



Trapping mobile Pt species by PdO in diesel oxidation catalysts: Smaller is better



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ARTICLE INFO

Article history:

Received 15 October 2015

Received in revised form

25 December 2015

Accepted 4 January 2016

Available online 16 February 2016

Keywords:

Diesel oxidation catalyst

Bimetallic Pt–Pd

Trapping Pt

Particle size effect

ABSTRACT

Pt is an active catalyst for treatment of diesel exhaust emissions but is known to sinter and form large particles under oxidizing conditions. Pd is added to suppress the sintering of Pt and improve the performance of the Pt catalysts through the formation of a Pt–Pd alloy. In a previous study, using model catalysts, we demonstrated that mobile Pt species can diffuse on the surface and get trapped on PdO particles, leading to the formation of metallic Pt–Pd alloys in flowing air at 650 °C. In this work we explore the implications of this trapping phenomenon to powder catalysts. We physically mixed Pt/MgAl₂O₄ and PdO/La–Al₂O₃ catalyst powders and aged them at 800 °C in air. Mobile Pt species emitted from the Pt/MgAl₂O₄ migrated through the vapor phase and were trapped by PdO nanoparticles located on the La–Al₂O₃ support. Since the Pt moved from the MgAl₂O₄ support to the PdO, we infer that PdO is better at trapping Pt than the MgAl₂O₄ support. We also investigated the effect of PdO particle size on the trapping efficiency for Pt. It was found that small PdO particles were more effective, leading to smaller size of Pt–Pd particles as confirmed by electron microscopy, X-ray diffraction and reactivity for methane oxidation.

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1. Introduction

Pt is a precious metal (0.003 ppb in the earth's crust) and is among the most active elements for NO oxidation in diesel oxidation catalysts (DOCs). However, Pt nanoparticles (NPs) sinter when the catalysts are used at high temperature under oxidizing conditions [1]. The mechanism of sintering is Ostwald ripening [2], which results in the loss of active surface area and drop in reactivity after use. Due to the high cost and low abundance of Pt, it is important to develop strategies to improve the durability of Pt catalysts by slowing the rate of sintering of Pt. We have recently demonstrated that the formation of a volatile oxide of Pt plays a significant role in the degradation of Pt catalysts when heated in air at 800 °C [3]. The high vapor pressure of Pt oxides is a significant contributor to the rates of catalyst sintering. A recent report suggests that MgAl₂O₄ as a support could help slow the rates of Pt sintering because it is possible to stabilize small Pt particles due to a strong affinity between Pt and the (1 1 1) facets of the MgAl₂O₄ support [4]. This previous study found that after aging in air at 800 °C, a significant fraction of the Pt was present in the form of large particles as detected by XRD. The authors reasoned this growth of Pt occurred because of

the limited availability of suitable sites on the spinel to stabilize Pt. In this study we explore whether the presence of PdO might help to trap this mobile Pt that leads to the growth of large particles.

It is known that the addition of a second metal, for example Pd, leads to improvements in the durability of Pt catalysts, the mechanisms are still a subject of study [1,5]. Pd has a very low vapor pressure under oxidizing conditions due to the formation of the stable oxide PdO and we see very little sintering of Pd only catalysts when heated in air at 800 °C [3]. We have also found that the presence of Pt helps to keep Pd in metallic form [6], and the Pd helps to lower the rates of emission of Pt to the vapor phase [3]. When Pt nanoparticles were deposited on a planar model SiO₂ support as a separate phase, heating for only 2 min at 650 °C in air caused the formation of bimetallic PtPd particles [7]. This previous work demonstrates that Pt species are mobile and can be effectively trapped by PdO at high temperatures in air, forming bimetallic PtPd particles which are thermodynamically more stable [7].

The migration and vapor phase transport of precious metals in automotive exhaust catalysts has been documented in the literature. Cavataio et al. [8] pointed out that trace amounts of precious metals were transported from Pt-based DOC catalysts to the SCR catalyst, negatively impacting the performance of the SCR catalyst. Yu-Yao and Kummer [9] reported that they were able to prepare low concentration precious metal catalysts via vapor phase transport from a metal foil to an alumina or ceria-alumina support. The

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transport of precious metals has also been found to lead to formation of alloys and bimetallic nanoparticles, as in the case of physically mixed Pt and Pd [10] catalysts and also Pt, and Rh catalysts [11]. In this previous work, the results were influenced by the catalyst formulation, for example the same nominal ratio of Pt and Pd gave very different extent of volatilization and transport. The role of particle size and morphology was not explicitly studied.

The objective of the present work is to investigate the trapping capability of PdO by physically mixing Pt/MgAl₂O₄ and PdO/La–Al₂O₃ catalysts, followed by aging in flowing air at 800 °C. Detailed STEM-EDX analysis was used to investigate the location and composition of Pt-containing particles. We separately aged the PdO/La–Al₂O₃ to generate PdO particles of differing size, so the role of particle size on the trapping capability of Pt could be studied. Methane oxidation was used as a probe reaction and the results show that smaller PdO crystallites are more effective at trapping the mobile Pt, which appears to move from the spinel phase via vapor phase transport and is captured on the PdO particles.

2. Experimental

2.1. Catalyst preparation and aging

La-alumina was obtained from W.R. Grace (MI-386), contained 4 wt.% La₂O₃, and had a BET surface area of 176 m² g⁻¹. MgAl₂O₄ spinel support (surface area: 7 m² g⁻¹) was synthesized following the method reported in the literature [4]. The Pt/La–Al₂O₃ and Pt/MgAl₂O₄ catalysts (1 wt.% Pt) were prepared by incipient wetness by using an aqueous solution of chloroplatinic acid (8 wt.% H₂PtCl₆). The as-prepared catalyst materials were calcined at 450 °C for 5 h in flowing air.

The PdO/La–Al₂O₃ catalysts (2 wt.% Pd) were prepared by incipient wetness using a 10 wt.% palladium(II) nitrate solution in 10 wt.% nitric acid. This sample was subjected to different thermal pretreatment to vary the PdO particle size. The PdO/La–Al₂O₃ catalysts were calcined in air at 350 °C (6 h) and 800 °C (10 h and 50 h, respectively). These catalysts were denoted as PdO/La–Al₂O₃-1, PdO/La–Al₂O₃-2 and PdO/La–Al₂O₃-3, respectively.

To investigate the trapping capability of PdO on Pt with different PdO sizes, Pt/MgAl₂O₄ was physically mixed with the above three PdO/La–Al₂O₃ catalysts with a mass ratio of 1:1, respectively. The physical mixture was then aged at 800 °C for 10 h in flowing air (100 mL/min). For comparison purposes, monometallic Pt/MgAl₂O₄ and Pt/La–Al₂O₃ catalysts were also aged at 800 °C for 10 h in flowing air (100 mL/min).

2.2. Characterization

XRD patterns for the samples were recorded with a Rigaku Smart Lab diffractometer using Cu K_α radiation and a Ni filter. N₂ physisorption was performed on a Quantachrome Autosorb-1. Scanning electron microscopy (SEM) was performed on a Hitachi S-5200. High resolution transmission electron microscopy was performed using a JEOL 2010F microscope. The powders were deposited on holey carbon support films after being dispersed in ethanol.

2.3. Methane oxidation

Methane oxidation [12] was used as a probe reaction to investigate the reactivity of these catalysts. We selected this reaction since it operates under lean conditions, where metallic Pd easily transforms into PdO. Hence, the reaction is useful for determining the extent of Pt–Pd contact, since the bimetallic nanoparticles remain in metallic form under oxidizing conditions [6]. The catalytic activity for methane oxidation over the physical mixtures

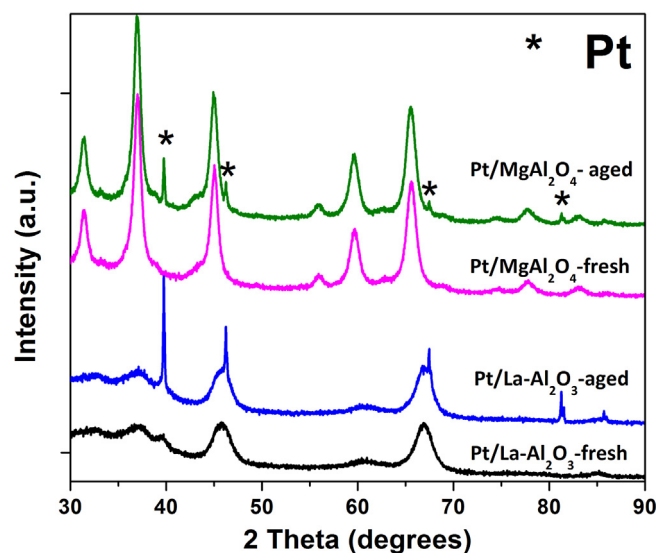


Fig. 1. XRD patterns of Pt nanoparticles supported on La–Al₂O₃ and MgAl₂O₄ before and after aging at 800 °C for 10 h in air. Scherrer analysis indicates the particle size of Pt >500 nm i.e., too large to be accurately determined by this technique.

(Pt/MgAl₂O₄–PdO/La–Al₂O₃) catalyst was measured in a plug-flow quartz tube reactor. A powder sample of 20 mg was placed in the middle of the reactor. Gas flow rates was measured by mass flow controllers. Reaction products were analyzed by an online micro-GC (Agilent 490). The reactant gas mixture contained 2% CH₄, 5% O₂ and He as balance. Light-off measurements were carried out with a heating rate of 2 K min⁻¹ from 100 °C to 600 °C, with a GHSV of 30,000 h⁻¹.

3. Results and discussion

3.1. Sintering behavior of Pt nanoparticles supported on MgAl₂O₄ and La–Al₂O₃ at high temperature in oxidation conditions

The sintering behavior of monometallic Pt nanoparticles supported on MgAl₂O₄ and La–Al₂O₃ was first investigated. The XRD patterns of Pt supported on MgAl₂O₄ and La–Al₂O₃ before and after aging are shown in Fig. 1. No diffraction peaks corresponding to Pt nanoparticles was found on the XRD patterns of the fresh Pt catalysts, indicating that Pt NPs are highly dispersed on the support. However, the sharp diffraction peaks corresponding to Pt crystallites are observed on the XRD patterns of Pt/MgAl₂O₄ and Pt/La–Al₂O₃ catalysts after aging. Calculation based on the Scherrer equation indicated that the average crystallite sizes of Pt after aging for both of the catalysts are larger than 500 nm. This means that the Pt catalysts on MgAl₂O₄ and La–Al₂O₃ sintered significantly suggesting that these supports do not stabilize Pt when exposed to high temperatures under oxidizing conditions.

The representative electron microscope images (SEM/TEM/STEM) of Pt/La–Al₂O₃ catalyst before and after aging in air are shown in Fig. 2. The Pt nanoparticles on the Pt/La–Al₂O₃ catalyst before the high temperature treatment are small and the Pt sizes are in the range of 1–5 nm before aging (Fig. 2a). However, after aging at 800 °C in air, micrometer-scale Pt particles (1–4 μm) are formed (Fig. 2b and c). These results confirm the observations of the Pt/La–Al₂O₃ via XRD indicating the severe sintering seen after aging the catalysts in flowing air for 10 h.

The representative TEM/STEM images of Pt/MgAl₂O₄ catalyst before and after aging in air are shown in Fig. 3. The Pt nanoparticle sizes on the Pt/MgAl₂O₄ catalyst are less than 1 nm in diameter before aging (Fig. 3a). After aging at 800 °C in air, we see

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