UNIVERSITI TEKNOLOGI MARA

DEVELOPMENT OF MONO- AND BI-SUPPORTED GOLD NANOPARTICLES FOR CATALYTIC REDUCTION OF *p*-NITROPHENOL

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of the requirements for the degree of
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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

The design of catalysts plays a crucial role in optimising their catalytic properties to enhance chemical reactions. The catalytic properties of gold (Au) catalysts, such as their activity, selectivity, and stability, are significantly influenced by their size and interaction with the supporting material. The supporting materials range from metal oxides, and activated carbon, to ordered porous structures. The current study aims to investigate the effects of using mono- and bi-supported Au catalysts for the reduction of *p*-nitrophenol (*p*-NP). The mono-supports consist of anodic aluminium oxide (AAO) and anodic titanium oxide (ATO) fabricated by the electrochemical anodisation method. The AAO and ATO fabricated through this method produce ordered porous structures in the form of thin membranes, providing improved features compared to conventional powdered metal oxide support. The bi-supported system includes carbon nanotubes (CNTs) coated on AAO and ATO. The deposition of Au on these supports was carried out using a deposition-precipitation (DP) method, and their morphologies were characterised via UV-Vis, FTIR, Raman, FESEM, TEM, XRD, TGA, and XPS, while ICP-OES was used for quantifying the Au loadings. The mono-support system (Au-AAO) exhibited excellent activity under optimised conditions: pH 6, 4 hours aging time, mild sonication, and AAO anodised at 80 V with APTES surface functionalisation. This resulted in 7.8 nm Au NPs size with a loading of 1.21%. The system achieved a rate constant (k) value of 1.41×10^{-2} s^{-1}, comparable to the well-engineered catalysts reported in the literature. The high porosity induced by 80 V anodisation contributed to the enhanced catalytic activity by improving mass transport and facilitating efficient electron transfer at the Au NPs interfaces. In contrast, the key finding for the Au-ATO system indicates decreased activity when Au NPs are densely populated on the ATO support with limited interparticle distance. The highest k values is 6.02×10^{-3} s^{-1} with 6.15 nm Au particle at a loading of 4.58%. The optimised parameters for this system are pH 8 and 2 hours aging time. For the bi-supported system, the highest activity observed in Au-CNTs/AAO is 3.21×10^{-2} s^{-1} and 3.55×10^{-2} s^{-1} for Au-CNTs/ATO. The addition of CNTs as the second support facilitates electron transfer from the CNTs to the Au NPs, resulting in an electron-rich Au state that further enhances interaction with the reactant (*p*-NP) and improves the catalytic activity. This effect is supported by XPS analysis, which shows a shift to lower binding energy (BE) in the $Au4f_{7/2}$ peak, indicating a change in the electronic environment of Au upon CNTs introduction compared to the mono-supported system. Variation in the concentration of *p*-NP during kinetic evaluation indicates a decrease in the observed rate constant at high initial *p*-NP concentration across the prepared Au-supported catalysts, suggesting a surface-mediated process which is consistent with the Langmuir-Hinshelwood kinetics. Meanwhile, the catalysts demonstrate excellent reusability, achieving 100% conversion to *p*-AP over four successive cycles. The k values of the fourth cycles for the respective Au-AAO, Au-CNTs/AAO, Au-ATO, and Au-CNTs/ATO catalysts were 6.1×10^{-4}, 6.6×10^{-4}, 7.3×10^{-4}, and 3.8×10^{-4} s^{-1}. Notable stability was also observed as the catalysts can be reused directly after a simple rinsing process for up to three cycles without any detectable leaching. This highlights the development of more efficient Au-supported catalysts that significantly enhance the reduction of *p*-NP.

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