



## Relating adatom emission to improved durability of Pt–Pd diesel oxidation catalysts



Tyne R. Johns<sup>a</sup>, Ronald S. Goeke<sup>b</sup>, Valerie Ashbacher<sup>a</sup>, Peter C. Thüne<sup>c</sup>, J.W. Niemantsverdriet<sup>c</sup>, Boris Kiefer<sup>d</sup>, Chang H. Kim<sup>e</sup>, Michael P. Balogh<sup>e</sup>, Abhaya K. Datye<sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Biological Engineering, University of New Mexico, Albuquerque, NM 87131, USA

<sup>b</sup> Sandia National Laboratories, P.O. Box 5800, MS 0959, Albuquerque, NM 87185-0959, USA

<sup>c</sup> Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

<sup>d</sup> Department of Physics, New Mexico State University, Las Cruces, NM 88003, USA

<sup>e</sup> General Motors Global R&D, 30500 Mound Rd., Warren, MI 48090, USA

### ARTICLE INFO

#### Article history:

Received 19 October 2014

Revised 23 March 2015

Accepted 24 March 2015

Dedicated to the memory of Haldor Topsøe.

#### Keywords:

Adatom emission  
Ostwald ripening  
Catalyst sintering  
Pt–Pd  
Diesel oxidation  
Exhaust treatment

### ABSTRACT

Sintering of nanoparticles is an important contributor to loss of activity in heterogeneous catalysts, such as those used for controlling harmful emissions from automobiles. But mechanistic details, such as the rates of atom emission or the nature of the mobile species, remain poorly understood. Herein we report a novel approach that allows direct measurement of atom emission from nanoparticles. We use model catalyst samples and a novel reactor that allows the same region of the sample to be observed after short-term heat treatments (seconds) under conditions relevant to diesel oxidation catalysts (DOCs). Monometallic Pd is very stable and does not sinter when heated in air ( $T \leq 800$  °C). Pt sinters readily in air, and at high temperatures ( $\geq 800$  °C) mobile Pt species emitted to the vapor phase cause the formation of large, faceted particles. In Pt–Pd nanoparticles, Pd slows the rate of emission of atoms to the vapor phase due to the formation of an alloy. However, the role of Pd in Pt DOCs in air is quite complex: at low temperatures, Pt enhances the rate of Pd sintering (which otherwise would be stable as an oxide), while at higher temperature Pd helps to slow the rate of Pt sintering. DFT calculations show that the barrier for atom emission to the vapor phase is much greater than the barrier for emitting atoms to the support. Hence, vapor-phase transport becomes significant only at high temperatures while diffusion of adatoms on the support dominates at lower temperatures.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

Low-temperature after-treatment catalysts are increasingly important due to a tighter regulatory environment in recent years and the demand for more efficient advanced combustion engine technologies [1]. Specifically, Pt and Pd are the precious metals used in diesel oxidation catalysts (DOCs) for hydrocarbon (HC), carbon monoxide (CO), and nitrogen oxide (NO) oxidation in engine exhaust. Previous reports in the literature indicate that Pt sinters and has poor durability under oxidizing conditions [2,3]. After high-temperature aging in air ( $>700$  °C), Pt can grow to form particles greater than 200 nm in diameter and approaching microns [4] which is detrimental to low-temperature reactivity, and a considerable economic loss in view of the high price of Pt. Adding Pd prevents the formation of large Pt particles, leading to

improved durability and performance [4–6]. There is, however, limited understanding of how Pd modifies the behavior of Pt. Learning how Pd helps Pt catalysts can have significant payoffs in the design of more robust catalysts for this and other high-temperature catalytic processes.

Previous work shows that Ostwald ripening—inter-particle transport of mobile species emitted from small particles—plays an important role in the sintering of supported metal catalysts [7,8]. When metal nanoparticles are heated in air, volatile metal oxides can be formed, but these are easily trapped within the pore structure of an industrial catalyst. Hence, role of vapor-phase processes in interparticle transport is not well understood. In this work, we have used planar model catalysts that allow measurements of the rate of emission to the vapor phase. By redirecting the emitted atoms back to the surface, we are able to simulate what might happen within a porous catalyst support. Besides being able to observe the same region of the sample before and after treatment, model catalysts allow studies via in-situ TEM where

\* Corresponding author.

E-mail address: [datye@unm.edu](mailto:datye@unm.edu) (A.K. Datye).

the sample can be observed in real time or after short-term treatments. But many of the in-situ TEM studies are performed at low pressures which can sometimes result in different sintering behaviors. In a recent study, Behafarid et al. [9] report that Pt is quite stable in O<sub>2</sub> up to 800 °C when studied via in-situ TEM at 1 Torr total pressure showing negligible growth in particle size over 30 min. In contrast, Chen and Schmidt [10] found rapid sintering and also documented a loss in Pt content when model catalysts were heated in air at atmospheric pressure. Using similar model catalysts, Simonsen et al. [8] found no loss of Pt when studying the samples via in-situ TEM, but at low pressures. It is clear that oxygen pressure is important, since the formation of metal oxides of Pt is first order in O<sub>2</sub> pressure [11].

Accelerated aging of Pt catalysts is generally carried out in air at atmospheric pressure where we see rapid sintering at elevated temperatures [12,13]. Furthermore, air aging leads to similar catalyst deactivation as that seen in vehicle aging [14]. Therefore to allow comparison with supported catalysts, we performed our experiments at atmospheric pressure. To preserve the benefits of model catalysts while allowing heating in air at elevated temperatures, we used custom-made Si TEM grids with Si<sub>3</sub>N<sub>4</sub> windows [15,16]. Rapid heating was made possible by using a heating device [17] that provides heating and cooling rates over 100 °C s<sup>-1</sup>. This setup allowed us to perform short-term aging of the model catalysts, so that we could capture the disappearance of individual nanoparticles which can occur on the timescale of seconds [18]. Such short-term observations cannot be performed in a tube furnace due to long heating and cooling times.

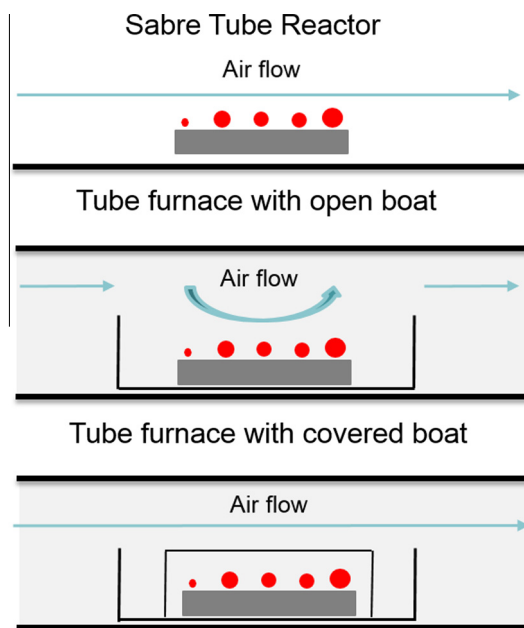
A notable feature of Pt is the high vapor pressure of Pt oxide which can cause a loss of weight in Pt crucibles, and cause massive restructuring of Pt foils heated in air [19,20]. But Pd on the other hand forms a stable oxide (PdO) in air that has negligible vapor pressure (~3 orders of magnitude less than that of Pd metal) [21]. If PtO<sub>2</sub> were the only mobile species, we would expect that Pt–Pd nanoparticles would slowly lose Pt, leaving behind the Pd and causing phase segregation of the catalyst. However, in supported catalysts rather than seeing segregation, we find that even a physical mixture of Pt/alumina and Pd/alumina leads to Pt–Pd alloy formation after aging in air [3]. This apparent “self-assembly” of Pt and Pd into bimetallic Pt–Pd particles occurs because PdO acts as a trap for the mobile Pt species. Therefore, metallic Pt–Pd particles are formed under conditions where Pd by itself would transform into stable PdO, and this is why the working state of Pt–Pd diesel oxidation catalysts consists of metallic Pt–Pd alloy particles [12]. What is not understood is how the presence of Pd slows the rates of sintering in these catalysts. Another unknown is the relative importance of vapor-phase and surface processes in these catalysts. As we show here, vapor-phase processes become increasingly important at elevated temperatures. At 650 °C, sintering appears to be largely occurring via surface migration of mobile species emitted from the particles, but at 800 °C it is the vapor-phase processes that become significant. This shift in mechanisms causes profound changes in the observed particle size distributions, and the vapor-phase processes appear to be responsible for the formation of abnormally large Pt particles. We conclude that the primary role of Pd is to slow the rates of emission of mobile Pt species from bimetallic nanoparticles.

## 2. Materials and methods

### 2.1. Imaging methods

The TEM grids were custom-made using a design developed in previous work at TU Eindhoven [16]. They have a 100 μm × 100 μm silicon nitride membrane window with a

thickness of 15 nm. The top and bottom 3 nm have been transformed into a surface oxide layer through calcination in air at 750 °C for 24 h. High-purity (99.999%) metals (platinum and palladium) purchased from Materion Corporation were used to fabricate these samples. The metals were deposited directly onto the 2 mm × 2 mm SiO<sub>2</sub> TEM grid surface using a 10 kV Temescal electron beam evaporator. This high-vacuum cryo-pumped system was pumped to a base pressure of 1 × 10<sup>-7</sup> Torr prior to deposition. The film thickness was controlled by a quartz crystal microbalance (QCM), while the deposition rate was controlled to 0.03 Å s<sup>-1</sup>. This system as configured is capable of controlling the film thickness to 0.1 Å. These noble metals are non-wetting on oxide surfaces, so a continuous film is not formed during deposition at these very low loadings. All films were deposited to a thickness equivalent to 5 Å (500 pm). The as-prepared samples were treated for 10 min at 700 °C in flowing 7% H<sub>2</sub>/N<sub>2</sub> (140 sccm) in a SabreTube™ furnace manufactured by Absolute Nano to allow the deposited films to dewet and form nanoparticles (an image of the furnace is provided in Fig. S1 in the Supporting information). The furnace allows for a 100 °C s<sup>-1</sup> heating rate over a 1-cm wide substrate. Temperatures up to 1000 °C are possible with the SabreTube™. The short, up to two-minute, aging treatments were performed in the SabreTube™ in flowing air at 140 sccm. The 1.5-h aging treatments were done with the sample placed in a ceramic boat within a quartz tube furnace in flowing air at 100 sccm. The quartz tubes have an inner diameter of 2 cm. The ramp rate of the furnace was 20 °C min<sup>-1</sup>, and the temperature was held for 1.5 h and then decreased to room temperature in the flowing air. In some of the experiments, we covered the ceramic boat with a smaller boat inverted on the sample to trap the emitted species—helping us simulate the conditions encountered in a porous catalyst structure. Fig. 1 shows a schematic diagram of the three catalyst structures used for aging the model catalyst samples. The major difference in these three arrangements is the mass transfer to the flowing air. The SabreTube™ being open allows the flowing air to sweep away any volatile oxides emitted to the vapor phase. The rate of emission is slower in the tube furnace since the



**Fig. 1.** Schematic diagram showing the nature of air flow over the TEM specimen for the three heating arrangements (with nanoparticles shown in red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/60773>

Download Persian Version:

<https://daneshyari.com/article/60773>

[Daneshyari.com](https://daneshyari.com)