

Article

Enabling High Activity Catalyst $\text{Co}_3\text{O}_4@\text{CeO}_2$ for Propane Catalytic Oxidation via Inverse Loading

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Abstract: Propane catalytic oxidation is an important industrial chemical process. However, poor activity is frequently observed for stable C–H bonds, especially for non-noble catalysts in low temperature. Herein, we reported a controlled synthesis of catalyst $\text{Co}_3\text{O}_4@\text{CeO}_2$ -IE via inverse loading and proposed a strategy of oxygen vacancy for its high catalytic oxidation activity, achieving better performance than traditional supported catalyst $\text{Co}_3\text{O}_4/\text{CeO}_2$ -IM, i.e., the T_{50} (temperature at 50% propane conversion) of 217 °C vs. 235 °C and T_{90} (temperature at 90% propane conversion) of 268 °C vs. 348 °C at the propane space velocity of 60,000 mL g^{−1} h^{−1}. Further investigations indicate that there are more enriched oxygen vacancies in $\text{Co}_3\text{O}_4@\text{CeO}_2$ -IE due to the unique preparation method. This work provides an element doping strategy to effectively boost the propane catalytic oxidation performance as well as a bright outlook for efficient environmental catalysts.

Keywords: propane catalytic oxidation; inverse loading; oxygen vacancy



Citation: Wang, X.; Liang, W.; Lin, C.; Zhang, T.; Zhang, J.; Sheng, N.; Song, Z.; Jiang, J.; Sun, B.; Xu, W. Enabling High Activity Catalyst $\text{Co}_3\text{O}_4@\text{CeO}_2$ for Propane Catalytic Oxidation via Inverse Loading. *Molecules* **2023**, *28*, 5930. <https://doi.org/10.3390/molecules28155930>

Academic Editor: Zhaohui Liu

Received: 30 May 2023

Revised: 30 July 2023

Accepted: 3 August 2023

Published: 7 August 2023



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1. Introduction

Environmental pollution, especially atmospheric environment pollution, is becoming an increasingly serious problem. Volatile organic compounds (VOCs) emission gained widespread attention in very recent years [1–3]. The term VOCs means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which has become a main pollutant in the whole world. VOCs come from manifold sources, such as the petrochemical industry, construction materials, the printing industry and the electronics industry. In addition to the direct health effects, such as mutagenesis, teratogenesis and carcinogenesis, VOCs form 2.5 micrometer particulate matter (PM_{2.5}) and damage the ozone layer through a series of photochemical reactions, thus seriously affecting the air quality around our living environment [4–6].

Propane, representing typical VOCs, is widely released from the energy activities involving liquefied natural gas (LNG), compressed natural gas (CNG) and liquefied petroleum gas (LPG), as well as other important industrial processes [7,8]. The effective treatment process of propane is catalytic oxidation for it provides high performance at a relatively low reaction temperature. However, there is still a problem in the catalytic oxidation of propane at low temperatures due to the stable C–H bonds in propane. Generally, precious metal (e.g., Au, Pd, Pt, Ru) catalysts show high activity in the propane catalytic oxidation [9–12]. Although noble metal catalysts, such as Pd and Pt, are supposed to be highly active and stable, their high expense, sintering rates, volatility, and the possibility of being poisoned by water or sulfur compounds limit their wide practical application. With

gradually increasing awareness of environmental protection and strict emission control regulations, highly efficient cleaning technologies of dilute propane are in great demand. More attention has been paid to transition metal oxides (such as manganese, cobalt, and copper oxides) in recent years [13–18]. Co_3O_4 and its composite oxides emerge to be competitive alternative catalysts for noble metal catalysts due to their advantages, such as varied Co valence (Co^{2+} and Co^{3+}), unfilled d orbitals, redox property, affluent active oxygen, rich resources and low prices. And it is one of the most effective active species in the cleavage of C–C and C–H bonds [19–21]. In the past decades, numerous efforts have been taken to improve the catalytic activity of Co_3O_4 based materials, for example, by controlling the size, dispersity and shape of the nanoparticles, the exposed crystal faces and the defect concentration of the surface [22–24]. New active sites can be constructed by surface engineering on the defects of Co_3O_4 based materials to regulate catalytic activity.

Oxygen vacancies (O_V), one type of common defects, were first proposed in the 1960s [25]. O_V can capture oxygen from the surrounding atmosphere and convert gaseous oxygen molecules into more reactive oxygen species. The mobility and activity of lattice oxygen species can be improved via the transmission effect of bulk vacancies. Later, researchers discovered that O_V can be used as reaction sites to change the structure of the material and the electronic and chemical properties of the surface [26–28]. CeO_2 acts as an attractive support for the catalyst to generate O_V when Ce^{4+} is reduced to Ce^{3+} that corresponds to Ce_2O_3 and CeO_2 . As the most abundant rare earth element, its content in the crust is 0.0046%. It is an acidic substance with plentiful Lewis acid sites and a few Brønsted acid sites. Acidic sites can improve the mobility of reactive oxygen species, enhance the adsorption of propane, promote the breaking of C–H bonds and thus contribute to catalytic oxidation of propane [29–32]. Moreover, O_V in the support can improve the dispersion and stability of catalysts by anchoring the active metal. However, as far as we know, there are few reports about the simple method for O_V of the Co_3O_4 -based catalyst for the propane catalytic oxidation. Thus, it is very necessary to develop a concise route to construct the O_V of the catalyst for high catalytic activity and low temperatures of propane catalytic oxidation.

In this study, we designed an inverse loading method, called ion–exchange method, and accordingly synthesized a catalyst $\text{Co}_3\text{O}_4@\text{CeO}_2\text{--IE}$ (Figure 1) possessing unique structure different from the traditional supported catalyst $\text{Co}_3\text{O}_4/\text{CeO}_2\text{--IM}$ synthesized by impregnation method. For traditional impregnation (IM) methods, an inorganic salt precursor, $\text{Co}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$ is used as the starting precursor to deposit the active species onto the outer surface of CeO_2 . These loading methods normally render limited contact area/density and relatively weak interfacial interaction between the active species and the support, resulting in easy aggregation of active species, simultaneously sharp reduction in the interfacial area/density during the pretreatment or reaction process and further impact on the catalytic performance (Figure 1a). In contrast, for the IE reaction, the $\text{Co}(\text{OH})_2$ nanosheet precursor was added into the solution of support CeO_2 precursor Ce^{3+} solution and the ion–exchange (IE) reaction took place driven by the difference of solubility product (K_sp), as shown in Figure 1b. Co^{2+} was replaced with Ce^{3+} to form $\text{Co}(\text{OH})_2@\text{Ce}(\text{OH})_4$ mixed metal hydroxide (MMH) structure. The $\text{Co}_3\text{O}_4@\text{CeO}_2\text{--IE}$ catalyst was obtained by the subsequent calcination of $\text{Co}(\text{OH})_2@\text{Ce}(\text{OH})_4$ MMH. $\text{Co}_3\text{O}_4@\text{CeO}_2\text{--IE}$ exhibits a T_{50} of 217 °C and T_{90} of 268 °C at propane space velocity of 60,000 $\text{mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, comparing to T_{50} of 235 °C and T_{90} of 348 °C for the $\text{Co}_3\text{O}_4/\text{CeO}_2\text{--IM}$. The investigations indicate that the enriched oxygen vacancies resulting from unique synthetic method, i.e., ion–exchange method, increase the propane catalytic oxidation efficiency.

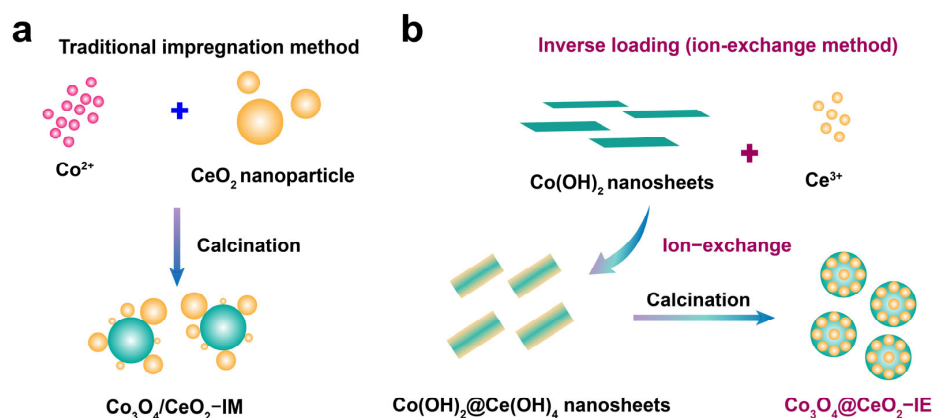


Figure 1. Schematic illustration of the synthesis of (a) Co₃O₄/CeO₂-IM prepared by impregnation method and (b) Co₃O₄@CeO₂-IE catalyst via inverse loading.

2. Results

2.1. Structure and Morphology of the Obtained Samples

Two sets of composite samples with different loading directions, i.e., the Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM, and similar chemical compositions were synthesized (Table S1 in the Supporting Information (SI)). The morphology and hierarchical structure of the composites were characterized by a high-resolution transmission electron microscope (HRTEM) and energy dispersive spectrometer (EDS) elemental mapping analyses. The transmission electron microscope (TEM) images of Co(OH)₂ show ultrathin nanosheets (about 10 nm) with clear lattice spacing of 0.26 nm (Figure S2). And the typical HRTEM images (Figure 2a) of Co₃O₄@CeO₂-IE shows the CeO₂ and Co₃O₄ particles are uniformly distributed. As shown in Figure 2b, the typical HRTEM images clearly show the Co₃O₄ (311), (220) and CeO₂ (111) with interlayer spacing of 0.243 nm, 0.288 nm and 0.310 nm, respectively. EDS elemental mapping further proves the homogeneous distribution, implying a sufficient contact between Ce and Co of the Co₃O₄@CeO₂-IE catalyst. (Figure 2c). In comparison, Co₃O₄/CeO₂-IM shows a heterogeneous distribution between Co and Ce, and the CeO₂ is reunited, meaning that there is a weak interaction between Co₃O₄ and CeO₂ (Figure 2d–f). These results suggest that Co₃O₄@CeO₂-IE mainly exposes the CeO₂ inserts into Co₃O₄ surface, while Co₃O₄/CeO₂-IM mainly stands on the surface of Co₃O₄. And the particle size of Co₃O₄@CeO₂-IE (10.8 nm) and Co₃O₄/CeO₂-IM (41.8 nm) was calculated by Scherrer equation, indicating that the smaller particles could be fabricated by ion-exchange methods.

The phase composition and crystallographic structure of Co₃O₄@CeO₂-IE samples and Co₃O₄/CeO₂-IM were examined by powder X-ray diffraction (PXRD). Figure 3a shows PXRD patterns Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM, which can be indexed to the composite phases of Co₃O₄ (JCPDS:42-1467) and CeO₂ (JCPDS:34-0394), further confirming the similarity in the effect of IE and IM methods on the preparation of the catalyst. However, there is a discrepancy in the intensity of the diffraction peaks. Co₃O₄/CeO₂-IM has higher intensity of the diffraction peaks than Co₃O₄@CeO₂-IE, suggesting that the former has better crystallinity than the latter and the uniform distribution affects the crystallinity of Co₃O₄ and CeO₂. Notably, the characteristic peaks of Co₃O₄@CeO₂-IE shift to lower 2θ values due to the diffusion of Ce⁴⁺ and Co²⁺, Co³⁺ into the opposite crystal lattice at the interface of Co₃O₄ and CeO₂ while smaller Co²⁺ (74.5 pm) and Co³⁺ (61 pm) than Ce⁴⁺ (97 pm) [33], thus forming a mixed phase. Co₃O₄/CeO₂-IM has almost the same peak positions as Co₃O₄ and CeO₂, indicating that interactions between the Co₃O₄ and CeO₂ seldom occur at the interface of Co₃O₄/CeO₂-IM, consistent with the results of HRTEM analysis. The analysis results of nitrogen adsorption isotherms of the catalysts demonstrate that Co₃O₄@CeO₂-IE (94.7 m² g^{−1}) has a much higher BET surface area than Ni-CeO₂-IM (24.3 m² g^{−1}), meaning that the IE method can expose more active sites for the following catalytic applications (Figure 3b).

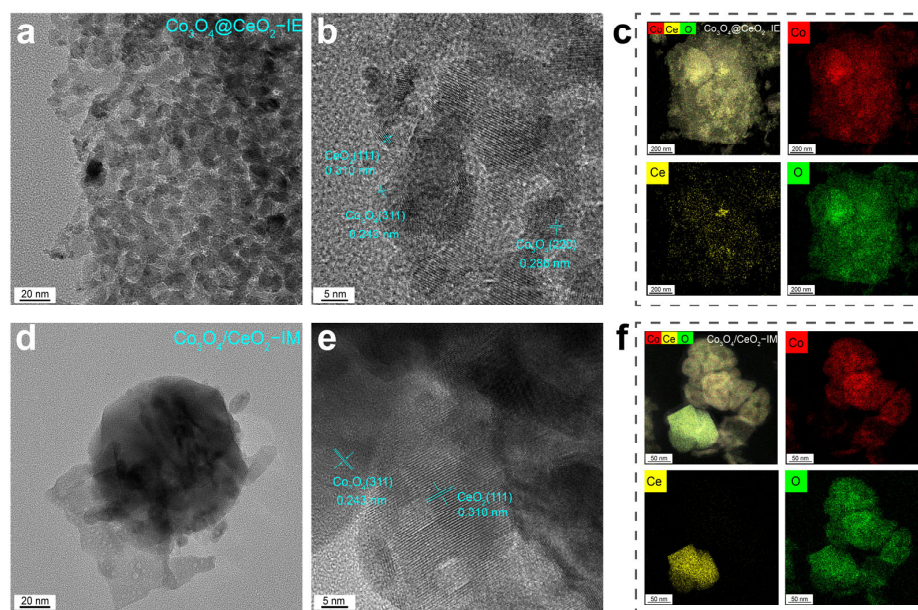


Figure 2. The typical HRTEM images of (a,b) Co₃O₄@CeO₂-IE catalyst. (d,e) Co₃O₄/CeO₂-IM catalyst, (c) EDS elemental mappings of Co₃O₄@CeO₂-IE and (f) Co₃O₄/CeO₂-IM.

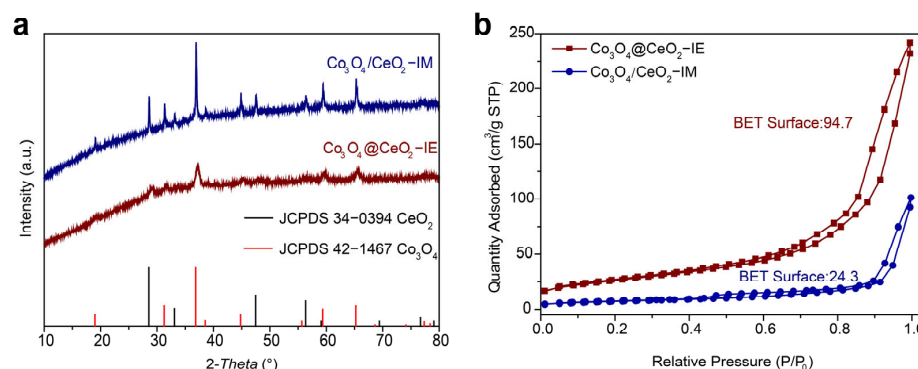


Figure 3. (a) Powder XRD patterns and (b) N₂ adsorption/desorption isotherms of Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM.

2.2. Catalytic Oxidation Performance

The propane catalytic oxidation test was performed in the fixed bed reactor at WHSV of 60,000 mL·g^{−1}·h^{−1}. The oxidative reactivity was evaluated by T₅₀ and T₉₀. Figure 4a shows that the Co₃O₄@CeO₂-IE has much higher activity than Co₃O₄/CeO₂-IM. Co₃O₄@CeO₂-IE as it participates in the propane catalytic oxidation reaction, with T₅₀ of 217 °C and T₉₀ of 268 °C, significantly superior to T₅₀ of 235 °C and T₉₀ of 348 °C for Co₃O₄/CeO₂-IM catalyst. The activation energies (E_a) were evaluated according to the Arrhenius plots in Figure 4b, demonstrating a much lower E_a value of 63.7 kJ·mol^{−1} for Co₃O₄@CeO₂-IE than Co₃O₄/CeO₂-IM (89.5 kJ·mol^{−1}). And Co₃O₄@CeO₂-IE shows a superior activity toward the total oxidation of propane to Co₃O₄/CeO₂-IM, and its reaction rate at 235 °C is 9.80 × 10^{−7} mol g^{−1} s^{−1}, is almost 1.5 times that of Co₃O₄/CeO₂-IM (6.91 × 10^{−7} mol g^{−1} s^{−1}). These findings confirm that Co₃O₄@CeO₂-IE exhibits higher catalytic activity (Table S2).

2.3. Surface Chemistry Analysis of the Catalysts

To gain deep insight into the origin of differences in catalytic behaviors between Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM, X-ray photoelectron spectroscopy (XPS) analysis was used to access the electronic state of the catalyst. The Ce 3d XPS spectra for the two catalysts were performed. And the spectra were deconvoluted into ten sub-peaks. The

peaks denoted as U and V are individually attributed to Ce 3d_{5/2} and Ce 3d_{3/2}, respectively. Among those ten peaks, U₀, U^I, V₀ and V^I are assigned to Ce³⁺ (red line) and the rest of them are related to Ce⁴⁺ (blue line) [34]. As depicted in Figure 5a, the XPS results reveal that the Ce³⁺ fraction (49.6%) on the surface of Co₃O₄@CeO₂-IE is nearly twice more than that of Co₃O₄/CeO₂-IM (28.6%). It is proposed that there are more oxygen defects on the surface of Co₃O₄@CeO₂-IE (Ce⁴⁺ + O_L → Ce³⁺ + O_V) [35,36]. The relative oxygen vacancy (O_V) proportion on the surface of Co₃O₄@CeO₂-IE (40.7%) is much higher than that of Co₃O₄/CeO₂-IM (25.0%). The peaks at 780.5 eV and 795.8 eV are attributed to the Co 2p_{1/2} and Co 2p_{3/2} core line of Co²⁺, respectively, whereas those at 779.2 eV and 794.2 eV are related to Co³⁺ [37]. The ratio of Co²⁺/Co³⁺ (2.64) in Co₃O₄@CeO₂-IE is much higher than that (1.96) in Co₃O₄/CeO₂-IM due to the fact that the oxygen defects of the catalyst can promote the reduction in metal ions (Figure 5c and Table S3).

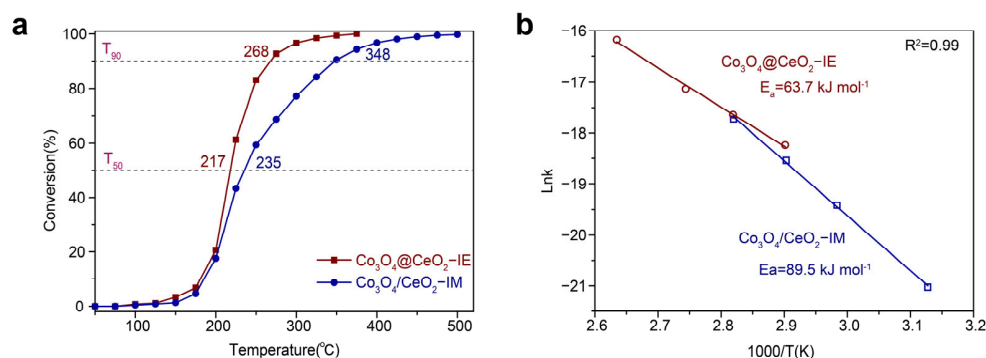


Figure 4. (a) Catalytic performance and (b) Arrhenius plots of Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM.

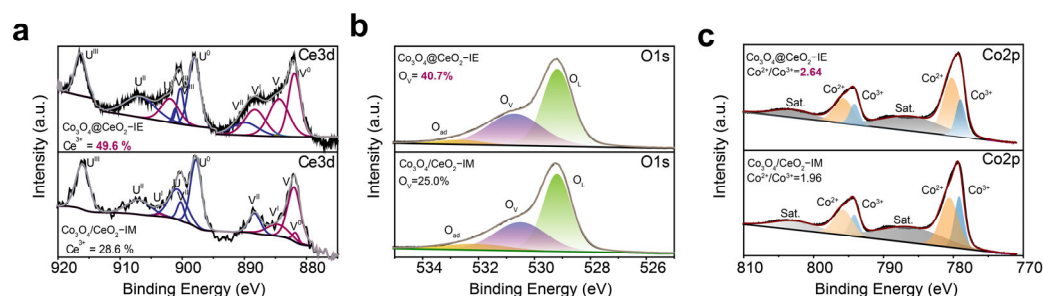


Figure 5. XPS spectra of Ce 3d (a) (Ce³⁺: V⁰, V^I, U⁰, U^I (red line); Ce⁴⁺: V, V^{II}, V^{III}, U, U^{II}, U^{III} (blue line)), (b) O 1s and (c) Co 2p for Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM.

The structures of oxygen vacancies were further investigated by electron paramagnetic resonance (EPR). Figure 6a,b show that the two catalysts have the g value of 2.004, which can be attributed to the unpaired electrons trapped in the O_V in the Co₃O₄/CeO₂ materials. Co₃O₄@CeO₂-IE has higher intensity of the peaks than Co₃O₄/CeO₂-IM. The intensity of the peaks, which is associated with the number/density of the O_V, implies that Co₃O₄@CeO₂-IE have more O_V.

The surface defects were further examined by the Raman spectroscopy (Figure 6c). Co₃O₄/CeO₂-IM exhibits the signals of 191 (F_{2g}¹), 474 (E_g), 516 (F_{2g}²), 615 (F_{2g}³) and 680 cm⁻¹ (A_{1g}), which correspond to pure Co₃O₄ [38], indicating that Ce seldom interacts with Co₃O₄ in Co₃O₄@CeO₂-IE (in accordance with the results of HRTEM and XRD analysis). All of the bands should be mainly assigned to the vibration mode of Co₃O₄. The sharp band at 461 cm⁻¹ (F_{2g} band) of CeO₂ can be assigned to the vibration mode of CeO₂ fluorite structure (Figure S3) [39,40]. The F_{2g} band of Co₃O₄@CeO₂-IE shows a red-shift of 16 cm⁻¹ to 445 cm⁻¹ with a sharp peak, which can be attributed to the Co–O–Ce bond induced by residual stress or lattice distortion in CeO₂ structure, further suggesting a strong interaction between Co₃O₄ and CeO₂ in Co₃O₄@CeO₂-IE [41].

O₂-TPD profiles were determined to recognize the oxygen species desorbed from the surface as a function of temperature. Figure 6d shows more obvious adsorption (225 °C–600 °C) and (725 °C–950 °C) of oxygen species in Co₃O₄@CeO₂-IE than in Co₃O₄/CeO₂-IM, indicating more O_V. The quantitative analysis shows that Co₃O₄@CeO₂-IE has nearly three times higher desorptive capacity of O (0.0838 mmol g⁻¹) than Co₃O₄/CeO₂-IM (0.0284 mmol g⁻¹). The defects O_V caused by Ce doping can strengthen the adsorption, activation ability of oxygen molecules and surface oxygen species migration ability, resulting in the generation of abundant active oxygen species at low temperatures.

The above analysis results indicate that the Ce³⁺ ions are partly exchanged with the Co²⁺ ions in Co(OH)₂, leading to a special interface between Co(OH)₂ and Ce(OH)₄ with the diffusion of Ce⁴⁺ and Co²⁺ into opposite crystal phases and thus more O_V of the interface in Co₃O₄@CeO₂-IE via inverse loading. There existed the lattice distortion due to the radius of Co²⁺ or Co³⁺ being smaller than Ce⁴⁺ and the charge imbalance for Co²⁺ or Co³⁺ and Ce⁴⁺ in Co₃O₄@CeO₂-IE, that may induce the more active oxygen species of Co–O–Ce in the interface than in the pure CeO₂ which induced the formation of more interfacial oxygen vacancies, while the Co₃O₄ and CeO₂ in Co₃O₄/CeO₂-IM exhibited poor interaction.

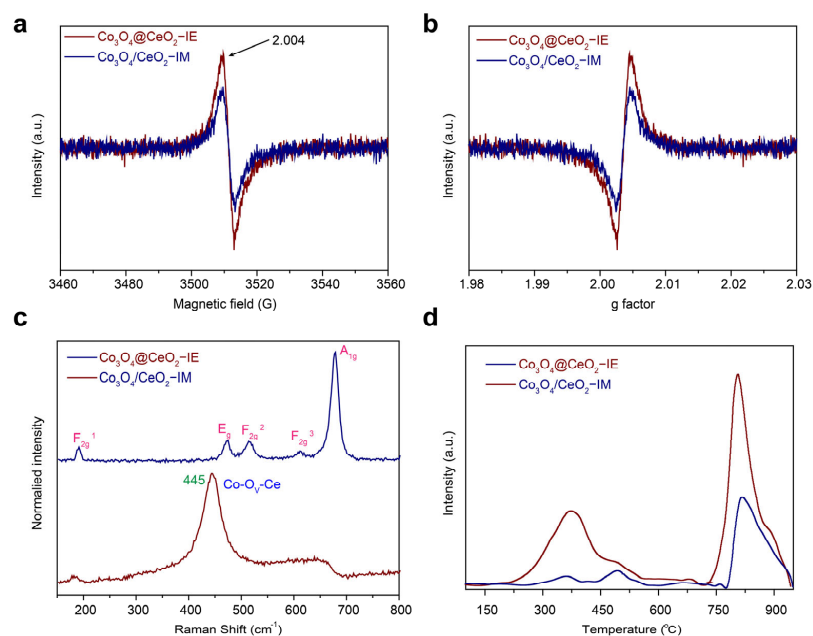


Figure 6. (a,b) EPR, (c) Raman spectra and (d) O₂-TPD profiles of Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM.

2.4. Catalytic Mechanism and Density-Functional Theory (DFT) Calculations

Marse-van Krevelen (MvK) mechanism is suitable for most non-metal catalysts to oxidize VOCs. MvK mechanism is based on redox reaction. Its essence is that the lattice oxygen in the catalyst oxidizes VOCs. In this reaction process, firstly, when VOCs react with lattice oxygen and generate oxygen vacancies, the metal oxides are reduced consequently. Secondly, oxygen vacancies are filled by oxygen in the air. The adsorption capacity and oxygen transfer capacity are the key contributing factors of the MvK mechanism. It is widely accepted that the dissociative adsorption of C₃H₈ on the catalyst surfaces triggers the catalytic oxidation process [42,43]. We calculated DFT in order to further elucidate the adsorption mechanism of Co₃O₄@CeO₂-IE. To simulate the sample, a Co₃O₄-(311) surface model was created to expose the most crystal faces in the experiments. The Co₃O₄-(311) surface, which contains O_V (Co–O_V) adjacent to Co atoms, was simulated first, and then Co₃O₄@CeO₂-IE was simulated by replacing Co atoms with Ce atoms in Co₃O₄. In the simulations, VO is adjacent to both Co and Ce atoms (Co–O_V–Ce). The reaction is initiated by the adsorption of propane to the surface, followed by the dehydrogenation of propane

to produce free radicals, which are finally oxidized to CO_2 and H_2O , where the desorption of generated propane radicals from the surface of the catalyst is the rate-limiting step for the entire reaction. Hence, the adsorption energies of propane adsorption are studied. Two substrate structures for adsorption are shown in Figure 7a,b. The calculated adsorption free energies (ΔE_{ads}) of propane on the two substrates are 0.17 eV and -0.85 eV, respectively. That indicates that propane is not favorable for adsorption on the $\text{Co}-\text{O}_V$ substrate, but is favorable for adsorption on the $\text{Co}-\text{O}_V-\text{Ce}$ surface. This is mainly due to the fact that Ce atoms have a greater number of outer electrons than Co atoms, and Ce doping in the system not only induces a large number of O vacancy defects, but also increases the free electrons of the system. The electronic density of Ce in the $\text{Co}_3\text{O}_4@\text{CeO}_2-\text{IE}$ system near the Fermi level can be analyzed according to the density of states in Figure 7c,d, conducive to electron exchange with propane. The density of states of the $\text{Co}-\text{O}_V-\text{Ce}$ structure suggests that the additional electrons provided by the Ce atoms are mainly populated above the Fermi energy level 0.3–0.7 eV above the Fermi energy level. In order to better investigate the adsorption property of propane by the extra electrons from Ce atoms, we calculated the crystal orbital Hamilton population (COHP) between Ce and H after adsorption of propane (Figure S4). We found that the extra electrons provided in the Ce atoms coupled with the H atoms favor the adsorption and dehydrogenation of propane [44]. As shown in the charge density difference in Figure 7e,f, the presence of Ce atoms leads to a greater exchange of electron density between the substrate and propane. When Ce fully invades the surface, $\text{Co}_3\text{O}_4@\text{CeO}_2-\text{IE}$ has more $\text{Co}-\text{O}_V-\text{Ce}$ structures than $\text{Co}_3\text{O}_4/\text{CeO}_2-\text{IM}$ [45], and is more conducive to the decomposition of propane.

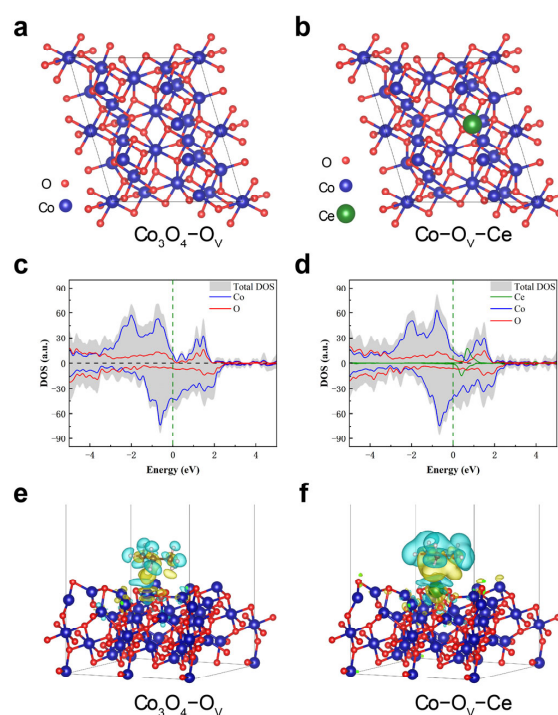


Figure 7. (a,b) The structures and (c,d) the electronic density of states (DOS) of the $\text{Co}_3\text{O}_4-\text{O}_V$ and $\text{Co}_3\text{O}_4-\text{O}_V-\text{Ce}$ substrates, respectively. The charge density difference of the substrate after propane adsorption is shown. The green dashed line represents the Fermi energy level (e,f), where the blue region represents a decrease in charge density and the yellow region represents an increase in charge density. The isosurface level is set at $0.002 \text{ e}/\text{\AA}^3$.

3. Discussion

In summary, we successfully fabricated a new kind of $\text{Co}_3\text{O}_4@\text{CeO}_2-\text{IE}$ catalyst by ion-exchange method. The obtained $\text{Co}_3\text{O}_4@\text{CeO}_2-\text{IE}$ presents superior catalytic activity in the propane catalytic oxidation. The results of XPS, EPR, Raman spectra and DFT calculations etc., indicate that $\text{Co}_3\text{O}_4@\text{CeO}_2-\text{IE}$ catalyst possesses abundant oxygen vacancies

on the surface of $\text{Co}_3\text{O}_4\text{-CeO}_2$, which adsorb the propane. This study not only presents a new kind of non-noble metal catalyst for efficient catalytic oxidation of propane, but also highlights a strategy for the design of the oxygen vacancy for an advanced catalyst.

4. Materials and Methods

4.1. Catalyst Preparation

4.1.1. Preparation of $\text{Co}(\text{OH})_2$

All chemicals were purchased from Aladdin, China, and used as received.

Synthesis of $\text{Co}(\text{OH})_2$ nanosheets. According to our previously reported hybridization route [46], the synthetic process for the $\text{Co}(\text{OH})_2$ was as follows: Commercial MgCO_3 was calcined at 750°C for two hours to obtain MgO . Then, the resultant MgO was put into distilled water with a MgO -to- H_2O mass ratio of 1:10 under stirring for 24 h. Finally, the white $\text{Mg}(\text{OH})_2$ product was separated by filtration, washed with deionized water and absolute ethanol three times and dried at room temperature. The resultant $\text{Mg}(\text{OH})_2$ (0.73 g equivalent to 0.0125 mol) was added to 25 mL of an aqueous solution containing 0.0125 mol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$. After stirring vigorously for two hours at room temperature, the green $\text{Co}(\text{OH})_2$ product was separated by filtration, washed with deionized water and ethyl alcohol three times and dried at room temperature overnight.

4.1.2. Preparation of $\text{Co}_3\text{O}_4\text{@CeO}_2\text{-IE}$ Catalyst

The $\text{Co}_3\text{O}_4\text{@CeO}_2\text{-IE}$ surrounded catalyst was synthesized by ion-change method. The fresh 1.86 g $\text{Co}(\text{OH})_2$ was added into the 40 mL solution including of 0.22 g $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and then stirred under room temperature for 30 min. And thus put the mixture into Teflon-lined stainless steel autoclave, sealed, and maintained at 120°C for 12 h. When cooled to the room temperature, the yellow-greenish products of $\text{Co}(\text{OH})_2/\text{Ce}(\text{OH})_4$ were separated by filtration, washed with deionized water and ethanol six times, and dried at 80°C overnight. The hydroxide products were calcinated at 300°C for 2 h in muffle furnace denoted as $\text{Co}_3\text{O}_4\text{@CeO}_2\text{-IE}$. The Co loading is 45.3 wt % and the Ce loading is 8.36 wt % which was determined by ICP.

4.1.3. Preparation of $\text{Co}_3\text{O}_4/\text{CeO}_2\text{-IM}$ Catalyst

The $\text{Co}_3\text{O}_4/\text{CeO}_2\text{-IM}$ catalyst was synthesized by wet impregnation method. CeO_2 support was prepared by reference method. 5.82 g $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was added into deionized 5 mL water solution and then added 0.09 g CeO_2 into the mixture. The slurry was evaporated under stirring at 110°C until dried thoroughly. And then followed the calcination denoted as $\text{Co}_3\text{O}_4/\text{CeO}_2\text{-IM}$. The Co loading was 45.4 wt % and the Ce loading was 8.38 wt % which was determined by ICP and the similar content as $\text{Co}_3\text{O}_4\text{@CeO}_2\text{-IE}$.

4.2. Characterizations

The morphology was characterized using a Hitachi S-4800 scanning electron microscope (SEM). The chemical composition of the solids was determined by an inductively coupled plasma-atomic core line spectroscopy (ICP-AES) (Thermo Fisher iCAP PRO (OES)). XRD patterns were performed on a Rigaku Miniflex 600 using Ni-filtered Cu K α radiation ($k = 0.15408\text{ nm}$) at 40 Kv and 40 mA, and the scope of data collection was $2\theta = 10\text{--}80^\circ$. The HRTEM images were obtained using a FEI Talos F200X G2 electron microscope operated at 200 kV. Results of element mapping were obtained on a super-x equipped with an Energy Dispersive Spectrometer (EDS). Brunauer-Emmett-Teller (BET) surface area measurement was conducted on a ASAP 2460 instrument. Before the BET surface area measurement, the samples were dried at 300°C for 4 h under vacuum. Temperature-programmed desorption of O_2 ($\text{O}_2\text{-TPD}$) was performed on a Tianjin XQ TP-5080B chemisorption instrument with a thermal conductivity detector (TCD). The sample (100 mg) was first at 300°C for 1 h to remove moisture under the steam (30 mL/min). After cooling to room temperature, 5 vol% O_2/N_2 mixture was switched on with a flow rate of $25\text{ mL}\cdot\text{min}^{-1}$ at 50°C for 1 h, and then cooled down to room temperature in the oxidizing atmosphere. Then continuously

purging in a He flow for 30 min, the measurement started from room temperature to 950 °C at a heating rate 10 °C·min^{−1} after the baseline of single was stable. Electron paramagnetic resonance (EPR, Bruker A300, Bremen, Germany) were tested by a FA-200 (JES) electron paramagnetic resonance spectrometer. Raman spectra were carried out on Renishaw inVia Qontor with 532 nm of incident light. X-ray photoelectron spectra (XPS) were recorded on Escalab 250Xi using Al K α radiation (1486.6 eV, 150 W) with binding energies (BEs) calibrated against the C1s peak of adventitious carbon at 284.8 eV.

4.3. Catalyst Evaluation

Propane oxidation test was carried out in a fixed-bed reactor using reactant of 0.5 vol% C₃H₈ and 21 vol% O₂, balanced with N₂. The Weight-Hourly-Space-Velocity (WHSV) was set at 60,000 mL·g^{−1}·h^{−1} with reaction temperature increased from room temperature to 500 °C (5 °C/min). The products were in situ tested by a gas chromatograph (Agilent, GC-7890B, Santa Clara, CA, USA). C₃H₈ conversion was acquired from the following formulas:

$$\text{C}_3\text{H}_8 \text{ conversion (\%)} = \frac{[\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}}}{[\text{C}_3\text{H}_8]_{\text{in}}} \times 100(\%)$$

where in, $[\text{C}_3\text{H}_8]_{\text{in}}$ and $[\text{C}_3\text{H}_8]_{\text{out}}$ represent the inlet and outlet C₃H₈ concentrations, separately.

To obtain the information of the apparent activation energy (E_a), the reaction was controlled at the kinetic regime (C₃H₈ conversion is under 10%). The equation below was used for the calculation of E_a by acquiring the slope:

$$\ln k = \frac{-E_a}{RT} + C$$

where k represents the reaction rate constant, T is the absolute temperature and R stands for the gas constant.

4.4. Computational Details

First-principles calculations were carried out using the projector-augmented wave method implemented in the Quantum ESPRESSO based on density functional theory (DFT) [47,48]. The Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) was adopted for electron exchange and correlation interaction [49]. The van der Waals interactions between layers were corrected using the DFT-D3 functional [50]. The ions relaxation was achieved until the force for per atom was less than 0.02 eV/Å and the total energy converged to 10^{−5} eV. A vacuum spacing of 15 Å was used to prevent interaction between adjacent slabs. The change in free energy for the adsorption (ΔE_{ads}) of the target by the catalyst substrate is defined by $E_{\text{q}}: \Delta E_{\text{ads}} = E_{\text{total}} - E_{\text{substrate}} - E_{\text{target}}$, where E_{total} is the total energy of the catalyst substrate and propane, $E_{\text{substrate}}$ and E_{target} are the energies of the substrate and free target molecule, respectively.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28155930/s1>, Figure S1: PXRD patterns of Co(OH)₂; Figure S2: Typical (a) TEM and (b) HRTEM images of Co(OH)₂ nanosheets; Figure S3: Raman spectrum of CeO₂; Figure S4: The crystal orbital Hamilton population between Ce and H atoms in the Co₃O₄-O_v-Ce adsorbed propane system. Table S1: Element compositions of the two catalysts analyzed by ICP technique; Table S2: The ration of Co, Ce and O ions from XPS; Table S3: Catalytic performances of Co₃O₄@CeO₂-IE and Co₃O₄/CeO₂-IM catalysts.

Author Contributions: Conceptualization: X.W., W.L. and N.S.; methodology: X.W. and W.L.; software: C.L.; validation: X.W., W.L., T.Z. and J.Z.; formal analysis: X.W.; investigation: X.W. and W.L.; resources: B.S. and W.X.; data curation: X.W. and C.L.; writing—original drat preparation: X.W.; writing—review and editing: Z.S.; visualization: X.W.; supervision: W.X., N.S. and Z.S.; project administration: J.J., B.S. and W.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by SINOPEC Research Institute of Safety Engineering Co., Ltd.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are available from the authors.

References

1. Mellouki, A.; Wallington, T.J.; Chen, J. Atmospheric chemistry of oxygenated volatile organic compounds: Impacts on air quality and climate. *Chem. Rev.* **2015**, *115*, 3984–4014. [\[CrossRef\]](#)
2. Ravi Kumar, Y.; Deshmukh, K.; Kovářík, T.; Khadheer Pasha, S.K. A systematic review on 2D materials for volatile organic compound sensing. *Coord. Chem. Rev.* **2022**, *461*, 214502. [\[CrossRef\]](#)
3. He, C.; Cheng, J.; Zhang, X.; Douthwaite, M.; Pattison, S.; Hao, Z. Recent Advances in the Catalytic Oxidation of Volatile Organic Compounds: A Review Based on Pollutant Sorts and Sources. *Chem. Rev.* **2019**, *119*, 4471–4568. [\[CrossRef\]](#)
4. Li, P.; Kim, S.; Jin, J.; Do, H.C.; Park, J.H. Efficient photodegradation of volatile organic compounds by iron-based metal-organic frameworks with high adsorption capacity. *Appl. Catal. B Environ.* **2020**, *263*, 118284. [\[CrossRef\]](#)
5. Yin, F.; Yue, W.; Li, Y.; Gao, S.; Zhang, C.; Kan, H.; Niu, H.; Wang, W.; Guo, Y. Carbon-based nanomaterials for the detection of volatile organic compounds: A review. *Carbon* **2021**, *180*, 274–297. [\[CrossRef\]](#)
6. Khatib, M.; Haick, H. Sensors for Volatile Organic Compounds. *ACS Nano* **2022**, *16*, 7080–7115. [\[CrossRef\]](#)
7. Nadjafi, M.; Abdala, P.M.; Verel, R.; Hosseini, D.; Safonova, O.V.; Fedorov, A.; Müller, C.R. Reducibility and Dispersion Influence the Activity in Silica-Supported Vanadium-Based Catalysts for the Oxidative Dehydrogenation of Propane: The Case of Sodium Decavanadate. *ACS Catal.* **2020**, *10*, 2314–2321. [\[CrossRef\]](#)
8. Zhang, M.; Sui, X.; Zhang, X.; Niu, M.; Li, C.; Wan, H.; Qiao, Z.-A.; Xie, H.; Li, X. Multi-defects engineering of NiCo₂O₄ for catalytic propane oxidation. *Appl. Surf. Sci.* **2022**, *600*, 154040. [\[CrossRef\]](#)
9. Liotta, L.F. Catalytic oxidation of volatile organic compounds on supported noble metals. *Appl. Catal. B Environ.* **2010**, *100*, 403–412. [\[CrossRef\]](#)
10. Scire, S.; Liotta, L.F. Supported gold catalysts for the total oxidation of volatile organic compounds. *Appl. Catal. B Environ.* **2012**, *125*, 222–246. [\[CrossRef\]](#)
11. Wang, B.; Wu, X.; Ran, R.; Si, Z.; Weng, D. IR characterization of propane oxidation on Pt/CeO₂-ZrO₂: The reaction mechanism and the role of Pt. *J. Mol. Catal. A* **2012**, *356*, 100–105. [\[CrossRef\]](#)
12. Chen, J.; Lv, X.; Xu, W.; Li, X.; Chen, J.; Jia, H. Utilizing Cl coordination to facilitate Ru-Ag self-assembling into alloy and recover thermally-inactivated catalyst for propane combustion. *Appl. Catal. B Environ.* **2021**, *290*, 119989. [\[CrossRef\]](#)
13. Chen, K.; Li, W.; Zhu, C.; Yuan, L. Construction of Hollow Cobalt Tetroxide Nanocages through the Metal Salt Bifunctional Etching Strategy for Catalytic Oxidation of Propane at Ultrahigh Space Velocity. *ACS Appl. Nano Mater.* **2022**, *5*, 6575–6584. [\[CrossRef\]](#)
14. Li, W.; Wang, J.; Gong, H. Catalytic Combustion of VOCs on Non-noble Metal Catalysts. *Catal. Today* **2009**, *148*, 81–87. [\[CrossRef\]](#)
15. Feng, C.; Jiang, F.; Xiong, G.; Chen, C.; Wang, Z.; Pan, Y.; Fei, Z.; Lu, Y.; Li, X.; Zhang, R.; et al. Revelation of Mn⁴⁺-O_{sur}-Mn³⁺ active site and combined Langmuir-Hinshelwood mechanism in propane total oxidation at low temperature over MnO₂. *Chem. Eng. J.* **2023**, *451*, 138868. [\[CrossRef\]](#)
16. Sun, L.; Liang, X.; Liu, H.; Cao, H.; Liu, X.; Jin, Y.; Li, X.; Chen, S.; Wu, X. Activation of Co-O bond in (110) facet exposed Co₃O₄ by Cu doping for the boost of propane catalytic oxidation. *J. Hazard Mater.* **2023**, *452*, 131319. [\[CrossRef\]](#)
17. Chen, K.; Li, W.; Zhou, Z.; Huang, Q.; Liu, Y.; Duan, Q. Hydroxyl groups attached to Co²⁺ on the surface of Co₃O₄: A promising structure for propane catalytic oxidation. *Catal. Sci. Technol.* **2020**, *10*, 2573–2582. [\[CrossRef\]](#)
18. Wu, S.; Liu, H.; Huang, Z.; Xu, H.; Shen, W. O-vacancy-rich porous MnO₂ nanosheets as highly efficient catalysts for propane catalytic oxidation. *Appl. Catal. B Environ.* **2022**, *312*, 121387. [\[CrossRef\]](#)
19. Xiao, Z.; Huang, Y.C.; Dong, C.L.; Xie, C.; Liu, Z.; Du, S.; Chen, W.; Yan, D.; Tao, L.; Shu, Z.; et al. Operando Identification of the Dynamic Behavior of Oxygen Vacancy-Rich Co₃O₄ for Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2020**, *142*, 12087–12095. [\[CrossRef\]](#)
20. Li, Z.; Zhang, Y.; Feng, Y.; Cheng, C.Q.; Qiu, W.K.; Dong, C.K.; Liu, H.; Du, X.W. Co₃O₄ Nanoparticles with Ultrasmall Size and Abundant Oxygen Vacancies for Boosting Oxygen Involved Reactions. *Adv. Fun. Mater.* **2019**, *29*, 1903444. [\[CrossRef\]](#)
21. Hu, J.; Zeng, X.; Wang, G.; Qian, B.; Liu, Y.; Hu, X.; He, B.; Zhang, L.; Zhang, X. Modulating mesoporous Co₃O₄ hollow nanospheres with oxygen vacancies for highly efficient peroxymonosulfate activation. *Chem. Eng. J.* **2020**, *400*, 125869. [\[CrossRef\]](#)
22. Iablokov, V.; Barbosa, R.; Pollefeyt, G.; Van Driessche, I.; Chenakin, S.; Kruse, N. Catalytic CO Oxidation over Well-Defined Cobalt Oxide Nanoparticles: Size-Reactivity Correlation. *ACS Catal.* **2015**, *5*, 5714–5718. [\[CrossRef\]](#)
23. Sun, H.; Ang, H.M.; Tadé, M.O.; Wang, S. Co₃O₄ nanocrystals with predominantly exposed facets: Synthesis, environmental and energy applications. *J. Mater. Chem. A* **2013**, *1*, 14427–14442. [\[CrossRef\]](#)
24. Xie, X.; Li, Y.; Liu, Z.Q.; Haruta, M.; Shen, W.-J. Low-temperature oxidation of CO catalysed by Co₃O₄ nanorods. *Nature* **2009**, *458*, 746–749. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Tompkins, F.C. Superficial Chemistry and Solid Imperfections. *Nature* **1960**, *186*, 3–6. [\[CrossRef\]](#)

26. Li, H.; Xiao, Z.; Liu, P.; Wang, H.; Geng, J.; Lei, H.; Zhuo, O. Interfaces and Oxygen Vacancies-Enriched Catalysts Derived from Cu-Mn-Al Hydrotalcite towards High-Efficient Water–Gas Shift Reaction. *Molecules* **2023**, *28*, 1522. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Jiang, W.; Loh, H.; Low, B.Q.L.; Zhu, H.; Low, J.; Heng, J.Z.X.; Tang, K.Y.; Li, Z.; Loh, X.J.; Ye, E.; et al. Role of oxygen vacancy in metal oxides for photocatalytic CO₂ reduction. *Appl. Catal. B Environ.* **2023**, *321*, 122079. [\[CrossRef\]](#)
28. Zhu, K.; Shi, F.; Zhu, X.; Yang, W. The roles of oxygen vacancies in electrocatalytic oxygen evolution reaction. *Nano Energy* **2020**, *73*, 104761. [\[CrossRef\]](#)
29. Zhang, G.; Zhou, Y.; Yang, Y.; Kong, T.; Song, Y.; Zhang, S.; Zheng, H. Elucidating the Role of Surface Ce⁴⁺ and Oxygen Vacancies of CeO₂ in the Direct Synthesis of Dimethyl Carbonate from CO₂ and Methanol. *Molecules* **2023**, *28*, 3785. [\[CrossRef\]](#)
30. Su, Z.; Yang, W.; Wang, C.; Xiong, S.; Cao, X.; Peng, Y.; Si, W.; Weng, Y.; Xue, M.; Li, J. Roles of Oxygen Vacancies in the Bulk and Surface of CeO₂ for Toluene Catalytic Combustion. *Environ. Sci. Technol.* **2020**, *54*, 12684–12692. [\[CrossRef\]](#)
31. Yang, M.; Shen, G.; Wang, Q.; Deng, K.; Liu, M.; Chen, Y.; Gong, Y.; Wang, Z. Roles of Oxygen Vacancies of CeO₂ and Mn-Doped CeO₂ with the Same Morphology in Benzene Catalytic Oxidation. *Molecules* **2021**, *26*, 6363. [\[CrossRef\]](#)
32. Lou, B.; Shakoor, N.; Adeel, M.; Zhang, P.; Huang, L.; Zhao, Y.; Zhao, W.; Jiang, Y.; Rui, Y. Catalytic oxidation of volatile organic compounds by non-noble metal catalyst: Current advancement and future perspectives. *J. Clean. Prod.* **2022**, *363*, 132523. [\[CrossRef\]](#)
33. Singha, R.K.; Shukla, A.; Yadav, A.; Sivakumar Konathala, L.N.; Bal, R. Effect of Metal-Support Interaction on Activity and Stability of Ni-CeO₂ Catalyst for Partial Oxidation of Methane. *Appl. Catal. B Environ.* **2017**, *202*, 473–488. [\[CrossRef\]](#)
34. Wei, X.; Wang, X.; Pu, Y.; Liu, A.; Chen, C.; Zou, W.; Zheng, Y.; Huang, J.; Zhang, Y.; Yang, Y.; et al. Facile Ball-Milling Synthesis of CeO₂/g-C₃N₄ Z-Scheme Heterojunction for Synergistic Adsorption and Photodegradation of Methylene Blue: Characteristics, Kinetics, Models, and Mechanisms. *Chem. Eng. J.* **2021**, *420*, 127719. [\[CrossRef\]](#)
35. Jiang, F.; Wang, S.; Liu, B.; Liu, J.; Wang, L.; Xiao, Y.; Xu, Y.; Liu, X. Insights into the Influence of CeO₂ Crystal Facet on CO₂ Hydrogenation to Methanol over Pd/CeO₂ Catalysts. *ACS Catal.* **2020**, *10*, 11493–11509. [\[CrossRef\]](#)
36. Chang, S.; Li, M.; Hua, Q.; Zhang, L.; Ma, Y.; Ye, B.; Huang, W. Shape-Dependent Interplay Between Oxygen Vacancies and Ag–CeO₂ Interaction in Ag/CeO₂ Catalysts and Their Influence on the Catalytic Activity. *J. Catal.* **2012**, *293*, 195–204. [\[CrossRef\]](#)
37. Han, X.; Li, J.; Lu, J.; Luo, S.; Wan, J.; Li, B.; Hu, C.; Cheng, X. High mass-loading NiCoLDH nanosheet arrays grown on carbon cloth by electrodeposition for excellent electrochemical energy storage. *Nano Energy* **2021**, *86*, 106079. [\[CrossRef\]](#)
38. Mo, S.; Zhang, Q.; Li, S.; Ren, Q.; Zhang, M.; Xue, Y.; Peng, R.; Xiao, H.; Chen, Y.; Ye, D. Integrated Cobalt Oxide Based Nanoarray Catalysts with Hierarchical Architectures: In Situ Raman Spectroscopy Investigation on the Carbon Monoxide Reaction Mechanism. *ChemCatChem* **2018**, *10*, 3012–3026. [\[CrossRef\]](#)
39. Spanier, J.E.; Robinson, R.D.; Zhang, F.; Chan, S.-W.; Herman, I.P. Size-Dependent Properties of CeO_{2-y} Nanoparticles as Studied by Raman Scattering. *Phys. Rev. B* **2001**, *64*, 245407–245414. [\[CrossRef\]](#)
40. Lin, J.; Li, L.; Huang, Y.; Zhang, W.; Wang, X.; Wang, A.; Zhang, T. In Situ Calorimetric Study: Structural Effects on Adsorption and Catalytic Performances for CO Oxidation over Ir-in-CeO₂ and Ir-on-CeO₂ Catalysts. *J. Phys. Chem. C* **2011**, *115*, 16509–16517. [\[CrossRef\]](#)
41. Chen, L.; Liu, F.; Li, X.; Tao, Q.; Huang, Z.; Zuo, Q.; Chen, Y.; Li, T.; Fu, M.; Ye, D. Surface adsorbed and lattice oxygen activated by the CeO₂/Co₃O₄ interface for enhance catalytic soot combustion: Experimental and theoretical investigations. *J. Colloid Interface Sci.* **2023**, *638*, 109–122. [\[CrossRef\]](#)
42. Wu, S.; Liu, H.; Huang, Z.; Xu, H.; Shen, W. Mn₁Zr_xO_y mixed oxides with abundant oxygen vacancies for propane catalytic oxidation: Insights into the contribution of Zr doping. *Chem. Eng. J.* **2023**, *452*, 139341. [\[CrossRef\]](#)
43. Zhu, W.; Chen, X.; Jin, J.; Di, X.; Liang, C.; Liu, Z. Insight into catalytic properties of Co₃O₄-CeO₂ binary oxides for propane total oxidation. *Chin. J. Catal.* **2020**, *41*, 679–690. [\[CrossRef\]](#)
44. Maintz, S.; Deringer, V.; Tchougreff, A.; Dronskowski, R. LOBSTER: A Tool to Extract Chemical Bonding from Plane-Wave Based DFT. *J. Comput. Chem.* **2016**, *37*, 1030–1035. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Song, C.; Zhan, Q.; Liu, F.; Wang, C.; Li, H.; Wang, X.; Guo, X.; Cheng, Y.; Sun, W.; Wang, L.; et al. Overturned Loading of Inert CeO₂ to Active Co₃O₄ for Unusually Improved Catalytic Activity in Fenton-Like Reactions. *Angew. Chem. Int. Ed.* **2022**, *61*, e202200406. [\[CrossRef\]](#)
46. Wang, X.; Song, H.; Ma, S.; Li, M.; He, G.; Xie, M.; Guo, X. Template ion-exchange synthesis of Co-Ni composite hydroxides nanosheets for supercapacitor with unprecedented rate capability. *Chem. Eng. J.* **2021**, *432*, 134319. [\[CrossRef\]](#)
47. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **2009**, *21*, 395502. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno Nardelli, M.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys. Condens. Matter* **2017**, *29*, 465901. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Van Setten, M.J.; Giantomassi, M.; Bousquet, E.; Verstraete, M.J.; Hamann, D.R.; Gonze, X.; Rignanese, G.M. The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table. *Comput. Phys. Commun.* **2018**, *226*, 39–54. [\[CrossRef\]](#)
50. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104. [\[CrossRef\]](#)

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