Graphical Abstract:

On the Functional Role of the Cerium Oxide Support in the $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ Catalyst for CO Oxidation

Jacob Good,[†] Paul N. Duchesne,[‡] Peng Zhang,[‡] William Koshut,[†] Meng Zhou,[†] and Rongchao Jin^{†*}

Abstract

The catalytic oxidation of carbon monoxide to carbon dioxide by gold nanoclusters loaded onto cerium oxide supports is an important reaction that has been increasingly tailored for use in hydrogen fuel cells. It has been known that there are simultaneous mechanisms that involve coordination of both the dioxygen and carbon monoxide to the gold, as well as one in which the dioxygen is contributed in the form of lattice oxygen while the gold still coordinates the carbon monoxide. The latter has been shown to be the more potent, and it is for this reason that modulating the cerium oxide support is of vital interest. The present work provides compelling evidence that the rate-limiting step in this process is the coordination of the lattice oxygen. Exploratory studies of the control of this step via doping the cerium oxide support are also presented.

Keywords: Gold nanocluster, cerium oxide, doping, catalytic oxidation

1. Introduction

Since the pioneering work of Haruta et al in the 1980s, gold nanoparticles have been the subject of much interest in the field of catalysis [1]. The original discovery by the Haruta group entailed the oxidation of carbon monoxide by gold nanoparticles on various metal oxide supports [1]. In the field of nanoscience, a recent research goal has been developing methods of synthesizing well defined gold nanoclusters containing a precise number of gold atoms [2-11] (as opposed to the polydisperse-sized ones [1]). These clusters are stabilized at precise atomic counts by protecting ligands such as thiolate [3]. In terms of the catalytic application of such gold clusters, their precise nature allows for precise analysis of the underlying mechanism of the activity [4-11]. Moreover, ligand-protected gold nanoclusters possess greater longevity than unprotected ones, a quality highly desirable for practical application.

A heterogeneous catalyst is typically composed of active particles adsorbed on an appropriate support. Cerium oxide has been employed as a support in a wide range of oxidative catalytic reactions due to its high propensity towards releasing and adsorbing large quantities of oxygen [5]. This reversible uptake and release of oxygen causes an oxidation state conversion. The cerium oxide support also aids in the catalysis of the oxidation of carbon monoxide by donating lattice oxygen to the carbon monoxide adsorbed on the gold nanocluster. Transition and rare-earth metals doped into the cerium oxide lattice primarily facilitate the release or retention of oxygen; consequently, this modulates the chemical potential between the Ce^{4+} and Ce^{3+} states through various physicochemical properties of the additives. Due to incongruent ionic radii, electronegativity, or ionic charge, the dopants may induce structural strain in the cerium oxide lattice, potentially producing more oxygen vacancies or reactive morphological facets [12,13]. These oxygen vacancies are produced by the ejection of an oxygen atom from the ceria lattice, reducing two Ce^{4+} ions at the site of oxygen ejection to Ce^{3+} . Intuitively, the Ce^{3+} sites are able to accommodate the incoming oxygen species, but both the Ce^{3+} and the Ce^{4+} sites are capable of participating in different reactive steps, due to their propensities towards reduction and oxidation between cerium oxidation states, respectively. These differences can be assessed by spectroscopy [14,15],

voltammetry [16], and theoretical modeling [17]. The analysis by doping is made easier by the fact that the cerium oxide is not distorted from the cubic fluorite crystal structure, even up to 20% dopant content [18]. However, because of their prominent juxtaposition, it has been unclear in many chemical reactions, with carbon monoxide oxidation being no exception, whether the oxygen vacancy or the Ce^{3+} acts as the reactive site [19,20].

More specifically, a vital contribution of the support is, in fact, the coordination of oxygen for oxidation of carbon monoxide (CO). Two prominent mechanisms are generally suggested to take place during CO oxidation catalysis: the Mars-Van Krevelen mechanism and the Langmuir-Hinshelwood mechanism [21]. If a small quantity of thiolate ligands is removed (e.g. at the cluster/ CeO_2 interface, Scheme 1), then the Mars-Van Krevelen mechanism is active and indeed it has been confirmed that this mechanism is most prominent, in which oxygen from the CeO_2 lattice rather than atmospheric oxygen is the source of the oxygen and the CO is coordinated by the nanocluster [21]. Wu et al found that the Mars-Van Krevelen mechanism operates about three times as fast as the Langmuir-Hinshelwood mechanism [21]. The depleted lattice oxygen atoms are then replenished by atmospheric oxygen. If further dethiolation occurs due to a higher temperature of pretreatment (Scheme 1), the Langmuir-Hinshelwood mechanism [22] may occur; in this mechanism, both the carbon monoxide and the atmospheric oxygen are coordinated by the gold nanocluster.

Scheme 1. Mechanisms of both the Mars-Van Krevelen and the Langmuir-Hinshelwood pathways, opened up by dethiolation.

The activation energy barrier for the CO oxidation reaction has been shown to depend on stoichiometry and, in turn, the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio. Hence, one could analyze the effect of the ratio of such components in a given system [23,24]. The redox process can be affected by

additives into CeO₂. It would be of interest to study whether the concentrations and ratios of the ionic Ce species can be used as indicators of catalytic activity. In addition, because certain ionic species are involved in certain steps, their concentrations and ratios may offer useful implications for the rate-limiting steps.

In this work we choose to study the Au₃₈(SR)₂₄ (where SR = -SCH₂CH₂Ph) nanocluster as the catalytic particles for the current work. One of the most prominent functions of the gold nanocluster is to coordinate the CO for catalysis. Within a single Au₃₈(SR)₂₄ nanocluster, there are differently charged gold atoms: Au⁺, partial positive (Au^{δ+}), neutral (Au⁰), and partial negative (Au^{δ-}) sites. It has been confirmed that the CO adsorbed at the partial positive site is most readily oxidized to CO₂ [21]. To investigate the Ce³⁺/Ce⁴⁺ effect, we introduce several dopants including Samarium, Lanthanum, Yttrium, and Gadolinium. The concentrations of Ce³⁺ and Ce⁴⁺ and their ratios are correlated with catalytic activity.

2. Experimental

2.1. Synthesis of Au₃₈(SR)₂₄ nanoclusters

The synthesis of atomically precise Au₃₈(SR)₂₄ follows the literature approach developed by Qian et al [25]. Briefly, the synthesis starts from gold salt (HAuCl₄), which is reduced/complexed by glutathione into a gold(I)-glutathione polymer. The polymeric intermediate was further reduced by NaBH₄ to polydisperse glutathione-protected nanoclusters; finally, the crude nanoclusters were subjected to a size-focusing process under heat and in the presence of excess 2-phenylethanethiol to form the thermodynamically stable, 38-atom nanocluster with molecular purity [25].

2.2. Synthesis of Supports

The general procedure for synthesizing cerium oxide involved the dissolution of metal nitrate salts in an aqueous solution and induced “assisted coprecipitation” by a complexing agent. The precipitate was washed, dried, calcined, and loaded with gold nanoclusters at 0.3 wt%. Detailed syntheses for the various CeO₂ supports are as follows.

The CeO₂ support reported by Nie *et al* [26] was synthesized by carbonate coprecipitation in the present work and used for comparison with the other types of CeO₂ supports bearing various dopants.

For the CeO₂ doped by La, Y, Gd, and non-doped one, we adopted a literature protocol [27]. Oxalic acid was used as a coprecipitating agent. 120mL of a 0.4M aqueous oxalic acid solution was prepared with a pH of roughly 1.3. A 0.2M nitric acid solution of pH ~2.6-3.3 was prepared and used to dissolve 0.0114 mol (4.9675g) of cerium nitrate hexahydrate and 0.00286 mol of the dopant (1.1616g lanthanum nitrate, 1.2405g yttrium nitrate tetrahydrate, 1.6136g gadolinium nitrate hexahydrate, or more cerium nitrate hexahydrate, in the case of pure undoped support) in the minimum quantity necessary. The metal and nitric acid solution was then added dropwise with stirring to the oxalic acid solution, causing the ceria to precipitate out in a white powder. The precipitate was vacuum filtered and washed with copious amounts of water to remove the remaining acids and nitrates. The precipitate was dried in a vacuum overnight and then calcined for one hour at 600 °C. 150mg of the ceria was then loaded with 0.5mg of the Au₃₈(SR)₂₄ catalyst (determined by UV-vis spectroscopy) by dissolving the nanoclusters in 1mL of dichloromethane, mixing them with the ceria, allowing the closed vial of this mixture to sit overnight, and then evaporating the solvent and drying the now-loaded Au₃₈(SR)₂₄/ceria in a vacuum.

The Samarium-doped cerium oxide, along with its analogous pure cerium oxide, were prepared using tetramethylethylenediamine as a coprecipitating agent [28]. The reason for the deviation from the above procedure employing oxalic acid was in order to make a full comparison with literature employing this procedure. First, 2.084g of cerium nitrate hexahydrate and 0.533g of samarium nitrate hexahydrate were dissolved in 60mL of deionized water. 2.7mL (that is, three times the mole count of the metal ions) of tetramethylethylenediamine was added dropwise and with stirring to the metal solution, at which point the white powder precipitated out. This mixture was allowed to stir overnight. Next, the supernatant was decanted and the precipitate was washed with water. Because the particles precipitated with this procedure were much finer than those synthesized with oxalic acid, it may be necessary to centrifuge instead of using a filter paper. The precipitate was dried

overnight and then calcined at 600 °C for two hours. Finally, the support (powder) was mixed with a CH₂Cl₂ solution of the nanoclusters; after overnight, the solvent was decanted and the Au₃₈(SR)₂₄/support was dried as described above.

2.3. Catalytic Evaluation and Characterization

The catalytic activity of each gold-loaded ceria sample was measured using a fixed-bed gas reactor feeding into a gas chromatograph. The sample was loaded into a glass tube cell and then pretreated (heated at 150°C) for two hours. The temperature was then set to points between 25°C and no higher than 180°C, so as to avoid catalyst aggregation. Gases were introduced into the fixed bed reactor at proportions of 0.068mL/s (for O₂ gas), 0.020mL/s (CO), and 0.56mL/s (helium). After passing over the catalyst, the resultant gas was fed into the gas chromatograph, separated on a carbon molecular sieve column, and analyzed on a thermal conductivity detector. Oxygen eluted first at around 8 minutes, then CO around 10 minutes, and finally CO₂ around 45 minutes. Actual times may vary with the flow rate. The areas of the signals were then integrated and scaled by their corresponding conversion coefficients for detector response (2.38 for CO and 2.08 for CO₂). These total quantities were then used to determine the percent of CO conversion.

X-ray powder analysis of the catalysts was performed on a Rigaku Theta/Theta X-Ray Diffractometer equipped with a Copper Target Tube for an X-Ray source (1.52 angstroms). X-ray photoelectron spectroscopy (XPS) analysis of the catalyst samples was conducted on a Multilab ESCA2000 (Thermo VG Scientific). An Al K_α source for X-Rays was used (1486.6 eV) with a pass energy of 30 eV, which affords a resolution of ~1eV. An energy step of 0.1eV, a dwell time of 1s, and a spot size of 0.6mm were used.

3. Results

The atomic structure of a fully thiolated Au₃₈(SCH₂CH₂Ph)₂₄ nanocluster is shown in Figure 1, which was determined by X-ray crystallography [29]. The cluster comprises a biicosahedral Au₂₃ inner core (resembling a rod) and two kinds of surface-protecting motifs

including -SR-Au-SR- (three total) and -SR-Au-SR-Au-SR- (three on one end of the Au₂₃ rod and another three on the other end of the rod).

Fig. 1. X-ray crystallographic structure of the Au₃₈(SCH₂CH₂Ph)₂₄ nanocluster. Top: total structure; bottom: the Au₃₈S₂₄ framework only, with the carbon tails omitted. Color codes: Grey: carbon, Magenta: gold, Yellow: sulfur, Blue: surface motif gold.

The CeO₂ and doped ones are loaded with Au₃₈(SR)₂₄ nanoclusters at 0.3 wt%. In order to boost the activity, the catalysts were pretreated for two hours at 150°C in oxygen flow [30]. We previously confirmed that the surface ligands were still present on the cluster surface, evidenced by Raman, IR and other analyses [30,31], but precise quantification of the percentages of the remained and removed ligands was difficult.

From initial observations of the catalytic activity of each cluster-loaded support, a clear trend appeared between compositions. The reaction temperature then ranged from 60°C to 180°C, going no higher to prevent total desorption of protecting ligands (occurring between 200-250 °C [25]), which might induce aggregation. Since the CO oxidation reaction temperature is kept below 200 °C (the onset temperature of ligand desorption), the clusters are stable.

3.1. Comparison of undoped CeO₂ supports prepared by various methods.

Pure cerium oxides (i.e. undoped) allow comparison of synthetic methods when comparing functionality, and also allows for unambiguous reference to the structural qualities such as facet exposure or defect quantification. In this work four types of pure CeO_2 are compared, including the commercial one and three others prepared by using oxalic acid, carbonate, and tetramethyl-ethylenediamine (TMEDA) as the respective coprecipitating agent.

Figure 2 shows the catalytic activity of each pure cerium oxide with $\text{Au}_{38}(\text{SR})_{24}$ loaded at 0.3wt%. With the commercial CeO_2 as a reference, one can see that the pure cerium oxide coprecipitated with oxalic acid exhibited the highest degree of catalytic activity enhancement, followed by carbonate-precipitated CeO_2 and then the TMEDA-precipitated one. This result is interesting as it implies that the surface properties (e.g. defects) of CeO_2 prepared by different methods are important in the catalytic system. It is likely that the coprecipitation method contributes to the structural aspects of CeO_2 necessary for catalysis. The mechanism of CeO_2 formation may involve interactions between coprecipitation agents, such as through hydrogen bonding to coordinate ions close to each other. It may also operate through abstraction of hydrogen ions from the water in solution to produce reducing hydroxide ions. Lastly, the degree of steric hindrance between coprecipitating agents may influence the production of defects, as they might not be able to coordinate cerium and oxygen atoms with perfect replication in a fixed pattern. Since plain CeO_2 (i.e. without gold clusters) does not exhibit appreciable activity in our investigated temperature range ($<180^\circ\text{C}$), the above observation indicates the important role of the CeO_2 /cluster interfaces. Of note, the CeO_2 samples exhibit considerable activity at 300°C and higher.

Fig. 2. Catalytic activities of the pure cerium oxide supports loaded with $\text{Au}_{38}(\text{SR})_{24}$ nanoclusters.

3.2. Comparison of doped CeO_2 supports.

To further gain insight into the functional role of CeO_2 in the catalytic reaction, we further prepared cerium oxides with 20% samarium, lanthanum, yttrium, and gadolinium dopant contents. A 20% dopant content was selected because the cubic fluorite crystal structure is still retained at this concentration [27]. The catalytic activity of each of these supports is shown in Figure 3. Lanthanum, yttrium, and gadolinium dopants all exhibit decreased catalytic activity relative to the pure cerium oxide corresponding to its oxalic acid procedure (Fig 3A). With respect to Samarium doping, the reference CeO_2 sample was prepared by using TMEDA coprecipitating method [28]; following a similar procedure the Sm-doped CeO_2 was prepared and the cluster-loaded sample exhibits a slightly increased catalytic activity with respect to the corresponding pure support (Fig 3B).

Fig 3. Catalytic activities of 20% doped cerium oxides. A) La, Y, Gd doped and pure CeO₂ (all prepared by the oxalic acid coprecipitation method), B) Sm doped and pure CeO₂ samples (both prepared with TMEDA). All supports are loaded with 0.3wt% Au₃₈(SR)₂₄ nanoclusters.

3.3. X-Ray Photoelectron Spectroscopy

We further performed quantitative analysis of the dopant and Ce³⁺/Ce⁴⁺ atomic percentages by XPS. A representative XPS spectrum can be seen in Fig 4, in which both Ce³⁺ and Ce⁴⁺ can be clearly identified. These quantities were determined by fitting a Gaussian-Lorentzian curve proportional to the intensity of each peak, the areas of which were then integrated and scaled according to the relative sensitivity factor for each element/oxidation state. The relative abundance of each element/oxidation state was finally determined by taking the respective peak area and dividing it by the total area of all peaks. It is important to note that the shake-off peaks at *ca.* 886 eV and 903 eV are not representative. In addition to their relative proportions, it was also determined that all three dopants were present in the 3+ oxidation state. Because extracting such information was not trivial, this process required each oxidation state of Ce to have constraints on peak width (equal full widths at half-maximum), area (3:2 ratio for 3d^{5/2} and 3d^{3/2}, respectively), and relative position (based on literature peak separation, for Ce⁴⁺ only). This method is consistent with previously published analyses of CeO₂ materials [32].

Fig 4. X-Ray photoelectron spectrum of pure cerium oxide coprecipitated with oxalic acid. Signals are fitted with Gaussian-Lorentzian curves.

As can be seen from Table 1, the lanthanum, yttrium, and gadolinium dopants in the oxalic acid coprecipitated ceria supports largely replaced the Ce^{4+} ion sites in the lattice rather than the Ce^{3+} sites. This substitution of the 4+ site was unexpected, considering that the dopants adopt a 3+ oxidation state and would normally replace Ce^{3+} for the isoelectric reason. Furthermore, a decrease in Ce^{3+} site concentration was reported with Samarium doping in the tetramethyl-ethylenediamine coprecipitated support [20].

Table 1

Compositional content of the cerium oxide supports as determined by XPS.

Sample	% Ce^{3+}	% Ce^{4+}	% Dopant	$\text{Ce}^{4+}/\text{Ce}^{3+}$	Ion radius (Å)
Non-Doped	12.5	87.5	none	6.97	1.110 (Ce^{4+})
La-Doped	9.7	63.5	26.6	6.44	1.300 (La^{3+})
Y-Doped	11.6	65.7	22.7	5.65	1.159 (Y^{3+})
Gd-Doped	13.8	53.7	36.5	3.88	1.193 (Gd^{3+})

By correlating with the catalytic activity, we found that the activity is proportional to the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio of each loaded support. Non-doped ceria showed the highest activity, followed by lanthanum-doped ceria, yttrium-doped ceria, and lastly gadolinium-doped ceria. This is the same ordering of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio. The results indicate that cerium ions are, both individually and in tandem, significant components in the catalytic cycle. The Ce^{3+} site is where atmospheric oxygen is integrated into the lattice. The Ce^{4+} site coordinates the lattice oxygen to react with the carbon monoxide that is coordinated by the gold nanocluster. Together, the Ce^{3+} and Ce^{4+} sites form a reversible redox couple allowing this cycle to take place upon atmospheric oxygen integration and release.

3.4. X-Ray Diffraction

The identity of the unit cell is a possible component for coordinating oxygen in the catalytic cycle and ought to be considered. Pure CeO_2 has a cubic fluorite crystal structure and it is largely very stable as such. However, the quantity of the dopant necessary to distort the crystal structure varies depending on the dopant. For a solid solution of iron oxide and cerium oxide coprecipitated in aqueous solution, the cubic fluorite phase is maintained up to 50 mole% iron [33-35]. The force exerted by dopants takes the form of stress and strain on the crystal lattice. This strain may result in the creation of oxygen vacancies and substitutions of dopants may result in fewer Ce^{3+} sites, both of which are potential influences on catalytic activity [36-39]. For this reason, the crystal structure ought to always be considered when doping the cerium oxide support.

X-Ray Diffraction was used to determine the structure of the supports (Fig 5), including the pure cerium oxides coprecipitated by oxalic acid (labeled “pure” in the figure) and by carbonate (labeled “Nie” [26]) and with each dopant coprecipitated by oxalic acid (La-doped, Y-Doped, and Gd-Doped). There is not significant difference in either diffraction angle or peak width between the different catalysts under investigation, indicating that the crystal structure of CeO_2 is not affected by doping. Some differences are observed in the relative signal intensity, which suggests differences in facet prominence, but a change in either diffraction angle or full-

width at half-maximum would be expected if this facet redistribution were significant enough to cause important crystal structure changes. No diffraction peaks for the oxides of dopant elements (e.g. Y_2O_3 , La_2O_3 , Gd_2O_3) are found.

Fig 5. X-Ray diffraction spectra of the pure cerium oxides coprecipitated by oxalic acid (labeled “pure” in the figure) and by carbonate (labeled “Nie”) and with each dopant coprecipitated by oxalic acid (La-doped, Y-Doped, and Gd-Doped).

4. Discussion

The catalytic activity of the two tetramethylethylenediamine samples showed a unique pattern of activity with increased dopant concentration. It has been debated in many chemical and biological reactions whether it is the Ce^{3+} or the oxygen vacancy that acts as the reactive center, because the ejection of an oxygen to produce an oxygen vacancy necessarily also reduces the Ce^{4+} at that site to Ce^{3+} . However, these cerium oxides have previously been characterized in literature as to their elemental and ionic compositions [20]. It has been shown that the pure cerium oxide has 21% of its metal in the form of Ce^{3+} , whereas when 20% of the metal is doped with samarium, that number drops to 6% Ce^{3+} , showing that samarium largely substitutes the Ce^{3+} sites [20], which is sensible considering that the 4+ oxidation state is highly

unfavorable for samarium. With that said, the 20% samarium doped cerium oxide still showed a noteworthy increase in activity with respect to the pure cerium oxide synthesized by tetramethylethylenediamine coprecipitation (see Fig 3B). The fact that an increased catalytic activity was observed despite the great decrease in Ce^{3+} sites proves that the Ce^{3+} ion is not critical in the CO oxidation and that the benefits provided by the cerium oxide support can be replicated by other supports, provided that the qualities necessary can also be replicated.

Probably the most telling data obtained thus far is from the XPS results. As shown above in Fig 4 and Table 1, a strong correlation has been shown between the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio and the catalytic activity of each loaded support. Pure oxalic acid coprecipitated ceria has greater activity than lanthanum doped ceria, which has greater activity than yttrium and gadolinium doped ceria. This activity trend is also the same order that is seen in the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio. If several steps of logic are followed, three critical and impactful conclusions can be drawn.

First, based upon our data, observing that the Ce^{4+} sites were replaced by dopants and the catalytic activity was lowered we can infer the necessity of these sites in the catalytic cycle; thus, we conclude that the coordination of the lattice oxygen with the carbon monoxide is the rate limiting step in this catalytic cycle. Ce^{4+} is bound to the lattice oxygen and the dopants replaced primarily the Ce^{4+} ions. The lattice oxygen is employed to oxidize the carbon monoxide in the Mars-Van Krevelin mechanism, and all dopants in the oxalic acid coprecipitated ceria series (La, Y, and Gd) resulted in lower catalytic activity because the reduction to lower states of the dopant metals by ejecting oxygen is less favorable and thus, these doped sites are less reactive towards oxidation of carbon monoxide.

The second conclusion can be drawn by contrasting the newly collected data with previous literature data regarding ionic composition from XPS [20]. The previous literature reported that as the samarium concentration was increased, the Ce^{3+} concentration decreased, indicating that samarium strongly prefers to replace the Ce^{3+} sites over the Ce^{4+} sites. This stands in contrast to the dopants used in the present experiment, which replaced the Ce^{4+} sites over the Ce^{3+} sites. The Sm-doped ceria is the only loaded support which shows an increase in activity relative to the pure support made by the same coprecipitating agent. Therefore, it is

this alternate substitution that accounts for the increased activity, which also suggests that the integration of atmospheric oxygen is significantly easier than the coordination of lattice oxygen with carbon monoxide. This also confirms the above conclusion that decreasing the Ce^{3+} concentration and implicitly increasing the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio increases the catalyst activity, which is shown in this paper.

Finally, working with Mars-Van Krevelen mechanism as the dominant mechanism for CO oxidation, it is confirmed that the rate limiting step is the coordination of lattice oxygen to the carbon monoxide by the Ce^{4+} site. When this ion is replaced by another ion less conducive towards reversible oxidation/reduction, it is also less likely to release oxygen for oxidizing the carbon monoxide and reducing the dopant metal site. In contrast, the cerium is able to both release oxygen from the lattice and incorporate atmospheric oxygen to replenish the supply of lattice oxygen.

5. Conclusions

The foremost conclusions of the research presented herein are each related to the process qualities of the CO oxidation. The first is the identification of the rate limiting step (the coordination of lattice oxygen to CO which itself is coordinated by the gold nanocluster) in the catalytic conversion of CO to CO_2 by gold nanocluster-loaded cerium oxide. The second is the determination of the substitution preferences and behavior of lanthanum, yttrium, gadolinium, and samarium as dopants. By identifying both the rate limiting step and its primary hindrance, supports can be further tailored towards easing this step. This will be approached more easily now that the behavior of dopants has been established. Future work would entail investigating what atomic factors determine which ion(s) the dopant is prone to substituting. This substitution may be dependent on the coprecipitating agent or the dopant itself, and can be investigated using a simple survey synthesis with XPS follow-up. For mechanism analysis, it can be determined what the mechanism of oxygen adsorption is on the support by employing mixed isotopes of dioxygen and observing any recombination. Given the presence of ligand on

the Au₃₈ cluster, it is of potential interest to investigate the ligand dependence of the catalytic activity of Au₃₈. Future work on Au₃₈ with different ligands will be pursued.

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References

- [1] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide, *J. Catal.* 115 (1989) 301-309.
- [2] G. Li, R. Jin, Atomically precise gold nanoclusters as new model catalysts, *Acc. Chem. Res.* 46 (2013) 1749–1758.
- [3] R. Jin, Atomically precise metal nanoclusters: stable sizes and optical properties, *Nanoscale* 7 (2015) 1549–1565.
- [4] C. Lavenn, A. Demessence, A. Tuel, Atomically well-defined Au₂₅(SR)_{17/18} nanoclusters deposited on silica supports for the aerobic epoxidation of trans-stilbene, *Catal. Today* 235 (2014) 72-78.
- [5] G. Li, R. Jin, Atomic level tuning of the catalytic properties: doping effects of 25-atom bimetallic nanoclusters on styrene oxidation, *Catal. Today*, 2016, doi:10.1016/j.cattod.2015.11.019.
- [6] S. Xie, H. Tsunoyama, W. Kurashige, Y. Negishi, T. Tsukuda, Enhancement in aerobic alcohol oxidation catalysis of Au₂₅ clusters by single Pd atom doping, *ACS Catal.* 2 (2012) 1519-1523.
- [7] J. Liu, K.S. Krishna, Y.B. Losovyj, S. Chattopadhyay, N. Lozova, J.T. Miller, J.J. Spivey, C.S.S.R. Kumar, Ligand-stabilized and atomically precise gold nanocluster catalysis: a case study for correlating fundamental electronic properties with catalysis, *Chem-Eur. J.* 19 (2013) 10201-10208.
- [8] A. Kogo, Y. Takahashi, N. Sakai, T. Tatsuma, Gold cluster-nanoparticle diad systems for plasmonic enhancement of photosensitization, *Nanoscale* 5 (2013) 7855-7860.
- [9] H. Yamamoto, H. Yano, H. Kouchi, Y. Obora, R. Arakawa, H. Kawasaki, N,N-dimethylformamide-stabilized gold nanoclusters as a catalyst for the reduction of 4-nitrophenol, *Nanoscale* 4 (2012) 4148-4154.
- [10] M.B. Li, S.K. Tian, Z. Wu, Catalyzed formation of alpha,beta-unsaturated ketones or aldehydes from propargylic acetates by a recoverable and recyclable nanocluster catalyst, *Nanoscale* 6 (2014) 5714-5717.
- [11] G. Li, H. Abroshan, Y. Chen, R. Jin, H. Kim, Experimental and mechanistic understanding of aldehyde hydrogenation using Au₂₅ nanoclusters with Lewis acids: unique sites for catalytic reactions, *J. Am. Chem. Soc.* 137 (2015) 14295-14304.
- [12] G. Avgouropoulos, M. Manzoli, F. Boccuzzi, T. Tabakova, J. Papavasiliou, T. Ioannides, V. Idakiev, Catalytic performance and characterization of Au/doped-ceria catalysts for the preferential CO oxidation reaction, *J. Catal.* 256 (2008) 237-247.
- [13] C. Castellarin-Cudia, S. Surnev, G. Schneider, R. Podlucky, M.G. Ramsey, F.P. Netzer, Strain-induced formation of arrays of catalytically active sites at the metal–oxide interface, *Surf. Sci.* 554 (2004) L120-L126.
- [14] A. Pfau, K. D. Schierbaum, The electronic structure of stoichiometric and reduced CeO₂ surfaces: an XPS, UPS and HREELS study, *Surf. Sci.* 321 (1994) 71-80.
- [15] F. Larachi, J. Pierre, A. Adnot, A. Bernis, Ce 3d XPS study of composite Ce_xMn_{1-x}O_{2-y} wet oxidation catalysts, *Appl. Surf. Sci.* 195 (2002) 236-250.
- [16] Z. Xie, F. Xiong, D. Zhou, Study of the Ce³⁺/Ce⁴⁺ redox couple in mixed-acid media (CH₃SO₃H and H₂SO₄) for redox flow battery application, *Energy & Fuels* 25 (2011) 2399-2404.
- [17] A. Migani, K.M. Neyman, F. Illas, S. T. Bromley, Exploring Ce³⁺/Ce⁴⁺ cation ordering in reduced ceria nanoparticles using interionic-potential and density-functional calculations, *J. Chem. Phys.* 131 (2009) 064701.

- [18] S. Patil, S. Seal, Y. Guo, A. Schulte, J. Norwood, Role of trivalent La and Nd dopants in lattice distortion and oxygen vacancy generation in cerium oxide nanoparticles, *Appl. Phys. Lett.* 88 (2006) 243110.
- [19] C.T. Campbell, C.H. Peden, Oxygen vacancies and catalysis on ceria surfaces, *Science* 309 (2005) 713-714.
- [20] I. Celardo, M.D. Nicola, C. Mandoli, J.Z. Pedersen, E. Traversa, L. Ghibelli, Ce^{3+} ions determine redox-dependent anti-apoptotic effect of cerium oxide nanoparticles, *ACS Nano* 5 (2011) 4537-4549.
- [21] Z. Wu, D.E. Jiang, A.K. Mann, D.R. Mullins, Z.A. Qiao, L.F. Allard, C. Zeng, R. Jin, S.H. Overbury, Thiolate ligands as a double-edged sword for CO oxidation on CeO_2 supported $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ nanoclusters, *J. Am. Chem. Soc.* 136 (2014) 6111-6122.
- [22] M.C. Kung, R.J. Davis, H.H. Kung, Understanding Au-catalyzed low-temperature CO oxidation, *J. Phys. Chem. C* 111 (2007) 11767-11775.
- [23] M. Nolan, J. E. Fearon, G.W. Watson, Oxygen vacancy formation and migration in ceria, *Solid State Ionics* 177 (2006) 3069-3074.
- [24] A. Trovarelli, Structural Properties and Nonstoichiometric Behavior of CeO_2 , in *Catalysis by Ceria and Related Materials*, 15-50, ISBN 1-86094-299-7.
- [25] H. Qian, M. Zhu, R. Jin, Size-focusing synthesis, optical and electrochemical properties of monodisperse $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ nanoclusters, *ACS Nano* 3 (2009) 3795-3803.
- [26] X. Nie, H. Qian, Q. Ge, H. Xu, R. Jin, CO oxidation catalyzed by oxide-supported $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters and identification of perimeter sites as active centers, *ACS Nano* 6 (2012) 6014-6022.
- [27] K. Higashi, K. Sonoda, H. Ono, S. Sameshima, Y. Hirata, Synthesis and sintering of rare-earth-doped ceria powder by the oxalate coprecipitation method, *J. Mater. Res.* 14 (1999) 957-967.
- [28] V. Esposito, E. Traversa, Design of electroceramics for solid oxides fuel cell applications: playing with ceria, *J. Am. Ceram. Soc.* 91 (2008) 1037-1051.
- [29] H. Qian, W.T. Eckenhoff, Y. Zhu, T. Pintauer, R. Jin, Total structure determination of thiolate-protected Au_{38} nanoparticles, *J. Am. Chem. Soc.* 132 (2010) 8280-8281.
- [30] X. Nie, C. Zeng, X. Ma, H. Qian, Q. Ge, H. Xu, R. Jin, CeO_2 -supported $\text{Au}_{38}(\text{SR})_{24}$ nanocluster catalysts for CO oxidation: a comparison of ligand-on and -off catalysts, *Nanoscale* 5 (2013) 5912-5918.
- [31] W. Li, Q. Ge, X. Ma, Y. Chen, M. Zhu, H. Xu, R. Jin, Mild activation of CeO_2 -supported gold nanoclusters and insight into the catalytic behavior in CO oxidation, *Nanoscale* 8 (2016) 2378-2385.
- [32] E. Bêche, P. Charvin, D. Perarnau, S. Abanades, G. Flamant, Ce 3d XPS investigation of cerium oxides and mixed cerium oxide ($\text{Ce}_x\text{Ti}_y\text{O}_z$), *Surf. Interface Anal.* 40 (2008) 264-267.
- [33] F.J. Pérez-Alonso, M. López Granados, M. Ojeda, P. Terreros, S. Rojas, T. Herranz, J. Fierro, J. R. Gancedo, Chemical structures of coprecipitated Fe-Ce mixed oxides, *Chem. Mater.* 17 (2005) 2329-2339.
- [34] H. Yahiro, Y. Eguchi, K. Eguchi, H. Arai, Oxygen ion conductivity of the ceria-samarium oxide system with fluorite structure, *J. Appl. Electrochem.* 18 (1988) 527-531.
- [35] H. Bao, X. Chen, J. Fang, Z. Jiang, W. Huang, Structure-activity relation of Fe_2O_3 - CeO_2 composite catalysts in CO oxidation, *Catal. Lett.* 125 (2008) 160-167.
- [36] C. Munnings, S.P.S. Badwal, D. Fini, Spontaneous stress-induced oxidation of Ce ions in Gd-doped ceria at room temperature, *Ionics* 20 (2014) 1117-1126.
- [37] S.P.S. Badwal, D. Fini, F. T. Ciacchi, C. Munnings, J. A. Kimpton, J. Drennan, Structural and microstructural stability of ceria-gadolinia electrolyte exposed to reducing environments of high temperature fuel cells, *J. Mater. Chem. A* 1 (2013) 10768-10782.
- [38] G. Vlaic, P. Fornasiero, S. Geremia, J. Kašpar, M. Graziani, Relationship between the zirconia-promoted reduction in the Rh-loaded $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ mixed oxide and the Zr-O Local Structure. *J. Catal.* 168 (1997) 386-392.
- [39] O.H. Laguna, F.R. Sarria, M.A. Centeno, J.A. Odriozola, Gold supported on metal-doped ceria catalysts (M= Zr, Zn and Fe) for the preferential oxidation of CO (PROX), *J. Catal.* 276 (2010) 360-370.