

**The Effects of Gold Nanoparticles on Isobutane
Oxidation by Phosphopolyoxomolybdates and
Metal Oxides**

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by

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Declaration

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other university or institution.

Hanadi Almukhlifi

Dedication

To my mum and dad.

Acknowledgment

Foremost, I would like to express my sincere gratitude to my supervisor Dr. Robert Burns for his support, motivation and enthusiasm through this course of the project. His guidance and patience helped me during the research and in the writing of this thesis. I am grateful to have had the opportunity to work and learn from him a lot. I would like to extend my thanks to my co-supervisor Dr. Warwick Belcher for his support and assistance.

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Abstract

This thesis describes a new approach for the preparation of oxidation catalysts that contain pure gold nanoparticles on their surfaces and within their pore structures. The prepared gold nanoparticles were loaded onto phosphopolyoxomolybdate and metal oxide surfaces and the resulting catalysts were used for the partial and complete oxidation of isobutane. The process involved the initial formation of *n*-hexanethiol-stabilised gold nanoparticles, followed by addition of a solution of the stabilised gold nanoparticles in *n*-hexane to the solid catalyst and allowing adsorption to occur. Following this, thermolysis converted the *n*-hexanethiolate-stabilised gold nanoparticles to pure gold nanoparticles loaded on the catalyst surface by decomposition of the thiolate ligand from the gold nanoparticle surface.

The *n*-hexanethiolate-stabilised gold nanoparticles were prepared using the Brust-Schiffrin method. Alkanethiol (in this work *n*-hexanethiol) was used as the ligand to prevent agglomeration of the gold nanoparticles. The produced *n*-hexanethiolate-stabilised gold nanoparticles were easily isolated from solution and stored in the form of a black powder. More importantly, for this work, the stabilised gold nanoparticles could be simply redissolved in an organic solvent (*i.e.* hexane) for future applications, in the present case heterogeneous catalysis.

In this study, two types of catalysis have been studied, partial oxidation of isobutane over phosphopolyoxomolybdate Keggin-type $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ catalysts, and complete oxidation (combustion) over the mixed oxidation state spinel-type metal oxides Mn_3O_4 and Co_3O_4 . A fixed-bed flow reactor was constructed as part for this study. Gas chromatography and infrared spectroscopy were used to analyse the products of both partial and complete oxidation, which included methacrolein,

methacrylic acid, acetic acid, isobutyric acid, CO and CO₂ for the former, and CO₂ and CO for the latter. Infrared spectroscopy was used to analyse the CO and CO₂.

For the partial oxidation of isobutane three series of compounds were synthesised with varying counter-cations: (Cs⁺)_{3-x}H_x[PMo₁₂O₄₀] (where x = 0, 0.5, 1 and 2), (Ag⁺)_{3-x}H_x[PMo₁₂O₄₀] (x = 0, 1 and 2) and (Cu²⁺)_{3-2x}H_{2x}[PMo₁₂O₄₀]₂ (x = 0, 1 and 2). These compounds, and the parent acid H₃[PMo₁₂O₄₀], were studied as selective oxidation catalysts for isobutane, along with analogous catalysts with a loading of 5 wt % gold nanoparticles. The size of the gold nanoparticles was estimated to be 6.0 nm using the Scherrer equation from X-ray powder diffraction studies. The series of catalysts, with and without gold nanoparticles, were characterised by a range of techniques including infrared spectroscopy, scanning and transmission electron microscopy, thermogravimetric and differential thermal analysis and X-ray photoelectron spectroscopy (XPS).

The catalytic activities of the phosphopolyoxomolybdate compounds for the partial oxidation of isobutane were examined before and after the addition of gold nanoparticles. The addition of gold nanoparticles affected both the % conversion and % selectivities to the products of the catalysts. This depended on the presence or not of H⁺ in the catalyst makeup of the counter-cations. In some cases it is likely that the gold nanoparticles blocked the surfaces of the catalysts, thereby reducing the effective surface area for isobutane adsorption. In other cases this was not the case, and this appeared to depend on the surface area of the catalysts. The presence of Au(I), likely as AuO⁻, was observed by XPS examination of the spent catalysts, and it likely that this species plays a significant role in the oxidation process.

In the complete oxidation studies, the spinel-type metal oxides Mn₃O₄ and Co₃O₄ (Fe₃O₄ was oxidised under the catalysis conditions to Fe₂O₃) in the form of

powders and nano-powders were used as supports for the gold nanoparticles (5 wt %). In this case the calculated sizes of supported gold nanoparticles ranged from 48 to 71 nm, respectively. Aggregation occurred on the surfaces of these metal oxides. The reason for this is not immediately obvious, and requires further study. The catalytic activities of Mn_3O_4 and Co_3O_4 gave apparent activation energies of 76 ± 7 and 95 ± 5 kJ/mol, respectively, which were lowered by the addition of the gold nanoparticles. Again the presence of Au(I) was observed in the spent catalysts and likely plays a role in the oxidation process.

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