Improving the Sonocatalytic Degradation of Caffeine by Organic Acids Treatment for Surface Modification of Ag/CeO₂

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Abstract. In this work, the surface of Ag/CeO₂ which was prepared using hydrothermal method was modified using three types of organic acid such as ascorbic acid, citric acid and oxalic acid as the post treatment of as-synthesized Ag/CeO₂ catalyst. The modified catalyst was further characterized using energy dispersive X-ray (EDX) for its elemental composition and BET surface area. The sonocatalytic degradation of caffeine under ultrasonic irradiation was examined to investigate the effect of these organic acids on the modification of Ag/CeO₂ catalyst. The result showed that ascorbic acid demonstrated the highest sonocatalytic degradation of caffeine compared to citric and oxalic acids. Meanwhile, the degradation of caffeine was improved from 72.8% to 78.9% for modified Ag/CeO₂ catalyst using ascorbic acid as the surface modifier. Thus, this result indicates that this kind of organic acid might have potential to modify Ag/CeO₂ catalyst surface and improve the sonocatalytic degradation of caffeine.

1. Introduction
Cerium oxide (CeO₂) or ceria based materials have been applied as the catalytic active species, promoters and support for several applications such as catalysis, fuel cell, environmental remediation, biomimeitcs and others [1]. As one of the most significant rare earth oxides or lanthanide metal, this compound has been widely used and has attracted much attention over the past decades in catalysis due to its catalytic performance such as in environmental catalysis, redox catalysis and wet catalytic oxidation of organic pollutants [2]. The catalytic properties of CeO₂ originates from the partial reduction of tetravalent (Ce⁴⁺) state to trivalent (Ce³⁺) state. These properties allow it to stores and release the oxygen, which generate the oxygen vacancies on the CeO₂ surface [3-4]. The oxygen vacancies promotes the number of active site and consequently lead to high catalytic activity [5]. Therefore, this unique properties has increased the industrial interest into CeO₂ or based-CeO₂ material and their widespread application in catalysis [6].

To further improve the catalytic activity of CeO₂, silver (Ag) has been introduced into CeO₂ catalysts, resulting in superior activity of Ag/CeO₂ catalysts for oxidation of soot [7] and photocatalytic degradation of organic pollutants [8]. In addition, Ag also demonstrates stable and is relatively inexpensive compared to other noble metals [8] like Pt, Pd and Au which cause this metal is
more practical for industrial applications. Therefore, the application potential of Ag/CeO₂ catalysts for sonocatalytic degradation of caffeine should be investigated in detail.

Morphologies, crystal surface, surface defect, synthesis method and others are among the factors which contribute the catalytic performance of CeO₂-base catalyst [1]. A recent study found a facile approach using chemical redox etching method with ascorbic acid and hydrogen peroxide to control the surface properties of CeO₂ such as specific surface area, oxygen vacancies and Ce³⁺ ions concentration [9]. Besides, ascorbic acid also was used to reduce graphene oxide (GO) into reduced graphene (rGO) for numerous applications in order to achieve the high yields of product with the controllable properties [10].

The motivation of this work is to prepared Ag/CeO₂ catalyst using hydrothermal method and organic acid is applied as post treatment of catalyst for a facile technique to modify the catalyst surface. Then, the catalysts are characterized its elemental composition and BET surface area. The effect of the organic acid on the performance of sonocatalytic degradation of caffeine is investigated. This preliminary result could demonstrate a better understanding of organic acid as surface modifier for the CeO₂-based catalyst.

2. Experimental

2.1. Synthesis of Ag/CeO₂ and Modified Ag/CeO₂ Catalysts
Cerium oxide nanoparticles was prepared using a hydrothermal method according to the published procedure [11]. An amount of Ce(NO₃)₃·6H₂O was dissolved in 5 mL of deionized water. Then, 75 mL of NaOH solution (6.4 M) was added drop wise into the ceria precursor solution under vigorous stirring for 30 min. The above mixture was then transferred into a Teflon-lined stainless-steel autoclave and heated up to 100°C for 24 h. The resultant precipitate was then washed with DI water and separated using centrifuge for several times. Then, the precipitate was dried in an oven at 60°C overnight.

The Ag/CeO₂ also was synthesized using hydrothermal method which was adapted from an article by Wei et al. [12]. A 2 mL of NaOH with a certain concentration and 10 mL of CeO₂ solution (2 g of as-synthesized CeO₂) were mixed. Then, 0.0202 g of AgNO₃ was dissolved in the NaOH solution. Both mixtures were stirred for 10 minutes. Then, the mixture of AgNO₃ with NaOH was dropped wisely into the CeO₂ solution under vigorous stirring for 30 minutes. The mixture was transferred into a Teflon-lined stainless-steel autoclave and was heated up similar temperature as-synthesis CeO₂ catalyst. Later, the precipitate was dried at 60°C for 8 h and was continued calcined at 500°C for 5 h.

The Ag/CeO₂ catalysts were modified its surface with using three types of organic acids such as ascorbic acid, citric acid and oxalic acid. A mixture of 1 mL ascorbic acid (0.5 M) and Ag/CeO₂ solution (0.5 g in 250 mL of DI water) was mixed and stirred for 30 minutes at medium speed. Then, the mixture was centrifuged and washed using DI water for several times before further dried in an oven for 12 hours at 60°C [9], [13]. The steps were repeated for another two types of organic acids.

2.2. Experimental Set-up and Degradation of Caffeine
The sonoionic and sonocatalytic degradation reaction of caffeine solution were carried out in a 250 mL Erlenmeyer flask as a reaction vessel under ultrasonic irradiation. The ultrasonic bath (Elmasonic S 60 H, Germany) was used for this purpose with a frequency and an output power of 37 kHz and 150 W, respectively. The sonocatalytic system was also equipped with two pumps, thermometer and holding tank. Throughout the process, the temperature of water bath was kept constant at 25±3°C by adding ice cubes in the holding tank in order to avoid the temperature rise in the ultrasonic bath. A 0.1 g of catalyst was added into a 100 mL of caffeine aqueous solution (5 ppm). Prior to the catalyst addition, the pH of the aqueous solution was adjusted to 10 and the suspension was agitated for 30 min in the dark condition to achieve the adsorption-desorption equilibrium. Subsequently, the suspension was sonicated for 120 min in the ultrasonic bath. During the process, 4 mL of sample was withdrawn and filtered through 0.22 μm syringe filter (PVDF) at 30 min of interval time. The absorbance of filtrate
was then determined at the maximum wavelength ($\lambda_{max}$) of 273.5 nm using Lambda 25 UV-VIS Spectrophotometer (Perkin Elmer, USA). Then, the concentration of sample was determined based on the standard calibration curve. Meanwhile, the removal performance for caffeine aqueous solution was calculated as follows: $(C_i - C)/C_i$, where $C_i$ is the initial concentration of caffeine aqueous solution and $C$ is the concentration of caffeine aqueous solution after sonication.

2.3. Characterization of Ag/CeO$_2$ and Modified Ag/CeO$_2$ Catalysts

The composition of element in the catalysts was obtained by energy dispersion energy dispersive X-ray (EDX) using Hitachi TM3030 scanning electron microscope (SEM) at accelerating voltage of 15 kV. The specific surface area and pore volume of catalysts were estimated via adsorption-desorption of N$_2$ using a Micromeritics instrument model ASAP 2020. The sample was degassed under vacuum at 250°C for four hours. The standard Brunauer–Emmet–Teller (BET) and a Barret-Joyner-Halenda (BJH) method was used to calculate the specific surface area and pore volume, respectively.

3. Results and Discussions

3.1. Effect of Different Organic Acids for Modification of Ag/CeO$_2$ Catalysts on Sonocatalytic Degradation of Caffeine

The results tabulate the warpage value for each run with the specified variable parameters condition which obtained from the DOE. The specified variable parameters condition was set and simulated in the AMI 2013 software. The effect of organic acids as the surface modification of Ag/CeO$_2$ catalyst on the sonocatalytic degradation of caffeine is shown in figure 1(a). From this figure, the highest sonocatalytic degradation of caffeine was obtained by AA-Ag/CeO$_2$ (ascorbic acid) catalyst follow by CA-Ag/CeO$_2$ (citric acid) and OA-Ag/CeO$_2$ (oxalic acid) with 78.9%, 63.8% and 43.0%, respectively. The occurrence of this behaviour might be related to the value of pKa whereas the values are 4.7, 2.79 and 1.46 for ascorbic acid, citric acid and oxalic acid, respectively. When the pKa value of the acid is lower, it tends to easily lose its proton and also the electron. Thus, it can increase the potential of converting more Ce$^{3+}$ ions from Ce$^{4+}$ ions on the surface of the catalyst whereas it is expected to gain electrons during the treatment process as can be ascribed in equation (1) [14]. Therefore, the condition of more Ce$^{3+}$ ions creates more oxygen vacancies on the catalyst surface.

$$\text{Ce}^{4+} + \text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{Ce}^{3+} + \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ \quad (1)$$

![Figure 1. (a) Surface modification of Ag/CeO$_2$ using three organic acids on sonocatalytic degradation of caffeine (Experimental conditions: [CAFF] = 5 mg/L, pH = 10, [Cat] = 1.0 g/L) (b) Comparison of different process for degradation of caffeine concentration (Experimental conditions: [CAFF] = 5 mg/L, pH = 10, [Cat] =1.0 g/L).](image-url)
Figure 1(b) shows the degradation of caffeine for four different systems; sonolysis (UV), absorption (ABS), Ag/CeO₂ (US+Ag/CeO₂) and AA-Ag/CeO₂ (US+AA-Ag/CeO₂). The degradation of caffeine was insignificant for the sonolysis process which low degradation (8.6%) achieved within 120 min. Meanwhile, when absorption process using of Ag/CeO₂ was applied, the degradation increased to 31.4% and increased further to 72.8% when ultrasonic radiation was employed in the catalytic system. This result demonstrates that there was a slight phenomenon of sonolysis occurred when the irradiation was used in the system. As expected, the caffeine degradation further increased to 78.9% when catalyst of AA-Ag/CeO₂ was used. The post treatment using ascorbic acid for modification of catalyst surface demonstrates positive effect by improving the degradation activity of caffeine compared to with non-modified catalyst, Ag/CeO₂. It can be correlated with the higher Ce³⁺ ions on the catalyst surface compared to non-modified catalyst. This is due to the surface site plays a crucial roles in the absorption of pollutant molecules [14]. However, analysis of chemical state for the surface properties of modified Ag/CeO₂ catalyst only can be verified by XPS analysis.

3.2. Characterization of Ag/CeO₂ Catalyst

The BET surface area and pore volume of the three types of catalysts are listed in the Table 1. The specific surface area of CeO₂ catalyst synthesized using hydrothermal method was found to be 126.62 m²/g and this method results in high specific surface area and hence the catalyst is porous in nature. After introducing Ag into the CeO₂ catalyst, the surface area of Ag/CeO₂ catalyst decrease to be 102.74 m²/g probably as a result of blockage of CeO₂ pores [15]. Meanwhile, the specific surface area and pore volume of Ag/CeO₂ catalyst are reduced to ~10% and ~15%, respectively after applying the ascorbic acid as the post treatment of the catalyst. The findings do not support most of the previous works which the surface area for single metal oxide of catalyst material such as CeO₂ nanorods [8] and nano-TiO₂ [16] was supposedly to be increased after applying the post treatment. However, it could be correlated with the pores might be occupied due to the interaction of ascorbic acid with Ag metal in CeO₂ catalyst and subsequently decrease its specific surface area and pore volume. The change of specific surface area also could be correlated with the change of average crystallite size. It is known that the pH has an important role on the change of the average crystallite size due to the value of pH or pKa of the organic acid applied on the catalyst surface. Thus, this behavior could be associated with the change of specific area [16].

| Catalyst          | S_BET (m² g⁻¹) | Pore volume (cm³ g⁻¹) |
|-------------------|----------------|----------------------|
| CeO₂              | 126.6          | 0.4869               |
| Ag/CeO₂           | 102.7          | 0.4132               |
| AA-Ag/CeO₂        | 93.3           | 0.3506               |

The elements present and purity of the as-synthesized Ag/CeO₂ and Ag/CeO₂-AA catalysts were investigated by EDX analysis as depicted in figure 2(a) and figure 2(b). As shown in the EDX spectrum of both catalysts, the strong peaks observed at 2.5, 2.9 and 4.8 keV are due to presence of oxygen (O), silver (Ag) and cerium (Ce) elements. It is evident that those peaks clearly ascribed to elements of both catalysts and no other impurities were found. The EDX pattern for AA-Ag/CeO₂ catalyst demonstrates the Ce peak is increased and the O peak is reduced compared to Ag/CeO₂ catalyst. This trend can be referred as well by its weight and atomic percent as shown in the same figure. It implies that Ce particles occupied the catalyst surface during the post treatment process and thus, content of oxygen element on the catalyst surface decreased [17].
4. Conclusions
As conclusion, this study demonstrated ascorbic acid has a potential in improving the sonocatalytic activity of Ag/CeO₂ by modifying its surface properties. It can be correlated with the increase the potential of converting more Ce³⁺ ions from Ce⁴⁺ ions on the surface of modified Ag/CeO₂ catalyst. Thus, post treatment of Ag/CeO₂ catalyst using organic acid provides a facile method to modify the surface properties for the sonocatalytic application.

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