Journal of Catalysis 364 (2018) 166–173

Contents lists available at ScienceDirect

Journal of Catalysis

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

Water activation by single Pt atoms supported on a Cu_2O thin film

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ARTICLE INFO

Article history:
Received 15 January 2018
Revised 2 April 2018
Accepted 21 April 2018

Keywords:
Single atom catalysis
Platinum
Water activation
Water scrambling
Oxidized copper
Density functional theory
Temperature programed desorption

ABSTRACT

Recent advances in single atom catalysis have sparked interest in their use as low-cost and high-efficiency catalysts in a wide variety of reactions. One such reaction that has been heavily studied with single atom catalysts is the water gas shift reaction. In addition, water participates in a rich variety of other industrially important catalytic processes, such as steam reforming reactions. However, much debate surrounds the structure and activity of single atoms toward water gas shift chemistry. By taking a model study approach, we determine the influence of atomically dispersed Pt atoms on the activation of water. Using a thin film Cu_2O/Cu(1 1 1) support, water activation is probed via isotopic scrambling temperature programed desorption experiments. We determine that the presence of supported single Pt atoms on the thin Cu_2O film will facilitate the low-temperature activation of water. Theory offers a viable water scrambling pathway on the supported Pt atoms, detailing the dynamic relationship between water, the Pt atom, and the support. The results reveal that single Pt atoms are capable of O-H bond activation when water interacts with such a catalyst.

1. Introduction

Supported single atoms are a rapidly growing class of catalysts that have shown promise as highly active, selective, and inexpensive materials [1–3]. The water gas shift reaction catalyzed by supported single atoms has been particularly heavily studied [4–10]. Interestingly, the reaction has been found to display remarkably similar reactivity on a variety of active single atom and support combinations [4–8]. Pt is one of the catalytic elements found to be active for the water gas shift reaction [6,9]. The reactivity of Pt single atoms [6,9,10], Pt clusters [11–16], and Pt alloys [17,18] toward water gas shift catalysis have previously been studied. However, in those cases, the optimal structure of Pt for the water gas shift reaction has been widely debated, with arguments made both for and against Pt single atoms versus Pt nanoparticles [6,9,15,19,20]. Here, we take a model study approach, creating isolated Pt single atoms dispersed on a well-defined support, to address fundamental questions of structure and reactivity. We have previously used this approach to demonstrate the oxidation of CO by Pt single atoms [21], and now use a similar methodology to study the activation of water.

The model support used in this study is a thin film Cu_2O(1 1 1)-like layer known as the "29" oxide. The "29" oxide is reproducibly formed by controlled oxidation of Cu(1 1 1), forming a single layer oxide film on the surface [22–25]. The atomic structure of the "29" oxide has been previously investigated through a combination of scanning tunneling microscopy (STM) and density functional theory (DFT) [24,25], and guided by previous surface science work [26]. The proposed structure of the "29" oxide is made up of six hexagonal rings, consisting of linear O-Cu-O bonds, per surface unit cell [24]. Within five of these porous rings resides an additional O adatom bound to the Cu(1 1 1) substrate [24]. In order to first understand water adsorption on the "29" oxide support, previous surface science studies can serve as a guide. Water interactions on oxidized Cu also have catalytic implications, as Cu-based

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https://doi.org/10.1016/j.jcat.2018.04.024
0021-9517/

catalysts are used industrially for the low-temperature water gas shift reaction and methanol steam reforming [27–36]. Generally, interfacial water structures are very complex, and have been heavily studied due to their broad application in many technologies [37–39]. Studies on single-crystal metal oxides have found that water molecules generally dissociate at defect sites on oxides, and in certain cases cause the surface to become hydroxylated [37–43]. The "29" oxide surface is largely defect free, with a defect density of approximately 0.02% of a monolayer with respect to the Cu(1 1 1) surface [24], which facilitates non-dissociative water adsorption. Water adsorption on oxidized Cu substrates has been studied by spectroscopic techniques [30,44,45]. Under near-ambient pressures, small amounts of surface hydroxyls were detected upon water adsorption to polycrystalline Cu_2O thin films [30], and water exposure under vacuum conditions also caused hydroxyl formation at submonolayer coverages of O on Cu(1 1 1) [44]. However, continuous and more complete Cu_2O films, such as the "29" oxide, have shown no evidence of water dissociation [44]. Recently, cyclic water hexamers on partially oxidized Cu(1 1 1) studied by STM were found to be surprisingly stable for non-dissociative water adsorption [46]. These results are also in line with DFT calculations that conclude water dissociation to be unfavorable on intact Cu_2O(1 1 1) [47,48]. Further work suggests that defects are the only active sites for water dissociation on bulk Cu_2O(1 1 1) [44,49].

The primary focus of this work is to study the activity of Pt single atoms toward water activation. To understand water adsorption and activation on supported single atoms, we must first investigate water adsorption and desorption on the bare "29" oxide. With this information, the "29" oxide surface will serve as a model support to assess the activity of atomically dispersed Pt atoms. Furthermore, isotopic labeling of the "29" oxide provides a way to quantify the degree of water activation. This approach allows for accurate DFT modeling, and in combination with experiment, this work provides fundamental insight into water interactions on supported Pt single atoms and the role of the support.

2. Methods

2.1. Temperature programed desorption (TPD)

TPD experiments were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of $<1 \times 10^{-10}$ mbar. The chamber was equipped with a quadrupole mass spectrometer (Hiden) and the Cu(1 1 1) crystal was able to be cooled to 85 K with liquid nitrogen and resistively heated to 750 K. The Cu(1 1 1) crystal was cleaned by Ar^+ sputtering and annealing to 750 K. The "29" oxide film was formed by exposure to O_2 gas (Airgas, USP grade), or $^{18}O_2$ (Aldrich, 97%) for isotopic scrambling experiments, at a pressure of 5×10^{-6} mbar for 3 min at a sample temperature 650 ± 20 K. The formation of the "29" oxide was verified by low energy electron diffraction (OCI Vacuum Microengineering). Pt depositions were performed on a cooled "29" oxide sample held at 85 K, using a Focus GmbH EFM3 electron beam evaporator. One monolayer (ML) is defined as the packing density of Cu(1 1 1), 1.77×10^{15} atoms cm^{-2}. High precision leak valves allowed for accurate exposure of deionized water obtained from a Nanopure water system, which was further purified by first boiling the water (to reduce the amount of dissolved gas in the liquid) and then proceeding with freeze-pump-thaw cycles. The background pressure of water in the UHV chamber was also used as a deposition source of water for low coverage experiments. TPD experiments were performed with a linear heating ramp of 1 K s^{-1}. H_2 from the background was found not to adsorb or react with the surface under our experimental conditions.

2.2. Density functional theory (DFT)

To examine the atomistic behavior of the system in question, DFT calculations were performed in which the interaction of water with the "29" oxide was modeled. The "29" oxide model structure used in these calculations was taken from previous studies [24,25] and consists of 4 atomic layers of metallic Cu(1 1 1) on which a single Cu_2O layer was placed. This oxide thin film is made up of fused hexagonal rings, each with six Cu atoms and six O atoms, buckling with linear O-Cu-O bonds. Additionally, we found that five O adatoms placed in the center on the hexagonal rings on the exposed Cu (1 1 1) surface were necessary in order to reproduce the experimental STM images of the "29" oxide [24]. Note that during optimizations, the bottom two Cu layers were held fixed in their bulk positions and all other atoms where allowed to relax.

All DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP) [50,51], which employs the projector augmented wave (PAW) method to project the pseudo core-electron wavefunctions onto the atomic centers [52–54]. Standard PAW projection sets released prior to 2012 were used in these calculations for all atoms. A cutoff energy of 500 eV was used for the determination of the plane-wave basis set. Throughout all calculations, wavefunctions were converged until total energy changes were $<10^{-6}$ eV and geometries were considered optimized when all interatomic forces were <0.02 eV/Å. A $(1 \times 2 \times 1)$ Monkhorst-Pack grid was used to sample the Brillouin zone in all calculations. The exchange-correlation energy was treated under the generalized gradient approximation (GGA) using the optB88-vdW functional [55,56] to compute water adsorption energies on the "29" oxide to capture nonlocal interactions. The "29" oxide was modeled as described previously [24], by a $\sqrt{13}R46.1$ Å $\times$ $7R21.8$ Å supercell, with (1×1) repetition, consisting of an oxide layer on the Cu(1 1 1) surface with that was four layers thick, where the bottom two layers of the slab were kept fixed in their bulk positions. This supercell is nearly rectangular with approximate dimensions of 18 Å by 9 Å.

Adsorption energies presented here were calculated using DFT energies. The contribution from zero-point energetics has been assessed in the Supplementary Content and is deemed negligible. Reaction barriers were also computed in VASP using the climbing image nudged elastic band (CINEB) [57,58] method to determine the transition state structure along with the associated reaction pathway energetics. Force optimizations along the pathway were handled using the fast inertial relaxation engine (FIRE) algorithm [59,60]. The Perdew-Burke-Ernzerhof (PBE) functional [61] was employed during reaction barrier calculations for all initial, transition, and final states, which optimized computational efficiency. All transition state structures were verified to have a single imaginary mode through vibrational analysis, with the wavefunction convergence criteria set to 10^{-8} eV and finite difference step sizes of 0.01 Å for the Hessian matrix construction. During the vibrational calculations, all copper layers were held fixed and vibrational modes corresponding to the "29" oxide layer, Pt atom, and adsorbed species were computed. The vibrational analysis was performed in part using homemade programs to process force outputs so as to create and diagonalize the dynamical matrix (following symmetrization), which allowed for parallelization of the necessary quantum chemical calculations.

3. Results and discussion

The desorption of water from the "29" oxide surface over a range of initial water coverages is shown in Fig. 1A, where 1 ML is defined as the saturation of the monolayer desorption peak. On weak binding metallic surfaces, such as Cu(1 1 1), water growth