

The catalytic nanodiode. Its role in catalytic reaction mechanisms in a historical perspective

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Catalytic nanodiodes, Pt/TiO₂ or Pt/GaN produce continuous flow of hot electron current during carbon monoxide oxidation for hours in the 80–150 °C temperature range at pressures of 100 Torr of O₂ and 40 Torr of CO. These observations provide proof of the Schottky diode model of oxide supported metal catalysis of many reactions that have been proposed by Schwab, Solymosi and others since the 1960s. The flow of hot electrons should influence chemistry at oxide–metal interfaces and the metal particle size dependence of catalytic activity and selectivity.

KEY WORDS: catalytic nanodiode; electron flow in catalysis; hot electrons.

We recently reported the continuous flow of hot electrons through a thin platinum film through semiconductor Schottky diodes of TiO₂ and GaN during the steady state catalytic oxidation of carbon monoxide (100 Torr of O₂ and 40 Torr of CO) in the 80–250 °C range [1,2]. The scheme of the nanodiodes is shown in figure 1 along with the cross sections of the nanodiodes used successfully in these experiments. Platinum acts both as an electrode and as a catalyst, and its film thickness has to be of the order of the elastic mean free path of electrons or smaller so that the charges could arrive at the metal–semiconductor interface without attenuation. The measured barrier height at the metal–semiconductor interface of both Pt/TiO₂ and Pt/GaN nanodiodes is 1.2 eV, and thus the electrons must have kinetic energies greater than 1.2 eV to be collected by the electrode on the semiconductor side. High conversion efficiency was reported for Pt/TiO₂ (three electrons for every four CO₂ molecules formed) and lower efficiencies for the Pt/GaN diode that was explained by the greater thickness of the Pt film and its discontinuity.

These definitive experimental confirmations of the flow of hot, high kinetic energy electrons away from the platinum surface where the catalyzed exothermic reaction occurs to the metal–semiconductor interface brings into focus the early suggestions of Schwab [3,4], Szabo and Solymosi [5] as well as Langenbeck *et al.* [6] who argued for the importance of the Schottky diode model of electron flow at oxide–metal interfaces for catalyzed reactions ranging from carbon monoxide oxidation, sulfur dioxide oxidation, formic acid decomposition, ethylene hydrogenation, cyclohexene hydrogenation/dehydrogenation to ammonia synthesis [5,7]. Their experimental strategies were through the use of “inverse catalyst” systems that were fabricated by depositing

oxides on films of transition metals that induced large changes in activation energies as a function of oxide thickness along with changes of turnover rates. However, these ideas of the importance of electron flow at the oxide–metal interfaces of these catalysts were strongly questioned [8] and found unacceptable by most catalyst researchers, mostly because of the absence of any experimental proof of current flow and its correlations to catalytic activity.

In light of the high hot electron currents that were detected through the oxide–metal interfaces of the catalytic nanodiodes [1,2], the classical ideas of electron transport that influences catalytic activity either at the metal or at the oxide surfaces must be revisited. There are several catalytic phenomena that deserve renewed attention in light of our results.

1. Catalysis at oxide–metal interfaces

Studies of ethylene hydrogenation using platinum nanoparticles deposited on alumina and silica surfaces revealed that when the reaction was poisoned by the adsorption of carbon monoxide the turnover rate became proportional to the oxide–metal periphery area without change in the activation energy for the reaction [9]. In contrast the CO poisoning of ethylene hydrogenation of the (111) crystal face of platinum gave turnover rates that were negligible with respect to the platinum nanoparticles on alumina or silica, and the activation energy increased to 22 kcal/mol as compared to the 10 kcal/mol on the unpoisoned surface [10]. The higher activation energy is equal to the heat of desorption of CO. Desorption of CO was necessary to make active metal sites available on the single crystal surface.

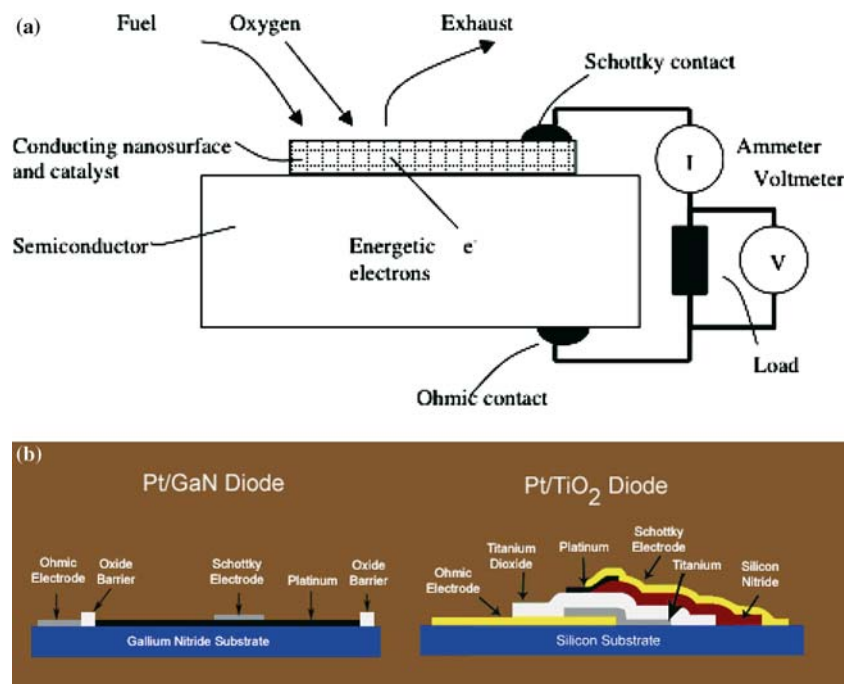


Figure 1. (a) Schematic representation of hot electron generation by exothermic catalytic reactions using a nanodiode. (b) Side views of Pt/GaN and of Pt/TiO₂.

The catalytic activity of gold nanoparticles supported on titanium oxide could be another example where hot electron flow during catalytic reactions could play an important role [11]. The particle size dependence of catalytic activity, the uniquely high turnover over small gold particles for CO oxidation could indicate a role of electron flow for gold particles with sizes that are smaller than the electron mean free path in the metal.

When various oxides are deposited on rhodium ranging from TiO₂, Nb₂O₅ to V₂O₅ and Fe₂O₃ large increases in CO hydrogenation were found in the presence of oxides with high Lewis acidity [12]. The turnover rates were at a maximum where the oxide-metal periphery area is at a maximum, indicating the important role of the interface in catalytic activity. In this circumstance the electric field, generated at the oxide-metal interfaces by hot electron flow, could be a contributor to enhancement of turnover rates.

Not only the turnover rates but also the catalytic selectivity is altered in the presence of various oxides for CO hydrogenation over nickel catalysts [13]. Although it is not clear how electron flow or electric fields at oxide-metal interfaces change selectivity it will be important to explore this using catalytic nanodiodes. Perhaps the application of an external bias voltage may reverse the direction of the current flow that can alter catalytic turnover rates, activation energies and reaction selectivities.

The hot electrons may also reduce the oxide at the metal-oxide interface that influences the bonding of the metal nanocluster and also influences the bonding and reactivity of adsorbates.

2. Catalyst particle size dependence of the reaction turnover rates

Catalytic reactions are often classified as structure sensitive or structure insensitive. Ammonia synthesis [14] and ethane hydrogenolysis [15] are among the many that belong to the structure sensitive reaction group while ethylene hydrogenation [16] belong to the other group. The catalytic activity changes with catalyst particle size for the first group while it does not for the second group. If hot electron production occurs during the catalytic reaction its magnitude should clearly be dependent on the metal particle size as the mean free path of electrons declines exponentially with increasing size.

It would be interesting to correlate size dependent catalytic activity with hot electron production with increasing thickness of the metal that catalyzes the reaction. It is not unreasonable to predict the possibility of such a correlation. Going one step further, the reaction selectivity in multipath catalytic reactions might also show a dependence on the hot electron flux.

Catalytic nanodiodes probe how reaction parameters alter the production of hot electrons. In turn, control of electron flow may permit alteration of reaction rates and selectivities. These new opportunities of catalytic chemistry will be explored in the near future in our laboratory and elsewhere.

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