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Facet-dependent Strong Metal Support Interactions Control the C-O Bond Activation

Song Shi^{1,2§}, Seungyeon Lee^{1§}, Chaochao Dun^{3§}, Weiqing Zheng¹, Jeffrey J. Urban³, Stavros Caratzoulas¹, Dionisios G. Vlachos^{1*}

Abstract

Reducible metal oxides are selective and effective C–O bond scission catalysts but are unstable under hydrogen exposure. Creating efficient redox centers while minimizing metal surfaces leads to highly selective catalysts. Single noble metal atoms activate the surface M–O bond, but the catalyst activity is limited due to low loading. Here, we report that the strong metal-support interaction (SMSI) between Ir and CeO₂ is facet sensitive, and certain facets regulate the C–O bond cleavage. At 300 °C reduction, Ir is mostly encapsulated on an octahedron by (111) facets but remains exposed by (110) facets. The former is selective whereas the latter is not. Density Functional Theory (DFT) indicates that Ir encapsulation is favored on (111) under reaction conditions, and oxygen vacancies more readily form on encapsulated Ir than on pristine ceria. This work showcases that the SMSI (encapsulation state) provides a general strategy for selective C–O bond activation.

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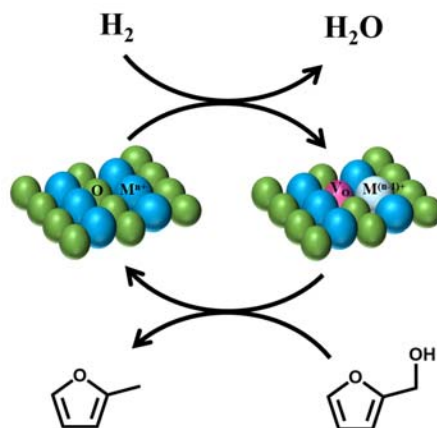
Selective C–O bond activation is essential for Fischer Tropsch synthesis, CO₂ utilization, and hydrodeoxygenation (HDO) for biomass upgrade.^{1–5} Catalysts developed for C–O bond scission include metals,⁶ metal oxides,⁴ carbons,^{7,8} and metal/acids.^{9,10} Although noble metals are active, they cause inevitable side reactions. In the case of functionalized furans and aromatics from cellulose, hemicellulose, and lignin, the selectivity is low due to the metal surfaces interacting strongly with the C=C bonds of the substrates.¹¹ Reducible metal oxides offer much higher selectivity than metals for transforming C–O side groups, due to repelling the unsaturated rings and curtailing ring chemistry, but are unstable.

Previous mechanistic investigations revealed that the C–O bond cleavage of furan rings over metal oxides follows the reverse Mars–van Krevelen mechanism.¹² Surface oxygen vacancies, created by hydrogen during the reaction, are active redox centers selectively cleaving C–O bonds (Scheme 1). The vacancy formation rate determines the C–O bond cleaving rate. Consequently, the more reducible the surface M–O bond, the higher the rate. However, readily reducible metal oxides convert to metals. This competition between activity and stability delimits the maximum activity at high selectivity.⁴ A highly efficient catalyst should have surface metal oxide reducibility but a stable bulk. For moderately reducible metal oxides, like CeO₂ and TiO₂, one can enhance the activation of the surface M–O bond by doping the oxide surface with a noble metal. However, metal nanoparticles lead to side reactions. Recently, we reported that an ultralow loading of metal dispersed into single atoms and small clusters could achieve this.⁵ This strategy avoids metal-nanoparticle-catalyzed reactions while increasing the rate over the bare oxide, but the rate enhancement is suboptimal due to the low metal loading.

The classic Strong Metal Support Interaction (SMSI) concept is epitomized by a sharp reduction in the CO and H₂ adsorption after the high-temperature reduction of supported metal catalysts.¹³ It usually occurs over the platinum group metals (PGMs) on reducible metal oxides, with Pt–TiO₂ being the most common pair, forming upon reduction at 500 °C. The most acceptable mechanism is encapsulation, wherein the reducible metal oxide overcoats the metal nanoparticles.^{14,15} A particle size-dependent SMSI and pairs beyond PGMs and reducible oxides, such as Ni/BN,¹⁶ Au/TiO₂,¹⁷ and Au/MgO,¹⁸ and adsorbate-mediated strong metal–support interactions (A-SMSI) have recently been introduced.¹⁹ While the facets of metal oxides possess different properties, their impact on the SMSI effect is less researched, except for TiO₂.^{20,21}

Here, we introduce a facet-dependent SMSI strategy for selective C–O bond activation. We expose that the SMSI between Ir and CeO₂ is facet sensitive and demonstrate that SMSI can regulate the HDO selectivity and rate. Density Functional Theory (DFT) calculations of work functions, oxygen vacancy formation energies, and binding energies

54 indicate that Ir encapsulation requires vacancies on the (111) facet and is thermodynamically preferred on the (110)
55 facet but kinetically not relevant at low reduction temperatures.



56 **Scheme 1.** Reverse Mars–van Krevelen mechanism for the C–O bond cleavage on a metal oxide catalyst. Oxygen vacancy (V_O) is shown in
57 pink.
58
59

60 Results

61 Catalyst preparation and characterization

62 CeO_2 nano-rod ($\text{CeO}_2\text{-R}$), nano-cube ($\text{CeO}_2\text{-C}$), and nano-octahedron ($\text{CeO}_2\text{-O}$) were prepared using
63 hydrothermal synthesis.²² TEM and SEM images show a well-ordered morphology (Figure 1, Figure S1). XRD
64 confirms the standard CeO_2 fluorite structure (Figure S2). The TEM-inferred lattice spacings of 0.31, 0.22, and 0.19
65 nm correspond to the (111), (110), and (100) facets, respectively, consistent with the XRD data. It is generally
66 accepted that the predominantly exposed facets of $\text{CeO}_2\text{-R}$ is the (110), of $\text{CeO}_2\text{-C}$ is (100), and of $\text{CeO}_2\text{-O}$ is (111)
67 (Table S1).^{23–25} The surface areas, measured using N_2 adsorption/desorption, are 120, 35, and 14 m^2/g , respectively
68 (Table S1, Figure S3). Ir was impregnated with a nominal loading of 1 wt% (order of magnitude higher than typical
69 single-atom catalysts). All samples were treated at 300 °C in H_2 to reduce the metal precursor and are hereafter
70 labeled as Ir- $\text{CeO}_2\text{-X-300}$ (X=R, C, or O). TEM images (Figure S4–S6) show that the nanoparticles retain their
71 morphology during impregnation. The particle size of Ir on Ir- $\text{CeO}_2\text{-C-300}$ and Ir- $\text{CeO}_2\text{-O-300}$ is around 1.0 and
72 1.3 nm, respectively (Figure S5a, S6b). Ir nanoparticles were not observed on Ir- $\text{CeO}_2\text{-R-300}$, indicating high
73 dispersion (EDS images in Figure 1) due to the high defect density of the crystals.

74 Ir 4f peaks of Ir- $\text{CeO}_2\text{-C-300}$ and Ir- $\text{CeO}_2\text{-O-300}$ (Figure S7) show metallic Ir^0 at 60.9 eV,²⁶ consistent with the
75 lattice spacings of the (111) and (200) facets (Figure S6f). For the Ir- $\text{CeO}_2\text{-R-300}$, the peak of Ir shifts to the higher
76 binding energy of 61.3 eV, due to its high dispersion, confirmed via TEM and CO adsorption (vide infra).

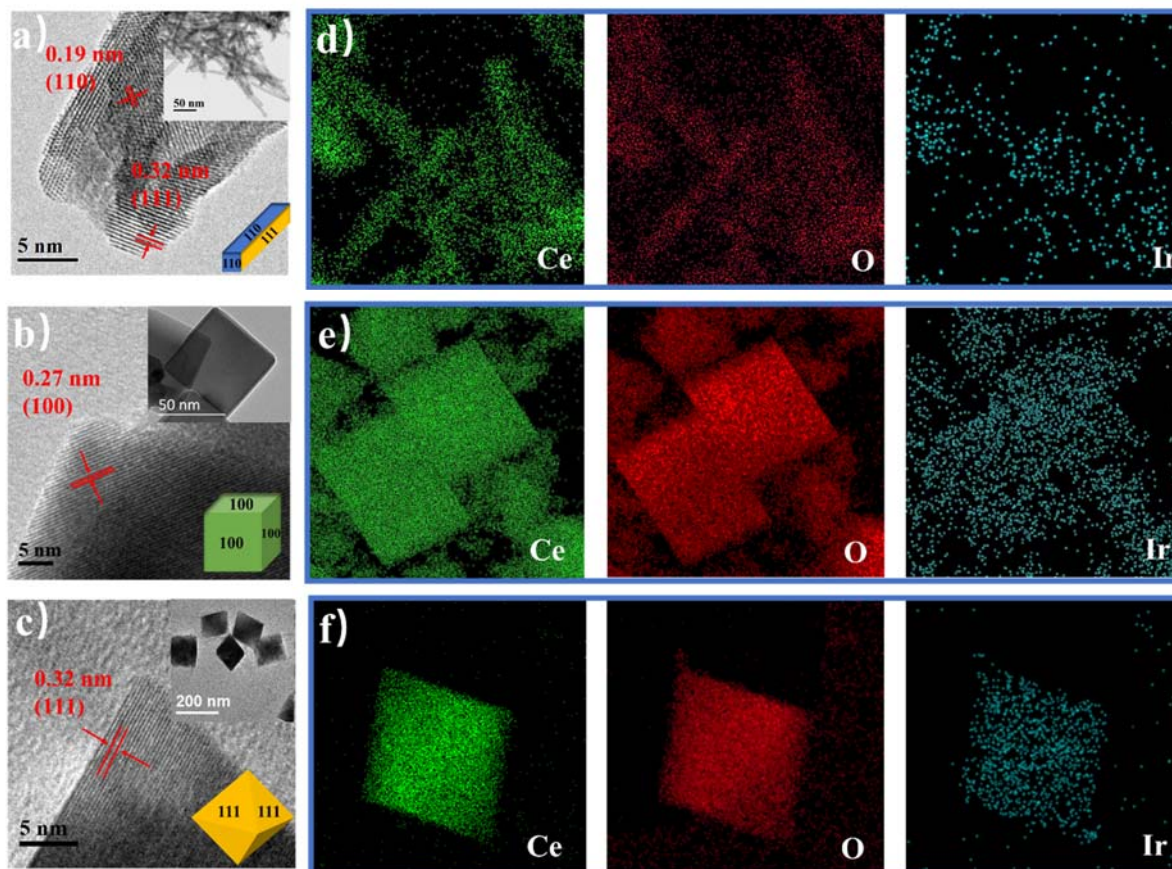
77 SMSI effect of the different CeO_2 structures

78 The interaction of Ir and CeO_2 was studied using CO pulse adsorption, CO Drifts-IR, HR-TEM, and DFT.
79 Pretreatment can minimize the effect of CeO_2 on CO adsorption.²⁷ At room temperature, the CO adsorption on Ir-
80 $\text{CeO}_2\text{-R-300}$ reaches 40.2 mmol/g (Figure 2a, Table S2), consistent with the high dispersion of Ir, whereas on Ir-
81 $\text{CeO}_2\text{-C-300}$ and Ir- $\text{CeO}_2\text{-O-300}$, is only 4.5 and 2.0 mmol/g, respectively. These results contradict the TEM
82 showing highly dispersed Ir nanoparticles.

83 SMSI of CeO_2 typically occurs at ~ 700 °C.^{28,29} However, SMSI can happen at as low a temperature as 300 °C
84 (same as our reduction temperature), for low loadings prepared by co-precipitation.²⁹ The low CO adsorption on Ir-
85 $\text{CeO}_2\text{-C-300}$ and Ir- $\text{CeO}_2\text{-O-300}$ samples suggest SMSI. To ensure full reduction of Ir, we reduced the catalyst at
86 500 °C (Figure 2b). No obvious difference on Ir- $\text{CeO}_2\text{-C}$ and Ir- $\text{CeO}_2\text{-O}$ was observed. Ir- $\text{CeO}_2\text{-R}$, on the other
87 hand, shows a classic SMSI evidenced by the dramatic CO adsorption drop at higher reduction temperatures (2
88 mmol/g at 700 °C reduction) comparable to that of Ir- $\text{CeO}_2\text{-O-300}$. No obvious sintering occurred during the high-
89 temperature treatment, except for a few particles (Figure S4g, h). The STEM-EDS mapping still shows highly
90 dispersed Ir, like that at 300 °C (Figure S8).

91 CO Drifts-IR (at room temperature, 1 atm of 0.3% CO/Ar) indicates a peak at 2068 cm^{-1} on Ir- $\text{CeO}_2\text{-R-300}$
92 from the CO adsorbing linearly on the metallic Ir (Figure 2b).³⁰ On Ir- $\text{CeO}_2\text{-C-300}$, a small peak occurs at ~ 2080
93 cm^{-1} .³¹ The peak shift implies more interfacial sites or potential electronic interaction between the particles and
94 substrate. On the Ir- $\text{CeO}_2\text{-O-300}$, only gas-phase peaks are detected. Considering the decreased CO adsorption of
95 Ir- $\text{CeO}_2\text{-R}$ with increasing reduction temperature, *in-situ* Drifts-IR of CO at various reduction temperatures was
96 conducted (Figure 2c). The CO adsorption peaks gradually decrease and ultimately disappear at 700 °C and the

97 peak at 2068 cm^{-1} (300 °C reduction) shifts to 2080 cm^{-1} (500 °C reduction), probably due to the electronic
98 interaction of Ir and CeO_2 (a characteristic of SMSI).
99



100
101 **Figure 1. Microscopy characterization and elemental mapping.** TEM images of a) CeO_2 -R, b) CeO_2 -C, c) CeO_2 -O, HAADF-STEM
102 images, and corresponding EDX elemental mappings: d) Ir- CeO_2 -R-300, e) Ir- CeO_2 -C-300, f) Ir- CeO_2 -O-300.
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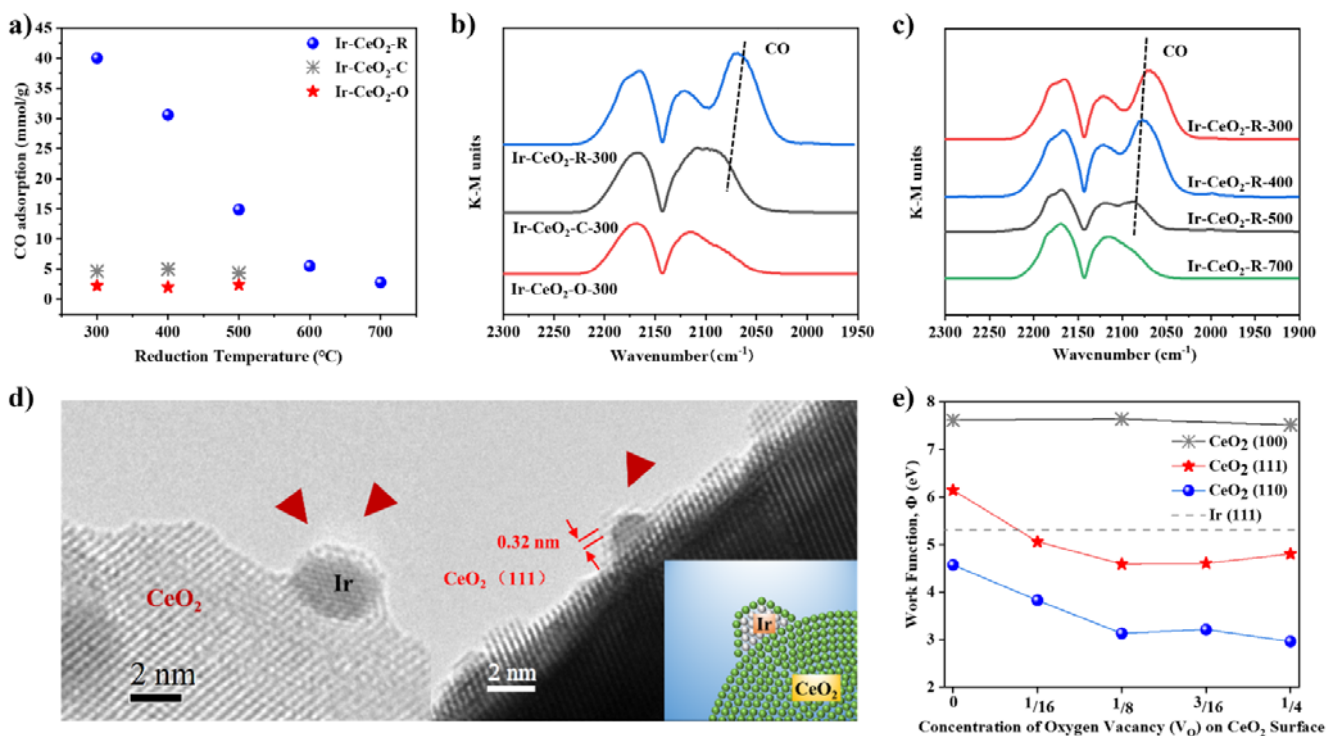
104 HR-TEM images show thin oxide layers over the Ir nanoparticles. On Ir- CeO_2 -O-300, nearly all Ir particles
105 were encapsulated by CeO_2 (Figure 2d, S6c-f). On Ir- CeO_2 -C-300, they were only partially encapsulated (Figure
106 S5c), enabling a slight CO adsorption (Figure 2a). Ir on Ir- CeO_2 -R-700 remains highly dispersed (Figure S8); a tiny
107 amount aggregates and is encapsulated by amorphous CeO_2 (Figure S4f). In addition, amorphous layers of Ir- CeO_2 -
108 O-300 without Ir after hydrogen reduction form, implying surface reconstruction (Figure S6a). This surface
109 reconstruction is likely responsible for the SMSI effect.

110 The above spectroscopic and microscopy results demonstrate that the SMSI effect sensitively depends on the
111 CeO_2 facet, a phenomenon not previously documented for CeO_2 . Prior studies have suggested that smaller metal
112 particles require higher reduction temperatures for encapsulation. To partially rule out size effects on various facets,
113 control experiments were performed by loading the same size of Ir particles ($\sim 1\text{ nm}$, Figure S9) on Ir- CeO_2 -R-np,
114 Ir- CeO_2 -C-np, and Ir- CeO_2 -O-np. CO adsorption shows a similar trend as direct impregnation (Table S2, entries
115 14-20). HR-TEM images highlight that the Ir particles on the Ir- CeO_2 -O-np are also encapsulated by an amorphous
116 shell (Figure S10d), indicating that the SMSI effect is independent of the initial Ir state. On Ir- CeO_2 -R-np, despite
117 some bare Ir particles (Figure S10b), most Ir nanoparticles are highly re-dispersed as in impregnation (Figure S10a).
118 Increasing the reduction temperature to 700 °C encapsulates the Ir nanoparticles (Figure S10c), like the
119 impregnation. We conclude this facet-dependent SMSI effect is weakly size-dependent over our studied particle
120 size range.

121 To further understand the encapsulation, we performed DFT calculations. For encapsulation to be
122 thermodynamically favorable between a metal and an oxide support, (i) the surface energy of the oxide has to be
123 lower than that of the metal; and (ii) the work function of the oxide has to be smaller than that of the metal as, then,
124 electron transfer from the oxide to the metal surface results in upward band bending at the oxide interface while the
125 positive electric field out of the oxide promotes migration of the oxide's cations.^{32,33}

126 The surface energies are: $\text{CeO}_2(111)$, $0.71 \text{ J/m}^2 < \text{CeO}_2(110)$, $1.00 \text{ J/m}^2 < \text{CeO}_2(100)$, $1.45 \text{ J/m}^2 < \text{Ir}(111)$, 2.50
 127 J/m^2 .³⁴ Based on these, Ir encapsulation by $\text{CeO}_2(111)$ is more likely than by $\text{CeO}_2(110)$ or $\text{CeO}_2(100)$. Next, the
 128 work function (Φ) at dilute oxygen vacancy (V_{O}) concentration is compared with Ir(111) (Figure 2e). On pristine
 129 CeO_2 , only (110) favors Ir encapsulation ($\Phi_{\text{CeO}_2(110)} < \Phi_{\text{Ir}(111)}$), while (100) is the least likely ($\Phi_{\text{CeO}_2(100)} > \Phi_{\text{Ir}(111)}$).
 130 Upon forming a single V_{O} , Φ of $\text{CeO}_2(111)$ decreases (6.14 eV for pristine, 5.06 eV with V_{O} , Table S3) below that
 131 of Ir(111), making encapsulation favorable. The work function of $\text{CeO}_2(111)$ and $\text{CeO}_2(110)$ decreases with the V_{O}
 132 concentration, in agreement with previous reports,³⁵ while Φ of $\text{CeO}_2(100)$ is rather independent of the V_{O}
 133 concentration and greater than Φ of Ir(111), suggesting that encapsulation by $\text{CeO}_2(100)$ is unlikely. Our data
 134 indicate that $\text{CeO}_2(110)$ is most likely to promote Ir encapsulation, while a small amount of V_{O} in $\text{CeO}_2(111)$ is
 135 necessary for encapsulation.

136 We hypothesize that encapsulation of Ir by $\text{CeO}_2(110)$ does not occur readily at low reduction temperatures,
 137 despite the favorable difference in Φ . The reason is that the top layer of $\text{CeO}_2(110)$ exposes the less coordinated
 138 Ce_{6c} atoms which function as intrinsic defects,³⁶ whereas $\text{CeO}_2(111)$ exposes evenly spaced Ce_{7c} atoms
 139 (Supplemental Note S1, Figure S11-S13). At high reduction temperatures, Ir encapsulation is also observed for Ir-
 140 CeO_2 -R (e.g., Ir- CeO_2 -R-700), as anticipated by the difference in Φ (Figure 2e) and supported by CO adsorption
 141 (Figure 2a) and HR-TEM images (Figure S4f). The significantly higher surface area of $\text{CeO}_2(110)$ than that of
 142 $\text{CeO}_2(111)$ ($120 \text{ vs } 14 \text{ m}^2/\text{g}$, Table S1) inhibits Ir aggregation. Lastly, we re-emphasize that while the (110) is the
 143 most exposed facet of CeO_2 -R, the presence of (111) or (100) facets must be kept in mind. There is an ongoing
 144 debate as to which two facets compose CeO_2 -R ((110)+(111) vs. (110)+(100)).²³⁻²⁵ Nevertheless, the (111) or (100)
 145 will reduce the probability of Ir encapsulation on CeO_2 -R.
 146



147 **Figure 2. Spectroscopic characterization, high-resolution imaging, and work function (Φ).** a) CO adsorption amount on different
 148 catalysts, b) *In-situ* Drifts-IR of CO on different CeO_2 supported catalysts, c) *in-situ* Drifts-IR of CO of Ir- CeO_2 -R under different
 149 reduction temperatures, d) HR-TEM images of Ir- CeO_2 -O-300. e) Computed work functions (Φ) for CeO_2 facets with varying concentrations of oxygen
 150 vacancies (V_{O}). Gray dashed line is the work function of Ir(111). Work function values are reported in Table S3.
 151
 152

153 Application to the HDO of furfuryl alcohol

154 HDO of furfuryl alcohol was employed as a model reaction to study the facet effect on the C-O bond cleavage.
 155 The chemistry entails C-O bond cleavage to 2-methyl furan (2-MF) and ring chemistry (hydrogenation and opening)
 156 (Figure S14). Consistent with previous work on reducible oxides, the three CeO_2 catalysts (without Ir) show high
 157 selectivity to HDO, with no ring hydrogenation,⁴ and different rates for C-O bond activation: CeO_2 -R is the most
 158 active and CeO_2 -O the least (Figure S15). The rates, after normalizing with the surface area (Figure 3a), are within
 159 a factor of two, following the order CeO_2 -O < CeO_2 -C < CeO_2 -R.
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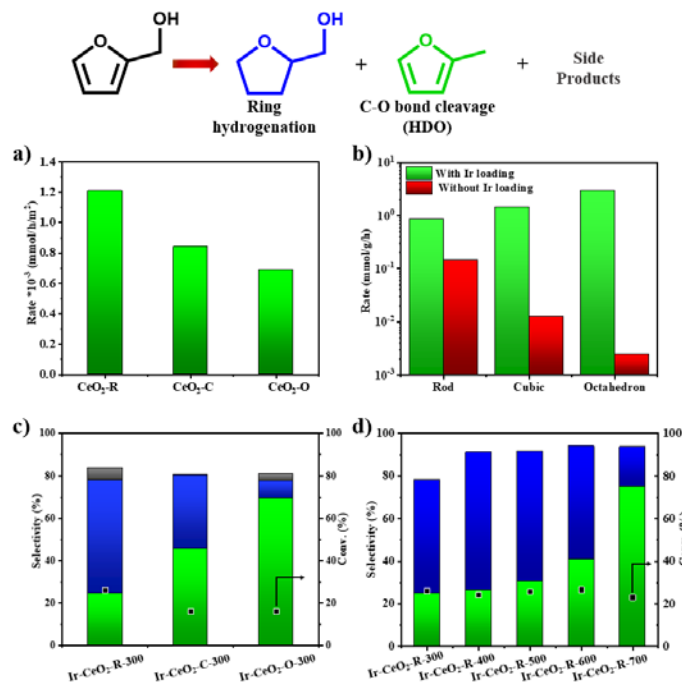


Figure 3. Catalyst evaluation in HDO over different catalysts. Top: schematic of reactions. a) HDO rate normalization with surface areas of CeO₂ on different facets. b) HDO rate of CeO₂ before and after Ir loading. c) Performance of different CeO₂-supported Ir catalysts. d) Performance of Ir-CeO₂-R catalyst reduced at different temperatures. Reaction conditions, 1 mmol furfuryl alcohol in 10 ml isopropanol, reaction temperature at 180 °C, 300 psi H₂ measured at room temperature. Green and red bars: 2-methyl furan, Blue bars: furfuryl alcohol, Gray bars: others.

The catalytic performance changes dramatically upon loading Ir on CeO₂ (Figure 3b). At a similar conversion, the selectivity of the products on Ir-CeO₂-O-300 is dominated by 2-MF (Figure 3c), while on Ir-CeO₂-R-300, the ring hydrogenation product, tetrahydrofurfuryl alcohol, dominates. The selectivity on Ir-CeO₂-C-300 is comparable to that of the other two catalysts. The rate increases upon loading Ir (Table S4, Figure 3b, S14). On Ir-CeO₂-O-300, it rises by almost three orders over the pristine oxide (from 0.0024 to 2.92 mmol/g/h), as Ir facilitates the Ce-O bond activation, forming HDO redox centers. The rate follows Ir-CeO₂-R < Ir-CeO₂-C < Ir-CeO₂-O, which is opposite of the pristine CeO₂. These performance differences stem from the SMSI effect stated above.

The selectivity differences can be attributed to the facet-dependent encapsulation. The metal surface is the primary site for ring hydrogenation.^{5,37,38} Ir-CeO₂-R-300 possesses the highest amount of metallic Ir sites, evidenced by CO adsorption and Drifts-IR, resulting in the most ring hydrogenation. Conversely, Ir-CeO₂-O-300 shows low ring hydrogenation due to the full encapsulation of Ir nanoparticles and minimally exposed metal. This is consistent with the slower hydrogenation for Ir-CeO₂-R when the metallic sites are reduced via higher temperature reduction (Figure S17). Since the metal oxide or the metal/metal oxide interface could also be active, even when encapsulated by the CeO₂, the Ir-CeO₂-O-300 still promotes C-O bond cleavage. These phenomena were also confirmed on Ir-CeO₂-R at various reducing temperatures (Figure 3d). By increasing the reduction temperature, ring hydrogenation decreases due to the decreased number of metallic sites (Figure S17). At 700 °C reduction temperature, the C-O bond cleavage dominates, consistent with the encapsulation (Figure 2a) occurring at 700 °C. The Ir-CeO₂-C and Ir-CeO₂-O state are insensitive to the reduction temperature, maintaining a constant selectivity (Figure S18).

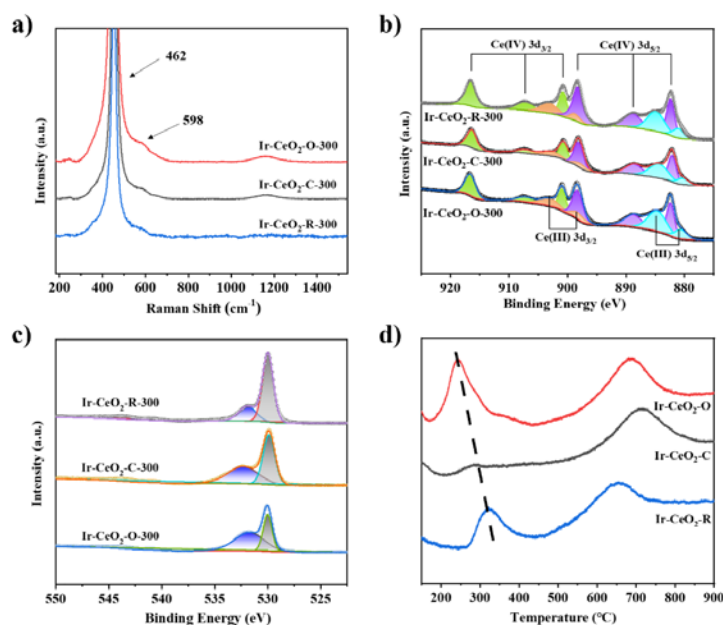
Unlike single atoms catalysis, the SMSI effect is fairly insensitive to the loading.³⁹ For CeO₂-O, even with a loading of 4 wt%, the C-O bond cleavage dominates (Figure S19). These results clearly show that the SMSI effect is an excellent knob to regulate selectivity.

Given the HDO rate is strongly affected by the oxygen vacancies, Raman, XPS, and H₂ TPR were used to explore the different morphologies systematically. In CeO₂, the Raman peak at 460 nm⁻¹ corresponds to the octahedral symmetry of the lattice, while peaks at 598 nm⁻¹ show the defect-induced mode (Figure S20).²³ The peak ratio of I₅₉₈/I₄₆₂, indicative of the oxygen vacancy density on the surface, followed the order CeO₂-O < CeO₂-C < CeO₂-R, rationalizing the reaction rate ranking. The oxygen vacancy density is also supported from XPS analysis of Ce and O (Figure S21).⁴⁰ For Ce 3d, peaks at 881.2, 884.9, 899.3, and 903.1 eV are attributed to Ce³⁺ species and the rest to Ce⁴⁺. The Ce³⁺ to Ce⁴⁺ species in CeO₂-R and CeO₂-O are 45.1 and 39.3%, respectively (Table S5). For O 1s, the peaks at 529.3 eV are due to the lattice oxygen and at 531.8 eV to the chemisorbed oxygen or oxygen vacancies.^{41,42} The latter is more active compared with the lattice oxygen according to the XPS peak shift. Thus, its

198 ratio can still be used to estimate the efficient redox center. For CeO₂-R and CeO₂-O, the ratio of chemisorbed
 199 oxygen is 52.2 and 49.7%, respectively (Table S5). XPS results of Ce 3d and O 1s support that the oxygen vacancy
 200 density follows the order CeO₂-O < CeO₂-C < CeO₂-R, consistent with the Raman results above. H₂ TPR further
 201 confirms the oxygen vacancy difference. Figure S22 shows two peaks in the three CeO₂ samples; the lower
 202 temperature one is assigned to surface Ce and the one at ~600 °C to the bulk oxide reduction.⁴³ The shift in the
 203 lower temperature peak, from 520 to 480 to 400 °C for CeO₂-O, CeO₂-C, and CeO₂-R, underscores the efficacy of
 204 reducing the various oxide facets, and its nice correlation to the facet-sensitive HDO rate and the reverse Mars–van
 205 Krevelen mechanism.

206 Metal doping is effective for activating the lattice oxygen and forming redox centers.⁴⁴⁻⁴⁶ The I₅₉₈/I₄₆₀ ratio of
 207 the Raman data (Figure 4a) follows the trend Ir-CeO₂-R-300 < Ir-CeO₂-C-300 < Ir-CeO₂-O-300. The XPS data
 208 (Figure 4b-c, S23-25, Table S6-8) shows that the Ce³⁺ species ratio increases from 46.3 to 57.0% and the
 209 chemisorbed oxygen ratio from 83.1 to 159.0%, consistent with the Raman data. The XPS data also follows a
 210 similar trend for the nanoparticle deposition method (Figure S26, Table S9), suggesting this oxygen vacancy
 211 difference is highly related to its intrinsic nature. Similarly, this trend was further confirmed by H₂ TPR (Figure 4d,
 212 S27). The peaks below 200 °C are due to the reduction of Ir, and the ones at 200-350 °C to the newly formed redox
 213 centers. Compared with pristine CeO₂, all samples are reduced at lower temperatures due to being activated by Ir.
 214 In contrast to the Ir-CeO₂-R catalyst (Figure S28a-b) which exhibits aggregation, the Ir-CeO₂-O is stable and can
 215 be recycled at least three times (Figure S29).

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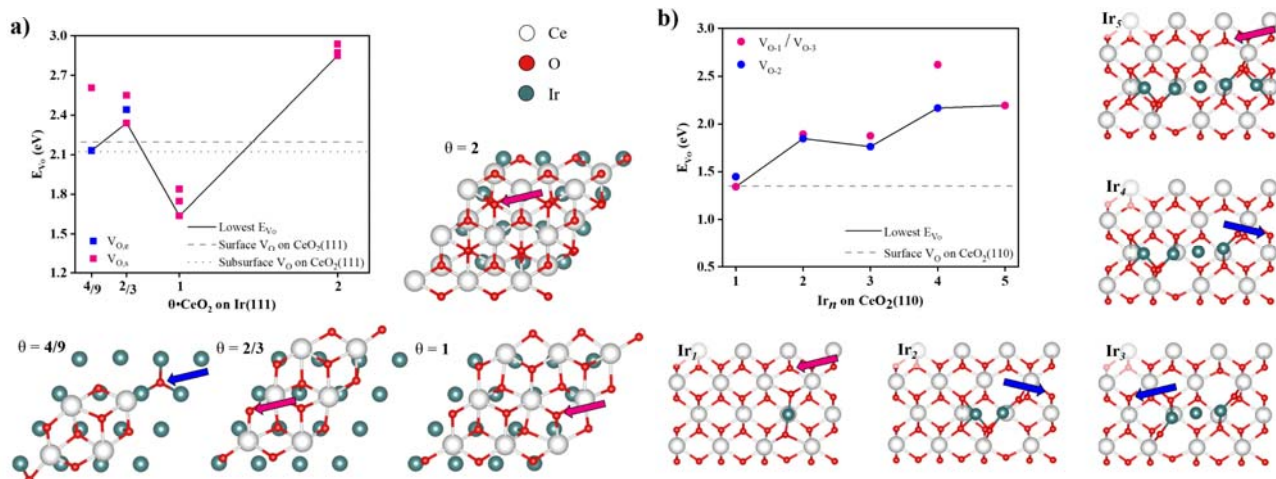


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Figure 4. Raman, XPS, and catalyst reduction data. a) Raman spectra of Ir-CeO₂-R-300, Ir-CeO₂-C-300, and Ir-CeO₂-O-300 b), c) XPS spectra and corresponding fitting curves of Ce 3d and O 1s in Ir-CeO₂-R-300, Ir-CeO₂-C-300, and Ir-CeO₂-O-300, Ce³⁺ species (881.2, 884.9, 899.3 and 903.1 eV), Ce⁴⁺ species (882.2, 888.2, 898.1, 900.7, 907.3, and 916.7 eV), chemisorbed oxygen (531.8 eV), lattice oxygen (529.3 eV). d) H₂ TPR of Ir-CeO₂-R, Ir-CeO₂-C, and Ir-CeO₂-O.

225 Next, we calculate the oxygen vacancy formation energy (E_{V_o}) and the adsorption energy of CO and furfuryl
 226 alcohol (FA) on Ir-CeO₂-O and Ir-CeO₂-R and compare them with the “pristine” surfaces (see Supplemental Note
 227 S2, Table S10-14, Figure S30-32). The Ir-CeO₂-O-300 model was informed by the TEM images and XPS
 228 measurements, which showed Ir⁰ (111) encapsulation under a thin layer of CeO₂. Ir(111) partially covered (4/9 or
 229 2/3 of the surface) to fully covered (mono or bilayer) by CeO₂ (111) (Figure 5a) represents Ir-CeO₂-O (hereafter
 230 $\theta \cdot \text{CeO}_2$, where $\theta = 4/9, 2/3, 1$ or 2). Overall, only 1•CeO₂ (hereafter Ir-O) has E_{V_o} lower than CeO₂(111) and
 231 effectively reflects the higher concentration of Ce⁺³ species in Ir-CeO₂-O-300 (36.2%, Table S8) compared to CeO₂-
 232 O (28.2%, Table S5). For the Ir-CeO₂-R-300 model, Ir^{+ δ} is slightly cationic and uniformly distributed on CeO₂-R.
 233 Different configurations of Ir_{*n*} ($n = 1-5$) were introduced in CeO₂(110) to investigate atomically dispersed Ir and
 234 small nanoclusters. Only Ir₁ (hereafter referred to as Ir-R) has E_{V_o} similar to that of pristine CeO₂(110) (1.34 vs
 235 1.35 eV), while the V_O's for Ir₂₋₅ requires more energy than pristine CeO₂(110), as shown in Figure 5b (1.63–2.62

236 eV vs 1.35 eV, Table S13). The comparable E_{V_o} between the CeO₂(110) and Ir-R captures the minimal change in
 237 V_o densities observed for CeO₂-R-300 (31.1 % of Ce⁺³, Table S5) and Ir-CeO₂-R-300 (31.6% of Ce⁺³, Table S6).
 238



239
 240 **Figure 5. Oxygen vacancy formation energies (E_{V_o}) of θ -CeO₂ ($\theta = 4/9, 2/3, 1, 2$) layers relaxed on Ir(111) (a) and Ir_n ($n = 1-5$) on
 241 CeO₂(110) (b) to model Ir-CeO₂-O and Ir-CeO₂-R, respectively. The surface geometries are displayed next to the plots (only the top
 242 surface is shown). Two different types of oxygens are removed for the two models (shown in pink/blue squares/circles). A solid black line
 243 highlights the lowest E_{V_o} per model of varying coverage or metal loading (blue/pink arrows indicate the corresponding oxygen removed).
 244 Gray dashed lines indicate E_{V_o} of pristine CeO₂. All E_{V_o} values are reported in Table S12 and Table S13 for (a) and (b), respectively.
 245**

246 We investigated the binding of CO and furfuryl alcohol (FA) on *Ir-O* and *Ir-R* with an oxygen vacancy as XPS
 247 data showed Ce⁺³ cations on Ir-CeO₂-R-300 and Ir-CeO₂-O-300 (Figure 4b-c). CO pulse adsorption implied
 248 exposed Ir atoms on Ir-CeO₂-R-300 (Figure 2a). This is reflected in the stronger CO adsorption on *Ir-R* ($E_{ad,CO} = -$
 249 1.62 eV) than on *Ir-O* ($E_{ad,CO} = -0.40$ eV) due to the direct binding of CO to the exposed Ir metal in *Ir-R*. In addition,
 250 we computed weaker CO adsorption on *Ir-R* than on Ir(111) (-2.02 eV) and stronger adsorption on *Ir-O* than on
 251 CeO₂ (~ 0 eV) (Table 1, Figure S29), reflecting changes in the electronic properties.

252 Next, the binding via the -OH group and the furan ring (C=C) was assessed on different surfaces. Oxide surfaces
 253 favor the adsorption of the -OH group and are selective for HDO, while metal surfaces bind the furan ring.⁴⁷ This
 254 is verified by the preferred adsorption geometries on CeO₂ and Ir (Table 1). Upon introducing Ir in CeO₂, we
 255 observe a strong preference for binding via the OH group on *Ir-O* ($E_{ad,FA} = -2.47$ eV via the OH group) and via the
 256 furan ring on *Ir-R* ($E_{ad,FA} = -0.95$ eV via the ring vs -0.79 eV via the OH group). The preferred binding geometries
 257 on *Ir-R* and *Ir-O* agree with the observed enhancement in hydrogenation and HDO activity on Ir-CeO₂-R-300 and
 258 Ir-CeO₂-O-300 (Figure 3c).
 259

260 **Table 1.** The adsorption energy of CO and furfuryl alcohol (FA) on Ir and CeO₂ surfaces with an V_o . The CO and FA adsorption geometries
 261 are presented in Figure S33. ($E_{ad,CO}$ or $FA = E_{surf,w,CO}$ or $FA} - E_{surface} - E_{CO}$ or $FA(gas)}$)

	$E_{ad,CO}$ (eV)	$E_{ad,FA}$ (eV) via	
		Furan ring (C=C)	Alcohol (-OH)
Ir (111)	-2.02	-2.57	N/A
CeO ₂ (111)	-0.05	-1.03	-1.65
CeO ₂ (110)	0.06	-1.05	-1.27
<i>Ir-O</i>	-0.40	-0.94	-2.47
<i>Ir-R</i>	-1.62	-0.95	-0.79

262
 263 In summary, these experiments and DFT results highly suggest that upon adding Ir, the C-O bond cleavage rate is
 264 determined by the oxygen vacancies by the reverse Mars-van Krevelen mechanism.
 265

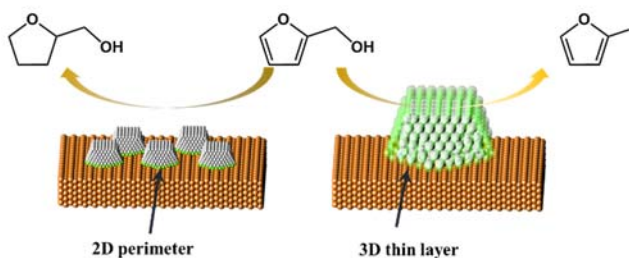
266 Discussion

267 The SMSI effect was discovered long ago, yet, the mechanism is still investigated. Recently, new SMSI effects
 268 have been discovered.⁴⁸⁻⁵¹ Oxide facets are important and TiO₂ was the first reported facet-sensitive material in
 269 SMSI.²¹ Here, we firstly reported that the SMSI effect of Ir and CeO₂ is facet controlled. The (111) facet more
 270 readily forms an encapsulated state at a low reduction temperature of 300 °C, far lower than the traditional 700 °C

271 of CeO₂. DFT calculations also revealed that Ir encapsulation is likely to occur into CeO₂(110) and CeO₂(111) with
272 oxygen vacancies, but unlikely to occur into CeO₂(100) due to the difference in the work functions (Figure 2e).

273 Owing to the encapsulation of the metal nanoparticles, SMSI usually decreases the rate of catalytic reactions
274 but exceptions have been reported.^{21,29,52,53} Until now, little attention has been paid to controlling the C-O bond
275 scission via the SMSI effect.⁵⁴ A facet-controlled SMSI effect enables the metal in different encapsulation states.
276 Encapsulation does not expose the metallic surface, staving off the side reactions such as the ring chemistry, but
277 provides more redox centers for HDO. Unlike the traditional loading method,⁵⁵ the whole thin layers over the noble
278 metal particles could be activated, changing the sites from the 2D perimeter to 3D. Here, Ir is almost fully
279 encapsulated on the octahedron CeO₂ and possesses the highest selectivity toward the C-O cleavage and the highest
280 C-O bond rate due to the highest oxygen vacancy density (Scheme 2).

281 DFT revealed that a single oxygen vacancy forms easier in *Ir-R* than *Ir-O* ($E_{V_o} = 1.34$ eV vs. 1.64 eV), while
282 HDO activity is higher on Ir-CeO₂-O-300 than on Ir-CeO₂-R-300. Moderate E_{V_o} values are preferable for high
283 activity as catalysts with low E_{V_o} values have a higher energy cost associated with surface regeneration.⁴ We found
284 that oxygen vacancies form more readily in *Ir-O* ($E_{V_o} = 1.64$ eV) than in pristine CeO₂(111) ($E_{V_o} = 2.20$ eV) and
285 prefer the -OH group of FA over the furan ring. Moreover, *Ir-O* has a larger active site, encapsulating the entire 3D
286 surface of Ir (Scheme 2) compared to *Ir-R* which is atomically dispersed, and the active site is restricted to the Ir-
287 CeO₂ interface. Moderate E_{V_o} and large active area of *Ir-O* compensate for the higher activity compared to *Ir-R* of
288 low E_{V_o} and smaller active area. The proposed strategy could be extended to other metal/metal oxide pairs.



289
290 **Scheme 2.** Proposed reaction mechanism and depiction of active sites.

291 **Methods**

292 **Preparation of catalysts**

293 *The CeO₂-rod (CeO₂-R) synthesis*

294 4 mmol Ce(NO₃)₂·6H₂O was dissolved in 80 ml 6 M NaOH aqueous solution, stirred for 20 min, and then placed in a hydrothermal synthesis
295 reactor at 100 °C for 24 h. The obtained solid was washed with water until neutral and then calcined at 350 °C for 6 hours.

296 *The CeO₂-cubic (CeO₂-C) synthesis*

297 4 mmol Ce(NO₃)₂·6H₂O was dissolved in 80 ml 6 M NaOH aqueous solution, stirred for 20 min, and then placed in a hydrothermal synthesis
298 reactor at 180 °C for 24 h. The obtained solid was washed with water for 6 times and calcined at 350 °C for 6 hours.

299 *The CeO₂-octahedron (CeO₂-O) synthesis*

300 2 mmol Ce(NO₃)₂·6H₂O dissolved in 80 ml 0.02 mM Na₃PO₄ aqueous solution, stirred for 20 min, and then placed in a hydrothermal
301 synthesis reactor at 170 °C for 12 h. The obtained solid was washed with water 6 times, and then calcined at 350 °C for 6 hours.

302 *Ir-CeO₂ synthesis*

303 The CeO₂-supported Ir catalysts were prepared using incipient wetness impregnation. Typically, CeO₂ was dispersed in the 1.0 wt % H₂IrCl₆
304 solution. The Ir loading was 1.0 wt%. Then the catalysts were reduced under pure H₂ for 6 hours. For the Ir nanoparticles, 4 mL of a solution
305 of NaOH at 0.5 M in ethylene glycol with an equal volume of a solution of H₂IrCl₆·6H₂O at 20 mM in EG was placed in a 20 ml vial. The
306 NaOH/Ir molar ratio is 25. The vials were replaced with N₂ and heated to 170 °C for 3 hours. The obtained Ir nanoparticles were washed with
307 HCl and re-dispersed in ethanol. To load them on CeO₂, a certain amount of CeO₂ was added into the solution, dried on the hotplate, and
308 then reduced under pure H₂ at a certain temperature for 6 hours.

309 **Characterization.** X-ray photoelectron spectroscopy (XPS) was performed on a Thermofisher ESCALAB 250Xi spectrometer using AlK α
310 radiation. The binding energies were calibrated using the C 1s level (284.8 eV). ¹³C cross-polarization magic-angle spinning nuclear magnetic
311 resonance (¹³C CP/MAS NMR) spectra were collected on Bruker AVANCE III HD 600 MHz. *In situ* Drifts spectroscopy measurements
312 were conducted on a Nicolet 6700 instrument equipped with a Harrick drifts cell. ATR measurements of the catalysts were conducted on a
313 Nicolet 6700 instrument equipped with golden state ATR accessories. The TEM images are obtained using the JEM2010F and JEM2100F.
314 The SEM images are recorded by Zeiss Auriga 60 High Resolution Focused Ion Beam & Scanning Electron Microscope. XRD patterns are
315 collected on Bruker D8 with Cu K α radiation. N₂ adsorption isotherm is collected on Micromeritics ASAP 2020 BET Analyzer. The CO
316 pulse adsorption and H₂ TPR experiment are performed using a Micromeritics ASAP 2020 BET Analyzer, before the CO pulse adsorption,
317 catalysts were reduced at 300 °C.

318 **Reaction procedures and products analysis.** Catalytic reactions were performed in a 125 mL autoclave reactor. Typically, 50 mg catalyst
319 and 10 mL IPA containing 1% furfural alcohol were added into the reactor. Then, the reactor was charged with 300 psi H₂ and heated to the
320 desired temperature under magnetic stirring. When the reaction was complete, the reactor was quenched with the ice bath, and then a small
321 amount of trimethyl benzene was added as an internal standard. The products were identified using an Agilent 7890N GC/5973 MS detector
322 and quantitated by Agilent 7890N GC equipped a CP-Volamine (30.0 m \times 0.320mm) column and flame ionization detector (FID).
323

324 Density-Functional Theory (DFT) Calculations

325 Spin-polarized periodic-DFT calculations were performed at the Perdew-Burke-Ernzerhof (PBE)⁵⁶ theory level with D3 dispersion⁵⁷
326 (Becke-Johnson damping⁵⁸) and dipole corrections. The projector-augmented wave (PAW)^{59,60} method was used to model core electrons.
327 Conventional valence configurations were employed for all elements. An energy cutoff of 400 eV (600 eV for bulk) and gaussian smearing
328 of 0.1 eV width were used for all structures. The SCF iterations were converged to 10⁻⁶ eV and geometries were optimized to 0.03eV/Å
329 (0.01 eV/Å) for slab (bulk) calculations. All DFT calculations were performed with the Vienna ab-initio simulation package (VASP, version
330 5.4.1).^{61,62} Bader charge analysis⁶³ was performed using the Henkelman *et al.* implementation.⁶⁴ The Visualisation for Electronic and
331 Structural Analysis (VESTA) package⁶⁵ was employed to visualize structures.

332 Bulk ceria ($Fm\bar{3}m$) with a calculated lattice constant of 5.462 Å (close to experimental value of 5.411 Å⁶⁶) was used to cleave the (111),
333 (110), and (100) facets for this study. For the (100) facet, the oxygen terminated surface with half the surface oxygens removed to the bottom
334 of the slab was used as reported in literature.^{67,68} A vacuum layer 20 Å thick in the direction normal to the surface was used in all cases.
335 Periodicity of (2 × 2) are employed for all three facets. Each slab is three layers thick (16•CeO₂ and 8•CeO₂ considered a layer for
336 (110)/(111)and (100), respectively) in which the bottom third of the atomic layers were held fixed to mimic the bulk properties. Monkhorst-
337 Pack k-point sampling of [3 × 3 × 1] was used for each facet. A +U value of 5 eV on 4f-orbitals of Ce was applied.⁶⁹ Effect of +U value on
338 the work function (Table S14) was tested and found to have a neglectable effect on the work functions of CeO₂(111) and (110) (varies by <
339 2%). The oxygen vacancy formation energy was computed from the equation

$$340 E_{V_o} = E_{CeO_{2-x}} + \frac{x}{2}E_{O_2} - E_{CeO_2} .$$

341 Author contributions

342 S. S. carried out the catalyst preparation, characterizations, analysis, tests and drafted the manuscript. S. L. and S. C. carried out the
343 DFT calculations and drafted the manuscript. C. D. and J. U. carried out the XPS, part of TEM and EDS mapping. W. Z. carried out part of
344 the TEM and assisted with the XPS deconvolution. D.G.V., S. L., C. D. and S. S. discussed the results and assisted with the manuscript
345 preparation. D.G.V led the project and revised the paper. All authors reviewed and commented on the manuscript.
346

347 Data availability

348 All data generated in this study are provided as supplementary dataset.
349

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356

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