

## Review

## Hot electron generation on metal catalysts under surface reaction: Principles, devices, and application

Ievgen I. Nedrygailov<sup>a</sup>, Hyosun Lee<sup>a</sup>, Si Woo Lee<sup>a,b</sup>, Jeong Young Park<sup>a,b,\*</sup><sup>a</sup> Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 305-701, Republic of Korea<sup>b</sup> Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

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## ABSTRACT

Understanding the fundamental mechanisms for charge transfer in supported catalysts is of great importance for heterogeneous catalysis. Several experimental and theoretical results suggest that charge flow through metal-support interfaces leads to the catalytic enhancement that is often observed in mixed catalysts. Therefore, it is crucial to directly probe this charge flow in metal-support catalysts during catalytic reactions. In this review, we consider the main aspects of research studying the processes that create and allow interfacial transfer of highly excited (hot) charge carriers in supported catalysts, and discuss the effect of this charge transfer on catalytic activity. We show a close connection between the phenomena of hot electron creation and chemical energy dissipation that accompanies catalytic reactions at both the gas/solid and liquid/solid interfaces. The intensity of hot electron flow is well correlated with the turnover rates of corresponding reactions, which opens up the possibility for developing new operando methodologies for studying chemical processes on catalytic surfaces.

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## 1. Introduction

Many industrial chemical processes associated with the synthesis of chemicals, environmental applications, and the production of clean energy are based on heterogeneous catalysis [1–4]. Therefore, studying the nature of heterogeneous catalysis has been an important practical task for decades. Diverse technologies have been developed to manufacture advanced catalysts that combine materials (e.g., metals, alloys, semiconductors, and oxides) with various properties, sizes, and shapes (e.g., nanoparticles, fine powders, porous materials) [1,2,5–7]. It is now possible to obtain catalysts with activities that are orders of magnitude greater than the activity of single-chemical catalysts. Nevertheless, even in the presence of such advanced catalysts, industrial chemical processes still occur at temperatures well above ambient temperatures. This makes the chemical industry one of the most energy-intensive technologies of our time, which motivates scientists around the world to search for new, more energy-efficient solutions in the field of heterogeneous catalysis.

One of the key technologies for increasing the activity and selectivity of heterogeneous catalysts is the use of catalytically

active metal nanoparticles in combination with a suitable support [2,8–12]. This technology is based on groundbreaking research by Schwab *et al.*, who in the 1960s discovered significant changes in the activity of fine metal particles when placed on the support of a metal oxide, even though the support itself is inactive for this reaction [13,14]. Called the “Schwab effect”, this phenomenon is attributed to the formation of a Schottky barrier at the metal-oxide interface with the subsequent transfer of charge carriers through the barrier, which affects the course of the surface reaction [1,9,13]. Later, it was also shown by Somorjai *et al.* that additional charge transfer through a metal-support interface can occur during exothermic surface reactions through the nonadiabatic creation of excited (hot) charge carriers in the metal [15–17]. It is expected that the creation of hot charge carriers can significantly affect the rate of reagent molecule adsorption on the catalytic surface and thus influence the overall rate of the reaction [1,5,18–21]. Although many studies have been performed to clarify the role of hot charge carriers in catalysis, a complete understanding of this phenomenon is still lacking because of the complexity of the quantitative description of interfacial charge transfer under reaction conditions.

The nature of hot charge carriers created in metal catalysts during nonadiabatic surface reactions is analogous to that of highly excited electron-hole (*e-h*) pairs generated by incident light absorption in semiconductor-based photocatalysts and plasmonic photocatalysts containing nanoparticles of noble metals [19,22–

\* Corresponding author.

E-mail address: [jeongypark@kaist.ac.kr](mailto:jeongypark@kaist.ac.kr) (J.Y. Park).

27]. However, the mechanism for the effect of hot charge carriers on the rate of chemical reactions is different. In photocatalysts, excited charge carriers are created by an influx of energy from external sources (e.g., the sun). After excitation, these charge carriers can transmit energy to molecules adsorbed on the catalytic surface and break old or form new chemical bonds, thereby converting photon energy into chemical energy. In exothermic reactions, the chemical transformations themselves are a source of energy sufficient for the generation of highly excited  $e-h$  pairs. In this case, the transfer of hot charge carriers only affects the rate of energy exchange between the metal catalyst and the support without introducing additional energy into the system. Thus, the creation of hot charge carriers from nonadiabatic energy dissipation is a process inverse to the generation of  $e-h$  pairs in photocatalysts.

This review considers the main aspects of research aimed at developing methods for studying the transfer of charge carriers through metal-support interfaces under catalytic reaction conditions. First, we review the mechanisms for hot electron excitation and transport through metal-oxide interfaces. We then show various schemes for detecting hot electrons that are generated during catalytic processes. In the end, we provide an overview of the latest results from the detection of hot electrons in supported catalysts during chemical reactions at both the gas/solid and liquid/solid interfaces and discuss the relationship between charge flow and reaction kinetics.

## 2. Principle of hot electron generation

The creation of hot charge carriers during gas-surface interactions has been known for a long time because of the observation of photon and electron exoemission from the highly exothermic reactions of alkali metals with various gases (e.g.,  $\text{Cl}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_2$ ) [28–38]. It is also known that the excitation of  $e-h$  pairs leads to a hot electron with energy above the Fermi level and to a hot hole with energy below the Fermi level. The excitation of an  $e-h$  pair takes place *via* a nonadiabatic process [2].

One view to justify the generation of hot electrons is related to the difference in heat capacity between electrons and phonons. Hot electrons thermalize within picoseconds by electron-phonon interactions. The phenomenon of hot electron creation can be rationalized as follows: The electronic heat capacity ( $C_{\text{electron}}$ ) of most metals in thermal equilibrium is about one hundred times smaller than the lattice heat capacity ( $C_{\text{lattice}}$ ) at 300 K. For example, for copper,

$$\frac{C_{\text{electron}}}{C_{\text{lattice}}} \approx \frac{\gamma T}{3R} = \frac{0.70 \times 10^{-3} \times 300}{3 \times 8.3} = 0.008 \quad (1)$$

where  $R$  is the gas constant and  $\gamma$  is the Sommerfeld's constant [ $0.70 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ] for Cu]. When heat is deposited from exothermic surface reactions or photon flux, electrons heat up much faster (femtoseconds) than the lattice (picoseconds) because their heat capacity is much lower.

The phenomenon of electron exoemission from highly exothermic reactions of alkali metals with various gases is an indication that the gas-surface system cannot effectively dissipate energy by generating heat and is therefore described in the framework of a nonadiabatic mechanism, as illustrated in Fig. 1. Here, one-dimensional potential energy curves (PECs) are shown for the cases of adiabatic and nonadiabatic interactions of a gas molecule with an atom on the metal surface. Such PECs are widely used in studies of the nonadiabatic phenomena that arise from charge-transfer reactions between reactants with very different electronegativities [28,29]. They can also be used to describe the dissociative chemisorption of diatomic molecules on metal

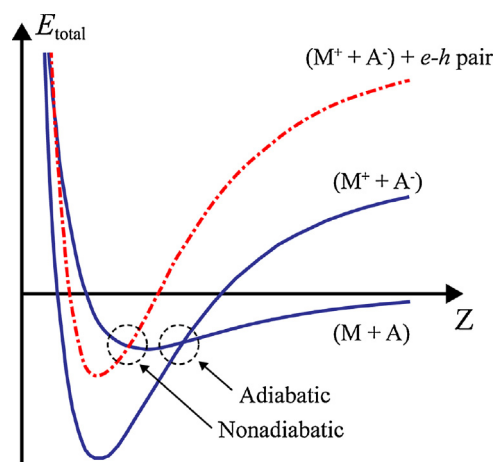


Fig. 1. One-dimensional PECs for the cases of adiabatic and nonadiabatic interactions of a gas molecule (A) with an atom on the metal surface (M). Adapted with permission [38]. Copyright 1991, AIP Publishing.

surfaces [21,39]. A gas molecule (A) approaches an atom on a metal surface (M) so that their interaction is represented by the ground-state PECs before ( $M+A$ ) and after ( $M^+ + A^-$ ) charge transfer. As shown in Fig. 1, the reaction may proceed either adiabatically or nonadiabatically. In the latter case, the transition of the system to a new state occurs at the point of intersection of the PEC for ( $M+A$ ) with one of the electronically excited states for ( $M^+ + A^-$ ), which leads to the creation of an  $e-h$  pair. The subsequent relaxation of the system to the ground state can occur by emission of a photon or an exoelectron [19,20,28,29].

Unlike adiabatic dissipation of chemical energy, which is characterized by the excitation of many phonons per elementary surface reaction, nonadiabatic reactions on metal catalysts most likely occur with the creation of a single  $e-h$  pair per exothermic reaction step [20,28]. This is due to the continuity of the electronic levels in metals, which allows the transfer of essentially any portion of chemical energy to the electronic system with a single excitation. Relaxation of one  $e-h$  pair happens on the femtosecond to picosecond timescale, and its mean free path is on the order of tens of nanometers. Therefore, hot charge carriers created during transient processes (e.g., gas adsorption) decay rapidly when transferred through the metal-support interface; thus, the whole system goes to an equilibrium state [28,40,41]. However, during a stationary exothermic reaction when charge carrier excitation occurs because of a multitude of elementary reactions taking place on the catalyst per unit time, a steady-state hot electron (or hole) flux can be generated [2,15,20,42]. Because hot electrons can transfer large amounts of energy, this flux can contribute significantly to the energy exchange process in the gas-surface system and thereby influence the reactivity of the catalyst [21,28,39,43].

It is important to consider the question of how to detect hot charge carriers that are excited in metal catalysts by an exothermic chemical reaction. There are two detection strategies: The first is to obtain sufficient time resolution for observing these excitations. The second is to use a nanometer-scale energy barrier for irreversible transfer of hot electron fluxes. For the first approach, two-photon time-resolved photoemission (TPTRP) spectroscopy has been employed to directly study the dynamics of optically excited electrons at metal and semiconductor surfaces. This technique has been applied to the direct measurement of hot electron relaxation in noble and transition metals [44] and surface-state dynamics on clean and adsorbate-covered metal surfaces [45], as well as charge carrier dynamics in semiconductors, where much work has been performed. As mentioned above, in the case of

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