of 4-NP at the initial and \( t \) moments, respectively. During this reaction, there is a linear relationship between \( \ln \left( \frac{C_t}{C_0} \right) \) and \( t \). The \( k_{app} \) can be estimated by linear fitting of experimental data. The catalysts of the experimental group with varying calcination time were tested for their performance according to the above method. The UV-Vis spectrum of the catalysts with different calcination times during the reaction process is shown in Figure 3(a–e). With the increase of reaction time, the peak strength of 4-NP at 400 nm decreased gradually, while that of 4-AP increased. When the absorption peak of 4-NP disappeared, and the absorption peak of 4-AP reached its maximum, it indicates the complete conversion of 4-NP to 4-AP. The linear fitting result of the reaction constant varies between 0.469 and 0.133, as shown in Figure 3(f). The results show that the rate of 4-NP reduction reaction decreases gradually when increasing the calcination time from 12 h to 60 h. That is, the catalytic performance of Ag/\( \alpha \)-Al₂O₃ for this reaction declined. In addition, according to the results of particle size analysis, the average particle size of Ag particles showed a significant increasing trend with the increase of calcination time. In the experimental group with varying calcination times, the results of performance tests and particle size measurements were consistent with the theory of particle size effect.

In order to explore the particle size effect during the variation of calcination temperature, UV-Vis spectroscopy was performed on the G2 samples. As shown in Figure 4(a–c), the characteristic peaks at 400 nm during the catalytic reduction of 4-NP were monitored for Ag/\( \alpha \)-Al₂O₃ samples calcined at 270°C, 290°C, and 310°C, respectively. It can be
seen from the UV-Vis curves that the reduction time of 4-NP was shortened from about 17 min to 7 min with the increase of calcination temperature. The linear fitting results of the reaction constants are shown in Figure 4(d), and the reaction constants for the three samples are 0.148, 0.328 and 0.527, respectively. It can be seen from the figure that with the increase of calcination temperature, the slope of the fitting line becomes larger and larger, the reaction rate constant increases successively. This result indicates that there is a positive effect of increasing the calcination temperature on improving the performance of the catalyst in the interval range of this experiment. Although the loading of Ag in the experimental group with adjusted calcination temperature was lower than that in the G1
experimental group, the catalytic performance of the catalyst obtained by calcination at 310 °C was better than that of the sample with the shortest calcination time in the G1 experimental group. However, with the increase of calcination temperature, the Ag particle size becomes larger, while the reaction constant decreases. This is quite contrary to the rule of changing the calcination time to regulate the particle size of the catalyst. The reason for this anomaly is discussed further below.

Ag is the main active phase of the catalyst Ag/a-Al2O3, and what determines its catalytic effect is not only the number of Ag atoms exposed on the catalyst surface (influenced by loading, particle size and dispersion), but also the redox ability of each exposed Ag site. Thus, the state of Ag also plays an important role in catalysis [31]. The two sets of samples were tested by XPS to evaluate the valence state of α-Al2O3 loaded elements, and the results are shown in Figure 5. The 3D spectrum of Ag has two characteristic peaks near 367.8 eV and 373.5 eV. According to previous studies, the Ag 3d5/2 binding energy at 368.7 eV is the characteristic peak of Ag0 [32], and the one at 367.7–367.8 eV belongs to the characteristic peak of Ag oxide [33]. And the binding energy of Ag 3d5/2 of both sets of samples is located in the middle of the binding energy of Ag0 and Ag2O [34]. Therefore, the XPS spectral results indicate that Ag coexists with Ag2O in the two groups of samples or that Ag in the samples exists in the intermediate valence state, that is, Agδ+ (0 < δ < 1) [35]. As can be seen from the figure, for the G1 experimental group, the binding energy of Ag 3d5/2 increased from 367.9 eV to 368.3 eV when the additional calcination time was increased from 12 h to 60 h. With the increase in calcination time,
more of the Ag species were converted to Ag$^0$, that is, the valence state of the Ag species decreased. For the G2 experimental group, with a small increase in calcination temperature in the experimental interval, the characteristic peak of Ag 3d$_{5/2}$ shifted slightly in the direction of decreasing binding energy, that is, closer to the characteristic peak of Ag$_2$O. This indicates that the valence state of Ag loaded on Al$_2$O$_3$ increases with the increase of calcination temperature. Combined with the above analytical results, we conjecture that for the catalytic reduction of 4-NP, an increase in the proportion of Ag$^+$ or an increase in the valence state of Ag species can improve the performance of the catalyst.

To verify this idea, we performed further oxidation of the sample in the G1 experimental group with a calcination temperature of 270°C. This sample was calcined at a constant rate of 5 K/min at 250°C and maintained in an O$_2$ atmosphere to fully oxidize the surface species Ag$^0$. The performance of the sample for catalytic 4-NP reduction was tested by UV-Vis spectroscopy (see Figure S5 in the supporting material for the results). The oxidized catalyst sample resulted in an increase of the reaction constant from 0.1483 to 0.1887. The results of the tests support our view that the oxidation or valence elevation of the surface Ag species leads to the better catalytic performance of the catalyst.

According to the above analysis, the principles of changing the calcination conditions to modulate the particle size of the catalyst and improve the catalytic performance are summarized below. The reduction process of 4-NP on the surface of metal catalyst [25] can be roughly divided into the following three parts: (1) p-nitrophenol anion and BH$_4$ are adsorbed on the metal particle surface simultaneously; (2) BH$_4^-$ adsorbed on the surface of the active center removes H$^+$ under the action of the metal particles to form metal-hydroxides; (3) 4-NP on the surface of metal nanoparticles was hydrogenated and reduced with H$^+$ to produce 4-AP. The 4-NP molecules are then desorbed from the catalyst surface and diffused into the solution. The reaction mechanism of the catalytic reduction of 4-NP by Ag/α-Al$_2$O$_3$ catalysts prepared from different calcination conditions is shown in Figure 6. When the calcination time is changed, the catalyst prepared at a shorter calcination time has better catalytic performance because of its larger specific surface area. As the calcination time increases, the Ag particles on the surface of the support gradually agglomerate, making the Ag less dispersed. Therefore, the active centers on the catalyst surface were reduced and the catalytic performance was weakened. The interaction of Al, O and Ag on Ag/α-Al$_2$O$_3$ increases with the increase of calcination temperature. This leads to a change in the electronic valence of the Al-oxygen bond [36] and a shift in electron density from Ag to Al with an increase in the chemical valence of Ag.
The higher valence Ag readily adsorbs more reactant anions. The more p-nitrophenol anions with BH$_4^-$ adsorbed to the catalyst surface, the correspondingly more reactive H$^+$ was produced, resulting in a faster reaction rate. In addition, the particle size of catalyst samples in G2 was smaller than in G1. The small Ag particles promote the redox transition between Ag$^0$ and Ag$^+$. And the relatively larger Ag particles tend to remain their metallic properties. The increase in the reactivity of small metal particles during oxidation has been confirmed by Bukhtiyarov et al. [37]. It is thus clear that the redox process and the particle size effect together influence the catalytic performance of metal catalysts.

4. Conclusion

In this work, the particle size of the Ag/$\alpha$-Al$_2$O$_3$ catalyst was tuned by varying the calcination conditions in a small range, and the catalytic performance was verified by the reaction rate of catalytic reduction of 4-NP. Due to the particle size effect, it is generally believed that a decrease in catalyst particle size is beneficial to improve the catalytic effect. The relationship between the size change of Ag particles and the change of their catalytic performance under different calcination time and calcination temperature treatments showed a completely opposite trend. When the calcination time was changed, the Ag particle size on the catalyst surface gradually increased with the increase of calcination time, while the binding energy of Ag 3d$_{5/2}$ moved toward Ag$^+$ and the catalyst performance became worse. When the calcination temperature was changed, the particle size of Ag gradually increased with the increase of calcination temperature, while the binding energy of Ag 3d$_{5/2}$ shifted toward Ag$_2$O, and the catalytic performance was significantly enhanced. The reason for this paradoxical change trend may be the interaction between Ag particles and their support $\alpha$-Al$_2$O$_3$, which elevates their valence state. As a result, more reactant anions are adsorbed on the catalyst surface, which increased the reaction rate. Our additional experiments also demonstrated that Ag$_2$O has better catalytic performance in the catalytic reduction reaction of 4-NP compared to pure metal Ag. This shows that the change in catalyst performance is the result of the synergistic effect of multiple factors such as particle size effect and redox properties. Through this work, the influence of the particle size and valence state of metal particles on the catalytic performance of catalyst surface was investigated. This will not only facilitate the rational design of improved catalyst performance, but will also have implications and insights into the research of industrial catalysis and environmentally friendly wastewater treatment.

Disclosure statement

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