



Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Communication

Unveiling the importance of reactant mass transfer in environmental catalysis: Taking catalytic chlorobenzene oxidation as an example

Kexin Cao^{a,b}, Xiaoxia Dai^{a,b}, Zhongbiao Wu^{a,b}, Xiaole Weng^{a,b,*}^a Key Laboratory of Environment Remediation and Ecological Health, Ministry of Education, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China^b Zhejiang Provincial Engineering Research Center of Industrial Boiler & Furnace Flue Gas Pollution Control, Hangzhou 310058, China

ARTICLE INFO

Article history:

Received 23 June 2020

Received in revised form 23 July 2020

Accepted 2 September 2020

Available online xxx

Keywords:

VOCs oxidation

Chlorinated organics

Reactant mass transfer

Secondary pollution

Catalyst design

Environmental catalysis

ABSTRACT

To date, investigations onto the regulation of reactants mass transfer has been paid much less attention in environmental catalysis. Herein, we demonstrated that by rationally designing the adsorption sites of multi-reactants, the pollutant destruction efficiency, product selectivity, reaction stability and secondary pollution have been all affected in the catalytic chlorobenzene oxidation (CBCO). Experimental results revealed that the co-adsorption of chlorobenzene (CB) and gaseous O₂ at the oxygen vacancies of CeO₂ led to remarkably high CO₂ generation, owing to their short mass transfer distance on the catalyst surface, while their separated adsorptions at Brønsted HZSM-5 and CeO₂ vacancies resulted in a much lower CO₂ generation, and produced significant polychlorinated byproducts in the off-gas. However, this separated adsorption model yielded superior long-term stability for the CeO₂/HZSM-5 catalyst, owing to the protection of CeO₂ oxygen vacancies from Cl poisoning by the preferential adsorption of CB on the Brønsted acidic sites. This work unveils that design of environmental catalysts needs to consider both of the catalyst intrinsic property and reactant mass transfer; investigations of the latter could pave a new way for the development of highly efficient catalysts towards environmental pollution control.

© 2020 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.
Published by Elsevier B.V. All rights reserved.

Environmental catalysis is of great importance in air pollution control, which converts the air pollutants into harmless products via a range of heterogeneous catalytic reactions [1]. Typical examples include selective catalytic reduction (SCR) of NO_x [2–4], catalytic destruction of organic wastes [5], the methane catalytic reforming with carbon dioxide [6], etc. Recent development in the environmental catalysis has been greatly accelerated by the increasingly stringent emission standards, while numerous techniques have been oriented to industrial-scale applications, making an important contribution to the improvement of air quality in China. As the core of environmental catalysis, rational design of environmental catalysts with an aim to maximize their catalytic activities have been extensively explored, which yields significant outcomes in terms of increasing the number of active sites [7,8] and enhancing the redox ability of catalysts [9–11]. However, since most of environmental heterogeneous reactions involve two or more reactants, the pollutant destruction efficiency

is not only dependent on the intrinsic properties of applied catalysts, but also on the mass transfer and collision probability of these multi-reactants. Current works put great efforts on modifying the catalyst intrinsic properties, while investigations onto how to regulate the reactants mass transfer rate has been paid much less attention; the latter is believed to play crucial role in determining the pollutant conversion efficiency and reaction selectivity.

Chlorinated volatile organic compounds (Cl-VOCs) are well-known with inherent bioaccumulation and potential carcinogenicity, many of which have been listed as priority control pollutants worldwide [12,13]. Catalytic destruction of chlorinated organics remains a great challenge in environmental catalysis, owing to it encounters problems of catalyst deactivation [14] and secondary pollution (i.e., abundant more toxic byproducts) [15,16], which severely hinders this technique towards industrial scale application [17–19]. This process is initiated by the scission of C–Cl bond at acidic (Brønsted/Lewis) sites or superficial oxygen vacancy and the activation of gaseous O₂ at oxygen vacancy, followed by the reaction between multi-adsorbates to convert the Cl-VOCs into CO₂, H₂O, HCl/Cl₂ and intermediates [20,21]. The involvement of Cl-VOCs and O₂ adsorptions at various active sites and the abundant reaction byproducts make the catalytic destruction of

* Corresponding author at: Key Laboratory of Environment Remediation and Ecological Health, Ministry of Education, College of Environmental and Resource Sciences, Zhejiang University, China.

E-mail address: xlweng@zju.edu.cn (X. Weng).

<https://doi.org/10.1016/j.cclet.2020.09.001>

1001-8417/© 2020 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

Cl-VOCs much ideal for exploring the importance of mass transfer in determining the pollutant destruction efficiency and product selectivity.

Herein, we choose CeO₂ nanorods as a model catalyst, because it has abundant superficial oxygen vacancies [22,23] that could provide sufficient adsorption sites for both of the Cl-VOCs and gaseous O₂. Chlorobenzene (CB) was selected as typical Cl-VOCs, the oxidation of which has shown to easily generate reaction intermediates [24], and can be used to evaluate the reaction selectivity.

Furthermore, to get a contrasted catalyst, a HZSM-5 zeolite with abundant Brønsted acidic sites was introduced by using a dry-mixing route in a ball miller. This catalyst was expected to provide separated adsorption sites for Cl-VOCs and gaseous O₂, as the Cl-VOCs were shown to preferentially adsorb on the Brønsted HZSM-5 sites. The separated adsorptions of Cl-VOCs and O₂ and the poor-mixing of CeO₂ and HZSM-5 effectively increased the mass transfer distance of their adsorbates, which should yield varied catalytic performance in comparison with their co-adsorption on the CeO₂ vacancies.

The reaction characteristics and byproducts generation of CeO₂ and CeO₂/HZSM-5 catalysts in the catalytic CB oxidation (CBCO) were evaluated using a range of analytical techniques, including powder X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature program reduction of hydrogen (H₂-TPR), temperature program desorption of oxygen (O₂-TPD), fourier transform infrared spectroscopy (FT-IR), gas chromatography mass spectrometry (GC-MAS), etc. XRD indicated the dry-mixing did not change the crystal structure of CeO₂ and HZSM-5 (Fig. S1 in Supporting information). The former exhibited characteristic patterns at 28.7°, 33.1°, 47.4°, 56.3°, 69.7° and 76.9° with a cubic fluorite structure (JCPDS No. 89-8436), and the latter revealed an MFI type framework at 7.9°, 8.8°, 23.0°, 23.9°, 29.8°, 45.5° and 55.1° (JCPDS No. 44-0002). Scanning electron microscope (SEM) revealed that CeO₂ was composed of monodispersed nanorods (200–500 nm in length) and in the CeO₂/HZSM-5, these nanorods were much shorter (50–200 nm) and showed certain agglomerations (Fig. S2 in Supporting information). Energy dispersive X-ray spectroscopy (EDX) mapping indicated the HZSM-5 and CeO₂ were not well mixed, owing to the use of dry mixing method (Fig. S3 in Supporting information). The Brunauer-Emmet-Teller (BET) surface area measurements showed the CeO₂ with a surface area of 96.0 m²/g, which was lower than that of CeO₂/HZSM-5 (120.1 m²/g), attributing to the HZSM-5 with a high BET surface area of 180.1 m²/g.

To confirm the existence of Brønsted acidity in the CeO₂/HZSM-5 catalyst, pyridine adsorption infrared spectroscopy (Py-IR) and NH₃ temperature programmed desorption (TPD) were conducted. As shown in Fig. 1a, the pyridine desorption peaks mainly located at 1595, 1545, and 1490 cm⁻¹, which correspond to the Lewis acidic site, Brønsted acidic site and the combination of them, respectively [25,26]. In comparison with CeO₂, the CeO₂/HZSM-5 catalyst exhibited a very intense peak at 1545 cm⁻¹, suggesting that the

introduction of HZSM-5 greatly enhanced the Brønsted acidity of the catalyst. This acidity was mainly derived from the proton H on the surface of HZSM-5. The amounts of acidic sites were also greatly increased by introducing the HZSM-5. In the NH₃-TPD profile, the type of acids can be divided into weak acid (below 200 °C), medium strong acid (200–400 °C), and strong acid (above 400 °C) based on the NH₃ desorption temperature. As shown in Fig. 1b, the CeO₂ exhibited two broad NH₃ desorption peaks centered at 99 °C and 464 °C, both of which were resulted from the Ce⁴⁺/Ce³⁺ (dominant) and the surface acidic hydroxyl group (bridged OH_{ad}) [27]. After loading the HZSM-5, the intensity of NH₃ desorption peaks were significantly enhanced, and shifted to 74 °C and 351 °C, respectively, suggesting that enriched weak and medium strong acidities were introduced to the CeO₂/HZSM-5 catalyst, consistent with the Py-IR results.

The selective adsorption of CB on the CeO₂ and CeO₂/HZSM-5 catalysts were confirmed using *in situ* FT-IR analyses. The spectra were collected at 150 °C in a stream of 500 ppm CB and 10 vol% O₂ within 30 min. As shown in Fig. 2a, the bands at 1591, 1479 and 1444 cm⁻¹ are assigned to C=C degenerate stretching vibrations of the aromatic ring [28]. According to the literature [29], on the dehydroxylated defect-free CeO₂ surface, CB adsorption was mainly through Ce⁴⁺...π-electron type interaction, while on the hydroxylated surface, this preceded *via* a dual-site interaction (OH...π-electron and OH...Cl). During the preparation of CeO₂ nanorods, a large number of hydroxyl groups remained on the catalyst surface after alcohol washing. As a result, the CB was shown to initially adsorb on the Ce–OH site. This is confirmed by the changes of –OH vibration, which exhibited inverted peaks in the range of 3750–3625 cm⁻¹ after CB adsorption. The appearance of 3600 cm⁻¹ band is considered as the result of the migration of these inverted peaks, owing to the disturbance of adsorbed species [29]. The bands in the range of 2000–1700 cm⁻¹ can be attributed to the out of plane distortion harmonics (combination and overtones) of the C–H bond [30], which are derived from the interaction of π electron cloud of benzene ring and electron center of oxide surface [31]. The characteristic bands at 3068 and 2829 cm⁻¹ are derived from the vibration of C–H on benzene ring [32]. These bands increased gradually in the first 10 min, and then decreased, suggesting that the OH groups on the CeO₂ surface were gradually consumed by CB adsorption.

After 10 min, a new band appeared at 1667 cm⁻¹, which gradually increased with the measuring time. This band has been assigned to the CB adsorption on Ce³⁺-Vo sites [33], which could result in the cleavage of C–Cl band, leaving the Cl at oxygen vacancies (Vo). The dissociated Cl at the Vo is inclined to attack the C⁺ of phenyl, leading to an electrophilic chlorination and the formation of (poly) chlorinated byproducts [34]. The continued growth of this peak indicated that after the complete consumption of surface hydroxyls in the CeO₂, the CB was mainly adsorbed on surface Vo sites. Additionally, the vibration bands at 1534 and 1174 cm⁻¹ are assigned to the intermediate products of maleic acid [28] and the inverted bands at 2935 and 2845 cm⁻¹ can be attributed to methylene (–CH₂–) and methyl (–CH₃) [29]. Fig. 2b illustrates the adsorption of CB on the CeO₂/HZSM-5 catalyst. It was noted that loading of the HZSM-5 effectively changed the adsorption model of CB on the catalyst surface, where the CB was found to mainly adsorb on the hydroxyls of HZSM-5, revealing the characteristic bands at 1578, 1478, 1444 and 1253 cm⁻¹ [35]. The *in situ* FT-IR analyses confirmed our assumption that the CB was preferentially adsorbed on the HZSM-5, which effectively separated the adsorption site with O₂, while this separated adsorption model made the two adsorbates have a comparatively larger mass transfer distance than co-adsorbed on the CeO₂.

To investigate the reaction characteristics of CeO₂ and CeO₂/HZSM-5 in the CBCO reaction, a CB-TPSR experiment involving a

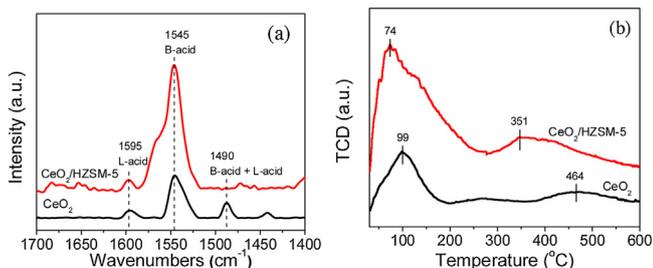


Fig. 1. (a) pyridine-IR and (b) NH₃-TPD profiles of CeO₂ and CeO₂/HZSM-5 catalysts.

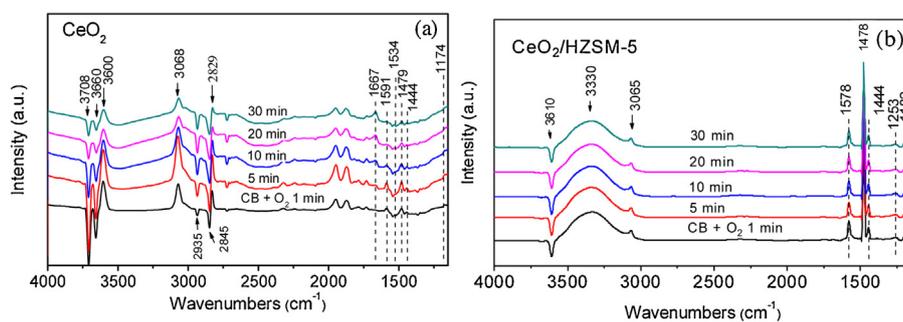


Fig. 2. *In situ* FT-IR spectra of (a) CeO₂ and (b) CeO₂/HZSM-5 catalysts at 150 °C in a stream of 500 ppm CB and 10 vol% O₂ within 30 min.

flow of 500 ppm CB and 10 vol% O₂ was conducted. The dynamic and timely generation of CO₂ from this reaction were *in situ* monitored. As shown in Fig. 3a, the different mass transfer distance in the CeO₂ and CeO₂/HZSM-5 indeed resulted in a distinct change in CO₂ generation, where the CeO₂ with short transfer distance yielded an intense CO₂ desorption peak in the temperature range of 225–450 °C. In comparison, the CeO₂/HZSM-5 with separated absorption sites of CB and O₂ exhibited a much lower and postponed CO₂ desorption peak. This result verifies that the mass transfer distance between the reactant adsorbates plays a crucial role in determining the CB destruction efficiency and CO₂ selectivity, where short distance yielded much higher destruction efficiency and CO₂ selectivity than the longer one. However, it was noted that the co-adsorption of CB and O₂ at the Vo resulted in severe Cl poisoning of the catalyst, where in a 250 °C stability test (Fig. 3b), the CeO₂ was shown to be rapidly deactivated, but the CeO₂/HZSM-5 displayed a much better long-term stability. Since the introduction of HZSM-5 was shown to not significantly alter the redox properties of CeO₂ catalyst (as confirmed by H₂-TPR and O₂-TPD analyses in Figs. S4-S5 in Supporting information), we believed that the higher long-term stability of CeO₂/HZSM-5 should be attributed to the preferential adsorption of CB at HZSM-5 that hindered the Cl occupation at Vo and ensured the continuous O₂ activation for CBCO reaction.

Reaction byproducts, particularly toxic polychlorinated organics in the off-gases were quantitatively analysed using a calibrated GC-MS system. As shown in Fig. 4, the CeO₂ and CeO₂/HZSM-5 catalysts both generated certain polychlorinated byproducts, including polychlorinated alkanes, polychlorinated alkenes and dichlorobenzenes, amongst which, the dichlorobenzenes should be paid the most concern as they are easily converted into dioxins, leading to severe secondary pollution to the environment [36–38]. The CeO₂ yielded approximately 2 μg/m³ of *p*-dichlorobenzene, while for the CeO₂/HZSM-5, the amounts of *m*-dichlorobenzene were measured at 5 μg/m³, and the *p*-dichlorobenzene was shown to be as high as 38 μg/m³. Such a difference was shown to originate from the excessive adsorption of CB on the HZSM-5 surface (Fig. S6

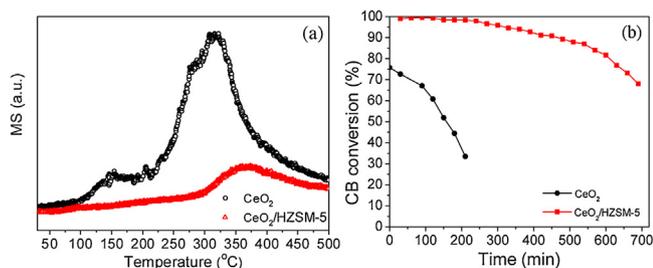


Fig. 3. (a) CB-TPSR profiles of CO₂ yield and (b) a stability test at 250 °C on the CeO₂ and CeO₂/HZSM-5 catalysts; Reaction conditions: GHSV = 10 000 mL g⁻¹ h⁻¹, 500 ppm CB, N₂ flow rate = 145 mL/min, O₂ flow rate = 15 mL/min.

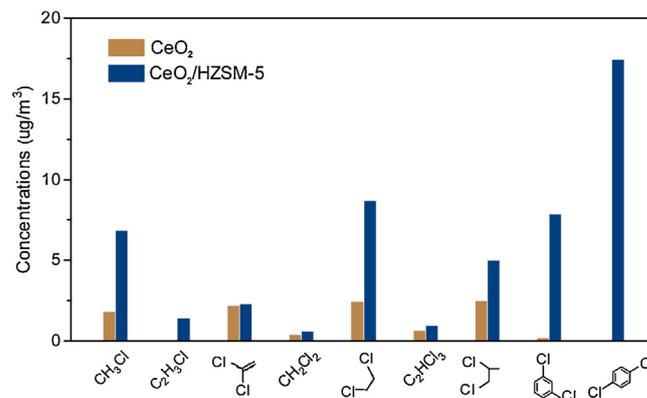


Fig. 4. Quantitative analyses of polychlorinated byproducts collected in the 350 °C off-gases of CeO₂ and CeO₂/HZSM-5 catalysts.

in Supporting information) that facilitated the electrophilic chlorination reaction. This reaction was assumed to precede through the electrophilic substitution of Cl over the Lewis acid sites of CeCl₄ [39] that attacked the accumulated CB at Brønsted HZSM-5 sites, leading to the formation of dichlorobenzenes in the off-gas.

In summary, we have fabricated CeO₂ and CeO₂/HZSM-5 catalysts that were employed in the CBCO reaction to unveil the importance of reactant mass transfer in environmental catalysis. The co-adsorbed CB and O₂ on the CeO₂ surface resulted in a remarkably high CO₂ generation, while those separately adsorbed on the CeO₂/HZSM-5 yielded a much lower CO₂ generation. This verifies our assumption that rational design of the mass transfer distance of reactant adsorbates can effectively regulate the pollutant conversion efficiency and product selectivity. The co-adsorption of CB and O₂ was shown to cause severe deactivation of the CeO₂ catalyst, as the dissociated Cl occupied the surface oxygen vacancy that hindered the O₂ activation. While in the CeO₂/HZSM-5, the CB was preferentially adsorbed on the Brønsted acidic sites of HZSM-5, which protected the oxygen vacancy from Cl poisoning, leading to a high long-term stability in CBCO reaction. However, the excessive adsorption of CB on the Brønsted sites distinctly promoted electrophilic chlorination reaction, which generated significant dichlorobenzenes in the off-gas, causing a severe secondary pollution to the environment. The work conducted herein unveils that the design of environmental catalysts needs to consider both of catalyst intrinsic property and reactant mass transfer, as they can both affect the pollutant conversion, product selectivity, reaction stability and secondary pollution. To date, modification of the reactant mass transfer has been paid much less attention in environmental catalysis. Such an investigation could pave a new way for the development of highly efficient catalysts for environmental pollution control.

Declaration of competing interest

The authors report no declarations of interest.

Acknowledgments

This work was financially supported by the National Key R&D Program of China (No. 2016YFC0202200), the National Natural Science Foundation of China (Nos. 21777140, 21922607) and the Outstanding Youth Project of Zhejiang Natural Science Foundation (No. LR19E080004).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccllet.2020.09.001>.

References

- [1] C. He, J. Cheng, X. Zhang, et al., *Chem. Rev.* 119 (2019) 4471–4568.
- [2] M. Shelef, *Chem. Rev.* 95 (1995) 209–225.
- [3] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B: Environ.* 18 (1998) 1–36.
- [4] L.P. Han, S.X. Cai, M. Gao, et al., *Chem. Rev.* 119 (2019) 10916–10976.
- [5] J. Wang, A. Yoshida, P.F. Wang, et al., *Appl. Catal. B: Environ.* 271 (2020) 118941.
- [6] B. Abdullah, N.A.A. Ghani, D.V.N. Vo, *J. Clean. Prod.* 162 (2017) 170–185.
- [7] Y.S. Kang, Y. Lu, K. Chen, et al., *Coord. Chem. Rev.* 378 (2019) 262–280.
- [8] H.X. Zhou, S.P. Wang, B.W. Wang, X.B. Ma, S.Y. Huang, *Chin. Chem. Lett.* 30 (2019) 775–778.
- [9] X.W. Wang, W.Y. Jiang, R.Q. Yin, et al., *J. Colloid Interface Sci.* 574 (2020) 251–259.
- [10] Y. Du, Y.B. Shen, Y.L. Zhan, et al., *Chin. Chem. Lett.* 28 (2017) 1746–1750.
- [11] W. Yu, D. Wei, W. Yifu, G. Limin, I. Tatsumi, *Mol. Catal.* 459 (2018) 61–70.
- [12] B.B. Huang, C. Lei, C.H. Wei, G.M. Zeng, *Environ. Int.* 71 (2014) 118–138.
- [13] P. Yang, S.S. Yang, Z.N. Shi, et al., *Appl. Catal. B: Environ.* 162 (2015) 227–235.
- [14] J. Liu, X. Dai, Z. Wu, X. Weng, *Chin. Chem. Lett.* 31 (2020) 1410–1414.
- [15] X.X. Dai, X.W. Wang, Y.P. Long, et al., *Environ. Sci. Technol.* 53 (2019) 12697–12705.
- [16] W.L. Wang, Q.J. Meng, Y.H. Xue, et al., *J. Catal.* 366 (2018) 213–222.
- [17] X.L. Liu, L. Chen, T.Y. Zhu, R.L. Ning, *J. Hazard. Mater.* 363 (2019) 90–98.
- [18] R.W. van den Brink, R. Louw, P. Mulder, *Appl. Catal. B: Environ.* 16 (1998) 219–226.
- [19] W.Y. Jiang, Y.L. Yu, F. Bi, et al., *Environ. Sci. Technol.* 53 (2019) 12657–12667.
- [20] H.A. Miran, M. Altarawneh, Z.T. Jiang, et al., *Catal. Sci. Technol.* 7 (2017) 3902–3919.
- [21] P.F. Sun, W.L. Wang, X.L. Weng, X.X. Dai, Z.B. Wu, *Environ. Sci. Technol.* 52 (2018) 6438–6447.
- [22] H. Huang, Q.G. Dai, X.Y. Wang, *Appl. Catal. B: Environ.* 158 (2014) 96–105.
- [23] S.Y. Zhao, S.P. Wang, Y.J. Zhao, X.B. Ma, *Chin. Chem. Lett.* 28 (2017) 65–69.
- [24] X.L. Weng, Q.J. Meng, J.J. Liu, et al., *Environ. Sci. Technol.* 53 (2019) 884–893.
- [25] C.A. Emeis, *J. Catal.* 141 (1993) 347–354.
- [26] M.A. Makarova, K. Karim, J. Dwyer, *Microporous Mesoporous Mater.* 4 (1995) 243–246.
- [27] Q. Dai, Z. Zhang, J. Yan, et al., *Environ. Sci. Technol.* 52 (2018) 13430–13437.
- [28] J. Lichtenberger, M.D. Amiridis, *J. Catal.* 223 (2004) 296–308.
- [29] M. Nagao, Y. Suda, *Langmuir* 5 (1989) 42–47.
- [30] M.A. Larrubia, G. Busca, *Appl. Catal. B: Environ.* 39 (2002) 343–352.
- [31] G. Ramis, G. Busca, V. Lorenzelli, *J. Electron Spectros. Relat. Phenom.* 64–65 (1993) 297–305.
- [32] M.A. Larrubia, A. Gutierrez-Alejandre, J. Ramirez, G. Busca, *Appl. Catal. A: Gen.* 224 (2002) 167–178.
- [33] H. Huang, Y.F. Gu, J. Zhao, X.Y. Wang, *J. Catal.* 326 (2015) 54–68.
- [34] Y.F. Gu, T. Cai, X.H. Gao, et al., *Appl. Catal. B: Environ.* 248 (2019) 264–276.
- [35] X.L. Weng, P.F. Sun, Y. Long, Q.J. Meng, Z.B. Wu, *Environ. Sci. Technol.* 51 (2017) 8057–8066.
- [36] S. Nganai, S.M. Lomnicki, B. Dellinger, *Environ. Sci. Technol.* 45 (2011) 1034–1040.
- [37] S. Nganai, B. Dellinger, S. Lomnicki, *Environ. Sci. Technol.* 48 (2014) 13864–13870.
- [38] M. Altarawneh, B.Z. Dlugogorski, E.M. Kennedy, J.C. Mackie, *Prog. Energy Combust. Sci.* 35 (2009) 245–274.
- [39] P.F. Sun, W.L. Wang, X.X. Dai, X.L. Weng, Z.B. Wu, *Appl. Catal. B: Environ.* 198 (2016) 389–397.