

Catalytic Evaluation of TiO₂-supported Cu-Ag Bimetallic Clusters in the Oxidation of Thymol Blue Solutions

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Abstract The synthesis of mono-metallic nanoparticles of silver and copper at three percent by mass supported on titanium dioxide by the precipitation deposition method is carried out. Elemental analysis by EDS spectroscopy shows that the synthesis method is efficient. Its catalytic activity is evaluated in the heterogeneous reaction of decomposition of aqueous solutions of thymol blue, which have a low activity. Silver-copper bimetallic nanoparticles supported on titanium dioxide are synthesized, keeping the percentage by mass of silver constant and varying the percentage of copper, a synergistic effect is observed which increases the catalytic activity providing practically one hundred percent reaction, also, this effect is also observed since the materials acquire greater stability and these can be used in consecutive reaction cycles without decreasing their activity. The synergy of bimetallic clusters is attributed to the fact that the particle size increases in bimetallic materials in contrast to monometallic ones which is observed by SEM spectroscopy.

Keywords: Catalytic assessment, TiO₂-supported Cu-Ag, bimetallic clusters

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1. Introduction

Since the last century, the development of the nanoscale has been presented, being essential in various areas such as pharmaceutical, petrochemical, catalysis, among others. Concepts such as nanoscience and nanotechnology have represented in recent years one of the most important scientific achievements. Although the use and study of nanostructured materials is not really so recent, since man used it for a long time without really knowing what he was working with since, at that time, there were no technological advances for the detection of nanostructures and their properties. Research on nanoscale materials has acquired great importance due to its properties or catalytic activity [1].

Transition metal nanoparticles are unsaturated metal aggregates containing from a few tens to hundreds of atoms of a metal, stabilized by ligands, surfactants, polymers, which in addition to stabilizing them protect their surface. Its size varies from one to hundreds of nanometers, but those with better catalytic activity are those that have a size of a few nanometers [2].

Nowadays, bimetallic nanoparticles, those composed of two different metallic elements, attract more attention than monoatomic ones since their catalytic performance and electronic, magnetic properties are improved compared to the monometallic particle [3].

Nanoparticle stabilization strategies can be divided into two categories: physical and chemical. In the physical approach, the nanoparticles are separated from each other by a physical barrier so that they cannot have direct contact. The most used tools are: stabilization by electrostatic forces, spherical stabilization and encapsulation in porous spheres (core-shell and yolk-shell structures). In the chemical approach, the support/nanoparticle ratio is modified and/or hybrid materials or alloys are synthesized, especially bimetallic nanoparticles [4].

During the formation of bimetallic nanoparticles, metals can combine and generate an alloy, in this case, the new catalytic surface has different physical and chemical characteristics to those shown by isolated metals, and even, thanks to their interaction, can present a synergistic effect. In the same way, it can happen that one of the metals is covered by a thin layer of the other, giving rise to structures of the core-shell type, it is also possible that the nanoparticles are deposited independently, as separate phases.

The formation of bimetallic gold particles can provide thermal stability to the nanoparticle and the ability to generate active oxygen species (which gold does not possess on its own) if a second material capable of dissociating O₂ is used [5]. Among the elements that may be suitable to form bimetallic nanoparticles with silver, the following stand out: Pt, Au, Ir, Ru and Cu [6,7,8].

Therefore, the objective of this work arises, which is to synthesize bimetallic nanoparticles Ag-Cu supported on TiO₂ using the method of successive deposit-precipitation

varying the charge of Cu and its evaluation in the reaction of decomposition of thymol blue by UV light.

2. Materials and Methods

Synthesis of nanoparticles: Monometallic catalysts. Place in the synthesis system 2 g of dry TiO_2 with 0.0618 g of AgNO_3 , add 75 mL of deionized water, add NaOH 0.1 M by drip until the pH of the solution is raised to 9.5 and leave the reaction for 4 h at 65 °C. Centrifuge the suspension at 8000 rpm for 7 minutes, resuspend in 100 mL of deionized water, repeat 3 more times. Resuspend in 100 mL in the synthesis system and add 1 mL of hydrazine and leave for one hour at 65 °C, centrifuge and dry at 100 °C (monometallic Ag catalyst). For the monometallic Cu catalyst repeat the same process, but weigh 0.0266 g $\text{Cu}(\text{NO}_3)_2$. **Bimetallic catalysts.** For each material add the following amounts of $\text{Cu}(\text{NO}_3)_2$ in the synthesis system: 0.0133 g (catalyst BM01), 0.0266 g (catalyst BM02) and 0.0399 g (catalyst BM03). Add 1 g of the monometallic Ag catalyst and repeat the same methodology as described for its synthesis.

Catalytic evaluation: Weigh 700 mg of each material and add them to the reaction system together with 100 mL of a solution of thymol blue 5 mg L^{-1} buffered at pH = 5. A UV light lamp (wavelength 254nm and intensity of $440 \text{ } \mu\text{W cm}^{-2}$) is immersed, the lamp is turned on and irradiation begins. The reaction is monitored by spectrophotometric measurements, every 10 minutes the lamp is turned off and approximately 3 mL of aliquot is extracted from the system, centrifuged at 5000 rpm for 5 minutes and the absorbance is determined by the supernatant in a spectrophotometer at 544 nm. Each material undergoes the same catalytic evaluation.

Catalytic stability of nanoparticles: Weigh 700 mg of the material and place them in the reaction system. Add 100 mL of a solution of thymol blue 5 mg L^{-1} adjusted to pH=5. The methodology of catalytic evaluation is followed. Once a reaction cycle is finished, it is recovered and subjected to the same reaction, this same is done five times in total.

Characterization of materials: UV-VIS spectrophotometry: The spectra were performed in a range of 200 nm to 800 nm in a Perkin Elmer soft lambda 18 UV-VIS spectrophotometer with integration sphere to measure diffuse reflectance, at a scanning speed of 180 nm min^{-1} , the reference spectrum was taken from a Teflon sample. **EDS spectroscopy:** The dry samples were analyzed after the deposit of the metals in a SEM JEOL 5900 with EDS microanalysis system Oxford ISIS. The analysis was performed by areas of $100 \text{ } \mu\text{m}^2$ and different areas of the same sample were analyzed, 15 zones per sample. **Transmission Electron Microscopy (TEM):** The catalysts were observed in the TEM JEOL 20 Fast Tem Electron Microscope with Z contrast detector.

3. Results and Analysis

Elemental analysis: To know the amount of metals deposited on the catalysts, the characterization was carried

out by elemental analysis to know what proportion of the theoretical total was deposited, the theoretical amount for monometallics of 3 % by mass of the metal (Ag or Cu) and for the bimetallics was maintained at 3 % by mass of Ag and the percentage by mass of Cu was varied to 1 %, 1.5% and 3%. Table 1 compares the theoretical values with the actual amount of silver and copper deposited (± 5).

Table 1. Comparison of the percentage of theoretical and actual deposited metal in Ag-Cu materials

Description	Deposited metal/ %mm			
	Theoretical		Experimental	
	Cu	Ag	Cu	Ag
Ag	0	3	0	3
Cu	3	0	3	0
Ag-Cu	1	3	0.9	2.8
Ag-Cu	1.5	3	1.3	2.8
Ag-Cu	3	3	2.7	2.7

As can be seen in Table 1, the amount of silver deposited was very close to the theoretical values (3%) either in the monometallic catalyst of Ag or in the Ag-Cu materials, while in the case of copper the amount deposited was 87% to 90% of the theoretical value, so that the technique described for the deposit of the materials is efficient.

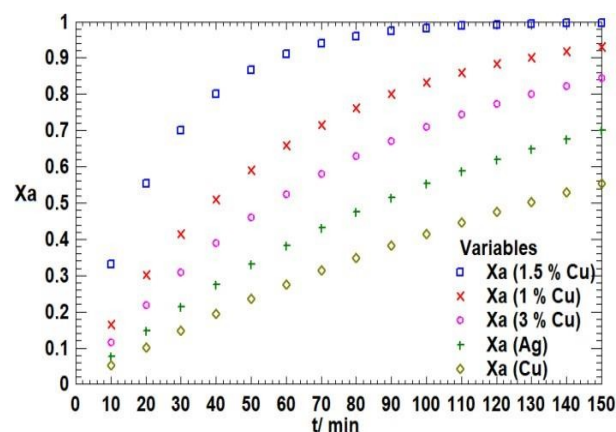


Figure 1. Conversion profile for the reaction as a function of time for different catalysts

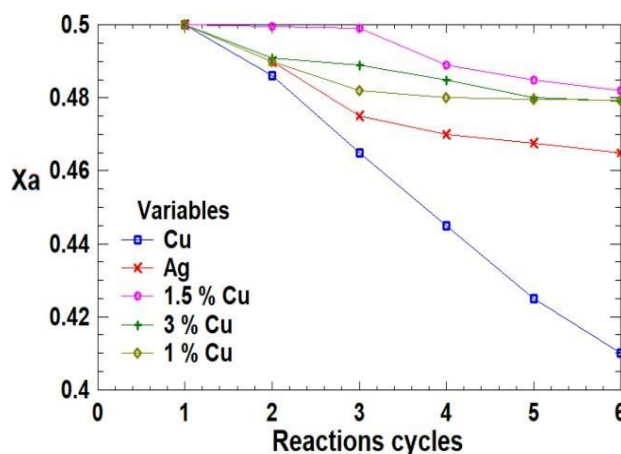


Figure 2. Determination of catalyst stability by testing consecutive reaction cycles

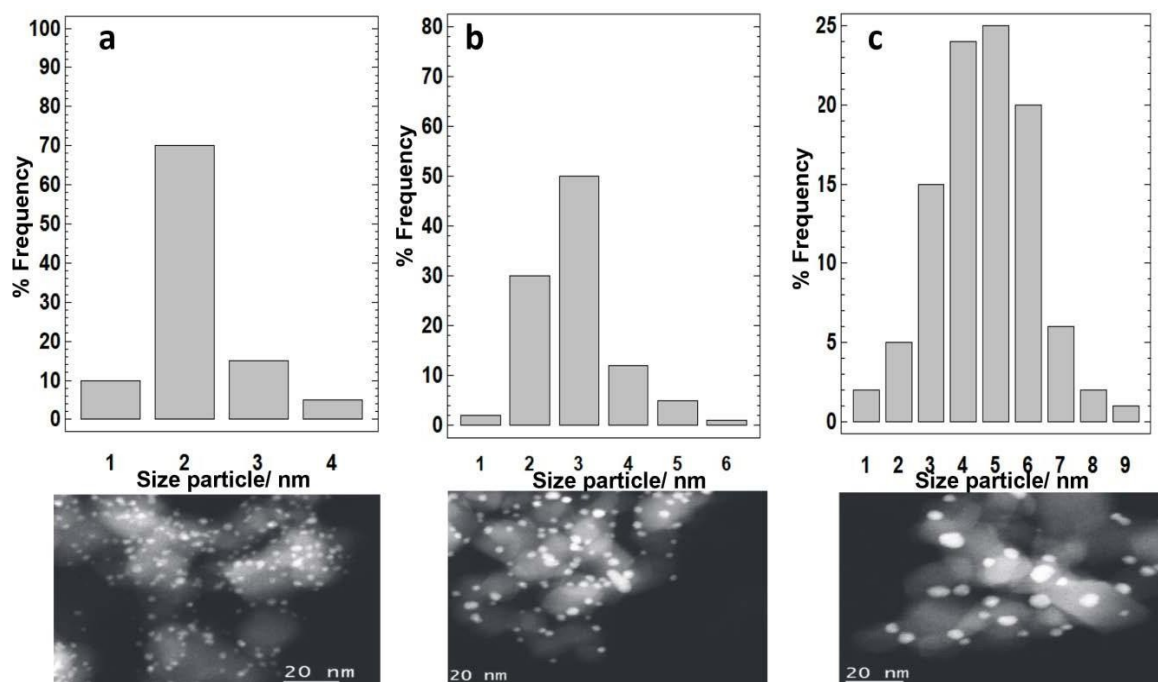


Figure 3. Particle size distribution histogram and micrograph for materials (a) Cu/TiO₂, (b) Ag/TiO₂ y (c) Ag-Cu/TiO₂ 3% Ag, 1.5% Cu

Catalytic tests: Each material was subjected to the reaction of decomposition by heterogeneous photocatalysis of thymol blue dye was determined the percentage of reaction at different times as shown in Figure 1.

As shown in Figure 1 monometallic catalysts have low catalytic activity, being the least active copper catalyst, however bimetallic have a higher activity being the most active containing 1.5% by mass of copper giving practically a total conversion. The addition of copper to the silver catalyst makes the resulting material have a synergistic effect and this increases its catalytic activity.

Catalytic stability: Catalytic activity is not synonymous with stability, since a material can provide high conversions in a reaction and for the same reaction, but carried out for the second or third time decrease its activity by effect of deactivation, aging or sintering. Therefore, monometallic and bimetallic materials were subjected to six consecutive reaction cycles to see if they could sustain 50% conversion as shown in Figure 2.

As shown in Figure 2 monometallic catalysts apart from being the least active are the most unstable, being monometallic copper the least stable losing 19% of activity in the sixth reaction cycle, also the synergistic effect of bimetallic catalysts is also observed since they provide stability in the reaction cycles, the most stable material is the bimetallic containing 1.5% Cu which only loses 4% activity until the sixth reaction cycle.

Transmission Electron Microscopy: The size of the deposited nanoparticles is an important factor in obtaining good catalytic activity. The micrographs of between 800 and 1000 particles were counted to obtain the average diameter and particle size distribution histogram.

As shown in Figure 3 the particle size histograms have a normal distribution, also the monometallic materials (Figure 3a and 3b) have the lowest size dispersion compared to the BM02 material that presents the highest

catalytic activity and stability. Particle sizes are presented in Table 2.

Table 2. Average particle size for different materials and their standard deviation

Catalyst	Average particle size/ nm	Standard deviation/ nm
Cu/TiO ₂	2.6	0.60
Ag/TiO ₂	3.3	0.71
Ag-Cu/TiO ₂ 1:1.5	5.4	1.81

As shown in Table 2 the monometallic copper catalyst has the smallest average particle size, 2.6 nm, while the silver material has an average size of 3.3 nm however the bimetallic catalyst BM02 has a larger particle size this may be due to the fact that during the synthesis coalescence occurs. However, the growth of the particle size does not affect the catalytic activity, based on Figure 2 this bimetallic material has the highest activity.

4. Conclusions

Silver and copper nanoparticles supported on titanium dioxide were synthesized by the method of deposit-precipitation at three percent by mass which have low catalytic activity in the heterogeneous oxidation reaction by ultraviolet light of aqueous solutions of thymol blue. The synthesis of bimetallic catalysts of silver-copper was carried out in different proportion by mass of copper keeping fixed 3% by mass of silver, the bimetallic material Ag (3%)-Cu (1.5%) by mass presented the highest catalytic activity above the bimetallic catalysts, that is, there is a synergistic effect of the metals providing practically 100% conversion in the decomposition of thymol blue. Also the synergistic effect is not only in high catalytic activity also provides stability to the catalyst,

which can maintain 50% conversion up to six consecutive reaction cycles. The synergy of bimetallic catalysts can be attributed to the fact that the average particle size is significantly larger compared to the size of monometallic silver and copper materials.

Author Contributions: C.M.O. was responsible for conducting the experimental design and performed the experiments A.E.O.V. made the original draft, and was in charge of the writing. Y.M.V.R. was responsible for the administration of the project and the acquisition of funds. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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