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Article

Lattice oxygen activation in transition metal doped ceria

Ya-Qiong Su, Long Zhang, Valery Muravev, Emiel J. M. Hensen *

Laboratory of Inorganic Materials & Catalysis, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 28 June 2019

Accepted 22 July 2019

Published 5 June 2020

Keywords:

Lattice oxygen activation

TM-doped CeO₂(111)

Density functional theory calculations

Oxygen vacancy

Square-planar coordination

Coordination transformation

CO oxidation

ABSTRACT

Density functional theory calculations were carried out to investigate the influence of doping transition metal (TM) ions into the ceria surface on the activation of surface lattice oxygen atoms. For this purpose, the structure and stability of the most stable (111) surface termination of CeO₂ modified by TM ions was determined. Except for Zr and Pt dopants that preserve octahedral oxygen coordination, the TM dopants prefer a square-planar coordination when substituting the surface Ce ions. The surface construction from octahedral to square-planar is facile for all TM dopants, except for Pt (1.14 eV) and Zr (square-planar coordination unstable). Typically, the ionic radius of tetravalent TM cations is much smaller than that of Ce⁴⁺, resulting in a significant tensile-strained lattice and explaining the lowered oxygen vacancy formation energy. Except for Zr, the square-planar structure is the preferred one when one oxygen vacancy is created. Thermodynamic analysis shows that TM-doped CeO₂ surfaces contain oxygen defects under typical conditions of environmental catalysis. A case of practical importance is the facile lattice oxygen activation in Zr-doped CeO₂(111), which benefits CO oxidation. The findings emphasize the origin of lattice oxygen activation and the preferred location of TM dopants in TM-ceria solid solution catalysts.

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1. Introduction

Ceria is extensively used as a support material in catalysis because of its high oxygen storage capacity [1]. In combination with transition metals, it can catalyze a large number of reactions, such as the water-gas shift reaction [2], CO₂ reduction [3], NO reduction [4], CH₄ combustion [5] and CO oxidation [6]. Besides the availability of lattice oxygen atoms of the support, the strong interaction of metals with ceria can boost the catalytic activity due to electron transfer. These effects are especially prominent for small particles [7–9]. In the extreme case, a catalyst can be made up of single atoms of a catalytically active transition metal (TM) supported on ceria. Such single-atom

catalysts (SACs) present a new frontier in heterogeneous catalysis research with the potential of extremely high TM utilization due to the highly under-coordinated nature of the isolated metal atoms [10–12]. In addition, the support may also play an important role in the catalytic cycle by providing specific functionalities. As such, there is an analogy between SACs and non-innocent ligands in homogeneous catalysts [13,14].

Generally, single metal atoms are more mobile on a support material than nanoparticles (NPs) and, therefore, SACs are prone to agglomeration [15–17]. Stabilization of single atoms by the support is therefore of critical importance to design stable SACs. Ceria can strongly interact with TMs, leading to a large metal-support interface [18,19]. These interactions are

* Corresponding author. Tel: +31-40-2475178; E-mail: e.j.m.hensen@tue.nl

This work was supported by The Netherlands Organization for Scientific Research (NWO) through a Vici grant and Nuffic funding. Access to supercomputing facilities was made possible by NWO. This work has also received funding from the European Union's Horizon 2020 research and innovation programme under grant No. 686086 (Partial-PGMs).

DOI: S1872-2067(19)63468-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 41, No. 6, June 2020

particularly strong between TM atoms and oxygen vacancies and step-edges. Another possibility is that TM cations substitute for Ce in the ceria lattice. Related to the latter, it has been found that substituting dopants into the ceria lattice can activate lattice oxygen, as most TM-O binding energies are lower than Ce-O binding energies in ceria [20,21]. The formation energy of oxygen vacancies (V_O) in TM-doped CeO_2 has been the topic of several theoretical investigations [22–26]. In all of these studies, a conventional structure of the TM dopant site has been adopted in which the octahedrally coordinated Ce ion is isomorphously substituted by a TM ion. Recently, we proposed another structure for Pd-doped $\text{CeO}_2(111)$, in which the Pd atom adopts a square-plane configuration surrounded by four lattice oxygen atoms [27]. The removal of the lattice oxygen atom connected to Pd dopant requires a higher energy than that of the perfect $\text{CeO}_2(111)$ surface, unlike the two-fold oxygen atoms that can be removed easily and generate oxygen vacancies. Therefore, it is necessary to thoroughly investigate the origination of the activated lattice oxygen in TM-doped CeO_2 .

In this study, we examine a series of TM-doped $\text{CeO}_2(111)$ (TM = Zn, Cu, Ni, Co, Fe, Ag, Pd, Rh, Zr, Au, and Pt) by density functional theory (DFT) calculations to explore the most stable configurations and V_O formation energies. We also included Zr in this study as mixed cerium-zirconium oxides are extensively used in oxidation reactions, the isomorphous substitution in ceria resulting in a higher availability of lattice oxygen atoms and boosting reactions such as CO oxidation [28,29]. Given the size of Zr^{4+} , isomorphous substitution for Ce^{4+} will lead to the retention of the octahedral coordination of the surface TM ion. In most of the other cases, doping ceria with TM ions leads to a structural transformation from an octahedral configuration around the TM dopant to a square planar one. For the most effective cation in terms of lattice oxygen activation (Zr), we explore catalytic CO oxidation.

2. Computational details

Spin-polarized calculations within the density-functional theory framework were carried out as implemented in the Vienna *ab initio* simulation package (VASP) [30]. The ion-electron interactions were represented by the projector-augmented wave (PAW) method [31] and the electron exchange-correlation by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [32]. The Kohn-Sham valence states were expanded in a plane-wave basis set with a cut-off energy of 400 eV. The Ce (5s, 5p, 6s, 4f, 5d), O (2s, 2p) and C (2s, 2p) electrons were treated as valence states. The DFT+ U approach was used, in which U is a Hubbard-like term describing the on-site Coulombic interactions [33]. This approach improves the description of localized states in ceria, where standard LDA and GGA functionals fail. For Ce, a value of $U = 4.5$ eV was adopted, which was calculated self-consistently by Fabris et al. [34] using the linear response approach of Cococcioni and de Gironcoli [35] and which is within the 3.0–6.0 eV range that provides localization of the electrons left upon oxygen removal

from ceria [36]. To model TM-doped $\text{CeO}_2(111)$, we used a periodic ceria slab with a (4×4) surface unit cell. For Brillouin zone integration, a 1×1×1 Monkhorst-Pack mesh was used. The bulk CeO_2 equilibrium lattice constant (5.49 Å) previously calculated by PBE+ U ($U = 4.5$ eV) was used [37]. The $\text{CeO}_2(111)$ slab model is three Ce-O-Ce layers thick and the vacuum gap was set to 15 Å. The atoms in the bottom layer were frozen to their bulk position and the top two Ce-O-Ce layers were allowed to relax. The climbing image nudged-elastic band (CI-NEB) algorithm [38,39] was used to identify the transition states in the elementary reaction steps of structural transformation and CO oxidation. A frequency analysis was performed to confirm that each transition state has only a single imaginary frequency in the direction of the reaction coordinate. The total energy difference was less than 10^{-4} eV and the relaxation convergence criterion was set at 0.05 eV/Å.

The TM dopants in $\text{CeO}_2(111)$ adopt octahedral and square-planar coordination, which are referred to as TM-dop-I and TM-dop-II, respectively. The creation of an oxygen vacancy through the removal of a lattice oxygen atom results in structures denoted by TM-dop-I- V_{O1} and TM-dop-II- V_{O1} , respectively. The formation energies of the first oxygen vacancy are defined as:

$$E(\text{I-}V_{O1}) = \frac{1}{2}E(\text{O}_2) + E(\text{TM-dop-I-}V_{O1}) - E(\text{TM-dop-I}) \quad (1)$$

$$E(\text{II-}V_{O1}) = \frac{1}{2}E(\text{O}_2) + E(\text{TM-dop-II-}V_{O1}) - E(\text{TM-dop-II}) \quad (2)$$

Similarly, the formation energies of the second and third oxygen vacancies (only considered for square-planar coordination) are defined as:

$$E(V_{O2}) = \frac{1}{2}E(\text{O}_2) + E(\text{TM-dop-II-}V_{O2}) - E(\text{TM-dop-II-}V_{O1}) \quad (3)$$

$$E(V_{O3}) = \frac{1}{2}E(\text{O}_2) + E(\text{TM-dop-II-}V_{O3}) - E(\text{TM-dop-II-}V_{O2}) \quad (4)$$

in which $E(\text{O}_2)$ is the energy of O_2 in the gas phase, approximated by the computed electronic energy. $E(\text{TM-dop-I})$ and $E(\text{TM-dop-II})$ are the electronic energies of TM-dop-I and TM-dop-II, respectively, $E(\text{TM-dop-I-}V_{O1})$ and $E(\text{TM-dop-II-}V_{O1})$ the electronic energies of TM-dop-I- V_{O1} and TM-dop-II- V_{O1} , respectively and $E(\text{TM-dop-II-}V_{O2})$ and $E(\text{TM-dop-II-}V_{O3})$ the electronic energies of TM-dop-II- V_{O2} and TM-dop-II- V_{O3} , respectively.

The relative thermodynamic stability between TM-dop-I and TM-dop-II is defined as:

$$\Delta E(\text{I-II}) = E(\text{TM-dop-II}) - E(\text{TM-dop-I}) \quad (5)$$

Similarly, the relative thermodynamic stability between TM-dop-I- V_{O1} and TM-dop-II- V_{O1} is defined as:

$$\Delta E(V_{O1}(\text{I-II})) = E(\text{II-}V_{O1}) - E(\text{I-}V_{O1}) \quad (6)$$

We used the *ab initio* thermodynamics approach of Reuter and Scheffler to assess the relative stability of various TM-doped states in ceria as a function of oxygen pressure and temperature [40]. The free energy of TM-doped surface states can then be obtained by:

$$\begin{aligned} \Delta G &= \Delta E + \frac{n}{2}\mu_{\text{O}_2}(T, P) \\ &= \left(E_{\text{TM-dop-}V_{O_n}} + \frac{n}{2}E_{\text{O}_2} - E_{\text{TM-dop}} \right) + \frac{n}{2}\mu_{\text{O}_2}(T, P) \end{aligned} \quad (7)$$

where $E_{\text{TM-dop}}$ and $E_{\text{TM-dop-}V_{O_n}}$ are the electronic ground state energies of the TM-doped $\text{CeO}_2(111)$ and its defective surface after removing n oxygen atoms, respectively, E_{O_2} the electronic ground state energy of gaseous O_2 , and $\mu_{\text{O}_2}(T, P)$ the chemical

Fig. 1. Configurations of a single TM atom doped in to CeO₂(111) surface, (left) the octahedral configuration obtained by isomorphous substitution and (right) a square-planar contribution (color code: white, Ce red, O; green, TM).

potential of gaseous O₂. The chemical potential of gaseous oxygen can be correlated to the thermodynamic state in the following manner:

$$\begin{aligned} \mu_{O_2}(T, P) &= \mu_{O_2}(T, P^\theta) + RT \ln \left(\frac{P_{O_2}}{P^\theta} \right) \\ &= [H_{O_2}(T, P^\theta) - H_{O_2}(0 K, P^\theta)] - T[S_{O_2}(T, P^\theta) - S_{O_2}(0 K, P^\theta)] + RT \ln \left(\frac{P_{O_2}}{P^\theta} \right) \end{aligned} \quad (8)$$

where the enthalpy $H_{O_2}(T, P^\theta)$ and entropy $S_{O_2}(T, P^\theta)$ of gaseous O₂ were obtained from the standard thermodynamic tables [41]. The entropy of the solids is neglected.

3. Results and discussion

3.1. Stability TM-doped CeO₂

TM-doped CeO₂ is extensively used as heterogeneous catalysts due to their high activity and stability in a wide range of reactions [29,42]. Earlier, a number of theoretical studies have verified that doping TM atoms into octahedral Ce locations in the surface of CeO₂(111) is thermodynamically favorable [25,27,43]. Fig. 1 shows the octahedral and square-planar coordination environments of TM doped into the CeO₂(111) surface. Alternative to this conventionally considered configuration (TM-dop-I), we also explored the square-planar configuration (TM-dop-II). This TM-dop-II configuration has been earlier considered by us for Pd [27]. In TM-dop-II, two lattice oxygen atoms that were initially three-fold coordinated in CeO₂(111) and TM-dop-I become two-fold coordinated.

For Zn, Pd, Pt and Rh, the two considered configurations show nearly similar stability, as follows from Table 1. For Cu, Ag, Au, Ni, Co and Fe, the square-planar TM-dop-II configuration is thermodynamically favored over the octahedral

TM-dop-I one. The exception is Zr for which Zr-dop-I is so strongly preferred that an initial Zr-dop-II spontaneously reverted to the octahedral configuration.

In a previous work [27], we showed that the activation energy barrier for the transformation from Pd-dop-I to Pd-dop-II is 0.53 eV, suggesting that under typical catalytic conditions this transformation can easily occur. We explored in this study the activation barriers for the similar transformation of other TM dopants in the ceria surface (Table 1). For Zn, Rh, Ag, Au and Ni, the transformation requires overcoming relatively low activation barriers of 0.27, 0.32, 0.32, 0.63 and 0.22 eV, respectively. The activation barriers are negligible for Cu, Co, and Fe. On the other hand, the barrier is significantly higher for Pt at 1.14 eV. This can well explain the experimentally observed preference for Pt⁴⁺ substitutions in Pt-ceria solid solutions [44–46]. The Pt oxidation states in Pt-dop-I and Pt-dop-II are 4+ and 2+, respectively.

The typical preference for TM-dop-II is related to the smaller size of the TM⁴⁺ ions Ni, Pd, Pt, Rh, the TM³⁺ ions Cu, Au, Co, Fe and the Zn²⁺ ion in TM-dop-I with respect to the Ce⁴⁺ ion [5]. This is confirmed by the data in Table 2. Only Zr⁴⁺ (0.86 Å) has a comparable ionic radius as Ce⁴⁺ (0.97 Å) and, therefore, prefers the octahedral configuration. Especially, Ni⁴⁺ has a small ionic radii of 0.48 Å. The substitution of TM cations with a small ionic radius results in a weak bonding between the TM ion and lattice O atoms in TM-dop-I. The Ce⁴⁺-O bond length in CeO₂(111) surface is 2.37 Å. Direct isomorphous substitution by TM atoms results in a tensile-strained lattice. Although Ag³⁺ has a large ionic radii of 1.26 Å, the resulting Ag-O bonds in Ag-dop-I are 2.15 and 2.18 Å, much smaller than Ce-O bond length. In TM-dop-II, TM atoms are generally in the +2 or +3 oxidation state and coordinated by four lattice O atoms, with TM-O bond lengths in the 1.9–2.0 Å range. These results indicate that the TM-dop-II configuration can provide a more suitable coordination environment for TM dopants, except for Zr.

3.2. Oxygen vacancy formation

The formation energy of oxygen vacancies provides an indication of the surface reactivity upon substitution of Ce by TM. The direct removal of one oxygen atom from TM-dop-I results in a configuration in which the TM atom is coordinated by two oxygen atoms in the top surface layer and two oxygen in the subsurface layer, as shown in Fig. 2. The removal of one oxygen atom from TM-dop-II results in a configuration in which the TM

Table 1
Thermodynamic and kinetic properties of TM-doped CeO₂(111) (all energies in eV).

TM elements	Cu	Ag	Au	Ni	Pd	Pt	Co	Rh	Fe	Zr	Zn
$\Delta E(I-II)$	-1.52	-0.55	-0.60	-1.41	0.01	0.02	-1.57	-0.03	-0.23	—	-0.01
$E_a(I-II)$	0.09	0.32	0.63	0.22	0.53	1.14	0	0.32	0.03	—	0.27
$E(I-VO_1)$	-0.22	-0.25	0.27	-1.56	0.84	1.60	-0.63	1.32	0.98	1.56	-0.90
$E(II-VO_1)$	0.05	0.08	0.08	-0.16	-0.57	-0.01	0.03	0.75	0.69	—	-0.83
$\Delta E(VO_1(I-II))$	-1.24	-0.22	-0.80	—	-1.40	-1.59	-0.92	-0.91	-0.52	—	0.06
$E_a(VO_1(I-II))$	0	0.01	0.48	0	0.07	0.37	0.28	0.12	0.40	—	0.13
$E(VO_2)$	1.21	1.35	1.24	1.24	1.09	1.23	1.27	1.32	1.21	1.54	1.34
$E(VO_3)$	1.70	1.24	1.69	2.57	2.87	3.11	2.33	3.02	1.76	2.30	1.21

E_a is the energy barrier associated with the transformation from TM-dop-I to TM-dop-II and from TM-dop-I-VO₁ to TM-dop-II-VO₁, respectively.

Table 2

Ionic radii of various TM cations (in Å).

TM elements	Ce	Cu	Ag	Au	Ni	Pd	Pt	Co	Rh	Fe	Zr	Zn
4+	0.97	—	—	—	0.48	0.63	0.62	0.53	0.62	0.59	0.86	—
3+	1.04	0.54	1.26	0.85	0.60	0.70	0.75	0.65	0.67	0.67	0.89	—
2+	—	0.73	—	—	0.69	0.64	0.80	0.78	0.72	0.78	—	0.74
+	—	0.46	1.02	1.37	—	—	—	—	—	—	—	—

Data from literature [5,47–53].

atom keeps the same coordination. We name these configurations, TM-dop-I- V_{01} and TM-dop-II- V_{01} , respectively. Table 1 lists the corresponding V_0 formation energies. The V_0 formation energy of the clean $\text{CeO}_2(111)$ surface is 2.38 eV, in comparison to $\frac{1}{2}\text{O}_2$ in the gas phase [54]. The V_0 formation energies of Pt-dop-I, Zr-dop-I, Rh-dop-I, Fe-dop-I and Pd-dop-I are considerably lower than this value. While the value for Au-dop-I is much lower at 0.27 eV, the V_0 formation process is exothermic for Zn-, Cu-, Ag-, Ni- and Co-dop-I. On the other hand, for nearly all TM the V_0 formation energies for TM-dop-II are negligible, for Rh-dop-II and Fe-dop-II with values of 0.75 and 0.68 eV, respectively. Moreover, we note that the TM-dop-II- V_{01} configuration is more stable than the TM-dop-I- V_{01} for most of the TM. We earlier computed activation barriers of 0.07 and 0.39 eV for Pd and Pt, respectively, for the transformation of TM-dop-I- V_{01} to TM-dop-II- V_{01} [27]. For the other TM, the activation barriers for this transformation are also very small (Table 1). For Ni, the TM-dop-I- V_{01} spontaneously relax to the corresponding TM-dop-II- V_{01} configuration, after removing one surface oxygen atom from the stoichiometric structures. These findings demonstrate that the TM-dop-I- V_{01} structures are unstable and will easily transform into TM-dop-II- V_{01} .

We also computed the energy cost for the formation of the second and third oxygen vacancy (TM-dop- V_{02} and TM-dop- V_{03}) for the TM-dop-II structure. We limited ourselves to these structures, as TM-dop-II- V_{01} is thermodynamically favored over TM-dop-I- V_{01} , except for Zr. TM-dop- V_{02} is preferentially obtained by removing another two-fold lattice oxygen atom, while TM-dop- V_{03} is obtained by removing the lattice oxygen atom connected to the TM dopant. It is worthwhile to mention that Zr-dop- V_{02} and Zr-dop- V_{03} are obtained by suc-

cessively removing lattice oxygen atoms connected to Zr in Zr-dop-I- V_{01} , as shown in Fig. 2. The TM-dop- V_{02} formation energies are typically between 1.09 and 1.35 eV, although it is higher for Zr (1.54 eV). The chemical potentials of gaseous O_2 are circa 0.55, 0.77 and 0.99 eV at $P_{\text{O}_2} = 1$ atm and $T = 300, 400$ and 500 K, respectively. Compared to these values, we can conclude that the second two-fold lattice oxygen atom is thermodynamically stable under reaction conditions relevant to catalysis. Therefore, we expect that only a single oxygen vacancy will be obtained under typical conditions. Notably, the TM-dop- V_{03} formation process involves large energy penalties for Ni, Pd, Pt and Rh. The energy costs of TM-dop- V_{03} formation for Co and Zr are both 2.33 eV. For Zn, Cu, Ag, Au and Fe, the V_{03} formation energies are 1.21, 1.70, 1.24, 1.69 and 1.76 eV, respectively. The results demonstrate that Cu, Ag, Au and Fe can substantially activate the lattice O atoms connected to them. Co and Zr can also slightly activate the lattice O atoms, compared to the lattice O atoms of the clean $\text{CeO}_2(111)$ surface. Ni, Pd, Pt and Rh suppress the reactivity of lattice O atoms.

Given the size of the relatively small TM cations in comparison to Ce^{4+} , it is also possible to replace one Ce cation with two TM cations [5]. One of the TM cations is exposed to the medium and can, therefore, be involved in adsorption and catalysis. In the optimized model, the additional TM atom binds to the TM dopant via the two-fold coordinated oxygen atoms. These oxygen atoms dictate the catalytic reactivity. Moreover, these doped TM cations present a very stable configuration and we earlier speculated that such sites can also act as nucleation center for supported TM nanoparticles. There are strong experimental indications for the importance of the combination of TM dopants with TM nanoparticles [55–57]. In this configuration, dopants such as Ni, Pd, Pt and Rh cannot activate lattice O atoms, while Cu, Ag, Au and Fe can effectively activate lattice O atoms.

3.3. Phase diagrams

We determined the formal oxidation state by counting the total number of excess electrons localized in empty Ce 4f-orbital, which is related to the formation of Ce^{3+} ions. For example, in Au-dop-II- V_{01} and Au-dop- V_{03} , one and three Ce^{3+} ions, respectively, are present as shown in Fig. 3. Thus, Au is formally in the +3 and +1 oxidation state, respectively, in these two structures. Another way of approximating the charge on the TM dopants is by Bader charge analysis. Such analysis shows that Au in Au-dop-I, Au-dop-II and Au-dop-II- V_{01} exhibits +1.24, +1.13 and +1.12 e oxidation states, respectively. The lower oxidation states derive from charge transfer from lattice

Fig. 2. Various oxygen vacancies for models I and II (color code: white, Ce; red, O; green, TM; pink, top-surface O connected to TM).

Fig. 3. Calculated iso-surfaces of the spin density in Au-dop-II-V₀₁ and Au-dop-V₀₃ (color code: white, Ce; red, O; green, Au).

O atoms, as confirmed by magnetic moments of lattice O atom in the Au-dop-I and Au-dop-II models of 0.67 μ_B and 0.83 μ_B , respectively. In Au-dop-II-V₀₁, the magnetic moment of the other lattice O atoms are zero, while the magnetic moment of one of the Ce atoms is 0.99 μ_B , consistent with the formation of one Ce³⁺. In Pt-dop-I, there are no excess electrons, implying that Pt remains formally in the +4 oxidation state, in agreement with experimental data [44–46]. On the other hand, for a Pd-CeO₂ solid solution, the dominant oxidation state is Pd²⁺ [58]. Our previous work demonstrated that the oxidation state of Pd atom in Pd-dop-II is Pd²⁺, owing to the electron donation of lattice oxygen atoms [27]. In our model, this is consistent with the facile transformation from Pd-dop-I to Pd-dop-II and the subsequent removal of one of the oxygen atoms. Zr and Pt preserve the +4 oxidation state in solid solutions with CeO₂, due to the kinetic limitation of structure transformation at room temperature. The other TM dopants prefer to adopt +2 and +3 oxidation states, after generating an oxygen vacancy.

Based on the computed oxygen vacancy formation energies, we constructed stability diagrams for several TM-doped CeO₂(111) surfaces (TM = Cu, Au and Zr). These are phase diagrams in the thermodynamic sense by considering the free energy of the system. Fig. 4 shows that Cu-dop-II-V₀₁ and Au-dop-II-V₀₁ are the dominant species under typical reaction conditions at relatively low temperature. On the other hand, the favorable structure is Zr-dop-I. It further verifies that the TM-dop-II-V₀₁ is an important candidate structure of transition metal-ceria solid solution, which is thermodynamically relevant for the realistic catalytic conditions.

Cu-CeO₂ is one of the relevant systems for environmental catalysis such as CO oxidation [59,60]. In Cu-CeO₂ solid solutions, Cu ions mainly remain in the +2 and +3 oxidation state

under oxygen-rich catalytic conditions [59,61,62]. In line with this, we computed that Cu in Cu-dop-II-V₀₁ has a close to +3 oxidation state. Adding more TM such as Cu results in a lower oxidation states, leading to the formation of Cu²⁺ and eventually Cu⁺ [5]. Similarly, the Au dopant remains in the +3 oxidation state in accordance with experimental observation [63]. On the other hand, Zr maintains the +4 oxidation state [64,65].

3.4. CO oxidation by Zr-doped CeO₂(111)

Given the importance of ceria-zirconia solid solutions, we also explored how activation of lattice oxygen by Zr insertion into CeO₂(111) affects CO oxidation. As outlined above, the Zr substitution remains in octahedral coordination after insertion in the surface. Due to the slightly smaller ionic radii of Zr⁴⁺ than Ce⁴⁺, the V₀ formation energy is lowered in the doped structure. Therefore, Zr is an important substitution for Ce atoms to synthesize highly active ceria-based catalysts with a high oxygen storage capacity [66–68]. A catalytic cycle for CO oxidation is shown in Fig. 5.

CO adsorption on the Zr cation in Zr-doped CeO₂(111) is weak ($E_{\text{ads}} = -0.51$ eV). Subsequent CO oxidation by one lattice O atom involves a negligible energy barrier ($E_a = 0.02$ eV). The following CO₂ desorption step is facile ($\Delta E = 0.43$ eV). The resulting Zr-dop-I-V₀₁ structure binds another CO with a slightly higher adsorption energy of -0.70 eV. The next CO₂ formation event requires overcoming an energy barrier of 0.29 eV and is followed by an easy CO₂ desorption ($\Delta E = 0.14$ eV). One O₂ molecule strongly adsorbs on the resulting Zr-dop-I-V₀₂ ($E_{\text{ads}} = -1.56$ eV), and then is dissociated overcoming an energy barrier of 0.67 eV. This closes the catalytic cycle. For CO oxidation over pure CeO₂(111), CO adsorption is weaker ($E_{\text{ads}} = -0.51$ eV), and the required energy barrier for the first CO₂ formation step is 0.37 eV. The second CO adsorption energy is -0.45 eV, and the subsequent CO₂ formation overcomes an energy barrier of 0.31 eV. One O₂ molecule strongly adsorbs on the resulting V₀₂ site ($E_{\text{ads}} = -2.35$ eV), and then oxygen dissociation requires an energy barrier of 0.82 eV. The CO₂ desorption energy is slightly endothermic by 0.48 and 0.40 eV, respectively. Obviously, the introduction of Zr can improve the reactivity of surface lattice oxygen atoms of CeO₂, owing to the lowered formation energy of oxygen vacancies. During the whole CO oxidation cycle, CO₂ desorption is facile and the rate-limiting step is

Fig. 4. Stability diagrams of Cu-, Au- and Zr-doped CeO₂(111) surfaces as a function of the temperature and the oxygen partial pressure based on an *ab initio* thermodynamic analysis using first-principles DFT data.

Fig. 5. Potential energy diagram of CO oxidation by Zr-doped $\text{CeO}_2(111)$ and pure $\text{CeO}_2(111)$ (color code: white, Ce; red, O; cyan, Zr; gray, C; pink O of molecular CO and O_2).

likely O_2 dissociation. We note that the rate of this system will be low because of a low CO coverage. Previously, we explored CO oxidation by Pt-doped $\text{CeO}_2(111)$ [43], where CO adsorption is strong ($E_{\text{ads}} = -1.69$ eV) and the required energy barrier for CO_2 formation is negligible. On the other hand, in this system CO_2 desorption costs 1.61 eV, indicative of a limited activity at low temperature. In comparison, CO_2 desorption costs 0.65 eV from the Pd-doped $\text{CeO}_2(111)$ surface [25]. The complete CO oxidation mechanism by Pt-dop-II- $\text{V}_{\text{O}1}$ and Pd-dop-II- $\text{V}_{\text{O}1}$ have been thoroughly investigated in our previous work [27,43]. The dopants in square-planar coordination exhibit a higher CO oxidation activity compared to the stoichiometric ceria surface. Although usually Zr-doped CeO_2 is used together with an active metal phase, presumably allowing for a stronger adsorption and therefore higher coverage of CO, these data show that Zr-doping can facilitate the availability of oxygen atom of the ceria surface.

4. Conclusions

We investigated the activation of lattice oxygen atoms in ceria by transition metal dopants. The doped metal atoms prefer to be square-planarly coordinated by four lattice O atoms over the conventional octahedral coordination, except for Zr and Pt. While the transformation from Pt-dop-I to Pt-dop-II requires a high kinetic barrier, these transformations are facile for the other transition metals considered. The ionic radius of tetravalent TM cations is much smaller than that of Ce^{4+} , resulting in a significant tensile-strained ceria lattice and a decreased oxygen vacancy formation energy. Under typical conditions of low-temperature reactions in the context of environmental catalysis, the thermodynamically favorable species is TM-dop-II- $\text{V}_{\text{O}1}$ (except for Zr), in which there is one oxygen vacancy and the TM atom adopts the square-planar coordination. Zn, Cu, Ag, Au and Fe as dopants activate the lattice oxygen connected to them. Zr as a dopant preserves its octahedral coordination in ceria lattice due to the comparable ionic radii of Zr^{4+} and Ce^{4+} . It leads to higher reactivity in a CO oxidation cycle in which CO adsorbs to a Zr surface cation followed by CO_2 formation. Our work provides a detailed insight into the changed coordination of most transition metal dopants in the surface of ceria with respect to conventionally considered isomorphous substitution models. The high stability and reactivity of the explored single-atom configurations doped into the surface are also of topical interest in the framework of single-atom catalysis.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 977–984 doi: S1872-2067(19)63468-6

Lattice oxygen activation in transition metal doped ceria

Ya-Qiong Su, Long Zhang, Valery Muravev, Emiel J. M. Hensen*
Eindhoven University of Technology, the Netherlands

Isomorphous substitution of Ce cations in the $\text{CeO}_2(111)$ surface by TM atoms results in a surface reconstruction to a square planar coordination and a tensile-strained lattice which account for the lowered oxygen vacancy formation energy.

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过渡金属掺杂铈中晶格氧的活化

Ya-Qiong Su, Long Zhang, Valery Muravev, Emiel J. M. Hensen *

埃因霍温理工大学, 舒伊特催化研究所, 无机材料与催化实验室, P.O. Box 513, 5600 MB 埃因霍温, 荷兰

摘要: 采用密度泛函理论计算研究了在铈表面掺杂的过渡金属(TM)离子对表面晶格氧原子活化的影响。为此, 测定了经TM离子修饰的CeO₂最稳定(111)表面终端的结构和稳定性。除了保持八面体氧配位的锆和钨掺杂剂外, TM掺杂剂在取代表面Ce离子时更倾向于正方形平面配位。除了Pt(1.14 eV)和Zr(正方形平面配位不稳定)外, 所有TM掺杂剂的表面结构从八面体到正方形平面都很容易。通常, 四价TM阳离子的离子半径比Ce⁴⁺的小得多, 从而导致了显著的拉伸应变晶格, 并解释了氧空位形成能量的降低。除Zr外, 当产生一个氧空位时, 优先形成正方形平面结构。热力学分析表明, TM掺杂CeO₂表面在典型环境催化条件下存在氧缺陷。一个具有实际意义的例子是钨掺杂CeO₂(111)中的晶格氧容易活化, 从而有利于CO氧化。研究结果强调了晶格氧活化的本质和TM掺杂剂在TM-铈固溶催化剂中的优选位置。

关键词: 晶格氧活化; 过渡金属掺杂CeO₂(111); 密度泛函理论计算; 氧空位; 正方形平面配位; 配位转换; 一氧化碳氧化

收稿日期: 2019-06-28. 接受日期: 2019-07-22. 出版日期: 2020-06-05.

*通讯联系人. 电话: +31-40-2475178; 电子信箱: e.j.m.hensen@tue.nl

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