International Journal of Mass Spectrometry 377 (2015) 263–277

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Reprint of “Mass-selected supported cluster catalysts: Size effects on CO oxidation activity, electronic structure, and thermal stability of Pd_n/alumina ($n \leq 30$) model catalysts”☆

Matthew D. Kane, F. Sloan Roberts, Scott L. Anderson*

Department of Chemistry, The University of Utah, 315 S. 1400 E, Salt Lake City, UT, USA

ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form 17 June 2014
Accepted 19 June 2014
Available online 10 August 2014

Keywords:
Size-selected cluster
Catalysis
CO oxidation
Supported catalyst
Temperature programed reaction (TPR)
Steady state reactivity

ABSTRACT

An intense, mass-selected cluster source for preparation of model supported clusters is described, and results are presented for cluster size effects on CO oxidation activity for Pd_n clusters supported on alumina films grown on Re(0001) or Ta(110) single crystals. The electronic structure of the samples was probed by X-ray and UV photoelectron spectroscopy, and low energy ion scattering was used to probe binding morphology. The Pd_n activity was monitored via both steady state and temperature-programmed reaction (TPR) methods. In both cases, the samples appear to be stable in repeated reaction cycles for temperatures up to 600 K. In the TPR experiments, CO oxidation activity *per* Pd atom varied by ~40% between the most and least reactive clusters, while under steady state conditions, the activity varied by ~55%, but with a different pattern of activity vs. size. The difference in the effects of cluster size is attributed to the fact that TPR experiments were done under conditions where the rate-limiting step is oxygen activation, while the steady-state reactivity conditions were most sensitive to the strength of CO binding. Two distinct types of CO binding were observed and characterized by a combination of temperature-programmed desorption (TPD), and temperature-dependent ISS (TD-ISS).

1. Introduction

Catalysts are important in 35% of the world GDP [1], thus, it is not surprising that there is extensive fundamental and applied research aimed at improving catalytic activity and selectively [2–18]. Typical supported catalysts are quite complex and difficult to characterize in detail, and an important research thrust uses model catalysts to simplify the problem and allow important properties to be varied and measured in detail, to extract mechanistic insight. Among other approaches to tuning catalyst properties, using bi- or tri-metallic combinations [7,19–22], or varying the size of the catalytic metal particles are common [2,23–28]. Understanding the effects of particle size is complicated by the fact that there is typically a broad distribution of sizes present, and it is generally not possible to vary size independently, without also changing other properties such as metal loading or support structure. Consider gold nanocatalysts, which have received tremendous attention over the past decade, using a wide variety of approaches [17,29–33]. Much of the original work focused on the properties of Au nanoparticles in the 2–5 nm size range, because these were the obvious species detectable in conventional electron microscopy [34–37]. Planar model catalyst work suggested that smaller gold structures were reactive [38–45], and size-selected cluster deposition experiments similar to those discussed here, showed significant activity for gold clusters as small as seven or eight atoms [15,17,30,46–50]. Development of aberration-corrected scanning transmission electron microscopes has allowed features on the atomic scale to be detected in supported catalysts, and allowed studies showing that clusters in the ~10 atom size range are highly active under realistic conditions [51,52].

Preparation of catalysts by deposition of mass-selected cluster ions on well characterized supports, provides a powerful mechanistic tool, allowing studies where cluster size, composition, density, and impact energy can be varied independently. Cluster deposition has applications in catalysis, magnetic and electronic materials, as well as being useful in studying the fundamental properties of nanostructures. Our group has focused on exploring size-dependent correlations between catalytic activity and

---

DOI of original article: http://dx.doi.org/10.1016/j.ijms.2014.06.018.

☆ This article is a reprint of a previously published article. For citation purposes, please use the original publication details “*International Journal of Mass Spectrometry*” 370 (2014) 1–15.

* Corresponding author. Tel.: +1 801 585 7289; fax: +1 801 5816681.
E-mail address: anderson@chem.utah.edu (S.L. Anderson).

http://dx.doi.org/10.1016/j.ijms.2014.07.044
1387-3806/

physical properties such as cluster electronic structure and morphology, using CO oxidation to probe systems such as Au/TiO_2 [49], Pd/TiO_2(110) [6,24,53,54], Pd/Al_2O_3 [55,56], and Pt/Al_2O_3 [57]. We also recently observed a very strong size-dependent correlation between Pt electronic structure and electrocatalytic activity for Pt/glassy carbon, where some sizes showed the expected Pt redox and oxygen reduction activity, but other sizes efficiently catalyzed electro-oxidation of carbon by water [2]. The Heiz group has reported numerous studies of catalysis with recent work including CO oxidation kinetics over Pd clusters deposited on MgO [13,14,58–61], optical spectroscopy of deposited clusters and adsorbates [62,63], studies of oxide support thickness effects on cluster activity [15,64], Pt_n deposition on CdS nanorod films for photocatalysis studies [65], and STM studies of cluster mobility on graphene/Ru(0001) Moiré supports [66]. In collaboration with Arenz, this group has also reported studies of electrocatalytic activity of supported Pt clusters [67–71]. Harbich and co-workers have carried out STM and reactivity studies of deposited clusters, and recently reported studies focusing on the fundamentals of CO oxidation over Pt_n/TiO_2 [72,73], and of electrocatalysis, using an approach where Pt clusters are deposited directly on a solid electrolyte, allowing electrochemistry to be studied *in vacuo* [7,74]. The Vajda group has an active program where size-selected catalysts are studied in a variety of reactors, recently focusing on *in operando* studies using tools such as X-ray scattering, to probe chemistry under realistic reaction conditions [4,9,10,75–83]. Buratto and co-workers have used cluster deposition in conjunction with STM and theory to examine stability and reactivity of several types of clusters on TiO_2(110), with recent work focusing on vanadia clusters on titania [84]. Ganteför and co-workers developed another instrument combining cluster deposition with STM and used this for a number of studies of Au_n deposited on several supports [85–88]. This work has proceeded in collaboration with Kim and co-workers in Korea, recently focusing on gold chemistry under ambient conditions [32,89–91]. Watanabe and co-workers have an instrument that allows STM, XPS, and high pressure reactivity studies of size-selected model catalysts [92] and have reported studies of CO oxidation over Pt_n/TiO_2(110) [11,93] and correlations with core level binding energies. White and co-workers studied properties and reactivity of Mo_4S_6 deposited on Au(111) [94], and used two photon photoemission to probe charging of several different size and stoichiometry Mo_xS_y clusters on alumina supports [95]. Chorkendorff and co-workers have developed a program using mass-selected cluster deposition to study chemistry and morphology changes under both UHV and high pressure reaction conditions [96–98]. Recently, Bowen and co-workers have reported work on deposited clusters including stability of size-selected Mo nanoparticles on highly ordered pyrolytic graphite (HOPG) [99], and gold clusters supported on TiO_2 showing single atom sensitivity to reactivity for CO oxidation [100].

For the system studied here, CO oxidation over Pd/alumina, there has been a tremendous amount of relevant work that provides valuable mechanistic insight. Briefly, using Pd single crystals and other bulk surfaces, it had been shown that CO and O_2 combine to form CO_2 via a Langmuir–Hinshelwood mechanism that entails adsorbed CO reacting with adsorbed O atoms [101–105]. It was also shown that oxygen and CO compete for the same binding sites such that a 60% saturation dose of CO prevents dissociative binding of O_2 on Pd(110). The kinetics of the CO oxidation reaction over Pd single crystals [103–106] and Pd/alumina nanoparticle catalysts [107–111] have been discussed in detail. Furthermore, it was determined for room temperature experiments, that CO and O_2 have reasonably high sticking coefficients of 0.5 and 0.4, respectively [112]. For Pd(111) it was shown that for greater than ∼0.15 ML coverage of oxygen, dissociative adsorption of further oxygen became an activated process [113]. In the temperature-programmed reaction (TPR) experiments discussed below, the samples were exposed to O_2 prior to CO, to avoid CO poisoning. There has also been considerable previous work on Pd clusters/nanoparticles on alumina films. For example, Goodman and co-workers investigated the Pd cluster size needed to transition from nonmetallic to metallic characteristics, [114] as well as the adsorption and further oxidation of Pd clusters in the size range of 25–70 nm on powdered alumina surfaces [115,116]. The Freund group did similar studies for Pd nanoclusters in the 0.5–14 nm range deposited on alumina films grown on NiAl(110), examining particle growth [117] and CO binding via infrared spectroscopy, to probe charge transfer between the particle and the alumina support [118]. The self-limiting, 0.5 nm thick alumina film that grows on NiAl(110) when heated in O_2 has been used in numerous model catalyst studies. We previously attempted to study CO oxidation over size-selected Pd_n deposited on alumina/NiAl(110), but no reaction was observed [56]. Experiments by Shaikhutdinov et al. on CO oxidation over Pd nanoparticles grown on the same support showed that the problem was that the alumina film was too thin to act as an efficient diffusion barrier, allowing oxygen activated on the Pd clusters to react with the NiAl substrate, in preference to CO [114]. In the experiments below, thicker alumina films are grown by aluminum evaporation in an O_2 atmosphere, following methods developed to produce alumina films on Ta, Re, or Ru single crystals [119–121]. Epitaxial growth of alumina on Ta and Re crystals provides an chemically inert, thermally stable support which is ideal for the size-dependent mechanistic studies discussed below [55,57]. The alumina support isolates the Pd clusters from the underlying metal support, but the oxide also influences the chemistry. For example, as discussed below, both the overall reactivity and its size dependence is substantially different for Pd_n supported on alumina films vs. TiO_2(110), under identical conditions.

2. Experimental

2.1. The apparatus

The experiments were done in the vacuum system shown in Fig. 1, which has been briefly described previously [49,50,55,122], however, a number of changes have been made to improve operation. The system consists of two main sections: a cluster deposition source/beamline (top) and an ultra-high vacuum (UHV) surface preparation/analysis system (bottom). The coaxial laser vaporization cluster ion source is shown in detail in Fig. S1 of the supplementary information. The beam from a frequency-doubled Nd:YAG laser (30 Hz, 30–60 mJ/pulse) is focused on the Pd target through the cluster exit nozzle, creating a Pd-containing plasma. Approximately 300–500 ms before the laser pulse, helium is pulsed into the elliptical source volume using a piezoelectric pulsed valve (4500 Torr through a 1 mm orifice for 1 ms) to help confine and cool the plasma, leading to supersaturation and cluster formation. The cluster size distribution can be controlled to some extent by changing the source residence time, via interchangeable exit tubes of various lengths.

The Pd target is glued to a spring-loaded aluminum block, which is mounted to an *X*–*Y* translation stage, allowing the target to be rastered, so that vaporization occurs uniformly over the target area (∼1 cm × 2 cm). A target can be used for about 100 deposition experiments before becoming rough enough to seriously degrade source stability. The target is then simply sanded flat and reused until the laser begins to penetrate through to the glue layer. Two targets, each good for >300 depositions, can be fabricated from a single 99.9% Pd one ounce bullion bar, making the target cost negligible. A good seal and low sliding friction between the target and source body is critical, and for this purpose, a 0.1 mm thick Teflon gasket is bonded around the edge of the target. Motion of the *X*–*Y*