Research Article

Effects of the Reaction Parameters and Light Hydrothermal Aging for Catalytic Combustion of Propane over Co-Mn-Ce Catalyst

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Received 10 September 2021; Accepted 17 January 2022; Published 10 February 2022

Academic Editor: Ajaya Kumar Singh

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A composite oxides' Co-Mn-Ce catalyst was synthesized by a coprecipitation method, and the experiment was carried out to study the effects of reaction parameters and light hydrothermal aging on propane combustion over the Co-Mn-Ce catalyst. The influence of reaction temperature, propane concentration, oxygen concentration, water vapor, and hydrothermal aging was studied during the catalytic combustion of propane. The propane conversion significantly decreased by 10% when the propane concentration increased at 300°C and then further decreased from 80% to 40% as water vapor concentration increased from 0 to 10 vol.%. In addition, water vapor also prolonged the time required to reach equilibrium. After hydrothermal treatment, the catalyst obtained the lowest oxidation capacity of propane. Furthermore, the results of in situ DRIFTS and O₂ temperature programmed desorption (O₂-TPD) demonstrated that there were fewer oxygen species after hydrothermal aging, and carbonates were the main intermediates formed during the catalytic oxidation of propane.

1. Introduction

Volatile organic compounds (VOCs) are atmospheric pollutants emitted from a wide range of industrial processes and motor vehicle fuel combustion and cause chemical smog, haze, and ozone generation [1–3]. Propane emission is a light alkane VOC that is mainly produced from petrochemical processes and engines that use fossil fuels. Catalytic oxidation is considered an effective method for VOCs degradation due to its low operating temperature range (300–600°C) and because it does not require additional fuel and produces less secondary pollution than thermal oxidation [4, 5]. The catalytic oxidation of propane commonly requires large amounts of energy and active oxygen species during the reaction. It remains challenging to develop catalysts that demonstrate high performance at low temperatures.

Generally, the catalysts used for the total oxidation of propane include noble metals, transition metal oxides, and molecular sieves [6–8]. Transition metal oxides are thermally

stable, nontoxic, and inexpensive [9–11], which have been investigated as substitutes for precious metal catalysts [12, 13]. Among transition metals, mixed oxides show synergistic effects that produce catalytic activities than single-metal oxides. Zhao et al. [14] added Mn to Co₃O₄ to form a solid solution with spinel structure, which can significantly improve the catalytic activity of pure Co₃O₄, and can completely oxidize toluene and ethyl acetate at 220 and 180°C. Tang et al. [15] reported that Mn-Co mixed oxide nanorod with porous structure and high surface area formed solid solution with spinel structure, which inhibited the growth of nanoparticles that led to its higher surface area. While, a strong synergistic effect of Mn-Co species in the oxide made a great contribution to its low-temperature reducibility which played a key role in VOCs oxidation. Castano et al. [16] discovered that the redox properties and the oxygen mobility played a determining role in the oxidation of the VOCs, with the oxygen mobility playing a more significant role in the cobalt oxides, whereas the redox properties were fundamental in the manganese oxides and in

the Co and Mn mixture. Tang et al. [17] revealed that the hierarchical layer-stacking Mn-Ce composite oxide possessed superior physiochemical properties such as good low-temperature reducibility, high manganese oxidation state, and rich adsorbed surface oxygen species which resulted in the enhancement of catalytic abilities. Geng et al. [18] found that Ce can maintain the structure of the catalyst and prevent Mn^{4+} and Mn^{3+} from reducing to Mn^{2+} , which had good stability. Meanwhile, Tian et al. [19] found out that with the substitution of cobalt cations with Mn^{3+} and Mn^{4+} ions, the ratio $\text{Co}^{3+}/\text{Co}^{2+}$ decreased and both electrical resistivity and thermal stability showed increasing trends, which attributed to the progressive incorporation of manganese induced structural defects favoring the formation of anionic vacancies and the restriction of the oxygen mobility. Feng et al. [20] prepared Cu-Mn-Ce catalyst and found that unpaired electrons on the catalyst surface and Mn replacement in the catalyst crystal played an important role in the catalytic process, and the three metal oxides had a strong synergistic effect to significantly improve the catalytic activity. Deng et al. [21] found out that a solid solution was formed with more active oxygen induced by Co doping, while strong interaction effects among Co-Mn-Ce-O were speculated as the main mechanisms underlying the high efficiency catalytic capacity. Gómez et al. [22] found that $\text{Co}_3\text{O}_4/\text{La-CeO}_2$ contained more lattice oxygen species caused by $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ couples, which contributed to increased performance for toluene degradation. Kan et al. [23] reported that $\text{Mn}_8\text{Co}_1\text{Ce}_1$ /cordierite presented the best activity and stability among all of the catalysts synthesized. The results were attributed to the synergistic effect of ceria, manganese, and cobalt, which could promote the formation of more lattice defects, more oxygen vacancies, and smaller crystallite sizes.

The influence of water vapor on adsorption, catalytic oxidation, and the deposition of coke during the catalytic combustion of VOCs was also studied to understand the catalytic oxidation mechanism [24, 25]. In the presence of water vapor, the adsorption sites occupied by water vapor resulted in inaccessible of VOCs to adsorption sites [26, 27], the competitive adsorption of water vapor. In addition, some researchers found that the catalytic oxidation performance could also be affected by catalyst deactivation and operating temperature [28–30]. Bae et al. [31] showed that Mn-doped $\text{CuOeCo}_3\text{O}_4\text{eCeO}_2$ catalyst significantly enhanced activity and durability due to better preserved Co_3O_4 phase.

Although some progress has been made using Co-Mn-Ce composite catalysts for the catalytic combustion of VOCs, there are still few reports about the effect of reaction temperature, water vapor, and reaction conditions on the catalytic activity of VOCs. In this work, a Co-Mn-Ce catalyst was synthesized via a simple coprecipitation method and then used in the catalytic combustion of propane. The factors influencing oxidation performances including reaction temperature, C_3H_8 and O_2 concentration, and hydrothermal aging were investigated. The chemical properties of the catalysts were characterized by O_2 -TPD and in situ DRIFTS. In addition, the chemical reaction mechanism of Co-Mn-Ce catalytic oxidation of propane was evaluated.

2. Materials and Methods

2.1. Catalyst Preparation. The composite oxides' Co-Mn-Ce catalyst ($\text{Co:Mn:Ce} = 3:1:2$, molar ratio) was prepared using a coprecipitation method. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water, while the pH value was kept around 9.0. After stirring at room temperature for 1 h, the as-obtained homogeneous solution was filtered, washed, dried overnight at 110°C , and calcined at 500°C for 4 h to acquire the Co-Mn-Ce catalyst. The sample was labelled as CMC. In addition, the fresh CMC catalyst was light hydrothermally aged in $(10\% \text{H}_2\text{O} + 10\% \text{O}_2)/\text{N}_2$ at 750°C for 4 h and labelled as CMC-HA.

2.2. Catalyst Characterization. Oxygen temperature programmed desorption (O_2 -TPD) analysis was carried out using a Micromeritics AutoChem (USA) with a thermal conductivity detector (TCD). Approximately 30 mg of samples were pretreated in He with a flow rate of 30 mL/min at 400°C for 1 h. When the catalyst cooled to 50°C , O_2 was introduced until adsorption saturation. Afterward, the catalyst was purged by He to remove residual oxygen. Finally, O_2 -TPD was performed by increasing the temperature from 50 to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$ under He flow.

In situ DRIFTS spectra were recorded using a Nicolet 6700 FT-IR spectrometer in the spectral range of $400\text{--}4000\text{ cm}^{-1}$. Before the reaction gas was introduced, samples were pretreated at 450°C under N_2 flow for 1 h. The background spectra were then collected in flowing N_2 . Subsequently, the catalysts were exposed to a $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2$ gas mixture to investigate their activity during catalytic combustion of propane.

2.3. Catalyst Performance. Catalytic performance was evaluated in a continuous quartz tubular fixed bed flow reactor ($\varnothing 8\text{ mm} \times 10\text{ mm}$) as shown in Figure 1. For each experiment, catalyst powdered (40–60 mesh) was placed in the middle of the flow reactor with the aid of glass fiber. The reaction temperature was measured by a thermocouple, in direct contact with the catalyst bed. The water content was controlled by a precision injection pump, and the heating belt was wrapped in tubular quartz to maintain a temperature over 100°C to prevent water vapor condensation. The data of reactant and products were collected at each temperature by infrared and electrochemical gas analyzers.

Due to the large amounts of water vapor in the exhaust, experiments were evaluated under different water vapor concentrations (0, 5, and 10 vol%). The feed was composed of 1000×10^{-6} v/v propane, 10% O_2 , and balance N_2 , and the reaction was carried out from 100 to 500°C . The propane concentration was varied (250×10^{-6} v/v, 500×10^{-6} v/v, 750×10^{-6} v/v, and 1000×10^{-6} v/v) to evaluate its impact at 300°C . To reflect the effect of hydrothermal aging treatment, the reaction was carried out in a 0 vol% water vapor atmosphere, at reaction temperatures from 100°C to 500°C . The total gas flow rate was 240 mL/min at a space velocity of $48,000\text{ h}^{-1}$.

FIGURE 1: Schematic of the catalytic flow reactor experimental system.

Catalytic activities of the CMC catalyst were studied at temperatures from 100°C to 500°C for acquiring propane conversion of 10, 80, and 90%, respectively (T_{10} , T_{80} , and T_{90}). The propane conversion capacity ($\eta_{\text{propane}}\%$) during the catalytic oxidation of propane was evaluated by the following equation.

$$\eta_{\text{propane}}\% = \frac{(C_3H_8)_{\text{in}} - (C_3H_8)_{\text{out}}}{(C_3H_8)_{\text{in}}} \times 100, \quad (1)$$

where $(C_3H_8)_{\text{in}}$ (v/v) and $(C_3H_8)_{\text{out}}$ (v/v) represent the concentrations of propane in the inlet gas and the outlet gas, respectively.

3. Results and Discussion

3.1. Reaction Testing

3.1.1. Effect of Reaction Temperature. The reaction temperature was investigated to understand the propane oxidation process under different water vapor conditions as shown in Figure 2. A significant decrease in propane concentration from 1000×10^{-6} v/v to 150×10^{-6} v/v occurred within 30 s (Figure 2(a) and Figure 2(b)), due to hysteresis during gas switching. Furthermore, the propane concentration increased from 200 to 300°C, and the increase at 200°C was the fastest. The rising rate of propane concentration gradually decreased with increasing temperature. At each temperature, the rate was tending towards stability after 1000 s. This resulted from increasing the temperature, provided more energy for the catalytic oxidation of propane. Notably, the outlet propane concentration reached 900×10^{-6} v/v without water at 200°C, and this temperature corresponded to a propane conversion of 10%, which indicated that CMC presented a good low-temperature catalytic activity. The propane concentration was 30×10^{-6} v/v at 350°C, and the propane conversion was 97%. T_{10} and T_{90}

under 5 vol% water vapor conditions were the same as 0 vol% water vapor. At 10 vol% water vapor, T_{10} and T_{90} were approximately 250 and 400°C (Figure 2(c)).

As shown in Figure 2(d), the propane concentration did not change with the reaction temperature below 200°C. The propane conversion was similar at 0 vol% and 5 vol% water vapor, indicating that the water did not impact the oxidation activity. At 10 vol% water vapor, the propane conversion decreased at different temperatures, possibly because H_2O had adsorbed on the active sites and inhibited oxidation.

3.1.2. Effect of Propane Concentration. The results of the propane oxidation experiments showed that the effect of propane conversion at 300°C decreased by approximately 40% when water vapor was introduced in feed gas. When the temperature was below 300°C, little propane conversion was observed. When the temperature exceeded 300°C, propane was almost completely oxidized. Therefore, the constant temperature oxidation experiments were carried at 300°C to further investigate the effect of propane concentration and water vapor.

The propane concentration curve and conversion diagrams of the CMC catalyst are shown in Figure 3. From Figures 3(a)–3(c), the propane concentration (250×10^{-6} v/v, 500×10^{-6} v/v, 750×10^{-6} v/v, and 1000×10^{-6} v/v) showed a significant decrease in the first 50 s, which was caused by switching the three-way valve to change the reaction gas path. At 0 vol% water vapor, the propane concentration at the outlet remained constant after 60 s (39×10^{-6} v/v, 107×10^{-6} v/v, 201×10^{-6} v/v, and 267×10^{-6} v/v), indicating a stable catalytic performance. At 5 vol% water vapor condition, the propane concentration remained unchanged after about 100 s. At 10 vol% water vapor, the reaction required 200 s to reach equilibrium at constant propane concentration. This indicated that water vapor inhibited catalytic oxidation reaction, and as the water vapor

FIGURE 2: Propane concentration curve and propane conversion curve under different temperatures. (a) 0 vol% water vapor. (b) 5 vol% water vapor. (c) 10 vol% water vapor. (d) Propane conversion.

concentration increased, the reaction took longer to reach equilibrium.

As shown in Figure 3(d), under the same water vapor concentration, the catalytic activity decreased as the propane concentration increased, especially in the absence of water. Notably, at 10 vol% water vapor, the propane conversion remained nearly unchanged when different propane concentrations were introduced.

3.1.3. Effect of O₂ Concentration. The propane concentration curve of the CMC catalyst under various O₂ concentrations is shown in Figure 4. At 0 vol% water vapor, when the O₂ concentration was 0%, the concentration of propane at the outlet was 1000×10^{-6} v/v, indicating no oxidation. Upon increasing the O₂ concentration from 5% to 10%, the outlet propane concentration reached 160×10^{-6} v/v, indicating the same propane oxidation. As shown in Figure 4(b), at 5 vol% water vapor, the outlet propane concentration was 1000×10^{-6} v/v when the O₂ concentration was 0%. Upon introducing O₂, the propane concentration at the outlet was stable at 355×10^{-6} v/v. As shown in Figure 4(c), at 10 vol%

water vapor, the propane concentration at the outlet was 630×10^{-6} v/v as the oxygen content increased to 5% and 10%. It can be seen from Figures 4(a)–4(c) that the time required to reach reaction stability increased upon increasing the water concentration. The outlet propane concentration also increased as the water concentration increased. This may be due to the adsorption of water on the active sites of the catalyst surface, which hindered contact between propane and O₂ molecules and active sites, thus inhibiting propane oxidation.

3.1.4. Effect of Hydrothermal Aging Treatment. Propane concentration as a function of time and conversion after hydrothermal aging of the CMC-1 catalyst is shown in Figure 5. As shown in Figure 5(a), the propane concentration rapidly stabilized at different reaction temperatures in the first 60 seconds, and then, it remained unchanged, indicating that the catalyst remained stable after hydrothermal aging treatment. As the temperature increased, the propane concentration at the outlet decreased, possibly due to the enhanced oxidation capacity. Figure 5(b) shows that

FIGURE 3: Propane concentration and propane conversion under different propane concentrations. (a) 0 vol% water vapor. (b) 5 vol% water vapor. (c) 10 vol% water vapor. (d) Propane conversion.

the propane conversion reached T_{10} above 250°C and T_{80} was at 500°C . It was found that after hydrothermal aging treatment, T_{10} and T_{80} increased by 60 and 80°C , respectively, indicating that the activity of the catalyst decreased significantly after hydrothermal aging.

3.2. Characterization of the Catalyst

3.2.1. O_2 -TPD. The type and migration ability of oxygen species in the catalysts were studied through O_2 -TPD. Figure 6 shows the O_2 -TPD experiments of Co-Mn-Ce catalysts. The desorption sequence of surface oxygen species was generally as follows: $\text{O}_2^-(\text{O}_{\text{ads}}) \rightarrow \text{O}^-(\text{O}_{\text{ads}}) \rightarrow \text{O}_2-(\text{O}_{\text{latt}})$. Three broad peaks were observed at 182°C , 510°C , and 700°C . The peak at 182°C was assigned to desorption of O_2^- and O^- , both of which are the reactive oxygen species involved in oxidation. The second peak was associated with the desorption of O_2^- [32, 33]. A strong peak was observed at

700°C , which corresponded to the desorption of bulk lattice oxygen [34]. After aging, all desorption peaks shifted towards a higher temperature, which indicated that oxygen mobility was significantly affected, and the utilization of surface oxygen became difficult. The desorption peak of the fresh catalyst was much larger than that after hydrothermal aging, indicating the former had a higher concentration of oxygen species.

3.2.2. In Situ DRIFTS. The DRIFTS spectra used to explore the propane adsorption on the catalyst in a flow of 0.2% propane and 10% O_2 are shown in Figure 7. From Figures 7(a) and 7(b), the spectra contained bands at 1422 and 1584 cm^{-1} , which were associated with uncoordinated CO_3^{2-} and $\nu_{\text{as}}(\text{COO})$, respectively [35]. These peaks suggested that surface oxygen species oxidized propane into intermediate species. The bands around 2300 – 2400 and 3730 cm^{-1} were attributed to gaseous CO_2 and

FIGURE 4: Propane concentration curve on CMC catalyst under different O_2 concentrations. (a) 0 vol% of water vapor. (b) 5 vol% of water vapor. (c) 10 vol% water vapor.

FIGURE 5: CMC-HA catalyst. (a) Propane concentration. (b) Propane conversion.

FIGURE 6: O_2^- TPD curves of the CMC and CMC-HA catalysts.

FIGURE 7: In situ DRIFTS spectra of propane adsorption on (a) CMC catalyst and (b) CMC-HA catalyst at 100–450°C.

$\nu_{as}(OH)$ [36, 37], suggesting the total oxidation of propane. The spectra of CMC-HA were similar to that of the CMC catalyst, indicating that the two catalysts followed the same reaction mechanism. CMC-HA catalysts exhibited similar behavior as shown in Figure 7(b), and the new bands attributed to $\nu_{as}(C-H)$ at 2969 cm^{-1} and $\delta_{as}(CH_3)$ at 1479 cm^{-1} . The intensity of the peaks at 1422 and 1584 cm^{-1} was lower than the CMC catalyst, probably due to the much lower surface area after hydrothermal aging.

4. Conclusion

In this study, the effects of various reaction conditions were investigated over CMC catalysts by propane oxidation experiments. The catalytic oxidation experiments indicated that propane conversion was significantly different at 300°C under various water vapor concentrations. Propane conversion exceeded 95% at 400°C . In addition, it also showed that the reaction times required to equilibrium extended upon increasing the water concentration. Under the same propane concentration, propane conversion decreased from 80% to 40% upon increasing the water concentration. Under the same water vapor concentration, propane conversion

decreased by 10% upon increasing the propane concentration due to the presence of fewer active sites. When the concentration of O_2 was 0%, the propane concentration was $1000 \times 10^{-6}\text{ v/v}$, which showed that O_2 limited propane oxidation by the CMC-1 catalyst. After light hydrothermal aging, the oxidation activity of the catalyst decreased significantly. Notably, O_2 -TPD experiments demonstrated that the number of oxygen species (O_2^- and O^-) decreased after light hydrothermal aging. The stored species existed mainly as oxygenating intermediate over the CMC catalyst, while the stored species during propane oxidation existed as carbonate species over the CMC-HA catalyst in the DRIFTS experiments. It indicated that the oxidation path followed the same surface reaction mechanism after hydrothermal aging.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51906089), Postgraduate Research and Practice Innovation Program of Jiangsu Province (SJCX20_1422), National Engineering Laboratory Open Fund for Mobile Source Pollution Emission Control Technology (NELMS2018A18), and Zhenjiang Science and Technology Support Project (GY2020016).

References

- [1] X. Zhu, S. Liu, Y. Cai et al., "Post-plasma catalytic removal of methanol over Mn-Ce catalysts in an atmospheric dielectric barrier discharge," *Applied Catalysis B: Environmental*, vol. 183, pp. 124–132, 2016.
- [2] X. Zhu, S. Zhang, X. Yu et al., "Controllable synthesis of hierarchical MnO_x/TiO₂ composite nanofibers for complete oxidation of low-concentration acetone," *Journal of Hazardous Materials*, vol. 337, pp. 105–114, 2017.
- [3] L. Chen, Y. Liao, S. Xin, X. Song, G. Liu, and X. Ma, "Simultaneous removal of NO and volatile organic compounds (VOCs) by Ce/Mo doping-modified selective catalytic reduction (SCR) catalysts in denitrification zone of coal-fired flue gas," *Fuel*, vol. 262, Article ID 116485, 2020.
- [4] K. Everaert and J. Baeyens, "Catalytic combustion of volatile organic compounds," *Journal of Hazardous Materials*, vol. 109, no. 1-3, pp. 113–139, 2004.
- [5] Y. Guo, M. Wen, G. Li, and T. An, "Recent advances in VOC elimination by catalytic oxidation technology onto various nanoparticles catalysts: a critical review," *Applied Catalysis B: Environmental*, vol. 281, Article ID 119447, 2021.
- [6] Q. Dai, S. Bai, J. Wang, M. Li, X. Wang, and G. Lu, "The effect of TiO₂ doping on catalytic performances of Ru/CeO₂ catalysts during catalytic combustion of chlorobenzene," *Applied Catalysis B: Environmental*, vol. 142-143, pp. 222–233, 2013.
- [7] S. Zuo, M. Ding, J. Tong, L. Feng, and C. Qi, "Study on the preparation and characterization of a titanium-pillared clay-supported CrCe catalyst and its application to the degradation of a low concentration of chlorobenzene," *Applied Clay Science*, vol. 105-106, pp. 118–123, 2015.
- [8] Q. Dai, S. Bai, X. Wang, and G. Lu, "Facile synthesis of HZSM-5 with controlled crystal morphology and size as efficient catalysts for chlorinated hydrocarbons oxidation and xylene isomerization," *Journal of Porous Materials*, vol. 21, no. 6, pp. 1041–1049, 2014.
- [9] S. Behar, N.-A. Gómez-Mendoza, M.-Á. Gómez-García, D. Świerczyński, F. Quignard, and N. Tanchoux, "Study and modelling of kinetics of the oxidation of VOC catalyzed by nanosized Cu-Mn spinels prepared via an alginate route," *Applied Catalysis A: General*, vol. 504, pp. 203–210, 2015.
- [10] X. Wang, W. Zhao, X. Wu et al., "Total oxidation of benzene over ACo₂O₄ (A = Cu, Ni and Mn) catalysts: in situ DRIFTS account for understanding the reaction mechanism," *Applied Surface Science*, vol. 426, pp. 1198–1205, 2017.
- [11] Y. Ma, Y. Li, M. Mao, J. Hou, M. Zeng, and X. Zhao, "Synergistic effect between photocatalysis on TiO₂ and solar light-driven thermocatalysis on MnO_x for benzene purification on MnO_x/TiO₂ nanocomposites," *Journal of Materials Chemistry*, vol. 3, no. 10, pp. 5509–5516, 2015.
- [12] C. He, Y. Yu, Q. Shen, J. Chen, and N. Qiao, "Catalytic behavior and synergistic effect of nanostructured mesoporous CuO-MnO_x-CeO₂ catalysts for chlorobenzene destruction," *Applied Surface Science*, vol. 297, pp. 59–69, 2014.
- [13] J. Zhu and Q. Gao, "Mesoporous MCo₂O₄ (M=Cu, Mn and Ni) spinels: structural replication, characterization and catalytic application in CO oxidation," *Microporous and Mesoporous Materials*, vol. 124, no. 1-3, pp. 144–152, 2009.
- [14] H. Zhao, H. Wang, and Z. Qu, "Synergistic effects in Mn-Co mixed oxide supported on cordierite honeycomb for catalytic deep oxidation of VOCs," *Journal of Environmental Sciences*, vol. 112, pp. 231–243, 2022.
- [15] W. Tang, X. Wu, S. Li, W. Li, and Y. Chen, "Porous Mn-Co mixed oxide nanorod as a novel catalyst with enhanced catalytic activity for removal of VOCs," *Catalysis Communications*, vol. 56, pp. 134–138, 2014.
- [16] M. H. Castaño, R. Molina, and S. Moreno, "Cooperative effect of the Co-Mn mixed oxides for the catalytic oxidation of VOCs: influence of the synthesis method," *Applied Catalysis A: General*, vol. 492, pp. 48–59, 2015.
- [17] W. Tang, X. Wu, G. Liu et al., "Preparation of hierarchical layer-stacking Mn-Ce composite oxide for catalytic total oxidation of VOCs," *Journal of Rare Earths*, vol. 33, no. 1, pp. 62–69, 2015.
- [18] L. Geng, B. Chen, J. Yang et al., "Synergistic effect between Mn and Ce for active and stable catalytic wet air oxidation of phenol over MnCeO_x," *Applied Catalysis A: General*, vol. 604, pp. 117774–117783, 2020.
- [19] Z.-Y. Tian, P. H. Tchoua Ngamou, V. Vannier, K. Kohse-Höinghaus, and N. Bahlawane, "Catalytic oxidation of VOCs over mixed Co-Mn oxides," *Applied Catalysis B: Environmental*, vol. 117-118, pp. 125–134, 2012.
- [20] S. Feng, J. Liu, and B. Gao, "Synergistic mechanism of Cu-Mn-Ce oxides in mesoporous ceramic base catalyst for VOCs microwave catalytic combustion," *Chemical Engineering Journal*, vol. 429, pp. 132302–132313, 2022.
- [21] L. Deng, Y. Ding, B. Duan et al., "Catalytic deep combustion characteristics of benzene over cobalt doped Mn-Ce solid solution catalysts at lower temperatures," *Molecular Catalysis*, vol. 446, pp. 72–80, 2018.
- [22] D. M. Gómez, V. V. Galvita, J. M. Gatica, H. Vidal, and G. B. Marin, "TAP study of toluene total oxidation over a Co₃O₄/La-CeO₂ catalyst with an application as a washcoat of cordierite honeycomb monoliths," *Royal Society of Chemistry*, vol. 16, no. 23, pp. 11447–11455, 2014.
- [23] J. Kan, L. Deng, B. Li et al., "Performance of co-doped Mn-Ce catalysts supported on cordierite for low concentration chlorobenzene oxidation," *Applied Catalysis A: General*, vol. 530, pp. 21–29, 2017.
- [24] C. Yang, G. Miao, Y. Pi et al., "Abatement of various types of VOCs by adsorption/catalytic oxidation: a review," *Chemical Engineering Journal*, vol. 370, pp. 1128–1153, 2019.
- [25] P. Wang, C. Cui, K. Li, J. Yi, and L. Lei, "The effect of Mn content on catalytic activity of the Co-Mn-Ce catalysts for propane oxidation: importance of lattice defect and surface active species," *Catalysis Letters*, vol. 150, no. 5, pp. 1505–1514, 2019.
- [26] M. Ghafari and J. D. Atkinson, "One-step hyper-cross-linking of porous styrenic polymers using dichloroalkane cross-linkers to maintain hydrophobicity," *Polymer*, vol. 116, pp. 278–286, 2017.
- [27] Q. Dai, X. Wang, and G. Lu, "Low-temperature catalytic combustion of trichloroethylene over cerium oxide and catalyst deactivation," *Applied Catalysis B: Environmental*, vol. 81, no. 3-4, pp. 192–202, 2008.

- [28] C. H. Bartholomew, "Mechanisms of catalyst deactivation," *Applied Catalysis A: General*, vol. 212, no. 1-2, pp. 17–60, 2001.
- [29] R. López-Fonseca, A. Aranzabal, and P. Steltenpohl, "Performance of zeolites and product selectivity in the gas-phase oxidation of 1,2-dichloroethane," *Catalysis Today*, vol. 62, pp. 367–377, 2000.
- [30] W. B. Li, M. Zhuang, T. C. Xiao, and M. L. H. Green, "MCM-41 supported Cu–Mn catalysts for catalytic oxidation of toluene at low temperatures," *The Journal of Physical Chemistry B*, vol. 110, no. 43, pp. 21568–21571, 2006.
- [31] J. Bae, B.-S. Kim, H. Jeong, and H. Lee, "Mn-doped CuO Co₃O₄CeO₂ catalyst with enhanced activity and durability for hydrocarbon oxidation," *Molecular Catalysis*, vol. 467, pp. 9–15, 2019.
- [32] L. Xue, C. Zhang, H. He, and Y. Teraoka, "Catalytic decomposition of N₂O over CeO₂ promoted Co₃O₄ spinel catalyst," *Applied Catalysis B: Environmental*, vol. 75, no. 3-4, pp. 167–174, 2007.
- [33] S. Xie, Y. Liu, J. Deng et al., "Three-dimensionally ordered macroporous CeO₂-supported Pd@Co nanoparticles: highly active catalysts for methane oxidation," *Journal of Catalysis*, vol. 342, pp. 17–26, 2016.
- [34] G. Yang, Y. Li, and Y. Men, "Synergistic catalysis effect of Mn-promoted BaAl₂O₄ catalysts on catalytic performance for soot combustion," *Catalysis Communications*, vol. 69, pp. 202–206, 2015.
- [35] X. Li, X. Li, X. Zeng, and T. Zhu, "Correlation between the physicochemical properties and catalytic performances of micro/mesoporous CoCeO mixed oxides for propane combustion," *Applied Catalysis A: General*, vol. 572, pp. 61–70, 2019.
- [36] S. Mo, Q. Zhang, Y. Sun et al., "Gaseous CO and toluene co-oxidation over monolithic core-shell Co₃O₄-based hetero-structured catalysts," *Journal of Materials Chemistry*, vol. 7, no. 27, pp. 16197–16210, 2019.
- [37] M. Guo, K. Li, H. Zhang et al., "Promotional removal of oxygenated VOC over manganese-based multi oxides from spent lithium-ions manganate batteries: modification with Fe, Bi and Ce dopants," *The Science of the Total Environment*, vol. 740, Article ID 139951, 2020.