Au nanoparticles loaded Hydroxyapatite catalyst prepared from waste eggshell: synthesis, characterization and application in VOC removal

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Abstract. Eggshell, which is made almost entirely of calcium carbonate, is among the most abundant waste materials from poultry production. In 2018, the worldwide egg production exceeded 78 million metric tons which contributed to over 8 million metric tons of eggshell waste. However, this waste can be converted into useful materials for several industrial applications. Herein, hydroxyapatite (HAp) of fine particles was prepared using a green synthesis procedure in water medium from eggshell waste. Then, HAp was utilized as support material for loading different contents of Au nanoparticles (0.2 and 0.5 wt%). The materials were characterized by Brunauer-Emmett-Teller (BET) surface area analysis, Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), X-ray diffraction (XRD). The prepared catalysts were used for VOCs oxidation of formaldehyde in continuous flow and humid condition. In this study, Au/HAp (0.2 wt%) exhibited superior catalytic activity with good low-temperature reproducibility and high dispersion of particles on the surface of hydroxyapatite. Hence, hydroxyapatite prepared from eggshell waste is considered as a promising support material for noble metal catalysts for VOCs oxidation.

1. Introduction

Volatile organic compounds (VOCs) are organic chemical compounds whose composition makes them volatile under normal, indoor atmospheric conditions of temperature and pressure [1]. VOCs are usually industrial solvents such as chloroform, dichloromethane, benzene, toluene, xylenes, etc. In recent years, the industries of chemicals, pharmaceuticals, automobiles, oil and gas, etc. are growing with the number of factories constantly increasing. The manufacturing processes of these plants produce large amounts of emissions containing VOCs which cause environmental problems. Indoor emission of VOCs are mainly released into the air through the use of products and materials that contain organic solvents. Exposure to VOCs can cause immediate or long-term harm to human health [2]. Today, human are more and more concerned about the quality of air indoor. Indoor air pollutants mainly contain nitrogen oxides (NOx), carbon oxides (CO and CO2), volatile organic compounds and particulates. The overall rate of elimination of a VOC species from the atmosphere can be used to calculate its atmospheric lifespan. This rate can be calculated by adding the rates of radical species reactions, photolysis rates, and wet and dry deposition rates. Therefore, VOCs need to be analyzed, evaluated, treated and controlled from sources that emit VOCs into the environment. Due to the negative effects on human health, it is necessary to take measures to treat and remove VOCs from the air. Methods for removing VOCs from the air include physical, chemical or biological methods and can be divided into two main groups: recovery or decomposition [3]. It can be seen that with the recovery method, there will be many ways to remove VOCs, typically absorption, adsorption, condensation and finally membrane filtration. Another side, with the decomposition method, thermal oxidation processes are preferred in most cases because of their reliability, the fact that no further treatment is usually required, and because of their ability to achieve high efficiency destruction of VOCs. The prevalence of combustion systems such as boilers, furnaces, furnaces and incinerators in a multitude of manufacturing and fabrication facilities has enabled operators to accept thermal oxidants. Most other treatment technologies require additional treatment of VOCs...
after they have been removed from the gas stream. In this work, decomposition method is chosen to formdehyde removal. The process of catalytic oxidation is comparable to the method of thermal oxidation. Despite its significant cost savings, catalytic oxidation has a number of drawbacks, including high catalyst costs, additional byproducts, the possibility of poisoning the catalyst after use if not properly managed, and sensitivity to non-VOCs (water, halogen and sulfur compounds). As a result, thermal oxidation methods are employed more frequently than catalytic oxidation methods.

Catalytic oxidation of VOCs is the most promising approach among them, as it can be done at lower temperatures, at a cheaper cost, and with a higher oxidation efficiency. Gold has long won the hearts of mankind. Gold, abbreviated Au, is the 79th element in the periodic table, belonging to group IB and having the structure [Xe]6s14d10. Because the energy of the 5d and 6s sublevels of Au is nearly identical, there is competition between them. As a result, electrons are extremely malleable, able to migrate between both states, resulting in a unique plasticity in Au and a diverse optical spectrum. Gold is found in ores created from rock with very small or very small fractions of gold. Au has metal properties such as being soft, ductile, and easy to laminate. When carefully cut, the golden tint of this metal can turn black, ruby, or purple. Gold is inert to most chemicals, however it dissolves in Aqua Regia and forms cloroauric acid, as well as reacting with alkali metal cyanide solutions. For millennia, it has been used in art, cosmetics, metallurgy and architecture. This element is considered to be the ultimate statement of prosperity and beauty. Initial experimental work involving surface characteristics and related calculations of density functions showed that, for Au, dissociative adsorption of H2 and O2 does not take place at temperatures lower than 473K , and thus it will not exhibit catalytic activity for hydrogenation and oxidation reactions [4]. This is why Au has not been of catalytic interest up to now, but this property disappears when gold is synthesized in the nanoscale, in 1987 when Haruta et al. found catalytic activity particularly unexpected effect of nanometer-sized gold nanoparticles on CO oxidation even at lower room temperature [5]. With the advancement of science and technology, numerous important properties of gold at the nanoscale, as well as their practical applications, have been found. In 1991, Hutching and his colleagues used gold nanoparticles (AuNPs) as catalysts in the hydrochlorination of acetylene [6]. When compared to its bulk state, golden has a number of unique features at the nanoscale. The power to change hue, from golden to red or light purple, is one of them. This is due to the fact that gold nanoparticles absorb and scatter light in a different wavelength spectral region than solid gold. Furthermore, even at high sulfur conditions, gold catalyst is difficult to poison. Recently, gold nanoparticles (Au NPs) gain valuable interest in various fields such as impact, sensing, optics and electrochemistry as active features high impact, high electrical conductivity, modification, stability, adjustable spoilage and good biocompatibility [7]. Furthermore, it is known that Au can exhibit the lowest temperature response compared to other metals, for which it is listed as the most “noble” [8]. Similar to most nanoparticle catalysts, Au NPs still exhibited limitation in uniformed distribution, difficulty to recover at nanoscale [9]. Thus, immobilizing gold nanoparticles on a suitable substance is important.

Despite the various potential uses of supported gold catalysts, sintering of gold nanoparticles at high temperatures is one of the most significant restrictions in their utilization. Certain applications would necessitate the catalyst’s ability to withstand high temperatures and remain functional for extended periods of time. It is well known that the choice of supports and the precise interaction between gold and the support have a significant impact on the catalytic activity and stability of supported gold. Hydroxyapatite (HAp) \([\text{Ca}_10(\text{PO}_4)_6(\text{OH}_2)]\), which has been extensively used for ion exchange, adsorption, dissociation/precipitation and formation of surface complexes have been recognized as removal mechanisms. The application of HAp in the fields of heterogeneous has received a lot of attention in recent years. The intrinsic acid-basic characteristics of HAp, as well as the possibility of a large specific surface area and thermal stability, make it a good catalytic material. \([11-15]\). The ability of HAp to remove hazardous metals from aqueous solutions has also been established at a laboratory scale. HAp has strong affinity for the fixation of different metals including lead, cadmium, copper, zinc, strontium, mercury, cobalt, etc. \([16-21]\). Furthermore, because of its outstanding chemical stability, bioactivity, and biocompatibility, the HAP nanomaterial has been extensively studied in biomedical and catalyst-promoter applications \([22-24]\). However, to the best of our knowledge, there are just a few industrial applications of HAp for the usage of support material. Furthermore, functional composite catalysts with different surface acid-base characteristics, which may display unexpected HCHO capture and auxiliary oxidation performance, have yet to be thoroughly explored for HCHO elimination. HAp has been shown to have superior CO oxidation activity and to improve the stability of gold nanoparticles against sintering at temperatures as high as 600°C when used as a support for nano-gold \([25,26]\). Although the cause of this stabilization is unknown, it has been attributed to the existence of the PO43- and OH- groups \([27]\). This catalyst's exceptional sintering resistance opens up new possibilities for the production of stable nano-gold catalysts. These factors lead to HAp is decided to use as support material for Au. In fact, for a process to be viable, costs must be kept to a minimum, especially for environmental reasons. There are various way to
synthesis HAp, as synthesized by precipitation method, sol-gel method, chemical ultrasound, spray drying method, electrochemical method, hydrothermal method, composite method or solid phase reaction method [28]. Precipitation method is commonly used to prepare HAp materials commercial because it is a simple method, has high economic efficiency and does not require complicated equipment. The principle of the precipitation method whereby starting materials containing Ca\(^{2+}\) and PO\(_{4}^{3-}\) ions are mechanically mixed together, using suitable agents to adjust the pH of the solution to obtain HAp. Thus, this method is beneficial for preparing HAp from rich sources of Ca\(^{2+}\) such as eggshells which are made of 95% of CaCO\(_{3}\). In this process precipitation method is used for samples preparation, which is known as the possibility of creating pure and homogenous. The advantage of this method is that it is possible to control the reaction parameters by interfering with the crystallization process to obtain nanometer-sized HAp products. The essence of this method is to go from ions in solution to form precipitated products with sizes that gradually increase from the original size. Therefore, the shape growth and crystallinity of the products can be controlled by changing the reaction conditions such as temperature, time, pH, solvent. Moreover, the reaction may not require frequent pH adjustment. In addition, this method uses easy-to-find chemicals, simple equipment and thus it is environmentally friendly and suitable for industrial production. It has been also demonstrated that materials prepared by precipitation method have many attractive properties for high technology applications, including high crystallinity, small particle size, high specific surface area, and high average pore diameter [29]. Over 78 million tons of eggs was produced in 2018 and created over 8 million eggshells as solid waste [30]. The majority of eggshells is usually disposed at landfill and considers as a toxic waste for the environment by the EU [31]. However, eggshells can be a valuable source of calcium for the production of hydroxyapatite because they are composed of primarily of calcium carbonate (>94%). Eggshell-derived hydroxyapatite can be very beneficial as it reduces the solid waste discharged into the environment and the prepared material has excellent properties for environmental remediation (e.g. heavy metallic ion adsorption [32]).

In this paper, hydroxyapatite was prepared from eggshells waste collected from a local restaurant in Ho Chi Minh City Vietnam. The prepared hydroxyapatite was used as support material for the loading of Au nanoparticles for the catalytic oxidation of HCHO in gaseous phase. Formaldehyde (HCHO), which can be emitted for a long time in an airtight area from adhesives, paints, and ornamental materials, is well known for its harmful effects on human health [33-37]. The effect of Au loading content, temperature and relative humidity on the catalytic activity was investigated. XRD, SEM-EDS and N\(_2\) adsorption-desorption isotherms were used to characterize the prepared materials.

2. Experimental

2.1. Samples preparation

Hydroxyapatite (HAp). Eggshells were collected, soaked and washed several times with deionized water, before being ground and calcined at 800°C to form CaO. Then, the CaO was dispersed 100 mL of H\(_2\)O, while stirring continuously at 80°C. Next, a solution of HPO\(_4\) (1M) was added dropwise into the above mixture. The reaction was carried out for 2 h and was settled overnight. The mixture was then filtered and dried overnight at 80°C. The solid was then ground and calcined at 350°C to stabilize and increase crystallinity. The final white powder was labeled HAp. The HAp have ratio Ca/P = 1.67 in theory.

As loaded hydroxyapatite (Au/HAp). 1.0g of HAp powder was dispersed in 100mL of H\(_2\)O. The temperature of the mixture was raised to 60°C and was kept throughout the procedure. An appropriated amount of HAuCl\(_4\) (0.0313M) solution was added corresponding to the desired final mass ratio (0.2 and 0.5 wt%) following by the addition of citric acid (1M) solution. The reaction was carried out for 2 h and the mixture was settled overnight. The pinkish slurry was filtered and dried overnight. The solid was ground and calcined at 350°C for 2 h and the final purple powder was labeled XAu/HAp with X=0.2 or 0.5.

2.2. Catalyst characterization

The crystalline structure of the prepared hydroxyapatite was determined using Bruker D2 diffractometer, with Cu K\(_\alpha\) radiation (\(\lambda = 1.54184\)Å) operated at 30 kV and 10 mA, the range 20 of 20° - 70°, the scanning step is 0.03° for a period of 0.7s per step in the temperature of 25°C. SEM-EDS images were obtained using Hitachi FE SEM S-4800 Scanning Electron Microscope with Energy Dispersive Spectroscopy. The specific surface area was determined using the NOVA 2200e Surface area and Pore size analyzer (Quantachrome Corp.).

2.3 Catalytic oxidation experiments

The initial nitrogen and oxygen sources of the system have the purity of >99.9% and each stream was controlled using a set of needle valve and flow meter. Three streams were divided from the original nitrogen source which included a HCHO feed stream, a water vapor feed stream and a dilute stream. The HCHO tank and water tank were placed in liquid baths with thermometers. Thus, the relative humidity (RH=5% or 65%)
could be controlled by changing the bath’s temperature and ratio of the streams. The three nitrogen streams and an oxygen stream were uniformly mixed in a chamber to form a model gas with CO2=20 % v/v. The outlet of the mixing chamber was divided into two streams, a bypass stream and a stream to the reactor using a 3-way valve. The catalyst samples were pressed, which pelleting equipment that are mainly used to produce pellets. The ring die pellet mill has a slot all over the die. It works by distributing the powder once it is fed into the die. It has one roller that are responsible for compressing the powder through the hole. After that crushing, and sieving, 0.1 g of HAp or Au/HAp was fixed in the reaction tube with 2 layers of glass wool (1cm thick of catalyst). Catalyst was activated at 300°C for 1h in a flow of N2 gas before reaction.

The experiment procedure consisted of three phases. Firstly, the catalyst was activated for 2h at 300°C and cooled down in a nitrogen stream. Next, the model gas was fed to the reactor by adjusting the 3-way valve for adsorption of HCHO. After reaching saturation, the temperature of the reactor was increased from 50 to 260°C to perform the catalytic oxidation reaction. At each temperature, the reaction is maintained until equilibrium reaching. The outlet of the reactor was connected with gas chromatography (Hewlett Packard 5890plus) equipped with a Flame Ionization Detector (FID) via a 6-way valve for online injection and monitor of HCHO concentration.

The conversion efficiency of formaldehyde was calculated using the following equation:

\[ \chi = \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}} \right) \times 100 \]

where \( \chi \) is the conversion efficiency, \( C_{\text{out}} \) is the outlet/inlet concentration of formaldehyde.

3. Results and discussion

Fig. 1 illustrated the XRD pattern of the prepared HAp sample. The prepared-HAp sample exhibited characteristic peaks at \( 2\theta = 26.2^\circ; 32.3^\circ; 39.5^\circ; 47.7^\circ; 48.7^\circ \) and 54.6° which was corresponding to hydroxyapatite (JCPDS no.09-0432). Furthermore, there is no record of secondary phase on the pattern indicating the prepared hydroxyapatite was pure. Washed eggshells had a specific surface of 4 m2g\(^{-1}\), which were investigated in the laboratory, while that of prepared HAp is 85 m2g\(^{-1}\), which were also analysed in the laboratory. Thus, it can be seen that the specific surface area had increase significantly by about 21 times. Thus, the prepared HAp sample was more suitable to be used as catalyst support then eggshell waste.

![Fig. 1 XRD patterns of HAp.](image-url)
The prepared HAp nanoparticles were relatively uniform in shape and size as shown in Fig. 2a and Fig. 2b. The nanoparticles in Fig. 2b had the shape of rice grains with an average length of 120±5 nm and an average width of 40±5 nm. Au NPs were not detected in Fig. 2 suggesting that they were small in size and had good distribution on the surface of prepared HAp NPs. EDS analysis also confirmed the presence of Au element on the final material which was associated with the successful doping of Au element on the prepared HAp nanoparticles.

Fig. 2 SEM image of Au/HAp and the corresponding EDS elemental image

Fig. 3 illustrated the HCHO adsorption capacity of the prepared materials at $C_{\text{HCHO}} = 90$ ppm, RH = 65% T = 30°C and $F = 3$ L h$^{-1}$. HAp, 0.2Au/HAp and 0.5Au/HAp all exhibited similar adsorption behavior with the highest adsorption percentage at the first 5 minutes and they gradually decreased overtime. This behavior was to be expected as the experiment was carried in a continuous flow as the adsorption sites would be occupied eventually with a continuous feed of HCHO. HAp sample had the highest adsorption performance after 5 minutes at nearly 45%. The presence of Au nanoparticles had reduced the adsorption capacity of the material. Because Au obstructs the location where HCHO can connect, the adsorption capacity is lowered. When the temperature is elevated, the Au's activity is clearly visible (as shown in figure 4). The role of Au nanoparticles in this work can clearly be observed as a catalyst for the production of oxidizing agents. The highest HCHO removal percentage by adsorption of 0.2Au/HAp and 0.5Au/HAp was 36% and 29%, respectively.
The experiments to investigate the effect of temperature on the catalytic performance were carried out at the temperature 50-260°C with $C_{HCHO} = 90$ ppm and RH = 65% and the results were shown in Fig.4. As shown in Fig. 4, HAp exhibited no catalytic activity throughout the experiment due to having no catalytic sites to generate oxidizing agents. Thus, HAp only plays the role of support material for distribution of Au NPs and adsorption sites of gas molecules (H$_2$O, O$_2$ and HCHO) in the feed flow. This would also highlight importance of the presence of Au NPs in improving the thermal catalytic oxidation of HCHO using the prepared composite. The HCHO catalytic oxidation over Au/HAp can be divided into two regimes: (I) 100-150°C, (II) 150-200°C and (III) 220-260°C. In the first (I) regime, the catalytic activity of both samples was insignificant. They both converted about 10% of HCHO at 120°C but reduced to about 10% of HCHO at 120°C. The second (II) regime exhibited a jump in the efficiency of the catalytic activity and it increased with the rise of temperature. Specifically, the HCHO conversion of the 0.2Au/HAp at 150, 180, 200°C was 44%, 53% and 65%, respectively. 0.5Au/HAp also achieved a small difference (2-5%) in the catalytic efficiency. However, in the third (III) regime, there was a difference in the performance of two samples. They both continued the positive trend of converting more HCHO but 0.2Au/HAp was better. The difference in performance ranged from 10-20%. At the end of the experiment, at 260°C, 0.2Au/HAp exhibited over 85% in efficiency while that of 0.5Au/HAp was about 75%. It can be seen that increasing the Au content on HAp resulted in a negative effect on the conversion of HCHO.
From Fig. 5 illustrated the effect of temperature on formaldehyde conversion. Experiments were carried at temperatures from 50-260°C, CHCHO = 90ppm, RH = 65% and 5%. HAp have OH- anion, which may affect the formaldehyde removal. Because on the surface of HAp have hydroxyl ion (OH-). Which may adsorbed oxygen moleculars, it leads to affect the formaldehyde conversion. So when humidity is changed, this will influence the catalyst performance. In this work the humidity is decided to investigated is RH = 65% and 5%. RH = 5% is chosen, it means at our laboratory did not supply the vapor water through the reaction process. Which have a huge different condition to compare the effect of humidity between RH = 65% and 5% on the catalytic oxidation performance. It can also be divided into three temperature regimes: (I) 50-120°C, (II) 150-200°C and (III) 220-260°C. Remarkably, the prepared HAp exhibited no catalytic activity throughout the experiment on both different humidity. In the first (I) regime, the reduction in relative humidity seemed to hinder the activity of Au/HAp samples by 2-5%. In the second (II) regime, the effect of RH was also negligible for the performance of both samples with the HCHO conversion at 150, 180 and 200°C were about 40, 50 and 60%, respectively. However, in the third (III) regime, there were opposite effects on the performance of 0.2Au/HAp and 0.5Au/HAp. The performance of 0.5Au/HAp catalyst has an improvement in activity. At RH=5%, the catalytic activity of 0.5Au/HAp at 240 and 260°C had increased by a margin of 7-9% compared to those at RH=65% and ended at over 82%. The changes in the HCHO conversion at RH=5% over 0.2Au/HAp in this regime was insignificant and also ended at over 82% at 260°C.

![Fig. 5](image)

**Fig. 5** Effect of relative humidity on the catalytic oxidation performance

**RH=65%** (left) and **RH=5%** (right)

| Year | Catalyst | Application | Removal efficiency | Reference |
|------|----------|-------------|--------------------|-----------|
| 2018 | Ag/egshell | Benzene oxidation | Above 90% at 270°C | [38] |
| 2016 | Pt/HAp | Formaldehyde oxidation | 54% after 1h reaction | [39] |
| 2015 | Au/HAp | Formaldehyde and benzene oxidation | Above 90% at 270°C | [40] |
| 2015 | Rh/HAp | N2O decomposition | Above 90% at 270°C with pH = 10.5 | [41] |

Comparison between Au/HAp with Pt/HAp, which is published by Zhihuaxu and partners [39]. At 0.2Pt/HAp the conversion of formaldehyde reached 54% after 1h reaction. Furthermore, reaching with Ag/egshell of Yunlong Guo and partners show that the benzene conversion when increasing the temperature to 260°C reach over 90%. Beside that when decreasing the humidity the benzen elimination dropped [38]. Although HAP has previously been demonstrated to be an effective support for nano-gold (1 wt%) for HCHO removal[40], it was
also discovered to help gold NPs resist sintering. Nonetheless, due of its depletable resource and high price, the catalyst’s high proportion of noble metal (1 wt%) as one of the principal faults hampers its practical implementation. However, achieving functional composite catalysts with modest noble metal loading while maintaining catalytic performance remains critical. The HAP-supported lowcontent Au (0.2Au/HAp and 0.5Au/HAp) catalyst was prepared and investigated for HCHO removal, taking into account its environmental friendliness, rich resource, and unique surface acid-base character; and the effect of the modifier introduced during the preparation process on the catalyst surface property and activity toward HCHO oxidation was investigated. Futhermore, with RH/HAp was investigated to N2O removal [41], which show above 90% N2O decomposition. This leads to a promising catalyst with HAp supported noble metal for removal VOCs.

4. Conclusion

This study had successfully synthesis HAp nanomaterial from waste eggshells which was confirmed in XRD pattern and prepared Au loading HAp nanomaterial for the catalytic oxidation of HCHO. The BET specific area of HAp was 85 m²g⁻¹ which was a significant improvement when compared with the eggshells. The oxidation activity of HCHO over Au/HAp catalyst was investigated based on the change of factors: reaction temperature (50-260°C), Au loading content (0.2 and 0.5 wt%) and relative humidity (RH = 5% and 65%). They both exhibited good catalytic activity throughout the experiments with at least 40% of HCHO was converted at 150°C. Furthermore, the 0.2Au/HAp sample had the most outstanding activity and the highest efficiency of 85% at 260°C and RH = 65%. In the future work for this research, different mass of Au loading on HAp, the stability of the catalyst are and different humidity will be investigated to find out the best condition of the catalyst.

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