

Nanocatalysts by QED induced EM radiation

T. V. Prevenslik
Discovery Bay, Hong Kong

Abstract

Gold has been regarded as a poor heterogeneous catalyst because it is generally considered a nonreactive metal. But as nanocatalysts, gold and other metals somehow significantly enhance reactivity. It is generally thought chemical bonds of reactants are weakened by adsorption to nanocatalysts thereby allowing reactions to proceed more rapidly, but how this reaction proceeds to completion is not well understood. Here gold nanocatalysts are treated as unsupported nanoparticles (NPs) in a solution of reactant molecules from which extensions are made to gold NPs supported on titanium dioxide. Whether the NPs are supported or unsupported, enhanced catalytic reactivity depends on absorbed thermal kT energy accumulated from prior collisions of reactant molecules. The accumulated kT energy is treated as electromagnetic (EM) thereby allowing frequency up-conversion by quantum electrodynamics (QED) to the confinement frequency of the NP, typically beyond the vacuum ultraviolet (VUV). By this theory, the chemical reaction of reactant molecules having bonds weakened by adsorption is completed by QED induced VUV photolysis.

Keywords: nanocatalysts, nanoparticle, gold, QED

1. Introduction

Density functional theory (DFT) has now well established [1] that nanocatalysts comprising metal NPs provide an interface whereby adsorption of reactant molecules decreases dissociation barriers to allow chemical reactions to proceed more rapidly. Indeed, gold NPs deposited on select metal oxides have recently been found [2] to be very reactive for the removal of offensive odor from gases while improving electrochemical reactions in aqueous media. More recently, gold NPs in catalyzed hydrocarbon oxidation have been attributed [3] to free radical mechanisms while in luminol-hydrogen peroxide solutions have been shown [4] to enhance chemiluminescence. But gold NPs are not unique among nanocatalysts. The oxidation of tetralin in the liquid-phase is found [5] to increase and saturate with the number of vanadium atoms in the NP heteropolyanion.

However, DFT only explains how bond weakening depends on the adsorption of reactants. No guidance is offered as to the source of EM energy necessary to complete the bond breaking and initiate the chemical reaction.

In this paper, the EM energy necessary to initiate chemical reaction is QED induced EM radiation from the kT energy accumulated in collisions of reactant molecules with supported or unsupported NPs, the accumulated kT energy frequency up-converted by QED to VUV levels. Here, k is Boltzmann's constant and T is absolute temperature.

NPs under molecular collisions find similarity with quantum dots (QDs) under near infrared (NIR) laser radiation [6] in that both NPs and QDs partially absorb EM radiation. In QDs, NIR laser radiation is absorbed; whereas, in NPs the kT energy at far infrared (FIR) frequencies is absorbed by molecular collisions. Like the QDs, the NPs are absent specific heat, and therefore cannot conserve the accumulated kT energy by an increase in temperature. Conservation may only proceed by the NPs inducing the accumulated kT energy to undergo frequency up-conversion to the EM confinement frequency of the NP, typically beyond the VUV.

Consider an unsupported NP having kT energy accumulated from prior collisions of reactant molecules A and B that by QED is induced to undergo frequency up-conversion to VUV levels. Subsequently, A and B molecules react to form AB by VUV photolysis as depicted in Fig. 1.

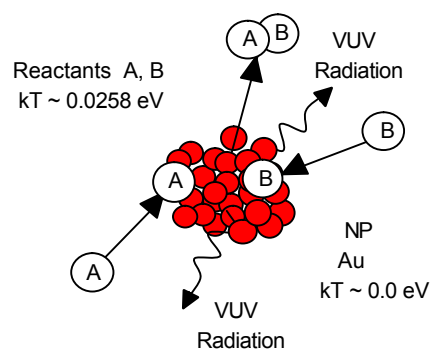


Figure 1. Catalysis of A and B Reactants by unsupported NP under QED induced EM radiation

Similar to photo-assisted [7] nanocatalysts, the reactant A and B molecules upon adsorption are excited by the VUV radiation induced within the NP to promptly initiate the chemical reaction,



where, h is Planck's constant and ν is the frequency of the EM confinement. By this theory, the QED induced VUV radiation in the NPs provides the EM energy necessary beyond bond weakening by adsorption necessary for the chemical reaction to form the product AB.

It is important to note the EM confinement frequency of the NP excited by FIR radiation from collisions of reactant molecules is not that of plasmon lattice vibrations at microwave frequencies. Instead, the quasi-bound Mie resonant radial mode [8] is excited at VUV frequencies that has sufficient Planck energy to activate adsorbed oxygen molecules, and if not leaks the VUV to the surroundings to excite the NP support or other reactant molecules in solution.

Under EM confinement, QED restricts the kT energy of the NP atoms to vanishing small levels; whereas, the colliding reactant A and B molecules absent EM confinement have full kT energy of 0.0258 eV. This may be understood by the Einstein-Hopf relation [9] for the harmonic oscillator at 300 K shown in Fig. 2.

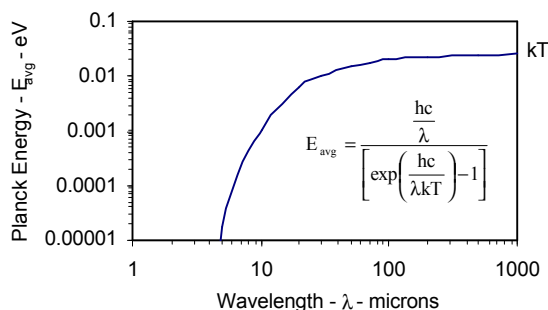


Figure 2. Harmonic oscillator at 300K.

In the inset, c is the speed of light, and λ is wavelength.

Typically, NPs as nanocatalysts [2] have diameters $D < 5$ nm. The EM confinement frequencies have wavelengths $\lambda < 2D = 10$ nm. Fig. 2 shows at $\lambda \sim 6$ microns, $kT = 10^{-4}$ eV, and therefore at $\lambda < 10$ nm, $kT \ll 10^{-4}$ eV. Hence, kT vanishes for NP atoms; whereas, colliding reactant molecules A and B not under EM confinement have full kT energy, say for $\lambda > 100$ microns in Fig. 2.

Collisions therefore transfer full kT energy to the NPs. But the absence of specific heat forbids the accumulated kT energy to be conserved by an

increase in temperature, and therefore conservation proceeds by the accumulation of Planck energy at the EM confinement frequency of the NP. For nanocatalysts having NP diameters $D < 5$ nm, the Planck energy exceeds 100 eV which is more than sufficient to complete the bond dissociation begun by adsorption to initiate the chemical reaction.

The generality of QED induced EM radiation finds application to EM radiation at VUV levels emitted from larger NPs than those used in nanocatalysts, e.g., the oxidation [10] of hydrocarbon liquids in flow electrification and aging by NP impurities having $D < 100$ nm.

2. Purpose

The purpose of this paper is to extend QED induced EM radiation to nanocatalysts under molecular collisions.

3. Theory

3.a EM Confinement

Before considering NPs absorbing EM radiation from molecular collisions, it is instructive to consider the QD theory [6] under NIR laser radiation for the case of $D > \lambda$ shown in Fig. 3. For clarity, a single NIR photon is depicted to excite the polar, radial, and equatorial modes [8] of the NP.

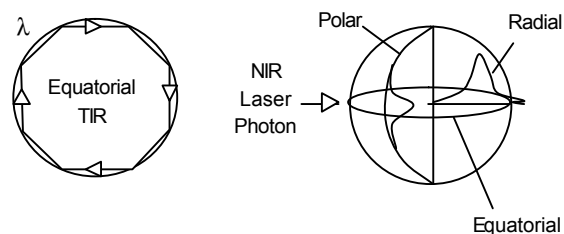


Figure 3 EM Energy Interaction with NP for $\lambda < D$

The equatorial mode shows the EM radiation trapped in the NP by total internal reflection (TIR). But the case of interest is $D \ll \lambda$ which can be understood by the number n of reflections of wavelength λ around the NP circumference, $n \sim \pi D / \lambda$. As $n \rightarrow 1$, the ratio $\lambda / D \rightarrow \pi$. For $n > 1$, the speed of light c is reduced in the NP, giving frequency f_{TIR} ,

$$f_{TIR} = \frac{c/n_r}{\pi D} = \frac{c}{\pi n_r D} \quad (2)$$

where, n_r is the index of refraction.

For NPs having $\lambda \gg D$, the TIR frequency f_{TIR} is modified [11] to a unity index of refraction,

$$f_{\text{TIR}} \sim \frac{c}{\pi D} \quad (3)$$

The radial Mie mode is analogous to the quantum mechanical analogy of creating photons of wavelength λ by supplying EM energy to a box having walls separated by $\lambda / 2$. For NPs the EM energy supplied is the absorbed kT energy accumulated from prior molecular collisions. With NP walls separated by diameter D , the QED photons created have wavelength $\lambda = 2D$. The frequency f_r of the radial mode,

$$f_r \sim \frac{c}{\lambda} = \frac{c}{2D} \quad (4)$$

3.b Vanishing Specific Heat

Upon absorption, the EM radiation is confined within the geometry of the NP. For the NP to conserve the absorbed EM radiation by an increase in temperature, the specific heat must be finite. Here, the specific heat of the NP generally follows the Einstein formulation, but differs in that instead of the specific heat given by atomic vibrations; it is given by the vibration of thermal photons, the atoms remaining stationary.

Prior to the absorption of kT energy, the thermal photons from the NP atoms are in equilibrium at temperature according to the Einstein-Hopf relation. But the absorbed kT energy disturbs the equilibrium during frequency up-conversion to the EM confinement frequency of the NP. Over this time, the NP momentarily has more kT energy than allowed by Bose-Einstein statistics at temperature. The specific heat is then given by the Einstein relation evaluated at the EM confinement frequency of the NP.

Although Einstein assumed the atoms are harmonic oscillators vibrating independent of each other, the thermal photons as oscillators vibrate coherently at the EM confinement frequency imposed by the NP, the coherent oscillations taking the shape of the Mie resonances shown in Fig. 3. For each atom, one thermal photon is assumed for each degree of freedom (DOF). The total Planck energy U of a NP with N atoms, each atom having 3 DOF is,

$$U = 3N \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1 \right]} \quad (5)$$

The NP specific heat C is,

$$C = \frac{\partial U}{\partial T} \quad (6)$$

In terms of the dimensionless specific heat C^* ,

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hc}{\lambda kT}\right)^2 \exp\left[\frac{hc}{\lambda kT}\right]}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]^2} \quad (7)$$

All BB photons are coherent at the EM confinement frequency f ,

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hf}{kT}\right)^2 \exp\left[\frac{hf}{kT}\right]}{\left[\exp\left(\frac{hf}{kT}\right) - 1\right]^2} \quad (8)$$

where, f is the frequency of the quasi-bound leaking radial mode, $f = f_r \sim c / 2D$. The dimensionless specific heat C^* in relation to wavelength λ at 300 K is observed to vanish at $D < 4$ microns in Fig. 4.

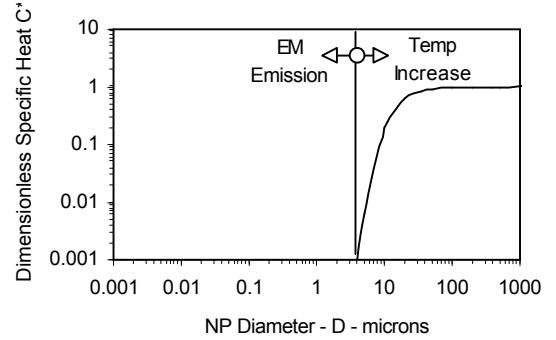


Figure 4. Dimensionless Specific Heat C^* at 300 K

3.b Collision Induced EM Radiation

The collisional EM energy Q_c transferred [12] to the NP is,

$$Q_c = \frac{\pi}{2\sqrt{3}} p P D^2 \sqrt{\frac{kT}{m}} \quad (9)$$

where, p is the probability of EM energy transfer, and P is the ambient pressure. The mass m of colliding molecules is, $m = MW / N_{\text{avag}}$ where MW is molecular weight and N_{avag} is Avagadro's number.

3.c QED Induced EM Energy and Rate

Absent an increase in NP temperature, the collisional EM energy Q_C is conserved by the emission of EM radiation,

$$E_p \frac{dN_p}{dt} = Q_C \quad (10)$$

where, dN_p/dt is the rate of QED photons produced in the NP having Planck energy E_p ,

$$E_p = \frac{hc}{2D}$$

$$\frac{dN_p}{dt} = \frac{\pi}{2\sqrt{3}} \frac{pPD^2}{E_p} \sqrt{\frac{kT}{m}} \quad (11)$$

For NPs having $D < 100$ nm, $E_p > 6.21$ eV and the EM radiation is emitted in the VUV where most reactant molecules are activated. For probability $p = 1$ of full kT transfer, the Planck energy E_p and power Q_C at Planck energy E_p for water and n-Hexane having MW = 18 and 86 are shown in Fig. 5.

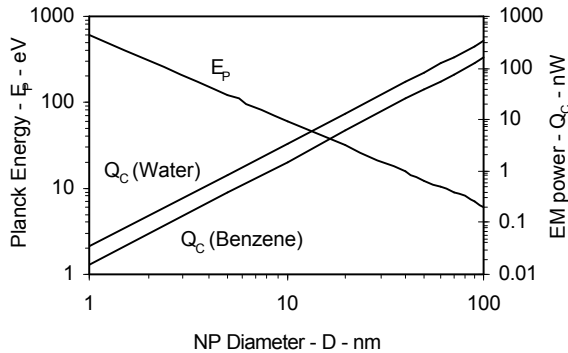


Figure 5. QED Induced Power Q_C - Planck Energy E_p

Under absorbed collisional kT energy, the NP is induced by QED to produce EM radiation at a power Q_C depending on its diameter D . For $D = 5$ nm NPs in Benzene and water, Fig. 5 shows the power $Q_C \sim 0.4$ nW of EM radiation at ~ 120 eV.

4. Extensions

When gold is deposited on select metal oxides as NPs, the long-standing notion that gold based on the fact pure gold surfaces do not adsorb oxygen, hydrogen, or carbon monoxide is somehow negated [2]. To this day, why this is so is an open question.

In the following, the theory for unsupported NPs is extended to hemispherical gold NPs supported on substrates. The metal oxide considered is TiO_2

because of high synergy [13] with gold in the catalytic oxidation of CO. Of importance are the QED effects of substrate size on the reactivity of attached gold particles. For Pt/ TiO_2 composites, the optimum TiO_2 size [14] is less than 35 nm, although TiO_2 substrates from 1 nm to 1 mm are cited in the literature.

4.a EM Confinement

The hemispherical gold NPs supported on the TiO_2 particle substrate absorbing EM radiation from molecular collisions is depicted in Fig. 6.

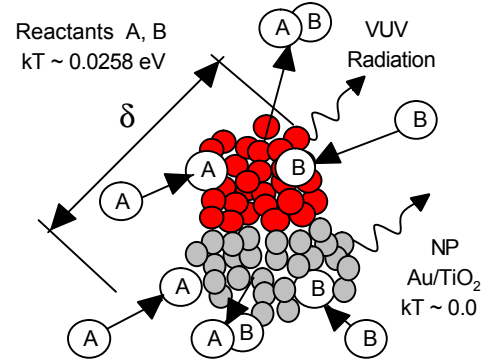


Figure 6. Catalysis of A and B Reactants by supported NP under QED induced EM radiation

Unlike the unsupported spherical gold NP, the geometry of the hemispherical gold NP on the TiO_2 particle is complex. The Mie EM confinement frequencies under TIR are even more complex as they are not simple in the unsupported spherical NP. For the purposes here, the fundamental Mie resonant frequency f_c for the Au/ TiO_2 composite is,

$$f_c \sim \frac{c}{2\delta} \quad (12)$$

where, δ is the longest dimension across the composite as shown in Fig. 6.

The EM confinement frequency includes the TiO_2 particle support having a large area to accumulate kT energy that may be transferred to the gold NP through the Au/ TiO_2 interface. Otherwise, the transfer of kT energy directly to the gold NP is far significant because of the small area compared to the TiO_2 particle.

4.b Vanishing Specific Heat

Upon absorption of kT energy from reactant molecules, the EM radiation is confined within the geometry of the Au/ TiO_2 composite. Fig. 4 shows the dimensionless specific heat C^* vanishes for $D < 4$ microns. Provided the longest dimension $\delta < 4$ microns, the Au/ TiO_2 composite may be considered to have vanishing specific heat.

4.c QED Induced EM Energy and Rate

Generally, optimum Pt/TiO₂ reactivity [14] is found for submicron TiO₂ supports having $\delta < 35$ nm. It is therefore likely that this would also be the case for Au/TiO₂. On this basis, the QED induced power Q_C may be estimated by taking $D = \delta$ in Fig. 5.

5. Discussion

Over the past decade, the emphasis in gold nanocatalysts has been prompted by the discovery [2] by Haruta that led to a review of gold in catalysis. However, the history of nanocatalysts by ubiquitous NPs began over 200 years ago.

In 1817, Davy showed [15] chemical reactions to occur between gaseous reactants at a metal surface without the latter being chemically changed. Davy used a fine Pt wire heated to a high temperature to catalyze the chemical reaction between H₂ and O₂ gases, although with finely divided Pt, the reaction could proceed at room temperature. By QED induced EM radiation, Davy's findings are interpreted in terms of the ubiquitous NPs: the finely divided Pt most likely included many NPs for the chemical reaction to be initiated at room temperature; but to initiate chemical reaction with the fine Pt wire, high temperature were required to raise the kT energy to compensate for the fewer NPs.

Like DFT, QED induced EM radiation is one of many theories [16] proposed to explain catalysis over the past decade. To limit the scope of this review, emphasis is placed on the activation of adsorbed oxygen in supported Au/TiO₂ thought [2] to enhance catalytic activity caused by surface defects. How QED induced EM radiation may supplement surface defects in activating oxygen adsorbed to Au/TiO₂ nanocatalysts is discussed as follows.

5.a Supported

With regard to CO oxidation to CO₂, gold can act as a novel catalyst once oxygen is activated on the defective surface *or* excited by other means [2].

In this regard, QED induced EM radiation from gold NPs provides a means by which oxygen may be activated other than by defective surfaces, say at the Au/TiO₂ interface. That QED induced EM radiation is a credible activation mechanism of oxygen is suggested [17] by the finding that gold deposited on the inside of the quartz tube of a CO₂ laser shows CO oxidation at room temperature only during laser operation.

Indeed, QED induced EM radiation may be considered a FIR laser converting the accumulated kT energy of colliding reactant molecules into VUV radiation having the Planck energy to activate adsorbed oxygen.

Currently, high Au/TiO₂ activity at low temperature is thought [18] caused by the contact structure which yields the longest perimeter interface, or equivalently the hemispherical gold bump geometry. But if the TiO₂ support particle is viewed as the area for gathering kT energy from colliding reactant molecules and transferring that EM energy to the gold NP through the contact area, the enhanced activity would also be consistent with a contact structure yielding the longest distance of perimeter interface.

In QED induced EM radiation, the size of the TiO₂ support particle is required to be submicron for the EM confinement to induce Planck energy at the necessary VUV levels to activate oxygen adsorbed on the gold bump, say $D < 35$ nm for Pt/TiO₂ composite [14]. Otherwise, the TiO₂ support induces low level Planck energy that cannot activate the adsorbed oxygen except by defect surfaces.

Hence, the reason for the enhancement of catalytic activity seen upon the addition of gold NPs to metal oxide supports may simply be the larger area of the supports that allows more kT energy to be absorbed from collisions of reactant molecules and subsequently transferred to the gold NP through the contact area. Indeed, the adsorption isotherms of CO by TiO₂ supports are almost the same as that of the Au/TiO₂ composite while that of the gold NP bumps is at least an order of magnitude less [13].

QED induced VUV photolysis is expected to liberate electrons leaving gold in a positive charged state. Indeed, Au⁺ and Au³⁺ but not Au⁻ are found [20] in the support surface consistent with QED induced VUV photolysis.

But the catalytic activity of gold NPs supported on metal oxides cannot rely on QED induced EM radiation alone as this would incorrectly imply activity is independent of defects and the chemical selectivity between the reactant molecules and support. Indeed, it is known [13] that gold supported on metal oxides other than SiO₂ and Al₂O₃ is much more active for CO while unsupported gold is more active for H₂ oxidation. All sources of oxygen activation need to be considered in enhancement of catalytic activity by nanocatalysts.

5.b Unsupported

Gold NP clusters are thought [21] reactive at room temperature with oxygen because of electrical charge and the number of atoms in the clusters. However, the gold clusters may be charged by QED induced EM radiation through the photoelectric effect.

But charging is inconsequential to excitation of adsorbed oxygen on the surfaces of the gold clusters that oxidizes CO to CO₂. It is the EM radiation at VUV levels induced by QED that activates adsorbed oxygen on gold NPs to oxidize CO to CO₂.

6. Conclusions

QED induced EM radiation relying on the transfer of kT energy to supported or unsupported nanocatalysts in collisions of reactant molecules acts to assist bond weakening of adsorbed reactant molecules thereby completing the bond breaking to initiate the chemical reaction.

Supported NPs on submicron metal oxide particles offer higher catalytic activation of adsorbed oxygen than unsupported NPs. But this is only true by activation under QED induced EM radiation at VUV levels as the activation mechanism. NPs supported on supramicron particles are not excited by VUV radiation, but rather low level IR Planck energy incapable of activating adsorbed oxygen. Supramicron particles require defective surfaces as the source of activation.

Similar to photo catalysis, QED induced EM radiation only provides a way of activating reactant molecules with VUV radiation, the VUV radiation almost independent of the nanocatalyst, say gold or another material. However, this does not imply that all nanocatalysts will catalyze a reaction more or less as gold. The chemistry of the nanocatalyst in relation the support must be considered to catalyze a particular chemical reaction.

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