

3D atom probe study of gas adsorption and reaction on alloy catalyst surfaces II: Results on Pt and Pt–Rh

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Abstract

The 3-dimensional atom probe (3DAP) is a unique instrument providing chemical analysis at the atomic scale for a wide range of materials. A dedicated 3DAP has been built specifically for analysing reactions at metal surfaces, called the catalytic atom probe (CAP). This paper presents an overview of results from the CAP on structural and chemical transformations to surface layers of Pt and Pt–17.4 at.%Rh catalysts following exposure to a number of gases typically emitted by vehicle engine exhausts, normally for 15 min at pressures of 10 mbar. Following exposure to the oxidising gases NO on Pt, and NO, O₂ or N₂O on Pt–Rh, both surfaces appear disrupted, while for Pt–Rh, Rh enrichment of the surface atomic layer is noted over the entire specimen apex for exposure temperatures up to 523 K. However, for oxidising exposures at 573–773 K relatively clean, Rh-depleted surfaces are observed on {001}, {011} and {012} crystallographic regions of Pt–Rh. It is suggested that this result is due to surface diffusion of oxide species over the specimen apex, towards the {111}-orientated areas where the oxides appear to be stabilised. In contrast, CO exposure appears to have little effect on the either the surface structure or composition of the Pt–Rh alloy. Finally, combinations of two gases (NO + CO, O₂ + NO) were also dosed onto Pt–Rh alloys in the same exposure. These revealed that while NO and CO can co-adsorb without interference, CO prevents the build up of oxide layers and reduces the extent of Rh segregation seen under NO exposure alone. On exposing Pt–Rh to NO after an oxygen exposure, heavily oxidised surfaces, Rh segregation and no intact NO molecules were seen, confirming the ability of oxidised Pt–Rh to dissociate nitric oxide.

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1. Introduction

Pt–Rh catalysts play a crucial role in automobile exhaust catalysis, removing the toxic gases NO_x and CO along with any unburnt hydrocarbons from engine exhausts. Despite their continuing successes at meeting increasing strict emissions legislation, the exact mechanisms of how such catalysts work at the atomic scale are poorly understood. Experimental work is generally carried out using catalyst-beds, effectively treating the catalyst as a “black-box” [1,2], or else using flat, single-crystal metal samples treated with low pressures ($\sim 10^{-8}$ mbar) of reac-

tants (e.g. [3]). While both methods continue to provide valuable information, it is often difficult to transfer findings between the two fields, due to the large materials and pressure “gap” that exists between them. There exists a need for a technique that can bridge this gap between the existing methods and the real catalyst environment. The 3D atom probe can provide atomic resolution chemical imaging of materials, and has been used with great success to study a range of materials including engineering alloys and magnetic multilayer films [4–6]. By including a high-pressure/temperature reaction cell within the vacuum system of a 3D atom probe, we have created a new instrument (the catalytic atom probe, CAP) capable of providing new insights into how heterogeneous catalysts function. The development and features of this instrument are described

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fully in an earlier paper [7], while a review of the distinctive aspects of 3D atom probe compared to conventional surface science techniques is also available [8]. This paper reports the results of a comparative study of gas adsorption and reaction on surfaces of platinum and a Pt–17.4 at.%Rh alloy using the new instrument. We have focussed mainly on the interaction of NO with different surfaces of Pt and Pt–Rh, followed by comparisons with other gases (O₂, CO, N₂O), before presenting some preliminary results from experiments using binary gas mixtures.

2. Experimental

Full details of the CAP have been previously published [7], so only a brief description is presented here. The instrument contains a field ion microscope (FIM) and 3-dimensional atom probe (3DAP) [5], which combines atomic-scale position mapping with time-of-flight mass spectrometry of single atoms removed from conducting needle-shaped specimens. The CAP can also be used for field emission microscopy (FEM), which has a lower spatial resolution than FIM, but it offers a way of performing an initial examination of a surface under a much lower, negative electric field. Specimens were made by electropolishing high-purity Pt metal or Pt–17.4 at.%Rh wires (Alfa-Aesar) in a molten salt mixture of 4:1 NaNO₃:NaCl. Before any treatments in gases were performed, each specimen was cleaned using field evaporation to produce a uniform adsorbate-free surface.

Located next to the atom probe vacuum chamber is a separate reaction cell which enables the treatment of a specimen in a mixture of gases (up to 1 atm) at elevated temperatures (up to 773 K). The aim of the experiments was to study catalytic surfaces that closely approximated those in real automotive catalytic converters. While in conventional surface science experiments specimens are typically atomically flat single crystals, in real catalysts the active metals are in the form of nanometre-sized particles deposited on a high-surface area material such as alumina. The specimen in an atom probe experiment however is in the form of an atomically sharp wire, with an end apex diameter of approximately 30–50 nm. The apex surface geometry provides a close approximation to a real catalyst particle, exposing multiple crystallographic planes for study. Such specimens are therefore a good model for the active metal particles deposited in real catalyst systems.

The gases used in the experiments were NO, CO, O₂ and N₂O, which are all typically present in engine exhaust in varying amounts. Nitrous oxide (N₂O) is present at trace levels, but was used in comparison with NO to explore effects of increased nitrogen on oxygen atom adsorption. Moreover, it is also a potent “Greenhouse gas” [9,10], and is the focus of increasing attention in pollution control.

Treatment durations were typically 15 min, unless stated otherwise, which was chosen to approximate the relatively short average duration of most automobile journeys. The treatment temperatures ranged from room temperature

up to a maximum of 673 K, which corresponded to the maximum likely temperature of automobile exhaust gases under normal engine operation. At the end of the treatment duration, the gas supply was switched off, allowing the differential pumping to reduce the cell pressure to around 10^{−4} mbar. This process was complete in less than one minute, during which time the cell was held at the treatment temperature. After gas purging was complete the specimen was moved back to the analysis chamber, which again took less than one minute. A gas pressure of 10 mbar was normally employed for exposures (again unless otherwise stated), which matched with the approximate partial pressure of CO in a typical engine exhaust.

Initially exposures of the specimens were performed using single gases in order to simplify the interpretation of the 3DAP data. However a set of experiments were also carried out using binary mixtures of gases on Pt–Rh. It is important to have an understanding of adsorption phenomena beyond single gases reacting on the catalyst surface, as clearly a number of species simultaneously arrive on a catalyst particle surface during the course of a real catalytic reaction. This was explored using mixtures of NO + CO, allowing investigation of the surfaces following treatment with an oxidising and reducing gas. The first set of experiments dosed both gases simultaneously over 15 min at a total pressure of 20 mbar (in a 50:50 ratio). The second set exposed the Pt–Rh specimens to 10 mbar of NO over 15 min before repeating the exposure with CO.

Finally, a major focus of current research in the automotive industry is the possible use of lean-burn engines, which have reduced CO₂ emissions. These operate under oxidising conditions, which causes problems in removing the NO component of engine exhaust [11]. A final set of experiments therefore exposed the Pt–Rh surfaces firstly to O₂ and then NO, both at 10 mbar over 15 min, in order to study the implications of using Pt–Rh catalysts with lean-burn engines.

Regardless of the treatment employed in the reaction cell, following exposure specimens were transferred back into the vacuum chamber for analysis at a temperature of 60 K. This enables resolution of atomic detail under the FIM/3DAP, while also limiting diffusion of any reaction products formed in the treatment. For atom probe analysis, a voltage pulse fraction of 20% was used, which provided measurement of the bulk alloy composition that was within 1% of the stated value. This pulse fraction was identical to that used by other atom probe groups to study Pt–Rh [12–14].

2.1. Results from single gases on Pt and Pt–Rh

2.1.1. Nitric oxide on Pt

Following treatment of pure Pt specimens with NO at temperatures ≥ 473 K morphological changes to the specimen apex were observed in the FIM. Fig. 1 shows a sequence of FIM images from a Pt specimen heated in NO at 573 K. The top-left image shows the surface just before

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