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A Density Functional Theory Study Of The Mechanism Of Formaldehyde Oxidation On Mn-doped Ceria

Hairong Wu,^{†,1} Sicong Ma,^{†,1} Weiyu Song,^{1,*} Emiel J. M. Hensen^{2,*}

¹State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum-Beijing, Beijing, 102249, P. R. China

²Inorganic Materials Chemistry, Eindhoven University of Technology, P.O.Box 513, 5600 MB Eindhoven, The Netherland

Abstract

Formaldehyde is an indoor pollutant, whose removal under mild conditions is of growing importance. Mn-doped CeO₂ is a promising catalyst for the oxidation of formaldehyde to water and carbon dioxide. We have theoretically investigated the origin of the high activity of Mn-doped ceria as compared with ceria. DFT+*U* calculations were used to identify adsorption modes and compare different reaction mechanisms. The reaction mechanism involves HCHO adsorption, two C-H bond cleavage steps involving reactive O atoms (either structural O atoms of the support or adsorbed O₂), H₂O formation and H₂O and CO₂ desorption. On the stoichiometric surface, a Mars-Van Krevelen mechanism occurs, which involves ceria surface O atoms. The lower coordination number of these O atoms in the stoichiometric Mn-doped ceria results in decreased barriers for C-H bond cleavage. In the presence of defects which will be ubiquitous in the Mn-doped surface, a Langmuir-Hinshelwood mechanism becomes feasible, as O₂ can strongly adsorb on the oxygen vacancy next to Mn where HCHO adsorbs. The adsorbed O₂ molecule is strongly activated by the reduced ceria surface. The barriers for C-H cleavage are lowest for reactions involved adsorbed O₂. We predict that the HCHO oxidation reaction proceeds with lowest overall barrier on the defective Mn-doped CeO₂ surface.

1. Introduction

Formaldehyde (HCHO) is a common chemical, found in many households and offices, in such products as carpets, upholstery, glues, dyes, permanent press clothes, markers, paints, and cigarettes. As long-term exposure to airborne formaldehyde may harm human health,¹ significant efforts are made to develop technologies to limit indoor formaldehyde levels. There are two methods that are suitable for eliminating formaldehyde from the atmosphere from the practical and economical point of view. Formaldehyde can be removed by absorption on, for instance, potassium permanganate or organic amines.^{2,3} Due to their limited capacity, these absorbents are effective only for a short period. Catalytic oxidation is more promising as the removal efficiency can be much higher and, if well designed, these systems can operate for much longer times. Catalytically, HCHO can be directly converted to CO₂ and H₂O. Therefore, seeking efficient catalysts that can catalyze HCHO oxidation under mild conditions at low cost has become important.

Oxide-supported noble metals and transition metal oxides have been explored as catalysts for formaldehyde oxidation.⁴⁻¹² Precious metal catalysts display excellent low temperature activity in HCHO oxidation, but their practical use is limited by high cost. Transition metal oxides are also promising and such oxides as Co₃O₄, MnO_x, and CeO₂ show comparable catalytic performance in HCHO oxidation reactions.^{1,7,13} Among them, MnO_x-CeO₂ mixed oxide catalysts have been extensively studied because of their high activity, durability and low toxicity. Tang et al. showed that a MnO_x-CeO₂ mixed oxide prepared by co-precipitation displayed very high activity in HCHO oxidation.⁷ Characterization indicated that good catalytic performance is associated with the high oxidation state of Mn and reactive surface oxygen species. Despite the importance of this topic, clear insight about the role of Mn is lacking.

Regarding the mechanism,^{14,15} different reaction pathways of HCHO decomposition have been proposed: direct decomposition (HCHO → CHO → CO → CO₂)¹⁶⁻¹⁹ or oxidation of HCHO first to dioxy-methylene, followed by successive dehydrogenation to carbon dioxide (HCHO → HCHO₂ → CHO₂ → CO₂).²⁰ It has also been demonstrated that neither pure CeO₂^{18,19} nor MnO₂¹ shows high activity for HCHO oxidation. MnO_x-CeO₂ mixed oxides, on the other hand, are able to convert formaldehyde completely to CO₂ at a temperature as low as 373 K.⁷ Despite these insights from experiment, a firm basis for the reaction mechanism of HCHO oxidation on Mn-Ce-oxide catalysts is lacking. As it was also demonstrated that oxygen vacancies in ceria-based catalysts are often

critical to catalytic performance,²¹⁻²³ it is important to study the influence of the oxygen vacancies as well.

Based on above considerations, density functional theory (DFT) calculations were performed to investigate the reaction mechanism on the most stable (111) termination of $\text{MnCe}_{1-x}\text{O}_2$ and $\text{MnCe}_{1-x}\text{O}_{2-y}$ mixed oxides with the aim to explore the effect of Mn doping and oxygen vacancies. First, the preferred adsorption mode of HCHO and O_2 on these surfaces were identified, followed by investigation of the mechanism of HCHO oxidation. We found that HCHO oxidation follows different reaction mechanisms on the $\text{MnCe}_{1-x}\text{O}_2$ and $\text{MnCe}_{1-x}\text{O}_{2-y}$ surfaces. We predict that the presence of Mn will introduce oxygen vacancies that greatly contribute to increased catalytic performance.

2. Computational details

All calculations were performed with the VASP code using the GGA-PBE electron exchange-correlation functional.²⁴ The valence electrons (5s, 4f, 3d for Ce; 2s, 2p for O and 4s, 3d for Mn) were expanded in a plane-wave basis set within a cut off energy of 400 eV, Γ -centered k -point meshes of $1 \times 1 \times 1$ were used. Stationary points were identified by the conjugate-gradient method until the forces acting on each ion were smaller than 0.05 eV/Å. It was verified that choosing higher cut off energy (500 eV), a larger k -point mesh ($3 \times 3 \times 1$) and a more stringent force convergence threshold (0.02 eV/Å) did not lead to significantly lower energies (Table S1). The energy criterion for convergence of the electron density was set at 10^{-4} eV. The projector augmented wave method was used to treat the core electrons.^{25,26} The location and energy of transition states were calculated with the climbing-image nudged elastic band method (CINEB).^{27,28} We used a Hubbard-like term (U_{eff}) describing the on-site Coulombic interactions to improve the description of localized states for the Ce 4f and Mn 3d orbitals, where standard LDA and GGA functionals fail. Although this approximation is rather empirical and system-dependent, we follow the approach explored by Fabris et al.²⁹ and Cococcioni and De Gironcoli³⁰ by setting $U_{\text{eff,Ce}} = 4.5$ eV which is within the 3.0-5.5 eV range reported to provide localization of the electrons left upon oxygen removal from CeO_2 .³¹ The use of the U correction for the Mn 3d orbital is based on the much better prediction of the structure of MnO .³² The strong deviation without the correction is due to the Coulombic interaction between Mn and O, which is reduced by the U correction. We should note however that this will affect some of the properties such as the oxygen vacancy energy.

1 The bulk equilibrium lattice constant of ceria ($a = 5.49 \text{ \AA}$) previously calculated by PBE+U ($U_{\text{eff}} = 4.5$
 2 eV) was used.³³ A 3×3 surface unit cell was used for CeO_2 (111) surface. A surface model for the
 3 Mn- CeO_2 mixed oxide was constructed by replacing one of the surface Ce atoms by a Mn atom.
 4 This structure is denoted as $\text{MnCe}_{1-x}\text{O}_2$. The six top atomic layers of the ceria slab were allowed to
 5 relax, while the three bottom layers were kept fixed to their bulk positions. The vacuum gap
 6 thickness was set to $15 \text{ \AA}$.

7 The adsorption energy was calculated by

$$8 \quad E_{\text{ads},X} = E_{\text{slab-X}} - (E_{\text{slab}} + E_X)$$

9 Where $E_{\text{ads},X}$ is the adsorption energy per X relative to the energy of the clean surface (E_{slab})
 10 and the energy of X (E_X); $E_{\text{slab-X}}$ is the energy of the surface covered by X .

11 The oxygen vacancy formation energy was calculated by:

$$12 \quad E_{\text{O}_v} = E_{\text{slab-O}_v} + \frac{1}{2}E_{\text{O}_2} - E_{\text{slab}}$$

13 Where E_{O_v} is the oxygen vacancy formation energy relative to the energy of the clean surface
 14 (E_{slab}) and the energy of gas phase O_2 (E_{O_2}); $E_{\text{slab-O}_v}$ is the energy of the defective ceria
 15 surface.

16 In the discussion on electron transfer, we make use of the analyzed spin magnetic moment changes
 17 of cations in the system. For the Ce^{4+} , the spin magnetic moment is $0 \text{ \mu B}$. If one electron is
 18 transferred to Ce, it will localize in its 4f orbital, reducing Ce from +4 to +3. Accordingly, the spin
 19 magnetic moment changes to $1 \text{ \mu B}$. For Mn atom, the calculated spin magnetic moments of 4.32
 20 $\text{\mu B}$ and $3.56 \text{ \mu B}$ are assigned to Mn^{3+} and Mn^{4+} , respectively.

21

22 **3. Results**

23 The optimized structure of $\text{MnCe}_{1-x}\text{O}_2$ is shown in Figure 1. The Mn atom coordinates to one surface
 24 O and three subsurface O atoms. The Mn-O bond distance is in the $1.93\text{-}2.03 \text{ \AA}$ range, and the spin
 25 magnetic moment of Mn is $3.56 \text{ \mu B}$, which can be assigned to the 4+ oxidation state. The details of
 26 the structure of the Mn-doped CeO_2 (111) surface have been described elsewhere.³⁴ Doping of Mn
 27 for Ce in the ceria lattice resulted in structural distortion. The two surface oxygen atoms
 28 neighboring the Mn atom change their coordination number from three to two (Figure 1). As will
 29 be shown in the following, this structural change of ceria surface plays an important role in HCHO

activation. The adsorption of HCHO and O₂ will be investigated on stoichiometric MnCe_{1-x}O₂ (111) and defective MnCe_{1-x}O_{2-y} (111) surfaces in sections 3.1 and 3.3, respectively. The reaction mechanism for formaldehyde oxidation for these two models will be presented in sections 3.2 and 3.4, respectively.

3.1 HCHO and O₂ adsorption on the stoichiometric MnCe_{1-x}O₂ (111) surface

The HCHO molecule was placed on the different adsorption sites of MnCe_{1-x}O₂ (111) surface. Optimized configurations of HCHO adsorption are presented in Figure 2. In the adsorption configuration (a), the oxygen atom of the carbonyl group interacts with the Mn atom ($d_{\text{Mn-O}} = 2.12$ Å). In configuration (b), the dioxy-methylene structure (O_{2c}-HCHO) is already formed with the carbonyl group's C and O atoms coordinating to the O_{2c} and Mn atoms, respectively. The Mn-O and C-O_{2c} distances are 1.93 Å and 1.40 Å, respectively. The dioxy-methylene adsorption mode is much stronger (-1.98 eV) than the end-on adsorption mode (-0.1 eV). We found that O₂ will only weakly adsorb on the MnCe_{1-x}O₂ (111) surface with an adsorption energy of -0.06 eV.

3.2 Reaction mechanism on the stoichiometric MnCe_{1-x}O₂ (111) surface

Figure 3 shows the complete reaction diagram, including important intermediate and transition-state structures for HCHO oxidation, while other transition-state structures and variations of the spin magnetic moments of Mn and Ce are shown in the Supporting Figures S1 and S2, respectively. The reaction pathway follows the Mars-van Krevelen (Mvk) mechanism. After HCHO adsorbs on surface (state *ii*, Figure 3), one of the C-H bonds dissociates with the H atom relocating to the oxygen atom of the carbonyl group followed by spontaneous migration to the O_{2c} atom of the ceria lattice (state *iii*, Figure 3). The activation barrier for this step is 1.09 eV, and the C-H dissociation step is exothermic by 3.43 eV. The transition state consists of a three-membered ring structure (state *TS1*, Figure 3) and the C-H bond distance is increased from its initial value of 1.12 Å to 1.33 Å. The bond distance in the transition state between O and H is 1.29 Å. This step generates two excess electrons. One electron occupies the Mn 3*d* orbital reducing Mn⁴⁺ to Mn³⁺, the other one occupies the Ce 4*f* orbital, leading the formation of Ce³⁺. In TS1 (Figure 3), electron transfer to the Mn atom is only limited. The magnetic moment of Mn changes from 3.59 μB to 3.89 μB. The electrons carried by the H atom are transferred to the surface Ce atom, only when the H atom migrates to the O_{2c} atom, involving partial reduction of the surface. Following C-H bond cleavage, the remaining formyl group may react in three different manners. One involves cleavage of the

1 other C-H bond with the H atom relocating to the surface O atoms (Figure S2). However, the
2 distance of the H atom to the surface neighboring O atoms are in the 3.82-5.08 Å, too long to lead
3 to interactions facilitating C-H cleavage. The other one involves cleavage of the other C-H bond
4 with the H atom relocating to the oxygen atom of the carbonyl group, thereby generating a COH
5 group (state *v*, Figure 3). This configuration results in close proximity of the second H atom to the
6 surface O_{2c}H group, which will facilitate water formation. Nevertheless, the activation barrier for
7 this step of 3.06 eV (state *TS2*, Figure 3) is very high and the reaction is endothermic by 1.58 eV.
8 Accordingly, we did not explore reaction steps further along this pathway.

9 Another more feasible pathway involves rotation of the formyl group in a way that the H atom will
10 point to another ceria support O atom (state *iv*, Figure 3). The reaction energy for the rotation is
11 0.31 eV. From this configuration, the formyl group dissociates by donating the H atom to the
12 neighboring O atom of the support. The remaining CO group binds to surface O_{2c} forming adsorbed
13 CO₂ (state *vi*, Figure 3). The activation barrier and reaction energy for this step are 0.51 eV (state
14 *TS3*, Figure 3) and -0.64 eV, respectively. The CO₂ product can desorb very easily from the surface,
15 leaving behind an oxygen vacancy. In this configuration, the surface contains four excess electrons
16 due to the two H atoms and the oxygen vacancy. Two excess electrons are localized in the Mn 3*d*
17 orbital, *i.e.*, the formal oxidation state of Mn is 2+, and the rest of electrons are localized on
18 neighboring Ce atoms. For the remaining H atoms, migration to other surface O atoms is not
19 possible due to the large distance. This finding indicates that the H atoms can only be removed by
20 formation of water with the adsorbed O₂ molecule, which will be discussed below.

21 In ceria-catalyzed oxidation of formaldehyde, two roles have been proposed for molecular oxygen.
22 It may directly participate as an oxidizing species in the reaction or it can heal the oxygen vacancy.
23 Direct participation of O₂ in the oxidation step requires co-adsorption with the other reactant. This
24 was examined and the adsorption energies for molecular oxygen are in the range of -0.03 eV to -
25 0.12 eV. It is accordingly not likely that O₂ will be involved directly in a Langmuir-Hinshelwood type
26 mechanism before an oxygen vacancy is formed. On the other hand, once the oxygen vacancy is
27 formed, molecular oxygen will adsorb on the defective ceria surface, *i.e.*, on the oxygen vacancy,
28 strongly with $\Delta E = -1.35$ eV (state *vii*, Figure 3). Two excess electrons, which were first localized on
29 the Ce and Mn atoms transfer to the O₂ molecule, effectively activating it. Evidence for this is in
30 the elongated O-O bond distance of 1.44 Å which is to be compared to the gas-phase value of 1.23

Å. It indicates the formation of a peroxide-type O_2^{2-} species. Then O_2 dissociates into two O atoms, which requires 0.35 eV (state *viii*, Figure 3). One of the oxygen atoms fills the oxygen vacancy and the other one is adsorbed on the top of Mn atom. The Mn-O bond distance is 1.81 Å. The remaining excess electrons localized on the Ce atom transfer to the O atom that fills the oxygen vacancy to form the O^{2-} ion. The O atom coordinating to the Mn ion has O^- character. O_2 dissociation is followed by successive migration of the two H atoms to the O^- species with activation barriers of 0.44 eV and 0.25 eV (state *TS4*, *TS5*, Figure 3). These steps lead to an OH group (state *ix*, Figure 3) and an adsorbed H_2O molecule (state *x*, Figure 3) with similar reaction energies for both steps of 0.24 eV. The final water desorption costs 1.05 eV, effectively closing the catalytic cycle.

3.3 HCHO and O_2 adsorption on the defective $MnCe_{1-x}O_{2-y}$ (111) surface

It has been reported before that doping will decrease the oxygen vacancy formation energy in ceria (E_{O_v}).²³ The oxygen vacancy formation energy for $MnCe_{1-x}O_2$ (111) surface is 0.08 eV, which is much lower than the oxygen formation energy of the stoichiometric CeO_2 (111) surface ($E_{O_v} = 2.13$ eV).³⁵ This implies that under typical reaction conditions the surface will be rich with oxygen vacancies. Accordingly, it is important to also investigate the catalytic mechanism of formaldehyde oxidation on the defective $MnCe_{1-x}O_{2-y}$ (111) surface. The $MnCe_{1-x}O_{2-y}$ (111) model was constructed by removing one surface O_{2c} (labeled in orange in Figure 1). One excess electron occupies the Mn 3d orbital reducing Mn^{4+} to Mn^{3+} . The other excess electron occupies the Ce 4f orbital leading the formation of Ce^{3+} .

Adsorbing HCHO on the $MnCe_{1-x}O_{2-y}$ (111) surface to form dioxy-methylene is exothermic by -1.32 eV. The Mn-O and C- O_{2c} bond lengths are 1.99 Å and 1.45 Å, respectively (Figure 4a). Molecular oxygen can adsorb on this surface with an energy of -0.78 eV. In this case, one of the oxygen atoms fills the oxygen vacancy and the other one is coordinated to the Mn atom with the Mn-O distance being 2.29 Å (Figure 4b). The excess electron initially localized on Ce is now present on the O_2 molecule, resulting in elongation of the O-O bond to 1.34 Å. This points to superoxide-type O_2^- character of adsorbed O_2 . We also explored co-adsorption of HCHO and O_2 on this surface. With HCHO being adsorbed, O_2 will adsorb on the $MnCe_{1-x}O_{2-y}$ (111) surface with an energy of -1.99 eV (Figure 4c). One of the oxygen atoms fills the oxygen vacancy and the other one is coordinated to a neighboring Ce atom. O_2 is again reduced to the superoxide O_2^- species. Contrary to the stoichiometric surface, co-adsorption of HCHO and O_2 is possible on the defective $MnCe_{1-x}O_2$ (111)

surface (section 3.1). This opens a different reaction pathway for HCHO oxidation on the latter surface, which will be presented in the next section.

3.4 Reaction mechanism on the defective $\text{MnCe}_{1-x}\text{O}_{2-y}$ (111) surface

Figure 5 shows the complete O_2 -participate reaction energy diagram for the oxidation of formaldehyde on the defective surface. Corresponding transition-state structures and spin magnetic moment analysis for Mn and Ce ions are shown in Figures S2 and S5, respectively. In the co-adsorbed state of HCHO and O_2 (state *iii*, Figure 5), one of the C–H bonds of HCHO dissociates resulting in the formation of an OOH species (state *iv*, Figure 5). C–H bond cleavage generates two excess electrons, one of which localizes on the HOO^- surface intermediate, yielding HOO^{2-} . This leads to elongation of the O–O bond to 1.46 Å. The other electron migrates to a surface Ce atom. The activation barrier for this step is only 0.17 eV (state *TS1*, Figure 5), and the C–H dissociation step is exothermic by 2.45 eV. C–H bond dissociation catalyzed by a surface oxygen has also been examined. The activation barrier of 1.50 eV for this step is much higher than the barrier for reaction with adsorbed O_2 species. This result is in line with experimental data,²³ and further indicates that, on the defective ceria surface, the possibility of co-adsorption of O_2 with the reactant plays a key role in enhancing the activity.

After the C–H bond cleavage step, the generated HOO^{2-} species reorients, with a cost of 0.16 eV, to a configuration convenient for accepting the second H atom (state *v*, Figure 5). From this configuration, the C–H bond of the CHO formyl group cleaves protonating the HOO group. This step leads to the dissociation of the O–O bond, and formation of CO_2 and H_2O (state *vi*, Figure 5). The activation barrier for this concerted step is 0.63 eV (state *TS2*, Figure 5). It is thermodynamically favorable ($\Delta E = -1.64$ eV) and is followed by desorption of water and carbon dioxide which cost 0.71 eV to close the catalytic cycle.

4. Discussion

Experimentally, it was observed that formaldehyde was completely converted into H_2O and CO_2 at a temperature as low as 373 K using the $\text{MnO}_x\text{-CeO}_2$ mixed oxide. In contrast, single MnO_x and CeO_2 oxides and their physical mixture displayed very low HCHO conversion under similar conditions.⁷ This result points to the important role of doping by Mn in enhancing catalytic HCHO oxidation. In this work we demonstrate the importance of Mn doping on HCHO and O_2 adsorption, C–H bond activation and the different mechanism opening up following Mn doping which is the

consequence of vacancy formation.

HCHO adsorbs much stronger on the more Lewis acidic Mn cation (-1.98 eV) than on the Ce cation (-0.86 eV) in line with literature.¹⁸ Bonding with HCHO involves interactions between the C 2*p* orbitals of formaldehyde and unoccupied frontier orbitals of the surface. The density of states (DOS) clearly shows that the unoccupied 3*d* states of Mn atom are located below the unoccupied 4*f* states of Ce atom (Figure 6), explaining the stronger bonding on the Mn-doped surface.

The explored reaction mechanisms contain two key elementary reaction steps, namely the first C-H bond cleavage in adsorbed HCHO and the second C-H bond cleavage in adsorbed CHO. For the first C-H bond cleavage, the dissociation barrier is 1.71 eV on the stoichiometric CeO₂ (111) surface. As this barrier is higher than the adsorption energy of HCHO, this reaction will not take place.¹⁸ The barrier decreases to 1.09 eV and 0.17 eV for the stoichiometric and defective Mn-doped CeO₂ (111) surfaces, respectively. For the second C-H bond cleavage step, the dissociation barriers are 0.53 eV and 0.63 eV for these two surfaces, which are also much lower than the barrier on the stoichiometric CeO₂ (111) surface of 2.28 eV.¹⁸ Clearly, doping with Mn strongly activates formaldehyde, consistent with the strong adsorption of formaldehyde on the Mn ions. On the stoichiometric Mn-doped surface, the reactivity of the O_{2c} atom is higher than that of the three-fold coordinated surface O atom (O_{3c}) on the stoichiometric ceria surface. On the defective surface, molecular oxygen participates in the reaction. In these cases, O₂⁻ is generated, which is more reactive than the O_{2c} atom. Both O₂⁻ and O_{2c} atoms are more reactive than the O_{3c} atom on the CeO₂ (111) surface.

The presence of Mn strongly decreases the oxygen vacancy formation energy of ceria to 0.08 eV, while it takes 2.13 eV to remove oxygen from the stoichiometric ceria surface. This implies that at ambient conditions the Mn-doped ceria surface will already contain a significant amount of oxygen vacancies. That is to say that the Mn-doped ceria surface is predicted to be defective under reaction conditions, whereas ceria itself will not expose vacancies. The oxygen vacancy will expose an under coordinated Ce atom, which enables O₂ adsorption. In this way, the defective Mn-doped ceria surface can operate in a Langmuir-Hinshelwood type of mode in which HCHO and O₂ can be simultaneously present at the surface. On contrary, the stoichiometric ceria surface will operate according to a Mars-Van Krevelen mechanism, which is very unfavorable due to the strong Ce-O bond energy. This difference helps to explain the promoting effect of Mn in ceria-catalyzed HCHO

1 oxidation.

2 **Conclusion**

3 In this work, we have performed DFT+U calculations to study the reactions between HCHO and O₂
4 on MnCe_{1-x}O₂ and MnCe_{1-x}O_{2-y} surfaces with the aim to understand the promoting effect of Mn
5 doping on HCHO oxidation. HCHO oxidation on the stoichiometric surfaces will occur via a Mars-
6 Van Krevelen-type mechanism involving oxidation of adsorbed HCHO with surface O atoms. Two H
7 atoms of adsorbed HCHO will be abstracted by lattice surface O atoms leading to hydroxyl groups
8 and CO₂. The resulting oxygen vacancy is healed by O₂ and one of its O atoms will be used to remove
9 the two H atoms as water. This catalytic cycle proceeds with lower activation barriers when Mn is
10 present in the surface due to stronger adsorption of HCHO on Mn than Ce and the higher reactivity
11 of the ceria surface O atom in the doped surface. On the other hand, Mn doping significantly lowers
12 the oxygen vacancy energy. On the resulting defective surface, O₂ can strongly adsorb so that the
13 mechanism becomes of the Langmuir-Hinshelwood type comprising reaction between adsorbed
14 HCHO and O₂. Adsorbed O₂ is partially reduced by the surface, explaining the lower barriers for C-
15 H bond cleavage. Mn doping of ceria leads to higher HCHO oxidation activity because of formation
16 of surface defects enabling co-adsorption of formaldehyde and molecular oxygen, and the
17 generation of more active oxygen atoms, effectively decreasing C-H bond cleavage barriers.

18 **Author Information**

19 **Corresponding Author**

20 Email: songwy@cup.edu.cn; tel.: +86-18801012455.

21 Email: e.j.m.hensen@tue.nl; tel.: +31-40-2475178.

22 **Author Contributions**

23 *These authors contributed equally.

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1 **Figures**

2

3 Figure 1. Structure of the $\text{MnCe}_{1-x}\text{O}_2$ (111) surface. The O atom labeled in orange is removed to
4 obtain the defective $\text{MnCe}_{1-x}\text{O}_{2-y}$ (111) surface.

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2 Figure 2. Two possible adsorption modes of HCHO on MnCe_{1-x}O₂ (111) surface (color scheme: white

3 - H; gray - C).

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2 Figure 3. Reaction mechanism for HCHO oxidation with O₂ to CO₂ and H₂O on the MnCe_{1-x}O₂ (111)
3 surface (color scheme: yellow - Ce³⁺;
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(a)

(b)

(c)

Figure 4. The most stable adsorption configurations of (a) HCHO, (b) O₂ and (c) HCHO + O₂ on the defective MnCe_{1-x}O_{2-y} (111) surface.

Figure 5. Reaction mechanism for the oxidation of HCHO with O₂ to CO₂ and H₂O on the MnCe_{1-x}O_{2-y} (111) surface.

- 1
- 2 Figure 6. Projected density of states for Ce $4f$ and Mn ($4+$, $3+$) $3d$ orbitals (all energies referenced
- 3 to the Fermi level indicated by the dashed line).
- 4

1 TOC

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