

Facet-dependent activity of Co₃O₄ catalyst for C₃H₈ combustion

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Graphic abstract



Highlights

- Co_3O_4 exposed different facets are synthesized and employed in C_3H_8 combustion.
- Co_3O_4 {111} exhibits the highest activity towards C_3H_8 combustion.
- Facile activation of C_3H_8 and better redox properties for the excellent performance.

Abstract

Clarifying the facet-dependent activity of Co_3O_4 towards C_3H_8 combustion is of great importance to have a deep understanding of reaction mechanism and develop highly active Co_3O_4 based catalysts for light hydrocarbon combustion. In this work, four different Co_3O_4 nanocatalysts which dominantly exposed {100}, {111}, {110} and {112} facets, respectively, were synthesized via hydrothermal method and further tested in C_3H_8 combustion. The catalytic activity of different crystal planes varied as the order of {111} > {100} > {110} > {112}. The Co_3O_4 catalyst with {111} facets exhibited the best catalytic performance with T_{50} and T_{90} as low as 209 and 239 °C, respectively. DRIFT and DFT calculations revealed that the facile activation of C-H bond on Co_3O_4 {111} planes is responsible for the high activity. Moreover, the higher activity of lattice oxygens and easy activation of gas phase oxygen could also contribute to the excellent catalytic performance.

Keywords: Co₃O₄; facet-dependent; C₃H₈ combustion; C-H activation.

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1. Introduction

Catalytic combustion is considered to be one of the most efficient means to eliminate the atmospheric pollutions like CO [1, 2], methane [3, 4] and various VOCs [5-7]. Catalysts based on precious metals such as Au [8], Pt [9] and Pd [10] are highly active towards catalytic combustion, but the high cost and facile deactivation due to poisoning [11] or sintering [12] have limited their large scale application.

Therefore, much attention has been paid to the non-noble metal oxide catalysts, for example Co₃O₄ [13], MnO_x [14], CeO₂ [15, 16] and mixed oxides such as spinels [17, 18] and perovskites [19]. Among them, Co₃O₄ is one of the most active catalysts towards catalytic combustion [20]. Currently, many studies have focused on the catalytic performance of Co₃O₄ with different morphologies including cubes [21, 22], octahedrons [21, 23], rods [24, 25], needles [26,27], belts [28,29], sheets [30,31] and plates [32,33]. The specific morphology possesses the dominantly exposed facets, which have significant impact on catalytic performance of reactions such as water splitting and catalytic combustion. Liu et al. [34] reported that the Co_3O_4 octahedrons enclosed by {111} facets exhibited the excellent activity in water splitting, because the {111} facets possessed the biggest dangling bond density, highest surface energy for the facial adsorption of ionized oxygen species and the smallest absolute value of Gibbs free energy for H adsorption. Xie et al. [35] fabricated the Co₃O₄ nanorods which could oxidize CO at -77 °C. The excellent performance was due to the abundant active Co^{3+} sites on the exposed {110} surface. Hu *et al.* [36] synthesized the Co₃O₄ nanosheets with {112} facets, which exhibited superior activity in methane combustion. The high activity was associated with the more open surface atoms arrangement of the $\{112\}$ planes. Therefore, it is meaningful to investigate the crystal plane effect on the catalytic activity

of different reactions.

 C_3H_8 , mainly comes from the LPG [37], is a kind of VOCs in atmosphere and should be eliminated through appropriate methods. Due to the high stability of C_3H_8 , it usually acts as a model reactant for catalytic combustion [38, 39]. Investigating the Co_3O_4 crystal plane effect on C_3H_8 combustion activity can help us to have a deep understanding of the reaction mechanism and develop highly active Co_3O_4 catalysts. However, to the best of our knowledge, few studies care about the influence of Co_3O_4 crystal plane effect on the catalytic performance of C_3H_8 combustion. Therefore, we intend to fabricate the Co_3O_4 catalysts with various exposed facets and investigate the effect of different crystal planes on C_3H_8 combustion activity.

Herein, four different Co_3O_4 catalysts with various shapes and crystal planes were synthesized through hydrothermal routes and further tested in C_3H_8 combustion. Co_3O_4 -H with {111} planes exhibited the best catalytic activity in terms of T_{50} and T_{90} as low as 209 and 239 °C, respectively. Through the combination of experimental results and DFT calculations, the mechanism of C-H activation process on the surface of Co_3O_4 as well as the reason for the superior activity of Co_3O_4 {111} planes was explored and the correlation between Co_3O_4 crystal planes with intrinsic catalytic activities was finally established.

2. Experimental

2.1.Preparation methods

All catalysts were synthesized through hydrothermal methods and roughly presented in Scheme 1. The detailed processes are shown as follows:

Preparation of Co_3O_4 nanocubes (Co_3O_4 -C): 3 mmol of $Co(OAc)_2 \cdot 4H_2O$ and 2.4 g PVP (Mw=10000) were dissolved in 114 mL of water with stirring for 15 min. Then, 6 mL of 1 M

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NaOH aqueous solution was added to the solution with further stirring for 20 min. After that, 0.2 g KClO₃ was added into the above solution with stirring for another 2 min. The mixture was transferred to a Teflon-lined autoclave, sealed and maintained at 180 °C for 24 h. After cooling down to room temperature, the product was collected by centrifugation and washed by water for several times. With further drying at 60 °C and calcination at 350 °C for 1 h, the catalyst was obtained.

Preparation of Co_3O_4 hexagonal nanoplates (Co_3O_4 -H): 3 mmol of $Co(OAc)_2 \cdot 4H_2O$ and 2.4 g PVP (Mw=10000) were dissolved in 114 of mL water under stirring for 15 min. Then, 6 mL of 1.5 M NaOH aqueous solution was added to the solution with stirring for another 2 min. The mixture was transferred to a Teflon-lined autoclave, sealed and maintained at 180 °C for 24 h. After cooling down to room temperature, the product was collected by centrifugation and washed with water for several times. With further drying at 60 °C and calcination at 350 °C for 1 h, the catalyst was obtained.

Preparation of Co_3O_4 nanorods (Co_3O_4 -R): 12.5 mL of concentrated NH₃ • H₂O was mixed with 20 mL of ethylene glycol to form a transparent solution. Then, 1 mL of 1 M Na₂CO₃ aqueous solution and 5 mL of 1 M Co(NO₃)₂ • 6H₂O aqueous solution was added in turn into the above mixture. After stirring for 20 min, the mixture was transferred to a Teflon-lined autoclave, sealed and maintained at 140 °C for 12 h. When cooling down to room temperature, the product was collected and washed with water for several times. Finally, the sample was dried and calcined at 350 °C for 1 h to obtain the catalyst.

Preparation of Co_3O_4 nanosheets (Co_3O_4 -S): 1.8 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 40 mL of water, which was mixed with 40 mL of hexamethylenetetramine (HMT) aqueous solution

(containing 1.7 mmol of HMT). Then, 10 M NaOH aqueous solution was added drop wise into the above solution and adjust the pH to 11. After stirring for 2 h, the mixture was transferred into a Teflon-lined autoclave, sealed and maintained at 110 °C for 24 h. When cooling down to room temperature, the product was collected and washed with water for several times. Finally, the sample was dried and calcined at 350 °C for 1 h to obtain the catalyst.

2.2.Characterization

Crystalline structure of catalysts were analyzed by X-ray powder diffraction (XRD) (PANalytical Empyrean X'pert powder diffractometer) with Cu K α radiation. The visible Raman spectra was recorded on a LabRAM HR Evolution Raman spectrometer with the 532 nm laser as excitation source. The specific surface area and the pore size distribution of catalysts were measured by the N₂ adsorption-desorption measurements on a Micromeritics ASAP 2460 equipment. The morphology and microstructures of the samples were characterized by transmission electron microscope (TEM, JEM-2100F) with accelerating voltage of 200 kV. X-ray photoelectron spectra was obtained by an AXIS ULTRA DLD X-ray photoelectron spectrometer, the binding energies of all elements were corrected by the standard C 1s line at 284.6 eV.

H₂-temperature programmed reduction (H₂-TPR) measurements were conducted on a TP-5080 chemical adsorption apparatus with a TCD detector. 30 mg of sample was loaded in the quartz tube. The feed gas (5 vol. % H₂ / N₂) flow was 30 ml/min. Each sample was heated from room temperature to 800 °C with the ramping rate of 10 °C/min.

 C_3H_8 -temperature programmed reduction (C_3H_8 -TPSR) profiles were measured by an on-line quadrupole mass spectrometer (MS, IPI GAM 200). 30 mg of sample was pretreated in the flow of 10 vol. % O_2 / Ar at 300 °C for 1 h. After cooling down to 50 °C, the sample was purged with 1

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vol. % C_3H_8 / Ar for 1 h to eliminate the physical adsorbed O₂. Following that, the sample was heated with a ramping rate of 10 °C/min from 50 °C to 800 °C. The effluent gas was monitored by a mass spectrometer and the mass signal of CO₂ (m/z=44) and C₃H₈ (m/z=29) were detected.

CO₂-temperature programmed reduction (CO₂-TPD) experiments were conducted on the same on-line quadrupole mass spectrometer (MS, IPI GAM 200). Typically, 150 mg of sample was pretreated in air flow at 300 °C for 1 h. After cooling down to room temperature, the sample was purged with 1 vol. % C₃H₈ / Ar to eliminate the physical adsorbed O₂ and then heated to 220 °C with a ramping rate of 10 °C/min. When cooling down to room temperature, the sample was purged with Ar for 1 h and heated to 900 °C with the ramping rate of 10 °C/min. The signal of CO₂ (m/z=44) was detected.

In-situ Raman spectra were measured on the LabRAM HR Evolution Raman spectrometer with excitation source of 532 nm. The sample was heated from room temperature to 300 °C under the oxygen atmosphere (0.5% vol. O₂/Ar) with the ramping rate of 10 °C/min. The spectra was recorded at 50 °C, 100 °C, 150 °C, 200 °C, 220 °C, 240 °C, 260 °C, 280 °C and 300 °C, respectively. Before recording of every spectra, the sample should be stabilized at that temperature for 15 min.

Diffuse reflectance infrared Fourier transform (in-situ DRIFT) was conducted on a Nicolet Magna 750 infrared spectrometer. First, the sample was loaded in the DRIFT cell and the spectra was recorded as the background. Then, the gas flow of 1% vol. C₃H₈/Ar was purged into the cell and the sample was heated from room temperature to 300 °C with the ramping rate of 10 °C/min. The spectra was recorded at 50 °C, 100 °C, 150 °C, 200 °C, 250 °C and 300 °C, respectively. Before recording, the sample should be maintained at that temperature for 15 min.

2.3. Evaluation of catalysts

The catalytic activity for C_3H_8 combustion was tested with a continuous flow fixed-bed reactor. Typically, 0.2 g catalyst mixed with 0.5 g quartz sands was loaded in the tubular reactor. The catalyst was heated under the feed gas (1 vol% C_3H_8 and 10 vol% O_2 balanced with N_2) at flow rate of 33.3 mL/min equivalent to the weight hourly space velocity (WHSV) of 10000 ml g⁻¹ h⁻¹. The feed and effluent gas was analyzed by gas chromatography equipped with a hydrogen flame ionization detector (FID).

3. Results and discussion

3.1. Structural, textural and morphological characterization

The crystalline structures of catalysts were characterized by XRD. As depicted in Figure 1, all samples show the similar diffraction patterns with intense peaks at 2θ =19.1°, 31.4°, 37°, 45°, 55.9°, 59.6° and 65.5°, which are indexed to the spinel Co₃O₄ (JCPDS No. 03-065-3103) and no peak attributed to CoO or any other impurities are detected, indicating the high purity and crystallinity of the fabricated Co₃O₄ catalysts.

Visible Raman spectra was conducted to further investigate the sub-lattice structures of catalysts. As seen in Figure 2, all samples possess five vibration modes located at 196 cm⁻¹, 522 cm⁻¹, 620 cm⁻¹, 482 cm⁻¹ and 693 cm⁻¹, which are matched well with the F_{2g} , E_g and A_{1g} symmetry of spinel Co₃O₄ [40]. It should be noted that the A_{1g} symmetry is corresponding to the Co³⁺-O²⁻ vibration in octahedral sites (CoO₆) of Co₃O₄ [41]. Any slight shift of A_{1g} symmetry reflects the change of Co-O bond, which can result in the lattice distortion in spinel structure [42]. As seen in the insertion of Figure 2, an obvious red shift of A_{1g} peak from 692 cm⁻¹ to 689 cm⁻¹ is observed in Co₃O₄-H, indicating lattice distortion in the catalyst. The lattice distortion can induce the formation of defective structures such as oxygen vacancies, which may promote oxygen activation

[43, 44]. Moreover, as the peaks at 196 cm⁻¹ and 691 cm⁻¹ are the characteristic of tetrahedral sites (CoO₄) and octahedral sites (CoO₆) of Co₃O₄, the intensity ratio of these two peaks may reflect the surface relative content of Co^{2+}/Co^{3+} [45]. As summarized in Table 1, the I₁₉₆/I₆₉₁ values follow the order of Co₃O₄-H > Co₃O₄-C > Co₃O₄-P > Co₃O₄-R, indicating more Co²⁺ on the surface of Co₃O₄-H. The results can be further confirmed by XPS, which will be shown latter.

The textural properties in terms of BET surface area and pore volume are listed in Table 1. All samples exhibit similar pore volume while the BET surface areas vary from 23.6 to 50 m² g⁻¹, the difference may be due to the various morphologies of samples obtained by different synthetic routes.

Figure 3 shows the TEM, HRTEM images of catalysts and the schematic diagrams of different Co_3O_4 facets. As seen in Figure 3a1, the Co_3O_4 -C sample exhibits uniform nanocubes with size of about 20 nm. Two sets of mutually perpendicular (220) planes with lattice space of 0.28 nm can be found and the corresponding FFT image spot array is well indexed as the [001] zone axis (Figure 3a2), indicating the dominantly exposed facets of Co_3O_4 -C are {100} planes. The Co_3O_4 -H sample presents the hexagonal nanoplates with the average edge length of approximately 150 nm (Figure 3b1). Three sets of (220) planes with lattice space of 0.28 nm and interfacial angle of 60° are observed in Figure 3b2, the corresponding FFT image is well indexed as [1-11] zone axis, demonstrating the preferentially exposed facets of Co_3O_4 -H are {111} planes. Figure 3c1 presents the morphology of Co_3O_4 -R, the nanorods with average length of about 250 nm can be observed. The HRTEM image in Figure 3c2 shows a set of (311) planes and a set of (222) planes with lattice space of 0.24 nm and 0.23 nm and a 79° interfacial angle, which means the mainly exposed facets of Co_3O_4 -R are {110} planes. As seen in Figure 3d1, the Co_3O_4 -P exhibits the morphology of

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irregular nanoplates with the average size of around 50 nm. HRTEM and the corresponding FFT image show the dominantly exposed facets of Co_3O_4 -P are {112} planes, which are normal to both the sets of (220) and (222) planes with lattice space of 0.28 nm and 0.23 nm.

3.2.XPS

The cobalt valance state and surface oxygen species were analyzed by XPS. Figure 4a presents the Co 2p spectra of samples. The intense peaks at around 795.0 eV and 779.8 eV are corresponding to the Co $2p_{3/2}$ and Co $2p_{1/2}$ spin-orbital peaks of Co₃O₄[33]. The Co $2p_{3/2}$ spectra can be further deconvoluted into Co³⁺ and Co²⁺ component peaks, which located at around 779.9 eV and 781.2 eV, respectively [46]. As summarized in Table 1, the Co²⁺/Co³⁺ values vary in the order of Co₃O₄-H > Co₃O₄-C > Co₃O₄-P > Co₃O₄-R, indicating higher concentration of Co²⁺ on the surface of Co₃O₄-H exposing {111} planes, which is consistent with the Raman results.

Figure 4b shows the O 1s spectra. It can be seen that all profiles can be fitted into four component peaks at around 529.9, 530.5, 531.5 and 533.5 eV, corresponding to the surface lattice oxygens (O_{latt}), surface adsorbed oxygen species (O_{ads}), oxygens in surface adsorbed OH- and the oxygens in surface adsorbed water of carbonates, respectively [47]. The deconvoluted results show the O_{ads}/O_{latt} values follow the order of Co₃O₄-H > Co₃O₄-C > Co₃O₄-R > Co₃O₄-P, which means the higher ratio of adsorbed oxygen species on Co₃O₄-H surface. It has been reported that O_{ads} are active species in catalytic combustion and usually participate in the reaction through superficial mechanism [48]. Hence, the more O_{ads} on Co₃O₄-H surface may be favored in C₃H₈ combustion. *3.3.Redox properties*

In order to investigate the redox properties of different Co₃O₄ catalysts, H₂-TPR measurements were conducted. As illustrated in Figure 5a, all samples present two distinct

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reduction peaks, which are attributed to the stepwise reduction of Co_3O_4 . Generally, the peak at lower temperature (< 400 °C) is assinged to the reduction of Co^{3+} to Co^{2+} , while the peak at higher temperature (> 400 °C) is associated with the reduction of Co^{2+} to Co^0 [49]. The H₂ consumption is calculated by integration of reduction peaks using the reduction peak area of CuO as calibration. As seen in Table 1, all samples exhibit similar H₂ consuption around 17 mmol g⁻¹ during H₂-TPR, which is close to the theoretical H₂ consumption of 16.6 mmol g⁻¹. The results further confirm that all samples are Co₃O₄ with high purity. As previously reported, the first reduction temperature is a sign of activity and mobility of lattice oxygen in Co₃O₄ [50], which is closely related to the catalytic performance in combustion reaction. It can be seen in Table 1, the first reduction temperature of Co₃O₄-H with {111} planes is 303 °C, lower than other samples, indicating the more active lattice oxygens in Co₃O₄-H, which is favored in combustion reaction. While the Co₃O₄-P with {112} planes presents the highest reduction temperature of 344 °C, which means the lattice oxygens are more difficult to be activated and participate in the reaction.

 C_3H_8 -TPSR measurements were conducted to investigate the reaction of C_3H_8 with surface lattice oxygens of catalyst. As shown in Figura 5b, the MS signals of C_3H_8 (m/z = 29) and CO₂ (m/z =44) were both detected during the experiments. The positive peaks in CO₂ signals represent the production of CO₂ and the negtive peaks in C_3H_8 signals represent the consumption of C_3H_8 . It can be seen that the temperatures of the positive peaks in CO₂ signals are in agreement with the temperatures of the negtive peaks in C_3H_8 signals, suggesting the C_3H_8 can react with surface lattice oxygens to form CO₂. It is reasonable that the peak temperatures and the peak areas in CO₂ signals can reflect the reactivity and amount of surface lattice oxygens. As seen in Table 1, the Co₃O₄-H with {111} planes exhibits the lowest reaction temperature of 441 °C, suggesting the surface lattice oxygens of Co_3O_4 -H are the most active among all samples. Co_3O_4 -C with {100} planes shows the largest peak area, indicating the abundant active lattice oxygens on the catalyst surface. These two catalytsts may exhibit higher activity towards C_3H_8 combustion. While the Co_3O_4 -P with {112} planes exhibits lower oxygen activity and fewer amount of surface lattice oxygens, which is possible to exhibit low activity in catalytic evaluation.

3.4.In-situ Raman

As mentioned above, C₃H₈ can react with the surface lattice oxygens. According to the MvK mechanism, the surface reaction is able to create oxygen vacancies which can be replenished through the activation of gas phase oxygen to form the new surface lattice oxygens and further participate in combustion reaction. The different oxygen activation abilities may have an impact on the catalytic performance of catalysts. Therefore, we employed the in-situ Raman to investigate the structural change of Co₃O₄ catalysts during the oxygen activation process and deduce the oxygen activation abilities of different catalysts. Figure S1 shows the change of the dominant peaks (A_{1g}) for all samples with increasing temperature in the stream of 0.5% vol. O₂/Ar. It can be seen that the peaks in all samples are weakened and shifted to lower wavenumbers with the temperature raised from 50 °C to 250 °C, indicating activation of gas phase oxygen on catalyst surface, which may lead to the formation of weakly bound oxygen species ($Co^{3+}-O_2^{-}-Co^{2+}$ or $Co^{3+}-O^{-}-Co^{2+}$) and affect A_{1g} symmetry [51]. In order to determine the oxygen activation ability of different samples, we analyze the change of peak intensity during the experiments. As seen in Figure 6, the peak intensity decreases more rapidly in Co₃O₄-H with {111} planes, which means the oxygen molecules are activated more easily on the catalyst surface. This will be benefit to the redox change of catalyst and result in the higher activity towards C₃H₈ combustion.

3.5.In-situ DRIFT

In addition to the oxygen activation, the adsorption and activation of C_3H_8 are also important to the activity of C_3H_8 combustion. Many studies have demonstrated that C_3H_8 can adsorb on catalysts surface through the C-H activation and C-H activation is the rate-determining step of combustion reaction [20, 52]. Therefore, we employed the in-situ DRIFT to reveal the C_3H_8 activation abilities of catalysts and investigate the possible transformation pathway of C_3H_8 after adsorption on catalysts surface. Figure 7 shows the in-situ DRIFT spectra over the Co_3O_4 catalysts in the stream of 1% C_3H_8/Ar with temperature increasing from 50 °C to 300 °C. The strong peaks at 1332 cm⁻¹ assigned to δ (CH) is observed over Co_3O_4 -H with {111} planes and Co_3O_4 -C with {100} planes at high temperature, but relatively weak for Co_3O_4 -R with {110} planes and almost absent for Co_3O_4 -P with {112} planes. As reported, C_3H_8 can be dissociatively adsorbed on catalyst surface through the C-H activation, which can form the methylene species [53]. The strong peaks at 1332 cm⁻¹ in the profiles indicates C_3H_8 is activated more easily on the surface of Co_3O_4 -H H and Co_3O_4 -C.

The adsorption peaks at 1440 cm⁻¹, 1550 cm⁻¹ and 1390 cm⁻¹, which are attributed to the carboxylic species (1440 cm and 1550 cm⁻¹) and bicarbonates (1390 cm⁻¹) [54, 55], can be observed for all samples. As the surface oxygen species may react with C_3H_8 to form carboxylic and bicarbonate species, the growing peak intensities with increasing temperature indicate that the reaction is promoted under high temperature. However, a decrease of the peak at 1440 cm⁻¹ is observed for $C_{03}O_4$ -P at 300 °C. As confirmed in the C_3H_8 -TPSR, the insufficient active oxygen species in $C_{03}O_4$ -P hinder the reaction with C_3H_8 , which may result in the less production of carboxylic species and lead to the decrease of the 1440 cm⁻¹ peak.

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Figure S2 illustrates the dynamic change of carboxylic species and bicarbonates on Co_3O_4 -H and Co_3O_4 -C by calculating the ratio of corresponding peak areas. There is an obvious accumulation of surface carbonates on the surface of Co_3O_4 -C compared with Co_3O_4 -H. The accumulation of surface carbonates may cover the active sites [56, 57] and hinder the reaction, which has a negative effect on catalytic performance. The CO₂-TPD after surface reaction with C₃H₈ was conducted to further confirm the results. As seen in Figure S3, the desorption peak of CO_2 for Co_3O_4 -C is much stronger than that of Co_3O_4 -H, demonstrating more surface carbonates on the Co_3O_4 -C after reaction with C_3H_8 .

It has been reported that C_3H_8 can dissociatively adsorb on catalyst surface and then react with surface oxygens to form carboxylic species which can be further oxidized into surface carbonates during C_3H_8 combustion [54]. Therefore, it can be inferred that C_3H_8 is dissociatively adsorbed on the catalyst surface and form CH species. This process is more favored on the surface of Co_3O_4 -H and Co_3O_4 -C. Then, the adsorbed C_3H_8 may react with surface oxygens and form carboxylic species. This process is promoted with increasing temperature except for Co_3O_4 -P, which has insufficient active surface oxygens to react with C_3H_8 . The carboxylic species can be further oxidized into carbonates, which is more likely to be accumulated on the surface of Co_3O_4 -C and cover the active sites.

3.6. Catalytic activity towards C₃H₈ combustion and DFT calculations

The catalytic performance of C_3H_8 combustion over Co_3O_4 catalysts is shown in Figure 8a. The T_{50} and T_{90} are employed as the evaluating indicators to compare the activities of different catalysts. It can be seen that the catalytic activity increases as the order of Co_3O_4 -P < Co_3O_4 -R < Co_3O_4 -C < Co_3O_4 -H and Co_3O_4 -H with {111} planes is the most active catalyst achieving T_{50} and

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 T_{90} as low as 209 °C and 239 °C. Moreover, the apparent activation energies (Ea) were also calculated from the Arrhenius plots presented in Figure 8b. It is noticed that the Co₃O₄-H exhibits the lowest E_a value of 90 kJ mol⁻¹ and the variation of E_a follows the order of Co₃O₄-H < Co₃O₄-H < Co₃O₄-C < Co₃O₄-R < Co₃O₄-P, which is the inversed trend of catalytic activity, confirming the best performance of Co₃O₄-H with {111} planes. In addition, the catalytic activity of Co₃O₄-H was also compared with that of other reported catalysts listed in Table 2. Obviously, the catalytic activity of Co₃O₄-H is better than the reported catalysts based on the T₅₀ and T₉₀ values.

However, as the specific area has a significant impact on catalytic performance, it is necessary to normalize the reaction rates to the specific surface areas of Co_3O_4 catalysts, which can reveal the intrinsic activities of different crystal planes. As shown in Figure 8c, the specific reaction rate decreases as the order of Co_3O_4 -H > Co_3O_4 -C > Co_3O_4 -R > Co_3O_4 -P, suggesting the activities of C_3H_8 combustion on different crystal planes follow the sequence of $\{111\} > \{100\} > \{110\} >$ $\{112\}$.

It has been reported that there is a positive relationship between the adsorption strength of dissociated C_3H_8 on different MnO_2 facets and the catalytic performance towards C_3H_8 combustion [64]. Base on this study, the adsorption ability of dissociated C_3H_8 could be a descriptor for the C_3H_8 combustion. During the adsorption of C_3H_8 , C-H activation is of great importance. The C-H activation can be proceeded through H abstraction by surface lattice oxygens which leads to the formation of hydroxyl and alkoxy species [65, 66]. Therefore, in this work, the DFT calculations were employed to analyze the adsorption behavior of dissociated C_3H_8 molecule (CH₃CHCH₃+H) on four different crystal planes of Co_3O_4 - {111} surface, {100}-O surface, {110}-B surface and {112} surface. Several possible adsorption sites involved with Co atoms or O atoms were studied.

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The most stable adsorption configurations on the four different crystal planes of Co₃O₄ are shown in Figure 9. The Co_3O_4 - {111} surface terminates to yield triply coordinated Co_{3c} atoms and triply coordinated oxygen atoms, which can be categorized into two types (seen in Figure S4a): O_{1st} are triply coordinated to the subsurface Co and O_{2nd} are doubly coordinated to the subsurface Co but also singly coordinated to the surface Co. In this case, the CH₃CHCH₃ and H species all favored to bind to O_{2nd} atoms (Figure 9a). On the {100}-O surface, the pentacoordinated Co_{5c} atoms are exposed. The four-fold coordinated Co_{4c} atoms are located in the first sublayer. The surface oxygen atoms includes two kinds of three-fold coordinated O atoms (denoted as O_{2-5c,1-4c} and O_{3-5c} in Figure S4b). The O_{2-5c,1-4c} atoms are linked to two Co_{5c} atoms and to one Co_{4c} atom, and the O_{3-5c} atoms are linked to three Co_{5c} atoms. The CH₃CHCH₃ species was adsorbed on the O_{2-5c,1-4c} atom, while the H atom was adsorbed on the O_{3-5c} atom (Figure 9b). The {110}-B surface has only one type of four-fold coordinated Co_{4c} atoms and two types of oxygen atoms: the two-fold coordinated O_{2c} atoms and three-fold coordinated O_{3c} atoms (seen in Figure S4c). On this surface, the CH₃CHCH₃ species preferred to bind to the O_{3c} atom and the H atom was binding to the O_{2c} atom (Figure 9c). The unusual $\{112\}$ surface has one type of two-fold coordinated Co_{2c} atoms and two types of three-fold coordinated Co_{3c} atoms. The surface oxygen atoms are categorized into one type of two-fold coordinated O_{2c} atoms and three types of three-fold coordinated O_{3c} atoms (Figure S4d). The CH₃CHCH₃ species favored to bind to the O_{2c} atom, while the H atom was adsorbed on the O_{3c} atom which is the nearest to the adsorbed CH₃CHCH₃ (Figure 9d). The adsorption is involved with O atoms on the four kinds of surfaces, which implies that the surface O atoms may play important roles in the adsorption and activation of C₃H₈ molecule. As presented in Figure 9, the adsorption energies on {111} surface, {100}-O surface, {110}-B surface and {112} surface

are -4.10 eV, -3.16 eV, -2.96eV and -2.43 eV, respectively. The results indicate that the binding strength between dissociated C_3H_8 molecule and the surface decreases in the order of {111} > {100}-O > {110}-B > {112}, which is consistent with the order of reaction activity in our experiments. The results confirm that the activation of C_3H_8 is crucial to C_3H_8 combustion to some extent.

As mentioned above, the activation of C-H bond is the rate-determining step during C_3H_8 combustion. Facile activation of C_3H_8 can increase the catalytic activity through the more efficient conversion from C_3H_8 to the intermediates such as carboxylates and carbonates, which can be further oxidized to CO₂. Moreover, the redox properties of catalysts can also influence catalytic performance. Higher lattice oxygen activity can make the oxygen species more accessible in the reaction and the facile activation of gas phase oxygen can promote replenish of oxygen vacancies which are created by reaction between surface intermediates and lattice oxygens. As a result, the catalytic activity is increased.

As confirmed by DRIFT and DFT calculations, the C-H activation is more readily achieved on the Co₃O₄ {111} planes. This may be the important reason for the high activity of the Co₃O₄-H with {111} planes. Moreover, the lattice oxygens in Co₃O₄-H are more active than other samples as confirmed in H₂-TPR and C₃H₈-TPSR, which enhances the interaction between the adsorbed C₃H₈ and the surface lattice oxygens and increase the catalytic activity. In addition, as illustrated in in-situ Raman, the more facile activation of gas phase oxygen on Co₃O₄-H surface can result in the more efficient replenish of oxygen vacancies created by surface reactions, which is also conducive to the catalytic activity. Therefore, the Co₃O₄-H with {111} planes can achieve the best catalytic performance towards C₃H₈ combustion. For Co₃O₄-C and Co₃O₄-R, the C-H activation

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ability as well as the redox properties is inferior to Co_3O_4 -H. As a result, the activities are relatively lower than Co_3O_4 -H. In terms of Co_3O_4 -P, the difficult activation of C-H bond and the lack of surface active species both lead to the poor activity towards C_3H_8 combustion.

4. Conclusion

Co₃O₄ nanocatalysts with different morphologies and different exposed facets were fabricated through hydrothermal routes. The obtained catalysts mainly exposed {100}, {111}, {110} and {112} planes, respectively. The catalysts were employed in C₃H₈ combustion and the catalytic activities of different facets varied as the order of {111} > {100} > {110} > {112}. The Co₃O₄-H with {111} planes exhibited the best activity with T₅₀ and T₉₀ as low as 209 and 239 °C, respectively. DRIFT and DFT calculations confirmed that the C-H activation was more facile on {111} planes, which was of great importance for the high activity. Moreover, the higher lattice oxygen activity and easy activation of gas phase oxygen also made the catalyst with {111} planes more active towards C₃H₈ combustion.

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Figure captions

Figure 1. Powder XRD patterns of investigated catalysts.

Figure 2. Visible Raman spectra of investigated catalysts.

Figure 3. TEM and HRTEM of investigated Co_3O_4 catalysts: (a1-a2) Co_3O_4 -C; (b1-b2) Co_3O_4 -H; (c1-c2) Co_3O_4 -R; (d1-d2) Co_3O_4 -P. Insets in a1 to d1 are the schematic diagrams of the corresponding catalysts. Insets in a2 to d2 show the FFTs of the HRTEM images. c3 to d3 present present the surface structures of the Co_3O_4 (100), (111), (110) and (112) surfaces, respectively. Figure 4. (a) Co 2p and (b) O 1s XPS of investigated catalysts.

Figure 5. (a) H₂-TPR and (b) C₃H₈-TPSR profiles of investigated catalysts.

Figure 6. The evolution of A_{1g} peak intensity vs temperature during the in-situ Raman experiments of investigated catalysts.

Figure 7. The in-situ DRIFT spectra over different Co_3O_4 catalysts in the stream of 1% C_3H_8/Ar with temperature increasing from 50 °C to 300 °C.

Figure 8. (a) C_3H_8 combustion activity vs temperature profiles of investigated catalysts; (b) Arrhenius plots of the invstigated samples; (c) Specific reaction rates of C_3H_8 combusiton over different Co_3O_4 catalysts.

Figure 9. The most stable adsorption configurations of dissociated C_3H_8 molecule (CH₃CHCH₃+H) and adsorption energy (E_{ads}) on the four different crystal planes of Co_3O_4 . (a) {111} surface, (b) {100}-O surface, (c) {110}-B surface and (d) {112} surface

Scheme 1. Schematic illustration of the synthetic routes for the investigated Co₃O₄ catalysts.























 $E_{\rm ads}$ = -2.43 eV

 $E_{\rm ads}$ = -2.96 eV

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Scheme 1



Table 1. Textural properties, redox properties, surface composition, catalytic activity and apparent activation energy of the investigated Co₃O₄ catalysts.

Catalyst	BET surface are (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Reduction temperature in H ₂ -TPR (°C)	H ₂ consumption (mmol/g)	Reaction temperature in C ₃ H ₈ -TPSR (°C)	I_{196}/I_{691}^{a}	XPS results		Catalytic activity		Ea
							Co ²⁺ /Co ³⁺	^b + Cads/Olatt ^b	T ₅₀ ^c (°C)	T ₉₀ ^c (°C)	(kJ mol ⁻¹)
Co ₃ O ₄ -C	50.2	0.16	317	17.0	450	0.073	0.83	0.78	214	242	92
Co ₃ O ₄ -H	41.6	0.18	303	17.1	441	0.075	0.88	0.85	209	239	90
Co ₃ O ₄ -R	43.9	0.17	310	17.5	443	0.059	0.72	0.69	220	245	94
Co ₃ O ₄ -P	23.6	0.16	344	17.2	497	0.069	0.80	0.44	251	283	131
^a Calculated fr ^b Calculated ba ^c The temperat	om peak inte ased on peaks ture at which	nsities in Ram area of XPS. the conversion	an spectra. 1 is 50 or 90%.					Accepted Mar			

Catalyst	WHSV (ml g ⁻¹ h ⁻¹)	C ₃ H ₈ concentration	T50	T90	Reference
Co ₃ O ₄ -H	10000	1%	209	239	This work
Co ₃ O ₄	12000	0.8%	250	2×0	[49]
Co_3O_4	15000	0.5%	225	075	[58]
Co_3O_4	6000	2%	335	350	[59]
Co ₃ O ₄ /ZSM-5	30000	0.2%	235	760	[39]
Co ₃ O ₄ /SiO ₂	30000	0.1%	280	3.21)	[60]
Mn _x Co _{3-x} O ₄	12000	0.3%	310	500	[61]
Ce _{1-x} Mn _x O ₂	30000	1%	232	268	[62]
NiCe	20000	0.8%	255	290	[63]
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Table 2 Catalytic testing condition (WHSV and propane concentration), catalytic activities (T₅₀ and T₉₀) of Co₃O₄-H and other reported catalysts