

# In situ gas-phase catalytic properties of TiC-supported size-selected gold nanoparticles synthesized by diblock copolymer encapsulation

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## Abstract

TiC-supported size- and shape-selected Au nanoparticles with well defined interparticle distances were synthesized by diblock copolymer encapsulation. Atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) have been used to investigate the correlation between the nanocatalyst morphological/electronic structure and its chemical reactivity. Using the low-temperature oxidation of CO as a model reaction, our TPD results showed an enhancement of the catalytic activity with decreasing particle size. Two desorption features were observed and assigned to kinks/steps in the gold surface and the Au–TiC interface. The role of the interparticle distance on the activity is discussed. AFM measurements showed drastic morphological changes (Ostwald ripening) on the nanoparticles after CO oxidation when the initial interparticle distance was small (~30 nm). However, no sintering was observed for Au nanoparticles more widely spaced (~80 nm).

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## 1. Introduction

Until the beginning of the 80s, gold was considered a poor candidate for heterogeneous catalysis applications, since reactive gases like O<sub>2</sub> do not adsorb on bulk gold surfaces [1]. Extensive studies conducted by Bond et al. [2] showed the unusual catalytic performance of small gold particles supported on silica for highly selective hydrogenation reactions. Later on, Haruta et al. [3] demonstrated the dramatic enhancement of the catalytic activity and selectivity of highly dispersed gold particles (<5 nm) supported on reducible metal oxides for a number of reactions including CO oxidation, combustion of hydrocarbons and reduction of nitrogen oxides [4]. This work also drew attention to the influence of the nanoparticle preparation method on the

catalyst's performance. "Coprecipitated" Au nanoparticles were found to be more active than "impregnated" nanocatalysts for low-temperature CO oxidation [5]. In the last 25 years, researchers have found that gold nanoparticles are excellent catalysts for many other technological and environmentally important reactions such as hydrogenation of CO<sub>2</sub> and CO into methanol and decomposition of halogenated compounds [4].

Since the first experimental observations, considerable efforts have been dedicated to the systematic investigation of the influence of nanoparticle size [4–9], shape [4], and nanoparticle–metal–oxide support interaction [4,10] on the catalytic activity [11].

One of the most broadly studied catalytic reactions is the low-temperature oxidation of CO. Despite the large amount of published work available, the origin of the unusual catalytic properties of supported metallic nanoparticles is still under discussion. Having as a common goal

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the understanding of catalysis at the atomic level, previous researchers proposed different models that could explain the high activity of small metallic nanoparticles [5,12–15]. Goodman's group suggested that the high activity of small gold particles is related to quantum-size effects generated by electrons confined within a small volume [6,16]. Based on scanning tunneling spectroscopy (STS) studies, a size-dependent metal-to-semiconductor transition was observed, and a correlation between the appearance of a band gap and catalytic activity established. In addition, they observed that bi-layer structure showed higher activity compared to monolayer structure [13,17]. However, recent density functional theory (DFT) calculations by Mills et al. [18] showed that the presence of a band gap might not be essential to the chemical activity of a cluster. Temperature programmed desorption (TPD) studies of CO desorption from different Au coverages deposited on FeO(111) carried out by Freund et al. [19] indicated that the reactivity of gold nanoparticles arises from the presence of highly uncoordinated gold atoms instead of quantum-size effects. Based on DFT calculations on gold surfaces, Mavrikakis et al. [15,20] found that CO, O and O<sub>2</sub> preferentially chemisorb on stepped surfaces. The authors concluded that the enhanced reactivity of small particles could be related to their high step densities. This is in agreement with previous experimental observations by Yates and coworkers [21,22]. Also it has been long accepted that the roughness play a vital role in the catalysis surfaces [23–25].

Haruta et al. [5] suggested that the catalytic activity of gold nanoparticles for CO oxidation depends strongly on the nanoparticle/support contact area, i.e., on the particle's shape. Different preparation methods yield different shapes, and hemispherical particles were found to perform better than spherical particles. These results also indicated that the catalytic reactions may occur at the perimeter interfaces around the Au particles, where the fraction of step sites increases significantly with decreasing particle size [5]. Hakkinen et al. [26] attributed the enhanced catalytic properties of small gold nanoparticles to charge transfer from the metal-oxide support to the nanoparticle surface. However, a recent review article by Lopez et al. [15] that compiled available experimental data on CO oxidation by gold concluded that the particle size (and not the support) was the determining factor controlling the catalyst's performance. Charge transfer from oxygen vacancies in the support to the gold particles as well as the interaction of adsorbates with the nanoparticle-support perimeter surfaces were found not to significantly contribute to the observed activity. The authors pointed out that the density of low-coordinate sites affects strongly the chemical activity and concluded that the activity follows a scaling law of  $\sim 1/d^3$ , with  $d$  being the particle diameter.

A non-monotonic size-dependent resistance towards oxidation was reported by Boyen et al. [27], where closed-shell Au<sub>55</sub> clusters (1.4 nm) encapsulated on (PPh<sub>3</sub>)<sub>12</sub>Cl<sub>6</sub> were found to remain inert under strong oxi-

dizing conditions. Later on, investigations by Roldan et al. [7,8] suggested that the ability of certain cluster sizes to stabilize larger amounts of Au<sup>3+</sup> upon O<sub>2</sub>-plasma exposure could be related to the enhanced catalytic performance of those particular particle sizes for CO electro-oxidation. The influence of the oxidation state of gold on its reactivity for CO oxidation is still under debate [28,29].

The present paper investigates the influence of particle size and shape on the chemical reactivity of gold. The low-temperature oxidation of CO on gold nanoparticles of sizes ranging from 2 nm to 6 nm supported on thin TiC films is used as a model reaction system. Transition metal carbides such as WC and MoC are known to exhibit reactivities similar to Pt-based catalysts for dehydrogenation, hydrogenolysis and isomerization reactions [30–33]. The catalytic properties of TiC for reactions involving water, SO<sub>2</sub> [34], ethanol [35,36] and methanol [37] have been investigated in the past. For example, Chen et al. observed that  $\sim 70\%$  of adsorbed water in the first monolayer reacts with TiC producing CO and H<sub>2</sub> [35]. Kojima et al. observed that TiC catalyzes the hydrogenation of CO to produce methane and higher molecular weight hydrocarbons [38,39]. To the best of our knowledge, there are no CO oxidation studies on TiC substrates in the literature.

The gold nanoparticles under investigation were synthesized by diblock copolymer encapsulation. This is a well-established method that results in nanoparticles with very narrow size distributions hexagonally arranged on the desired substrate [40]. Information on the nanoparticle structure, size and dispersion were obtained by high-resolution transmission electron microscopy (HR-TEM) and atomic force microscopy (AFM). Details on the nanoparticle and support chemical compositions were obtained by X-ray photoelectron spectroscopy (XPS), and insight into their catalytic activity was obtained by TPD. The following study will show that pure TiC is inactive for CO oxidation at low temperature. However, size-dependent catalytic activity is observed when gold nanoparticles are dispersed on ultrathin TiC films.

## 2. Experimental section

Size- and shape-selected gold nanoparticles with narrow size distributions have been synthesized by inverse micelle encapsulation [41]. A detailed description of the preparation method used can be found in Refs. [7,8]. Nanoparticles of different sizes and interparticle distances were synthesized using commercially available diblock copolymers, polystyrene-block-poly(2-vinylpyridine) (PS( $x$ )-*b*-P[2VP]( $y$ ), Polymer Source Inc.) as encapsulating agents, chloroauric acid (HAuCl<sub>4</sub> · 3H<sub>2</sub>O) as metal seed, and toluene as solvent. Keeping constant the concentration of HAuCl<sub>4</sub>, the nanoparticle size and interparticle distance can be tuned by changing the length of the diblock copolymer head (P2VP) and tail (PS), respectively (see Fig. 1). Further control over the nanoparticle size can be gained by changing the relative concentration of HAuCl<sub>4</sub> versus P2VP ( $r = \text{HAuCl}_4 / \text{P2VP}$

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