Ag₂O-Ag/CAC/SiO₂ composite for visible light photocatalytic degradation of cumene hydroperoxide in water

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A visible light-active composite, Ag₂O-Ag/CAC/SiO₂, was produced by loading an aqueous silver salt solution onto the layer of hydrated calcium aluminate cement coating on porous SiO₂ sphere. The mild cement hydration condition induced the formation of in situ Ag₂O precipitates on the cement surface which were partially decomposed to metallic Ag after drying and appropriate heat treatment at 200 °C to enhance both decomposition and crystallinity of Ag₂O. The coexistence of Ag₂O and Ag in the composite was clearly confirmed by XRD and XPS, and the mechanisms for the formation of Ag₂O particles on the hydrated cement layer and for the photocatalytic degradation of CHP were also suggested. The photocatalytic activity of Ag₂O-Ag/CAC/SiO₂ composite (calcined at 200 °C), evaluated under UV and visible lights irradiation through the photodecomposition of CHP in water quantified by HPLC, was two times higher than that of Ag₂O-Ag/CAC/SiO₂ composite (dried at 45 °C), and able to completely decompose CHP in 5 h. Additionally, the photostability of Ag₂O-Ag/CAC/SiO₂ photocatalyst remained unchanged for 5 recycling tests.

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1. Introduction

In the petrochemical industry, production of phenol based on the cumene method has become a major source of environmental pollutants. With many chemical reactions carried out in the production line, a wide variety of organic compounds are formed as direct and side reaction products such as cumene hydroperoxide (CHP), α-methylstyrene (α-AMS), dimethyl phenyl carbirnol (DMPC), acetophenone (ACP), phenol and acetone [1–3]. They can enter water used throughout all the processing steps in the phenol plant. Before discharge of production wastewater into the environment, a proper treatment must be operated to prevent the penetration of these organic compounds into natural ecosystems. Most of the organic compounds present in phenolic wastewater are
chemically stable, highly toxic and difficult biodegradable. In particular CHP and phenol are shown to be potentially carcinogenic substances in addition to their acute effects [4–6]. Biological treatment with microorganisms is commonly utilized for removing organic chemicals in water. However, the biodegradation of CHP was found to be a very difficult task because it resisted microbial treatment, and in a high concentration, could destroy microorganisms resulted in inhibition of other toxic compound degradation [4]. This situation led to an ineffective treatment of multicomponent phenolic wastewaters. Although some classes of the microorganisms discovered could effectively destruct this resistant compound [1], the metabolic activity was time consuming, hence not suitable for a large scale of the continuous treatment process. As mentioned above, an efficient technique with practical uses for the elimination of CHP or other resistant pollutants not readily treatable by the common biological method is urgently required.

Recently, heterogeneous photocatalysis using semiconductors has been widely accepted for environmental clean-up, in particular water and air purification [7,8]. Many kinds of chemical contaminants are completely removed through redox processes occurred at the irradiated semiconductor surface [9]. However, very few scientific reports have been published in the literature regarding the utilization of semiconductor photocatalysis for treating CHP. Among these, P25-TiO2 was reported to successfully degrade CHP under UV irradiation [10]. However, besides reusability, another drawback in the application of powdered photocatalysts is difficulty in separation of the catalysts from the treated water after use due to their very fine particles. As a solution to this problem, we attempted to find out cost-effective materials and a simple method for producing a novel photocatalyst having high potentiality and practicality. From our previous work [11], we immobilized TiO2 nanoparticles on porous silica supports using calcium aluminate cement (CAC) as a binding material by granulation method, which was practical to produce experimental samples in a large scale. This technique helped to create a spherical shape with controllable size of photocatalytic composites. The obtained photocatalytic result indicated that the prepared composite could potentially decompose CHP to intermediates that are known to be less toxic, and biodegradable [2,12,13]. Significantly, the composites were easy recovered and retained good mechanical stability after repetitive applications. Although CAC and other hydraulic cements modified with TiO2 powder have previously been reported to be effective for environmental purification [14–17], their photocatalytic activities have not yet been addressed on the degradation of CHP. Theoretically, the operation of TiO2 photocatalyst is limited to the range of UV light region due to its wide band gap energy (Eg = 3.2 eV) [9]. For practical applications, the operation limit has to be extended to visible light region. Therefore visible light-active composites based on cement material are our research interest.

To date, quite a number of narrow band gap semiconductors have been widely investigated for their photocatalytic performance in the visible light region. Among them, silver oxide (Ag2O) has attracted great attention because it can absorb visible light and exhibit excellent photocatalytic activity in degrading organic pollutants [18–22]. Ag2O is a p-type semiconductor with a narrow band gap energy varying from 1.2 to 1.5 eV [23–26], depending on the preparation method. Due to its optical and electronic properties, this versatile material can be utilized in many fields [27–31]. Although precipitation starting from aqueous silver salt solutions and strong alkali is a procedure commonly used to produce Ag2O [19–21], from our preliminary experiment, we found that such Ag2O precipitate was very agglomerate and could not provide a homogeneous mixture with cement powder. Hence, in the present work, Ag2O is loaded on the surface of cement supports by the green chemistry precipitation. Herein, cement-coated silica beads are chosen as the supports. The combination of Ag+ in silver salt solution and OH− generated from the cement hydration resulted in the formation of in situ Ag2O on the support surfaces. It should be noted that this invention uses no external chemical as a precipitating agent. To the best of our knowledge, this is the first time that the novel Ag2O-Ag/CAC/SiO2 composites are produced by this method, and their photocatalytic activities are evaluated under UV and visible lights via the photodecomposition of CHP in water.

2. Materials and methods

2.1. Materials

Calcium aluminate cement (CAC, 80% Al2O3) obtained from KERNEOS was used as an inorganic binder. Porous silica beads (diameter ~3–5 mm) were supplied from Siamese Ecolite Co. (Thailand). Cumene hydroperoxide solution (C6H5(CH3)3COOH, 80%) as a representative organic compound in wastewater was purchased from Sigma-Aldrich. Silver nitrate (AgNO3) obtained from Merck Chemical Co. was analytical grade reagent, used without further purification. Reverse osmosis (RO) water (TCC Siam drinking water Co., Thailand) was used throughout this work.

2.2. Preparation of CAC/SiO2 beads

Coating of CAC on porous silica bead surface was performed by granulation method. Briefly, 20 ml of the porous silica beads were moistened with water and well coated with 1.5 g of CAC in a pan granulator to obtain the 1st layer coating, then cured in air for 1 day and followed by curing in water for 6 h at room temperature. Later this process was repeated to obtain the 2nd coating layer using 5 g of CAC. After the second granulation, the cured granules were again well coated with 7 g of CAC to obtain the 3rd coating layer followed by curing in air and water at room temperature for 1 day and 5 days, respectively.

2.3. Preparation of Ag2O-Ag/CAC/SiO2 composites

Coating of Ag2O on CAC/SiO2 was carried out through a simple precipitation method, followed by a heat treatment as follows: The hydrated CAC/SiO2 beads were firstly dried at 45 °C for 30 min and followed by immersing into 20 ml of 0.1 M AgNO3 aqueous solution for 30 min to get a brown precipitate on the surface. The coated samples were collected and washed thoroughly with RO water for several times. Finally, the obtained
composites were dried at 45 °C for 12 h and then calcined at 200 °C for 1 h. All the above operations were carried out in darkness.

2.4. Characterization and analytical method

Crystalline phases of the samples were identified by X-ray powder diffractometer (XRD, Bruker, D8 Advance). HITACHI S-4800 field-emission scanning electron microscope (FE-SEM) was used to observe the morphologies of the samples. The chemical compositions were investigated via energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). UV–vis diffuse reflectance spectra (DRS) of the samples were obtained using a UV–vis spectrophotometer (UV-3600, Shimadzu). The absorption spectra of the test solutions were recorded using a UV–vis Spectrophotometer (Perkins Elmer, Lambda 35). The concentration of the test solution was measured by high performance liquid chromatography (HPLC, HP HEWLETT PACKARD SERIES 1100) equipped with a column (Thermoscientific® Hypersil Gold particle size 1.9 µm diameter 3 mm).

2.5. Photocatalytic activity

Photocatalytic activities of the samples were evaluated through the decomposition of CHP in aqueous solution under UV and visible lights irradiations. Each photocatalytic experiment was performed in a borosilicate bottle with CHP solution (10 ml, 475 ppm) and 20 composites beads. Prior to irradiation, the bottle containing the beads and CHP solution was kept in the dark for 3 h to reach a maximum solution pH at 10.5 and to obtain the equilibrium adsorption state. The visible light source, 2 × 9 W LED bulbs (Phillips), and the UV light source, 2 × 18 W UV lamps (TL-D, Phillips) were each focused onto both sides of the glass bottle. The light illuminated from a side with a distance of 10 cm away from the glass surface. At a given irradiation time, the test solution was separated, and then analyzed using a UV-VIS spectrophotometer to record the absorption spectra of CHP during the photocatalytic process. The concentration of the remaining CHP and its decomposition products in the test solution were quantified by HPLC.

3. Results and discussion

3.1. Characterization of Ag2O–Ag/CAC/SiO2 composites

Fig. 1a shows a photograph of the porous silica beads (~3-4 mm in diameter) used as support in this study. The beads float on water due to their low density. Fig. 2a shows an SEM image of the outer surface of a bead, which is rough and porous (pore sizes ~50-100 µm). The XRD pattern shown in the inset of Fig. 2a illustrates poor crystalline SiO2 existing in the material. With an appropriate property (shape, surface and density), these silica beads were easy to handle during granulation, and provided very good adherence to the moist CAC particles.

Fig. 1b shows the surface of hydrated CAC/SiO2 beads (~6-8 mm in diameter). The hydration behavior of CAC is known to depend on curing temperature. Therefore various temperature dependent hydration products, calcium aluminate hydrates (CAH10, C2AH8 and C3AH6), crystalline gibbsite (AH3) and amorphous aluminium hydroxide or alumina gel are reported [32,33]. The concentrations of Ca2+ and Al(OH)4− give a strong impact on the process of dissolution-precipitation and formation of those hydrates [34,35]. The XRD pattern of the hydrated CAC coating on silica, water cured at room temperature, is shown in Fig. 3a. It is observed that no any hydrated calcium aluminates are found as predominant hydration product but a considerable amount of gibbsite (AH3) is detected at this temperature. Intensity and sharpness of the gibbsite diffraction peaks indicate that the formed AH3 phase is well crystallized which confirms the SEM observation of plate-like crystals, mainly found in the CAC matrix, Fig. 2b, and the dense texture of the CAC matrix observed in some area attributes to the formation of alumina gel. The predominant AH3 is imparted from the pre-carbonation of curing water exposed to atmosphere which causes the formation of calcite (CaCO3) in the hydrated sample. This consequently reduces the concentration of Ca2+ in the solution, resulted in the increase of Al(OH)3− ion which induces a large precipitation of AH3 crystals as compared to other calcium aluminate hydrates [35]. Moreover, the unreacted CA and α-Al2O3 are detected as additional phases. A high amount of α-Al2O3 present in the XRD pattern might be due to the co-grinding of cement clinker with calcined alumina to reach the targeted alumina level in the refractory type CAC [36,37].

During the precipitation-deposition of Ag2O particles from AgNO3 solution onto the surface of hydrated CAC/SiO2, the exposed surface obviously changed in color from white to intense yellow, and then became dark brown. This occurrence is similar to the formation of Ag2O through the precipitation reaction using AgNO3 and NaOH as a precursor and a precipitating agent, respectively [38]. However, in our work, the reaction spontaneously took place without introducing a strong alkali hydroxide. Under our experimental conditions, all the Ag2O precipitates could be easily obtained and deposited on the hydrated CAC surface since no suspending precipitates were visible in the transparent AgNO3 solution. The operating solution pH remained stable at 5.5–6 throughout a reaction time of 30 min. Thus, it could be implied that the precipitates were only formed on the surface of the hydrated CAC coating. The appearance of final products after filtering and drying at 45 °C for 12 h was shown in Fig. 1c.

To confirm the formation of Ag2O particles, the outer surface layer of the dried photocatalyst composite samples was verified by the XRD analysis and the result is presented in Fig. 3b. It can be seen that the strong diffraction peak at 2θ = 32.7° and two weak peaks at 2θ ~ 38° and 55° belong to cubic Ag2O (JCPDS No. 41-1104). This result indicates that Ag2O crystals are directly formed on the hydrated CAC surface by a simple chemical method different from the other procedures [24,25,39,40]. A possible mechanism for the formation of Ag2O particles on the surface of the hydrated CAC/SiO2 is schematically illustrated in Fig. 4, and also suggested through the following equations:

\[ \text{CaAl}_2\text{O}_4(aq) + 4\text{H}_2\text{O} \rightarrow \text{Ca}^{2+}(aq) + 2\text{Al(OH)}_3^{-}(aq) \] (1)

\[ \text{Al(OH)}_4^{-}(aq) \rightarrow \text{Al(OH)}_3(aq) + \text{OH}^{-}(aq) \] (2)
OH\textsuperscript{−} (aq) + Ag\textsuperscript{+} (aq) → AgOH(s) (3)

2AgOH(s) → Ag\textsubscript{2}O(s) + H\textsubscript{2}O(4)

According to the literature [34,35], the hydration process of CAC (Eq. 1–2) starts with the dissolution of calcium monohalominate (CaAl\textsubscript{2}O\textsubscript{4} or CA), a major component, in water to Ca\textsuperscript{2+} and Al(OH)\textsubscript{4}\textsuperscript{−}. The Al(OH)\textsubscript{4}\textsuperscript{−} species partially dissolves to favor precipitation of crystalline gibbsite with some amount of amorphous alumina gel. This reaction generates OH\textsuperscript{−} species which increases the pH(s) of the solution. When the hydrated CAC/SiO\textsubscript{2} beads are immersed in the AgNO\textsubscript{3} solution, Ag\textsuperscript{+} reacts with OH\textsuperscript{−} generated from gibbsite precipitation to form AgOH(s). The AgOH product is thermodynamically unstable [20,30], hence converts rapidly to Ag\textsubscript{2}O(s).

When the dried Ag\textsubscript{2}O-Ag/CAC/SiO\textsubscript{2} composites are calcined at 200 °C for 1 h, they appear to be brownish black, as shown in Fig. 2d. The XRD pattern of the calcined composite is shown in Fig. 3c. Compared to the composite dried at 45 °C, the samples heated at higher temperature shows a slight enhance in the intensity of the peak at 2θ = 38° due to improved crystallinity and a new diffraction peak at 44° is observed corresponding to metallic Ag (JCPDS card no. 87-597). The coexistence of Ag\textsubscript{2}O and Ag metal in the surface of composite sample resulted mainly from partial decomposition of Ag\textsubscript{2}O during heat treatment processes [20].

The surface morphology and microstructural detail of Ag\textsubscript{2}O-Ag/CAC/SiO\textsubscript{2} composites obtained at 200 °C were investigated by FE-SEM observation and results are shown in Fig. 2c. Compared to the sample dried at 45 °C (Fig. 2b), the major peaks of AH\textsubscript{3} crystals are not clearly seen, indicating that the whole surface of CAC substrate is covered by spherical Ag\textsubscript{2}O particles. The covered areas with higher magnification are shown in Fig. 2d and e. These images display the Ag\textsubscript{2}O crystals in their regular shape (cubic) with sizes ranging from about 50–100 nm, uniformly distributed on CAC surface. The EDS results of the calcined composite are presented in Fig. 2f-h. Each spectrum area reveals that the spherical particles deposited on the CAC surface composed of O, Al, Ag and Ca elements. This result also confirms the presence of Ag\textsubscript{2}O in the obtained composites.

3.2. Photocatalytic activity

Based on the above mentioned results, heat treatment at a temperature of 200 °C clearly induces some amounts of crystalline Ag in the composite. In order to investigate the co-effect of the Ag\textsubscript{2}O-Ag metal, a preliminary test on photocatalytic activities of the dried and calcined composites are evaluated by the photodegradation of CHP in aqueous solution under visible light irradiation. For comparison, the activities of the blank CAC samples (without photocatalyst) and self-degradation of CHP (photolysis) are also performed under the
Fig. 2 – FE-SEM images of the sample surfaces. (a) porous silica bead (inset shows its XRD pattern, 70×), (b) hydrated CAC/SiO$_2$ granule (dried at 45 °C/12 h, 1000×), (c)–(e) Ag$_2$O-Ag/CAC/SiO$_2$ composite granule (calcined at 200 °C/1 h) at magnification of 1000×, 20,000× and 50,000×, respectively, and (f)–(h) EDS spectra (50,000×), analyzed in some area of calcined composite with three spectrum (inset shows the corresponding atomic %).
Fig. 3 – XRD patterns of the sample surfaces. (a) hydrated CAC/SiO$_2$ granule (dried at 45°C/12 h), (b) Ag$_2$O-Ag/CAC/SiO$_2$ composite granule (dried at 45°C/12 h), and (c) Ag$_2$O-Ag/CAC/SiO$_2$ composite granule (calcined at 200°C/1 h). The insets show the enlarged XRD patterns of (b) and (c).

Fig. 4 – Schematic illustration of formation process of Ag$_2$O particles.

same conditions. The photodegradation efficiency of CHP can be calculated using the following equation:

$$\text{CHP degradation(%) = 100 \times \frac{C_0 - C}{C_0}}$$

where $C_0$ and $C$ are the equilibrium concentrations of CHP before and after light irradiation, respectively. Upon exposure to visible light, a very small amount of CHP is removed by direct photolysis which is thought to have negligible effect on photocatalytic reaction as shown in Fig. 5. In this figure, both dried and calcined Ag$_2$O-Ag/CAC/SiO$_2$ composites exhibit strong photocatalytic activity, indicating that they are responsive to visible light region. After 5 h of visible light irradiation,
the photodegradation efficiency for CHP of the calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite is 99.3% and tends to be stable even after a long irradiation time of 7 h, which is much higher when compared to 75.7% of the dried composite. Obviously, the improved photocatalytic activity of the latter is resulted from the presence of well crystalline metallic Ag, partially formed by a thermal decomposition. The superior photocatalytic performance of the calcined composite may be attributed to the better separation of electron-hole pairs. During the visible light photocatalytic process, it is possible that the photogenerated electrons on the Ag$_2$O photocatalyst are transferred to Ag species. The metallic species could trap those electrons resulting in suppressing the recombination of electrons and holes [20]. The obtained results prove that the synergistic effect of Ag$_2$O and Ag plays an important role in improving the photocatalytic activity. From this finding, therefore, only calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite is selected for further photocatalytic investigation.

According to the photocatalytic results, we speculate that the enhanced photocatalytic activity of Ag$_2$O-Ag/CAC/SiO$_2$ composite would result from the presence of metallic Ag which acts as electron trap in the composite. To verify our speculation, the optical properties of various samples are investigated by UV–vis diffuse reflectance spectroscopy (DRS). As shown in Fig. 6, it can be seen that the CAC/SiO$_2$ bead mainly absorbs light in the UV region. After depositing Ag$_2$O particles on its surface, a strong absorption in the UV and visible light ranges of 200–800 nm is remarkably observed in both dried and calcined Ag$_2$O-Ag/CAC/SiO$_2$ composites. This is due to the narrow band gap of Ag$_2$O that can be excited by photon energy in the whole UV–vis wavelengths. In general, the optical band gap energy of a semiconductor is derived from UV–vis absorption data using the Tauc plot method. Ag$_2$O is considered as a direct semiconductor [41]. Thus, the Tauc’s equation for the direct band gap can be written as:

$$(a
\nu)^2 = A(\nu - E_g)$$

where $a$ is the absorption coefficient, $\nu$ is the photon energy, $A$ is a constant and $E_g$ is the band gap energy [42]. The plots of $(a
\nu)^2$ versus the photon energy for dried and calcined Ag$_2$O-Ag/CAC/SiO$_2$ composites are shown in the inset of Fig. 6. The band gap values of these composites were estimated by extrapolating the straight line of the linear part to the photon energy intercept (x-axis). From the Tauc plots, the obtained band gaps are 1.40 eV and 1.25 eV for the dried and calcined Ag$_2$O-Ag/CAC/SiO$_2$ composites, respectively.

Moreover, both composites possess high absorption of light because of the black color of Ag$_2$O particles. Interestingly, as for the calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite, the absorbance at the range of 500–800 nm is higher than that of the dried composite, which is attributed to the characteristic absorption of surface plasmon resonance (SPR) of metallic Ag on Ag$_2$O surface leading to more intense visible light absorption [21]. This result is consistent with the photocatalytic test as mentioned before and well support our interpretation of the enhanced photocatalytic activity of the calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite under visible light irradiation.

To further investigate the mechanism of CHP decomposition, the spectral changes during the photocatalytic degradation of CHP solution in the presence of the calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite under visible light irradiation were recorded by the UV–VIS spectrophotometer, and the results are shown in Fig. 7a. Also, the photocatalytic activity of the calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite under UV irradiation was performed in the same manner for comparison, and the results are presented in Fig. 7b. As shown in Fig. 7a, it can be seen that an absorption spectrum of initial CHP solution (475 ppm, pH 6) exhibits several peaks in the UV region. The peak at 257 nm is expected to be the characteristic of CHP [43]. In the presence of composite samples and standing in the dark to reach equilibrium state, there is a slight change in CHP spectrum (Fig. 7a, grey line), indicating that a small portion of CHP was probably oxidized to other products due to the base-catalyzed decomposition [44]. It is well known that the hydration reaction of hydraulic cements produces large amount of OH$^-$ ions, in addition to major hydrates. Certainly, the OH$^-$ ions produced in the calcined Ag$_2$O-Ag/CAC/SiO$_2$ composite can release into the initial CHP solution and retain a high pH. In our experimental conditions, the pH of CHP solution in the presence of the composite
reaches a maximum value at 10.5 when kept in the dark for 3h. It is noticeable that further increase of time from 3 to 10h in the dark, the pH of CHP solution as well as the UV spectrum remain unchanged. Since the CHP decomposition is commonly controlled on the basis of the reaction temperature [45], the small degradation of CHP at room temperature in the dark in our experiment suggests that the temperature of 25°C is not high enough to induce much decomposition of CHP. Therefore, it can be concluded that the degradation reaction of CHP in a high pH medium is negligible and does not substantially affect photocatalytic tests. When exposed to visible light, the spectral change of CHP is dramatically obvious as the spectrum band becomes stronger in the UV range of 200-270 nm and 280-290 nm along with the increasing irradiation time. The change in characteristic peaks of CHP under visible light irradiation indicates the occurrence of the photocatalytic reaction using the calcined Ag2O-Ag/CAC/SiO2 composite as catalyst. A similar trend is found under UV irradiation but not as much change at the same irradiation time (Fig. 7b), suggesting that the CHP degradation over the calcined composite is also dependent on the light source. The change in CHP spectra after light irradiation is attributed to the presence of intermediate products due to the decomposition of CHP.

To measure the concentration of the remaining CHP and the generated intermediate products, the collected solution at each irradiation time was analyzed by HPLC. The results present in Fig. 8a and b are indicative of DMPC (dimethyl phenyl carbino) and ACP (acetophenone) as the major products formed via the decomposition of CHP. It can be seen that CHP disappears rapidly while the formations of DMPC and ACP proceed continuously during photocatalytic reaction and become constant after the disappearance of CHP. The results obtained from the visible light photocatalysis indicate a complete decomposition of CHP after irradiation for 5 h. However, DMPC and ACP do not continue to decompose into other products for their contents remain constant in the test solution even after prolonged irradiation time for 7 h. When the concentration of DMPC become high to a point that its low solubility triggers precipitation, noticeable as dark brown precipitates covering the surface of the composite which might prevent Ag2O particles from light and result in inhibiting of further photocatalytic reaction.

The retardation of CHP degradation observed from the UV test is attributed to the fraction of Ag/Ag2O altered during photocatalytic reaction. As described in previous reports [20], the proper Ag/Ag2O fraction is necessary to achieve a high activity for organic degradation. To better understand the difference in the photocatalytic activities of the composite under UV and visible light irradiations, the mineral phases of the composite samples at the end of various irradiation times and weight fraction of Ag/Ag2O were analyzed by XRD and XPS, respectively. As seen in Fig. 9, the diffraction peak corresponding to metallic Ag at 2θ=44° decreases slightly after 1h of visible light irradiation (Fig. 9c). Subsequently, it turns to be almost the same as that of the fresh catalyst (Fig. 9b) and remains almost constant after 3h irradiation (Fig. 9d). The slight change in an intensity of metallic Ag during visible light photocatalytic reaction may be due to the interconversion of Ag2O/Ag occurred in aqueous solution with pH>7 [46]. From Fig. 10, on the contrary, a stronger peak of Ag metal is formed after 1h of UV irradiation and tends to decrease gradually after 3h irradiation time. It has been reported that partial Ag2O particles can be reduced to Ag metal when exposed to UV and the excessive Ag nanoparticles induced by UV might cause center recombination of photogenerated electron-hole pairs [20], and also shield the available irradiation sites on the Ag2O particles. These may be reasons why the performance of Ag2O-Ag/CAC/SiO2 composite under UV irradiation is inferior to that under visible light. The XPS results in Fig. 11 not only confirm the coexistence of Ag/Ag2O in the calcined composite.

Fig. 6 – UV–vis diffuse reflectance spectra of different samples.
but also in the dried composite which cannot be previously detected by the XRD due to poor crystallinity. Moreover the XPS results show a slight variation in the concentration ratios of the metallic Ag and AgO present in the samples: dried, calcined and 5-cycling test which are shown in Fig. 11 b, c and d as 1:17, 1:10, and 1:13, respectively.

3.3. Photocatalytic stability

It has been known that resistance to photochemical corrosion is a major drawback of Ag-based semiconductors [18] and to overcome this problem is a great challenge for practical applications. In addition to the high ability of the calcined Ag₂O-Ag/CAC/SiO₂ composite to degrade CHP, it photostability was evaluated in the recycling experiment. We selected a condition of 5 h irradiation in this study. After the first cycle, the visible light photocatalytic degradation of CHP was repeated for further four times using the same samples. Before reuse in the next cycle, the used samples of each test were washed by immersing in RO water for 15 min to remove residual degradation products. The results of the repetitive use of the calcined Ag₂O-Ag/CAC/SiO₂ composite are shown in Fig. 12. It is found that the photocatalytic activity of the calcined Ag₂O-Ag/CAC/SiO₂ composite remains almost unchanged after five cycles. When the recycling times increase, the composite shows the same activity in CHP degradation reaching 99% with a slight fluctuation concentration of degradation products, DMPC and ACP. Moreover, no obvious change in the size of composite particle is observed throughout the experiments. This can be implied that the prepared composite shows a very good mechanical stability, hence the hydraulic binder provides an excellent adhesion of Ag₂O and metallic Ag particles on
its hydrated surface. To investigate the obtained results, the exposed composite surface after each cycling test were characterized by XRD technique. As shown in Fig. 13, the XRD patterns of used samples after each cycle are only slightly different. The peak intensity of metallic Ag shown in the 2nd cycle was slightly weaker than those of the other cycles but insignificantly reduces the photoactivity of the composite. Referring to the XPS results mentioned previously, it can be suggested that a proper range of Ag/Ag_2O concentration present in the sample be maintained throughout the cycling test. Thus, the results indicate a good stability and reusability of the calcined Ag_2O-Ag/CAC/SiO_2 composite.

### 3.4. Mechanism of CHP degradation

On the basis of the above experimental results and discussion, a possible mechanism for CHP photocatalytic degradation in the presence of Ag_2O-Ag/CAC/SiO_2 composite is suggested as follows: When Ag_2O-Ag/CAC/SiO_2 composite is irradiated by UV or visible light, Ag_2O deposited on the surface of a cement can be excited to generate electrons (e\(^-\)) and holes (h\(^+\)) according to Eq. (7). The photogenerated holes left in the valence band (VB) of Ag_2O react with surface-bound H_2O or a hydroxyl group (OH\(^-\)) or H_2O to produce the hydroxyl radical species \(\cdot\text{OH}\) which is highly strong oxidant for the degradation of organic compounds (Eqs. 8–9). According to the previous report [20], the photogenerated electrons present in the conduction band (CB) could freely move to the metallic Ag through the junction between Ag_2O and metallic Ag, which decreases the recombination rate of the photogenerated electron-hole pairs on Ag_2O. Then the lifetime of electrons transferred to metallic Ag are prolonged in the conduction band of Ag_2O to be captured by dissolved O_2 in the CHP solution to produce \(\cdot\text{O}_2^-\) radicals. These radicals can react with H_2O to generate H_2O_2,
and subsequently converting into more reactive •OH radicals (Eqs 10–13), which strongly improve the photocatalytic activity. In general, hydroxyl radicals act as a strong oxidizing agent which is highly reactive with a broad range of organic compounds [47,48]. Thus, in this study, the photogenerated •OH radicals are considered as the major active species responsible for the photocatalytic degradation of CHP (Eqs. 14).

\[
AgO + h^+ \rightarrow e^- + h^+ (7) \\
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{•OH} + \text{H}^+ (8)
\]

\[
h^+ + \text{OH}^- \rightarrow \text{•OH} (9)
\]

\[
e^- + \text{O}_2 \rightarrow \text{•O}_2^- (10)
\]

\[
\text{•O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{•OH} (11)
\]
reaction of °OH radicals with peroxo anion induced by the base-catalyzed reaction \[^{[41]}\]. Subsequently, the CHP radicals are further oxidized to DMPC, ACP by °OH radicals. Due to the complication of CHP decomposition, we believe that more complex intermediates could be formed in the irradiated solution. However, only two of the compounds, DMPC and ACP, are detected as intermediates by HPLC in this study.

4. Conclusions

The visible light-active composite, \(\text{Ag}_2\text{O-Ag/CAC/SiO}_2\), was successfully produced by loading an aqueous silver salt solution onto the layer of hydrated cement coating of porous \(\text{SiO}_2\) spheres. The mild cement hydration condition induced the formation of in situ \(\text{Ag}_2\text{O}\) precipitates on the cement surface which partially decomposed to metallic Ag after drying and appropriate heat treatment. The coexistence of \(\text{Ag}_2\text{O}\) and Ag was maintained in an appropriate fraction in the composites under the high pH condition of CAC hydration, thus enhanced the photocatalytic reaction by reducing the electron-hole recombination rate, allowing a continuous formation of active °OH radicals, which effectively conducted a complete photocatalytic decomposition of CHP within 5 h to intermediates, DMPC and ACP. The recycling test results (5 times) indicated the good photostability and reusability of the \(\text{Ag}_2\text{O-Ag/CAC/SiO}_2\) composite.
Fig. 13 – XRD patterns of the used Ag₂O-Ag/CAC/SiO₂ composite after each cycling test.

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