Article

Insights into the Morphological Effect of Co_3O_4 Crystallite on Catalytic Oxidation of Vinyl Chloride

Chao Wang ¹ , Wenchao Hua ², Guangtao Chai ², Chuanhui Zhang ^{1,*} and Yanglong Guo ^{2,*}

¹ Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China; chao.wang@qdu.edu.cn

² Key Laboratory for Advanced Materials and Research, Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China; huawenchao88@126.com (W.H.); gtchai@163.com (G.C.)

* Correspondence: zhangch@qdu.edu.cn (C.Z.); ylguo@ecust.edu.cn (Y.G.); Tel.: +86-531-85951496 (C.Z.); +86-21-64252923 (Y.G.)

Received: 3 April 2019; Accepted: 27 April 2019; Published: 30 April 2019

Abstract: Co_3O_4 catalysts of cube and sphere shapes were prepared by one-step hydrothermal synthesis with different controlled amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH . The morphological effects on both physicochemical properties and catalytic activities of vinyl chloride oxidation were investigated by material characterization and performance evaluation. The obtained results showed that the morphology, resulting in the exposure difference of crystal planes, significantly affected the catalytic property. The catalytic activity for vinyl chloride oxidation followed a descending order of Co_3O_4 cube ($\text{Co}_3\text{O}_4\text{-c}$) > Co_3O_4 sphere ($\text{Co}_3\text{O}_4\text{-s}$) > Co_3O_4 commercial ($\text{Co}_3\text{O}_4\text{-com}$). The cube-shaped Co_3O_4 presented higher catalytic activity and stability than Co_3O_4 spheres despite their similar crystallographic structures as well as physicochemical and redox properties. Accordingly, the different catalytic behaviors should be attributed to a morphological effect. The Co_3O_4 cube with a preferential exposure of (001) plane presented higher abundance of surface Co^{2+} cations and adsorbed oxygen species, which acted as the active sites responsible for the improvement of its catalytic activity.

Keywords: Co_3O_4 ; morphological effect; crystal plane; catalytic oxidation; vinyl chloride

1. Introduction

A current global environmental issue is the atmospheric pollution arising from the emission of volatile organic compounds (VOCs), released from the combustion of fossil fuel and commercial waste exhausts such as petrochemical, industrial printing, and dry-cleaning processes. These emissions have adverse impacts on human health and the environment. As one of the promising technologies, catalytic oxidation could degrade VOC pollutants into harmless products with high selectivity. Thus, one of the most important research objectives for VOC oxidation is the preparation of highly efficient catalysts with good reaction stability.

Transition metal oxides are one kind of catalyst for VOCs oxidation, and are slightly less active than materials based on noble metals [1–3]. Nevertheless, their low cost and good resistance against poisoning by chlorine and sulfur species during the catalytic reaction are significantly highlighted. Among all, Co_3O_4 has been widely applied in many catalytic application [4–8], including VOC oxidation [9–13].

Co_3O_4 presents a spinel structure with an Fd-3m crystallographic space group, where oxygen atoms are arranged in a cubic close-packed matrix and the Co^{3+} and Co^{2+} cations are positioned in the octahedral and tetrahedral lattice sites, respectively [14,15]. The Co_3O_4 particles usually expose the lower index plane with (110), (111), and (001) planes [16], while the catalytic activity is likely related to high bulk oxygen mobility and highly active oxygen species [17,18]. Recent research has established that the tunable morphology of Co_3O_4 nanocrystals has a notable effect on CO or

hydrocarbon oxidation [19], which was ascribed to the reactive preferential crystal planes with different shapes. For example, the nanorod-shaped Co_3O_4 privileges the presence of active Co^{3+} species on (110) planes, which were demonstrated to be the most active sites for CO adsorption. Thus, this nanorod structure can also catalyze the oxidation of CO at temperatures as low as -77°C , keeping a constant stability in moist conditions [20]. Furthermore, it has been demonstrated that Co^{3+} species on (011) planes in nanobelt structures are more reactive than those on (001) planes in nanocubes [21]. From this viewpoint, a clear clarification of the morphology–activity relationship is of great significance for the development of novel catalytic materials. However, the correlation between the morphological features and catalytic activity of Co_3O_4 for chlorinated VOC oxidation has rarely been studied.

In this study, a Co_3O_4 catalyst with different morphologies (cube and sphere) was prepared, characterized, and investigated for the oxidation of vinyl chloride (VC), and the morphological effect of Co_3O_4 on both physicochemical characteristics and catalytic activities was extensively studied.

2. Results

2.1. Characterization Results

The inductively coupled plasma results in Table 1 show that all catalysts presented nearly the same weight percentage of Co (approximately 70 wt. %), which agree well with the theoretical value of Co_3O_4 . The scanning electron microscope (SEM) images of the catalysts in Figure 1 demonstrate that the morphology of Co_3O_4 varied depending on the amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH during the preparation process, which is in agreement with previous reports [22]. Obviously, the synthesis with a lower concentration of cobalt nitrate resulted in the formation of the $\text{Co}_3\text{O}_4\text{-c}$ with a particle size around 250 nm, seen in Figure 1a, while $\text{Co}_3\text{O}_4\text{-s}$ could be obtained using a higher concentration of cobalt nitrate with similar particle size as $\text{Co}_3\text{O}_4\text{-c}$ (Figure 1b). In contrast, Figure 1c shows that $\text{Co}_3\text{O}_4\text{-com}$ presented an irregular particle size from 100 to 300 nm. In addition, the morphology of $\text{Co}_3\text{O}_4\text{-c}$ was also confirmed by the transmission electron microscope (TEM) images in Figure 1d. According to the literature [23,24], the dominant exposed planes of cubic Co_3O_4 are six (001) planes.

Table 1. The Co content, crystallite size and surface atomic ratios of the Co_3O_4 catalysts.

Catalysts	Co content (wt. %)	Crystallite size (nm)	$\text{Co}^{3+}/\text{Co}^{2+}$ (at./at.)	$\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ (at./at.)
$\text{Co}_3\text{O}_4\text{-c}$	71.6	62	1.35	0.60
$\text{Co}_3\text{O}_4\text{-s}$	71.6	100	1.41	0.53
$\text{Co}_3\text{O}_4\text{-com}$	70.2	93	1.46	0.49

Figure 1. Cont.

Figure 1. SEM images of (a) $\text{Co}_3\text{O}_4\text{-c}$, (b) $\text{Co}_3\text{O}_4\text{-s}$, (c) $\text{Co}_3\text{O}_4\text{-com}$, and a TEM image of (d) $\text{Co}_3\text{O}_4\text{-c}$.

The X-ray diffraction (XRD) patterns of the Co_3O_4 catalysts are presented in Figure 2. All diffraction peaks were indexed as the standard pure crystalline phase of Co_3O_4 (JCPDS file No. 42-1467) without any detection of impurities. $\text{Co}_3\text{O}_4\text{-c}$ and $\text{Co}_3\text{O}_4\text{-s}$ presented analogous XRD patterns with similar characteristic peaks. As seen in Table 1, the average crystallite size was estimated by applying the Scherrer equation. It was 62 nm for $\text{Co}_3\text{O}_4\text{-c}$, whereas it increased to 100 and 93 nm for $\text{Co}_3\text{O}_4\text{-s}$ and $\text{Co}_3\text{O}_4\text{-com}$, respectively. Moreover, no obvious difference in the specific surface area of each catalyst was observed, which were 7, 7, and 6 $\text{m}^2\cdot\text{g}^{-1}$ for $\text{Co}_3\text{O}_4\text{-c}$, $\text{Co}_3\text{O}_4\text{-s}$, and $\text{Co}_3\text{O}_4\text{-com}$, respectively.

Figure 2. XRD patterns of the Co_3O_4 catalysts.

Chemical surface compositions and valence states were determined by X-ray photoelectron spectroscopy (XPS), and the spectra of Co 2p and O 1s are displayed. In Figure 3a, the binding energy (B.E.) value of Co 2p_{3/2} and Co 2p_{1/2} was around 780 and 795 eV, respectively [14,25]. The satellite peaks at 785 eV confirmed the existence of Co^{2+} species in the octahedral sites [26–28]. Herein, the Co 2p spectra were resolved using a fitting procedure partially based on that suggested by Biesinger et al. [29]. The contributions from Co^{3+} and Co^{2+} cations were identified at 779.5 and 781.1 eV, respectively [30]. Additionally, two satellite peaks, S₁ and S₂, at 785.3 and 789.4 eV appeared due to electron correlations and final state effects in Co^{2+} and Co^{3+} cations, respectively [31]. In turn, the satellite S₃ was attributed to the spin orbit contributions of Co 2p_{1/2} and also from satellites S₁ and S₂ [32–34].

Based on the quantitative analysis results in Table 1, the $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio over the Co_3O_4 catalysts followed an increasing order of $\text{Co}_3\text{O}_4\text{-c} < \text{Co}_3\text{O}_4\text{-s} < \text{Co}_3\text{O}_4\text{-com}$. The lower molar ratio of $\text{Co}^{3+}/\text{Co}^{2+}$ over $\text{Co}_3\text{O}_4\text{-c}$ indicates that higher abundance of Co^{2+} cations were presented on the (001) plane of $\text{Co}_3\text{O}_4\text{-c}$, which could be a crucial factor for the catalytic oxidation of VOCs [14,35]. The O 1s spectra in Figure 3b were also decomposed into two peaks. The peaks located at 529.7 and 531.2 eV could be ascribed to lattice oxygen (O_{latt} , i.e., O^{2-}) and adsorbed oxygen onto surface oxygen vacancies (O_{ads} , i.e., O^- , O_2^{2-} , OH^-), respectively [36,37]. According to the quantitative analysis of O

1s spectra, the O_{ads}/O_{latt} ratio of Co_3O_4 -c was higher than that obtained from other catalysts (Table 1), which indicates that Co_3O_4 -c provided more surface-active oxygen species than others.

Figure 3. (a) Co 2p and (b) O 1s XPS spectra of the Co_3O_4 catalysts.

The H_2 -TPR profiles show that two reduction peaks were clearly observed over the Co_3O_4 -c and Co_3O_4 -s catalysts in Figure 4a. The two peaks at 285 and 330 °C were assigned to the reduction of Co^{3+} to Co^{2+} and Co^{2+} to metallic cobalt, respectively [38]. Comparatively, the Co_3O_4 -com catalyst showed an overlapping peak, indicating a successive reduction behavior of Co^{3+} into Co^{2+} and Co^0 . Additionally, the temperature of reduction peaks maximum over Co_3O_4 -c and Co_3O_4 -s were relatively lower than that over Co_3O_4 -com, suggesting that the cube- and sphere-shaped Co_3O_4 catalysts presented better reducibility. The low-temperature reducibility could be evaluated by the initial H_2 consumption rate (less than 25% of oxygen consumption in the first reduction band of the H_2 -TPR profile) [39,40]. Figure 4b shows the initial H_2 consumption rate versus inverse temperature over the Co_3O_4 catalysts. The initial H_2 consumption rate over the catalysts decreased in the order of Co_3O_4 -c > Co_3O_4 -s > Co_3O_4 -com, indicating that Co_3O_4 -c exhibited the highest low-temperature reducibility. This trend is in good agreement with the order of the O_{ads}/O_{latt} ratio.

Figure 4. (a) H_2 -TPR profiles and (b) the initial H_2 consumption rate as a function of inverse temperature of the Co_3O_4 catalysts.

2.2. Catalytic Performances for VC Oxidation

The catalytic performances of the Co_3O_4 catalysts were tested for the oxidation of VC, which acted as a model reaction for chlorinated VOCs. Based on the light-off curves shown in Figure 5 and the T_{50} and T_{90} values listed in Table 2, it could be found that the catalytic activity for VC over the catalysts followed Co_3O_4 -c > Co_3O_4 -s > Co_3O_4 -com, which is similar to the TPR results.

Figure 5. The light-off curves of vinyl chloride (VC) oxidation as a function of reaction temperature over the Co_3O_4 catalysts (reaction conditions: 1000 ppm VC, air balanced, and weight hourly space velocity (WHSV) = $48,000 \text{ mL g}^{-1} \text{ h}^{-1}$).

Table 2. T_{50} and T_{90} values for the catalytic oxidation of vinyl chloride (VC) over the Co_3O_4 catalysts.

Catalysts	T_{50} ($^{\circ}\text{C}$)	T_{90} ($^{\circ}\text{C}$)
$\text{Co}_3\text{O}_4\text{-c}$	308	340
$\text{Co}_3\text{O}_4\text{-s}$	320	372
$\text{Co}_3\text{O}_4\text{-com}$	372	431

The final products in the effluent gas were water (H_2O), carbon dioxide (CO_2), and hydrogen chloride (HCl), which were identified by online mass spectrometry. However, during the reaction of VC oxidation, highly chlorinated by-products were yielded and quantitatively determined. The major chlorinated organics were namely 1,1,2-trichloroethane ($\text{CH}_2\text{ClCHCl}_2$), dichloromethane (CH_2Cl_2), trichloromethane (CHCl_3), and tetrachloromethane (CCl_4). As presented in Figure 6, the concentrations of the chlorinated organics over $\text{Co}_3\text{O}_4\text{-c}$ or $\text{Co}_3\text{O}_4\text{-s}$ were relatively lower than those over $\text{Co}_3\text{O}_4\text{-com}$ catalyst, which could be owing to their higher catalytic activity. Moreover, the temperature corresponding to the maximum formation of chlorinated organics in Figure 6 indicates that $\text{Co}_3\text{O}_4\text{-c}$ or $\text{Co}_3\text{O}_4\text{-s}$ also presented higher chlorination activity compared with $\text{Co}_3\text{O}_4\text{-com}$. Regarding the formation mechanism, $\text{CH}_2\text{ClCHCl}_2$ might be produced from the addition reaction between VC and the surface active chlorine species. Then, it could undergo catalytic cracking on Co_3O_4 catalysts, resulting in the formation of CH_2Cl_2 , CHCl_3 , and CCl_4 .

Figure 6. The chlorinated by-product distributions for vinyl chloride (VC) catalytic oxidation over the Co_3O_4 catalysts: (a) 1,1,2-trichloroethane ($\text{CH}_2\text{Cl}-\text{CHCl}_2$), (b) dichloromethane (CH_2Cl_2), (c) trichloromethane (CHCl_3), and (d) tetrachloromethane (CCl_4) (reaction conditions: 1000 ppm VC, air balanced, and WHSV = $48,000 \text{ mL g}^{-1} \text{ h}^{-1}$).

Figure 7 displays the selectivities of HCl and CO₂ at different reaction temperatures. At higher temperature, all VC was oxidized into HCl without the detection of other chlorinated by-products. However, the lowest HCl selectivity was obtained over Co₃O₄-c at the temperature range of 240 to 320 °C, which could be due to the simultaneous formation of high amounts of chlorinated by-products. The selectivity of HCl rose back to 100% with the temperature continuously increased, indicating the complete decomposition of chlorinated by-products. However, the selectivity for CO₂ always remained above 90% over the Co₃O₄-c and Co₃O₄-s catalysts beneficially due to their higher reaction activity, confirming the good carbon balance in the reaction.

Figure 7. The selectivity for (a) CO₂ and (b) HCl over the Co₃O₄ catalysts (reaction conditions: 1000 ppm vinyl chloride (VC), air balanced, and WHSV = 48,000 mL g^{−1} h^{−1}).

Finally, the catalytic durability for VC oxidation in long-term experiments (i.e., 40 h) was evaluated over the Co₃O₄ catalysts, as shown in Figure 8. Co₃O₄-com exhibited relatively poor stability, with the conversion at 40% at 360 °C. Comparatively, approximately the same VC conversion of 80% was observed over the Co₃O₄-c and Co₃O₄-s catalysts at lower temperatures of 330 °C and 350 °C, respectively. Co₃O₄-s maintained stable activity during the initial 15 h but gradually deactivated with more time, giving the conversion of 60%. Ultimately, Co₃O₄-c presented the relatively more stable VC conversion of 80%, confirming its higher catalytic stability.

Figure 8. Long-term catalytic durability as a function of time on stream for vinyl chloride (VC) oxidation over the Co₃O₄ catalysts (reaction conditions: 1000 ppm VC, air balanced, and WHSV = 48,000 mL g^{−1} h^{−1}).

Considering all of the results above, the lower catalytic activity and durability of Co₃O₄-com in the reactions could be associated with its poorer low-temperature reducibility, as well as the lower surface abundance of Co²⁺ and O_{ads} species compared to those Co₃O₄ catalysts of unique morphology. However, despite the close crystallographic structure and similar physicochemical properties, Co₃O₄-c presented higher catalytic activity and stability for VC oxidation than Co₃O₄-s, which reveals the close relation of catalytic reactivity with the morphological effect. Especially, the Co₃O₄-c catalyst

with a preferential exposure of (001) planes possesses more Co^{2+} cations on the surface of cubic structure. It was proven that the higher abundance of Co^{2+} correlated well with higher oxygen mobility, thus resulting in the significant improvement of catalytic activity.

3. Materials and Methods

3.1. Co_3O_4 Preparation

All chemicals throughout the experiment were analytically pure and not further purified. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH were provided by Sinopharm Chemical Reagent Co., Ltd. The Co_3O_4 catalyst was prepared by a hydrothermal process as reported in [22,23] with some modifications. Specifically, both $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH were dissolved in 30 mL deionized water and kept stirring for 30 min. Subsequently, the solution was transferred into a Teflon-lined stainless-steel autoclave and then treated at 180 °C for 3 h. After cooling down to room temperature, the obtained product was filtrated, washed several times with ethanol, and further dried at 60 °C. Finally, a calcination at 500 °C for 3 h in air was conducted to yield the Co_3O_4 material. For the synthesis of Co_3O_4 cube ($\text{Co}_3\text{O}_4\text{-c}$), the amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH was 8.73 g and 0.30 g, respectively. A total of 17.46 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.30 g NaOH were used for the preparation of Co_3O_4 sphere ($\text{Co}_3\text{O}_4\text{-s}$). For comparison, a commercial Co_3O_4 ($\text{Co}_3\text{O}_4\text{-com}$) purchased from Aladdin Co. Ltd was also used.

3.2. Characterizations

Elemental analysis of Co content in the catalysts was conducted using inductively coupled plasma (ICP) on a HORIBA Jobin Yvon Activa instrument (HORIBA, Paris, France). X-ray diffraction (XRD) patterns of the catalyst were recorded by a Bruker D8 Advance A25 with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154184$ nm) at 50 kV and 35 mA. The nitrogen sorption was measured at 77 K on a Micromeritics ASAP 2020 apparatus after a degassing pretreatment. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Temperature-programmed reduction of hydrogen (H_2 -TPR) was performed on a Micromeritics AutoChem 2920 apparatus using 10 vol% H_2/Ar ($50 \text{ mL}\cdot\text{min}^{-1}$) as the reducing gas. The reduction temperature increased from 50 to 800 °C at a rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and the H_2 consumption was measured by a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis Ultra DLD electron spectrometer using an $\text{AlK}\alpha$ (1486.6 eV) radiation source. The binding energy of C 1s electron (284.6 eV) was used to calibrate the spectra. Scanning electron microscopy (SEM) was performed on a JEOL JSM-7800F microscope (JEOL, Tokyo, Japan), while transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 microscope (JEOL, Tokyo, Japan).

3.3. Catalytic Tests

Catalytic oxidation of VC was performed using a fixed-bed reactor at atmospheric pressure. A total of 0.10 g of the Co_3O_4 catalyst was used under the flow rate of $80 \text{ mL}\cdot\text{min}^{-1}$ containing 1000 ppm VC diluted by air. VC and other organics were analyzed by an online PerkinElmer Clarus 580 GC with a flame ionization detector (FID) in a steady state.

The VC conversion was determined according to Equation (1),

$$\text{VC conversion (\%)} = (1 - [\text{VC}]_{\text{out}}/[\text{VC}]_{\text{in}}) * 100, \quad (1)$$

where $[\text{VC}]_{\text{in}}$ and $[\text{VC}]_{\text{out}}$ represent the VC concentrations of inlet and outlet, respectively. The HCl and CO_2 selectivity were calculated based on Cl and C balance according to Equations (2) and (3), respectively. $[\text{HCl}]$ and $[\text{CO}_2]$ represent the HCl and CO_2 concentrations of the outlet.

$$\text{HCl selectivity (\%)} = [\text{HCl}]/([\text{VC}]_{\text{in}} - [\text{VC}]_{\text{out}}) \quad (2)$$

$$\text{CO}_2 \text{ selectivity (\%)} = 0.5 * [\text{CO}_2]/([\text{VC}]_{\text{in}} - [\text{VC}]_{\text{out}}) \quad (3)$$

4. Conclusions

In this work, we prepared Co_3O_4 catalysts with different shapes (cubic and spherical) and comparatively evaluated their catalytic performances for VC oxidation with that of the commercial Co_3O_4 material. The Co_3O_4 -c catalyst exhibited the optimum catalytic activity and stability in the reaction, which could be attributed to its higher abundance of exposed Co^{2+} cations on the surface of the cube structure, acting as the active sites for oxidation reaction. This work provides clear evidence of the morphological effect on the catalytic behavior in VOC oxidation processes.

Author Contributions: Funding acquisition, C.W., C.Z., Y.G.; investigation, C.W., W.H., G.C.; supervision, Y.G.; writing—original draft preparation, C.W.; writing—review and editing, C.Z.

Funding: This research was funded by the National Key Research and Development Program of China (2016YFC0204300), the National Natural Science Foundation of China (21577035 and 21607163), the China Postdoctoral Science Foundation (2017M622139 and 2018M630754), and the Qingdao Postdoctoral Application Research.

Acknowledgments: We are grateful to Sonia Gil (S.G.) and Anne Giroir-Fendler (A.G.). We thank all the co-workers in the group of A.G. from Institut de Recherches sur la Catalyse et l'Environnement de Lyon. C.W. and C.Z. were as a joint student under the supervision of A.G, while G.C. is now as a joint student in this group.

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

References

1. Yu, Q.; Wang, C.; Li, X.; Li, Z.; Wang, L.; Zhang, Q.; Wu, G.; Li, Z. Engineering an effective MnO_2 catalyst from LaMnO_3 for catalytic methane combustion. *Fuel* **2019**, *239*, 1240–1245. [[CrossRef](#)]
2. Luo, D.; Chen, B.; Li, X.; Liu, Z.; Liu, X.; Shi, C.; Zhao, X.S. Three-dimensional nitrogen-doped porous carbon anchored CeO_2 quantum dots as an efficient catalyst for formaldehyde oxidation. *J. Mater. Chem. A* **2018**, *6*, 7897–7902. [[CrossRef](#)]
3. Zhang, C.; Huang, H.; Li, G.; Wang, L.; Song, L.; Li, X. Zeolitic acidity as a promoter for the catalytic oxidation of toluene over $\text{MnOx}/\text{HZSM-5}$ catalysts. *Catal. Today* **2019**, *327*, 374–381. [[CrossRef](#)]
4. Du, Y.; Huang, W.; Hua, Z.; Wang, Y.; Cui, X.; Wu, M.; Shu, Z.; Zhang, L.; Wang, J.; Chen, H.; et al. A facile ultrasonic process for the preparation of Co_3O_4 nanoflowers for room-temperature removal of low-concentration NO_x . *Catal. Commun.* **2014**, *57*, 73–77. [[CrossRef](#)]
5. Park, J.-Y.; Lee, Y.-J.; Karandikar, P.R.; Jun, K.-W.; Ha, K.-S.; Park, H.-G. Fischer–Tropsch catalysts deposited with size-controlled Co_3O_4 nanocrystals: Effect of Co particle size on catalytic activity and stability. *Appl. Catal. A* **2012**, *411–412*, 15–23. [[CrossRef](#)]
6. del Río, L.; López, I.; Marbán, G. Stainless steel wire mesh-supported Co_3O_4 catalysts in the steam reforming of ethanol. *Appl. Catal. B* **2014**, *150–151*, 370–379. [[CrossRef](#)]
7. Bi, L.; Shafi, S.P.; Da'as, E.H.; Traversa, E. Tailoring the Cathode–Electrolyte Interface with Nanoparticles for Boosting the Solid Oxide Fuel Cell Performance of Chemically Stable Proton-Conducting Electrolytes. *Small* **2018**, *14*, 1801231. [[CrossRef](#)] [[PubMed](#)]
8. Wang, B.; Bi, L.; Zhao, X. Liquid-phase synthesis of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ cathode material for proton-conducting solid oxide fuel cells. *Ceram. Int.* **2018**, *44*, 5139–5144. [[CrossRef](#)]
9. Teng, F.; Chen, M.; Li, G.; Teng, Y.; Xu, T.; Hang, Y.; Yao, W.; Santhanagopalan, S.; Meng, D.D.; Zhu, Y. High combustion activity of CH_4 and cataluminescence properties of CO oxidation over porous Co_3O_4 nanorods. *Appl. Catal. B* **2011**, *110*, 133–140. [[CrossRef](#)]
10. Garcia, T.; Agouram, S.; Sánchez-Royo, J.F.; Murillo, R.; Mastral, A.M.; Aranda, A.; Vázquez, I.; Dejoz, A.; Solsona, B. Deep oxidation of volatile organic compounds using ordered cobalt oxides prepared by a nanocasting route. *Appl. Catal. A* **2010**, *386*, 16–27. [[CrossRef](#)]
11. de Rivas, B.; López-Fonseca, R.; Jiménez-González, C.; Gutiérrez-Ortiz, J.I. Synthesis, characterisation and catalytic performance of nanocrystalline Co_3O_4 for gas-phase chlorinated VOC abatement. *J. Catal.* **2011**, *281*, 88–97. [[CrossRef](#)]
12. Li, G.; Zhang, C.; Wang, Z.; Huang, H.; Peng, H.; Li, X. Fabrication of mesoporous Co_3O_4 oxides by acid treatment and their catalytic performances for toluene oxidation. *Appl. Catal. A* **2018**, *550*, 67–76. [[CrossRef](#)]

13. Bai, B.; Arandiyán, H.; Li, J. Comparison of the performance for oxidation of formaldehyde on nano-Co₃O₄, 2D-Co₃O₄, and 3D-Co₃O₄ catalysts. *Appl. Catal. B* **2013**, *142–143*, 677–683. [\[CrossRef\]](#)
14. Cai, T.; Huang, H.; Deng, W.; Dai, Q.; Liu, W.; Wang, X. Catalytic combustion of 1,2-dichlorobenzene at low temperature over Mn-modified Co₃O₄ catalysts. *Appl. Catal. B* **2015**, *166–167*, 393–405. [\[CrossRef\]](#)
15. Wang, X.; Chen, X.; Gao, L.; Zheng, H.; Zhang, Z.; Qian, Y. One-dimensional arrays of Co₃O₄ nanoparticles: synthesis, characterization, and optical and electrochemical properties. *J. Phys. Chem. B* **2004**, *108*, 16401–16404. [\[CrossRef\]](#)
16. Hu, L.; Peng, Q.; Li, Y. Selective synthesis of Co₃O₄ nanocrystal with different shape and crystal plane effect on catalytic property for methane combustion. *J. Am. Chem. Soc.* **2008**, *130*, 16136–16137. [\[CrossRef\]](#)
17. Wang, C.; Zhang, C.; Hua, W.; Guo, Y.; Lu, G.; Gil, S.; Giroir-Fendler, A. Catalytic oxidation of vinyl chloride emissions over Co-Ce composite oxide catalysts. *Chem. Eng. J.* **2017**, *315*, 392–402. [\[CrossRef\]](#)
18. Zhang, C.; Wang, C.; Zhan, W.; Guo, Y.; Guo, Y.; Lu, G.; Baylet, A.; Giroir-Fendler, A. Catalytic oxidation of vinyl chloride emission over LaMnO₃ and LaB_{0.2}Mn_{0.8}O₃ (B=Co, Ni, Fe) catalysts. *Appl. Catal. B* **2013**, *129*, 509–516. [\[CrossRef\]](#)
19. Wang, C.; Zhang, C.; Hua, W.; Guo, Y.; Lu, G.; Gil, S.; Giroir-Fendler, A. Low-temperature catalytic oxidation of vinyl chloride over Ru modified Co₃O₄ catalysts. *RSC Adv.* **2016**, *6*, 99577–99585. [\[CrossRef\]](#)
20. Xie, X.; Li, Y.; Liu, Z.-Q.; Haruta, M.; Shen, W. Low-temperature oxidation of CO catalysed by Co₃O₄ nanorods. *Nature* **2009**, *458*, 746–749. [\[CrossRef\]](#)
21. Hu, L.; Sun, K.; Peng, Q.; Xu, B.; Li, Y. Surface active sites on Co₃O₄ nanobelt and nanocube model catalysts for CO oxidation. *Nano Res.* **2010**, *3*, 363–368. [\[CrossRef\]](#)
22. Xia, S.; Yu, M.; Hu, J.; Feng, J.; Chen, J.; Shi, M.; Weng, X. A model of interface-related enhancement based on the contrast between Co₃O₄ sphere and cube for electrochemical detection of hydrogen peroxide. *Electrochem. Commun.* **2014**, *40*, 67–70. [\[CrossRef\]](#)
23. Xiao, X.; Liu, X.; Zhao, H.; Chen, D.; Liu, F.; Xiang, J.; Hu, Z.; Li, Y. Facile shape control of Co₃O₄ and the effect of the crystal plane on electrochemical performance. *Adv. Mater.* **2012**, *24*, 5762–5766. [\[CrossRef\]](#)
24. Zhang, Y.; Ding, F.; Deng, C.; Zhen, S.; Li, X.; Xue, Y.; Yan, Y.-M.; Sun, K. Crystal plane-dependent electrocatalytic activity of Co₃O₄ toward oxygen evolution reaction. *Catal. Commun.* **2015**, *67*, 78–82. [\[CrossRef\]](#)
25. Konsolakis, M.; Sgourakis, M.; Carabineiro, S.A.C. Surface and redox properties of cobalt-ceria binary oxides: on the effect of Co content and pretreatment conditions. *Appl. Surf. Sci.* **2015**, *341*, 48–54. [\[CrossRef\]](#)
26. Barreca, D.; Massignán, C.; Daolio, S.; Fabrizio, M.; Piccirillo, C.; Armelao, L.; Tondello, E. Composition and microstructure of cobalt oxide thin films obtained from a novel cobalt(II) precursor by chemical vapor deposition. *Chem. Mater.* **2001**, *13*, 588–593. [\[CrossRef\]](#)
27. Wei, W.; Chen, W.; Ivey, D.G. Rock salt-spinel structural transformation in anodically electrodeposited Mn-Co-O nanocrystals. *Chem. Mater.* **2008**, *20*, 1941–1947. [\[CrossRef\]](#)
28. Tian, Z.; Tchoua Ngamou, P.H.; Vannier, V.; Kohse-Höinghaus, K.; Bahlawane, N. Catalytic oxidation of VOCs over mixed Co-Mn oxides. *Appl. Catal. B* **2012**, *117–118*, 125–134. [\[CrossRef\]](#)
29. Biesinger, M.C.; Payne, B.P.; Grosvenor, A.P.; Lau, L.W.M.; Gerson, A.R.; Smart, R.S.C. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* **2011**, *257*, 2717–2730. [\[CrossRef\]](#)
30. Díaz-Fernández, D.; Méndez, J.; Bomati-Miguel, O.; Yubero, F.; Mossaneck, R.J.O.; Abbate, M.; Domínguez-Cañizares, G.; Gutiérrez, A.; Tougaard, S.; Soriano, L. The growth of cobalt oxides on HOPG and SiO₂ surfaces: A comparative study. *Surf. Sci.* **2014**, *624*, 145–153. [\[CrossRef\]](#)
31. Lykhach, Y.; Faisal, F.; Skála, T.; Neitzel, A.; Tsud, N.; Vorokhta, M.; Dvořák, F.; Beranová, K.; Kosto, Y.; Prince, K.C.; et al. Interplay between the metal-support interaction and stability in Pt/Co₃O₄ (111) model catalysts. *J. Mater. Chem. A* **2018**, *6*, 23078–23086. [\[CrossRef\]](#)
32. Chen, J.; Shi, W.; Yang, S.; Arandiyán, H.; Li, J. Distinguished roles with various vanadium loadings of CoCr_{2–x}V_xO₄ (x=0–0.20) for methane combustion. *J. Phys. Chem. C* **2011**, *115*, 17400–17408. [\[CrossRef\]](#)
33. Wang, Y.; Jia, A.; Luo, M.; Lu, J. Highly active spinel type CoCr₂O₄ catalysts for dichloromethane oxidation. *Appl. Catal. B* **2015**, *165*, 477–486. [\[CrossRef\]](#)
34. Gautier, J.L.; Rios, E.; Gracia, M.; Marco, J.F.; Gancedo, J.R. Characterisation by X-ray photoelectron spectroscopy of thin Mn_xCo_{3–x}O₄ (1≥x≥0) spinel films prepared by low-temperature spray pyrolysis. *Thin Solid Films* **1997**, *311*, 51–57. [\[CrossRef\]](#)

35. Aristizábal, B.H.; de Correa, C.M.; Serykh, A.I.; Hetrick, C.E.; Amiridis, M.D. In situ FTIR study of the adsorption and reaction of ortho-dichlorobenzene over Pd-promoted Co-HMOR. *Microporous Mesoporous Mater.* **2008**, *112*, 432–440. [[CrossRef](#)]
36. Valeri, S.; Borghi, A.; Gazzadi, G.C.; di Bona, A. Growth and structure of cobalt oxide on (001) bct cobalt film. *Surf. Sci.* **1999**, *423*, 346–356. [[CrossRef](#)]
37. Zhang, C.; Wang, C.; Hua, W.; Guo, Y.; Lu, G.; Gil, S.; Giroir-Fendler, A. Relationship between catalytic deactivation and physicochemical properties of LaMnO₃ perovskite catalyst during catalytic oxidation of vinyl chloride. *Appl. Catal. B* **2016**, *186*, 173–183. [[CrossRef](#)]
38. De Rivas, B.; López-Fonseca, R.; Jiménez-González, C.; Gutiérrez-Ortiz, J.I. Highly active behaviour of nanocrystalline Co₃O₄ from oxalate nanorods in the oxidation of chlorinated short chain alkanes. *Chem. Eng. J.* **2012**, *184*, 184–192. [[CrossRef](#)]
39. Liu, Y.; Dai, H.; Du, Y.; Deng, J.; Zhang, L.; Zhao, Z.; Au, C.T. Controlled preparation and high catalytic performance of three-dimensionally ordered macroporous LaMnO₃ with nanovoid skeletons for the combustion of toluene. *J. Catal.* **2012**, *287*, 149–160. [[CrossRef](#)]
40. Liu, Y.; Dai, H.; Du, Y.; Deng, J.; Zhang, L.; Zhao, Z. Lysine-aided PMMA-templating preparation and high performance of three-dimensionally ordered macroporous LaMnO₃ with mesoporous walls for the catalytic combustion of toluene. *Appl. Catal. B* **2012**, *119–120*, 20–31. [[CrossRef](#)]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).