

Removal of salicylic acid on perovskite-type oxide LaFeO_3 catalyst in catalytic wet air oxidation process

Min Yang, Aihua Xu, Hongzhang Du, Chenglin Sun*, Can Li*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

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Abstract

It has been found that salicylic acid can be removed effectively at the lower temperature of 140°C on perovskite-type oxide LaFeO_3 catalyst in the catalytic wet air oxidation (CWAO) process. Under the same condition, the activities for the CWAO of phenol, benzoic acid and sulfonic salicylic acid have been also investigated. The results indicated that, with compared to the very poor activities for phenol and benzoic acid, the activities for salicylic acid and sulfonic salicylic acid were very high, which are attributed to their same intramolecular H-bonding structures. With the role of hard acidity of intramolecular H-bonding, salicylic acid and sulfonic salicylic acid can be adsorbed effectively on the basic center of LaFeO_3 catalyst and are easy to take place the total oxidation reaction. However, at temperatures higher than 140°C , the intramolecular H-bonding structure of salicylic acid was destroyed and the activities at 160 and 180°C decreased greatly, which confirms further the key role of intramolecular H-bonding in the CWAO. Moreover, the LaFeO_3 catalyst also indicated a superior stability of activity and structure in CWAO of salicylic acid.

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Keywords: Catalytic wet air oxidation (CWAO); Perovskite-type oxide LaFeO_3 catalyst; Salicylic acid; Intramolecular H-bonding

1. Introduction

The aqueous effluents from chemical and related industries contain organic pollutants, which are toxic and cause considerable damage and threat to the ecosystem in water bodies and human health [1,2]. Wet air oxidation (WAO) is a liquid phase oxidation process, in which toxic or poorly biodegradable organic compounds are oxidized into carbon dioxide and water under the stringent conditions of temperature (180 – 315°C) and pressure (2 – 15 MPa) [3,4]. Because the process requires relatively severe reaction conditions [5], a particular attention has been devoted to more effective and economically competitive catalytic wet air oxidation (CWAO) processes. In this respect, many investigators have studied heterogeneous catalysts because, unlike homogeneous ones, these catalysts can be easily separated from the treated wastewater [6,7].

The high efficiency and very stability of several kinds of supported noble metal catalysts for the CWAO of various pollutants have been demonstrated [8–11]. However, the noble metals are

expensive, affecting greatly the economics of the corresponding processes. As an alternative, transition metal oxide catalyst and supported transition metal oxide catalyst are widely researched in the CWAO processes [12–14]. As copper is a very effective homogeneous catalyst [15], the main active component of transition oxide catalyst and supported transition oxide catalyst is also Cu [13,16]. Moreover, Mn and Co are often employed to prepare the CWAO catalysts [12,14]. However, the CWAO processes based on these catalysts until now, for large run-times, induce a partial solubilisation of and solubilisation of transition metal ions due to the strong oxidation conditions of the processes so that an additional process is necessary to recover toxic transition metal ions.

To some extent, the leaching of transition metal catalyst during the CWAO process is unavoidable, so the toxicity of transition metal is the main factor that restricts its wide application. To overcome this drawback, we suggest here to use Fe to prepare the CWAO catalyst because Fe is the unique transition metal without any biologic toxicity in the transition metals. However, with its poor redox activity, Fe is rarely applied in CWAO. On the other hand, it is well known that ABO_3 perovskite-type oxides, including LaFeO_3 , are characterized by great stability at high temperature, high mobility of oxygen and

* Corresponding authors. Fax: +86 411 84694447.

E-mail addresses: cslun@dicp.ac.cn (C. Sun), canli@dicp.ac.cn (C. Li).

stabilization of unusual cation oxidation states in the structure [17,18], which lead to oxygen non-stoichiometry that makes them suitable for exhaust gas, such as NO_x [19] and volatile organic compounds [20,21] depollution processes. Therefore, to improve the oxidation activity of Fe catalyst, the perovskite-type oxide LaFeO_3 is considered. However, besides in photodecomposition of water [22,23], the perovskite-type oxide catalysts are rarely applied to liquid-phase oxidation reaction system.

Thus, the aim of this work is to investigate the activity and stability of perovskite-type oxide LaFeO_3 catalyst for CWAO of salicylic acid, which is a important raw material for the wide variety of organic compounds, dyes, pharmaceuticals, plasticizers, antioxidants, etc. In order to understand clearly the degradation of salicylic acid, the other three similar organic compounds with a benzene ring substituted by both (either) hydroxyl and (or) carboxylic groups, including phenol, benzoic acid and sulfonic salicylic acid, were also employed as model pollutant to study further the catalytic activity of LaFeO_3 . A mechanism is proposed and discussed in the light of the role of the intramolecular H-bonding of salicylic acid in its degradation on the LaFeO_3 catalyst in CWAO.

2. Experimental

2.1. Materials

Chemical grade phenol, benzoic acid, salicylic acid and sulfonic salicylic acid were dissolved in deionized water to prepare model wastewaters, respectively. Their concentrations are 2200, 2000, 2000 and 5000 ppm respectively, and corresponding chemical oxygen demand (COD_{cr}) are 5033, 3888, 3192 and 4030 mg/l, respectively. With the lower value of maximum solubility of salicylic acid at ambient temperature, the COD_{cr} value of salicylic acid is less than the other model pollutants.

La_2O_3 and Fe_2O_3 catalysts were prepared with $\text{La}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively. The two salts were dried in air at 120°C for 6 h, and then the resulting materials were heated in air from room temperature to 700°C at a rate of $3^\circ\text{C}/\text{min}$ and calcined at this temperature for 6 h, respectively.

LaFeO_3 was prepared with sol–gel preparation method [24,25]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) were used as raw materials. The gel precursor was prepared as follows. 0.06 mol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.06 mol $\text{La}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ and 0.2 mol $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were dissolved in 400 ml of deionized water. The solution was stirred for 1 h at 80°C , and then was heated to evaporate the water at the same temperature. The gel precursor was dried in air at 120°C for 6 h, and then the resulting material was heated in air from room temperature to 700°C at a rate of $3^\circ\text{C}/\text{min}$ and calcined at this temperature for 6 h.

2.2. Catalyst characterization

XRD measurements: crystalline phases of LaFeO_3 samples before and after catalytic wet oxidation reaction were detected

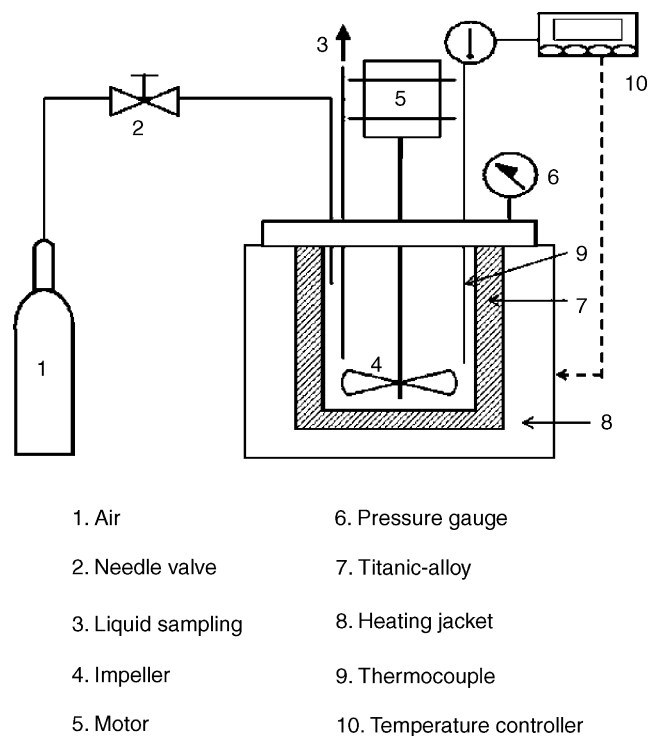


Fig. 1. Schematic diagram of experimental apparatus.

by X-ray diffraction using the packed powder method, on a Rigaku Rotaflex Ru200B diffractometer with a $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray diffraction pattern of the LaFeO_3 catalyst showed characteristic reflections for the perovskite-type oxide without other phases.

2.3. Experimental setup

Experiments were conducted using a commercial titanicalloy autoclave (Tongda Company, China) with an inner volume of 250 ml schematically represented in Fig. 1, which can efficiently prevent from corrosion by hot acid solution. The reactor was equipped with a stirrer, a thermocouple, a sampling tube and a safe valve. The reaction temperature was kept at the prescribed constant temperature by controlling the electric power supply to an electric heater surrounding the outer wall of the reactor [26].

2.4. Experimental procedure

The catalytic activity was determined in a typical run: 100 ml of treated wastewater and 0.8 g of catalyst was loaded into the autoclave. The system was pressured to 2.5 MPa by air, which was sufficient for complete oxidation of all C and H molecules in organic compound to be converted to CO_2 and H_2O , then heated to required temperature, and maintained at this temperature for 2 h keeping a stirrer rotating at a speed of 300 rpm. Representative samples were withdrawn from the reactor and analyzed.

2.5. Product analysis

Reaction intermediates produced during the CWAO of salicylic acid were qualitatively analyzed by UV–vis spectra. UV–vis spectra were recorded following the diffuse reflectance technique (UV–vis/DR) on a Varian Cary-50 spectrometer, using 15 nm slits and deionized water as reference.

A high performance liquid chromatography (HPLC) using a UV–vis spectrometric detector (DEAIC, Echrom98) served for quantification purpose, comparing the reaction products to extend standards. Phenol was analyzed on a ODS-BP column, the mobile phase was methanol 40 vol.%, a UV–vis was used at 270 nm wavelength; benzoic acid, salicylic acid and sulfonic salicylic acid were analyzed on a ODS-BP column, the mobile phases were ammonium diacid phosphate 0.02 M, a UV–vis was used at 240, 300 and 300 nm wavelength, respectively.

The amount of the chemical oxygen demand (COD) was analyzed by the closed microwave dichromate method using a quick COD_{cr} microwave sealed digestion measuring system type WMX [27]. COD proved to be useful in assessing the degree of total oxidation to CO₂ and some little molecular organic acids.

The conversion of salicylic acid, S , is defined in:

$$S = (C_0 - C_t) / C_0 \quad (1)$$

where C_0 is the initial concentration of salicylic acid, C_t the concentration of salicylic acid at any reaction time, t .

The degree of removal of COD_{cr}, C , is evaluated by the following relation:

$$C = ([\text{COD}_{\text{cr}}]_0 - [\text{COD}_{\text{cr}}]_t) / [\text{COD}_{\text{cr}}]_0 \quad (2)$$

where $[\text{COD}_{\text{cr}}]_0$ is the initial concentration of COD_{cr} and $[\text{COD}_{\text{cr}}]_t$ is the contraction of COD_{cr} at any reaction time, t .

The quantity of Fe and La leached out from catalyst were determined in the solution at the end of the reaction time (90 min) with ICP-AES spectrometer (Leeman USA, type Plasma-Spec-II). Fe and La were measured at 238.204 and 379.478 nm, respectively. The pressure and flow rate of assistant gas were 5.0 psi and 0.5 l/min, respectively; the pressure and flow rate of cooling gas were 5.0 psi and 12.0 l/min, respectively; the pressure and flow rate of nebulizer gas were 40.0 psi and 0.5 l/min, respectively.

3. Results and discussion

3.1. CWAO of salicylic acid on the different catalysts in the CWAO processes

We prepared three catalysts: La₂O₃, Fe₂O₃ and LaFeO₃, which were evaluated for the CWAO of model pollutant compound of salicylic acid with the temperature increasing from 100 to 180 °C. To compare with the results of catalyzed runs, a blank test without catalyst has been also performed. The activities for COD_{cr} removal of the model wastewater of salicylic acid at the different temperatures in these runs are shown in Fig. 2.

The observed trends of COD_{cr} removal exhibited in the runs catalyzed by La₂O₃ and Fe₂O₃ are similar to that in the uncat-

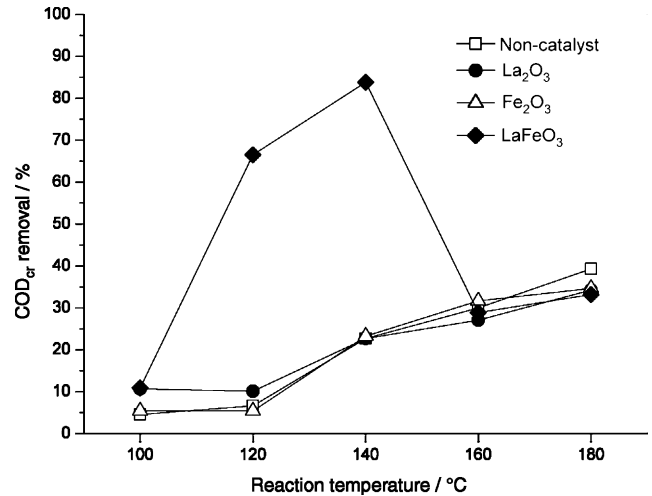


Fig. 2. The evolution of COD_{cr} removal with reaction temperature in the CWAO of salicylic acid on La₂O₃, Fe₂O₃ and LaFeO₃. Reaction conditions: 0.5 MPa O₂ initial, 300 rpm, and 2000 ppm salicylic acid_(aq) initial.

alyzed run. The COD_{cr} removals increased slowly with the reaction temperature increasing and, even at the highest temperature, the COD_{cr} removals of the above three runs are 34%, 35% and 39%, respectively. It suggests that the catalytic activities of La₂O₃ and Fe₂O₃ catalysts are very poor. On the other hand, it is interesting to find that, in the interval of 100–140 °C, the COD_{cr} removals of the catalyzed run by LaFeO₃ catalyst increased greatly with reaction temperature increasing and reaches a maximum of 84% at 140 °C, indicating a very high catalytic activity compared to La₂O₃ and Fe₂O₃. However, with temperature up to 160 and 180 °C, it is unexpected that the COD_{cr} removal values decreased drastically to 29% and 33%, which are both close to the COD_{cr} removal values of uncatalyzed run at the same temperatures.

3.2. The evolution of reaction intermediates and leaching of LaFeO₃ with the temperatures increasing from 140 to 180 °C

In order to clarify the above unexpected results, the model wastewater treated at 140, 160 and 180 °C were investigated by UV–vis spectroscopy, which are shown in Fig. 3.

It is seen from Fig. 3A that there is a small absorption band at 300 nm assigned to salicylic acid in the UV–vis spectra of the model wastewater treated at 140 °C, which not only indicates that most of salicylic acids undergoes a ring-open reaction and is oxidized to CO₂ (mainly) and small molecule carboxylic acids [20], but also is well agreement with the high COD_{cr} removal value of 84%. As shown in Fig. 3B, compared to the UV–vis spectra of the treated wastewater at 140 °C, the UV–vis spectra of the treated wastewater at 160 °C indicated two new characteristic peaks at 270 and 280 nm assigned to some kinds of organic intermediates with benzene ring, such as phenol and its derivatives [28]. When the reaction temperature reached to 180 °C, the two characteristic peaks became more intensive as indicated in Fig. 3C. This means that the yield of intermediate products increases greatly with temperature increasing. It suggests that

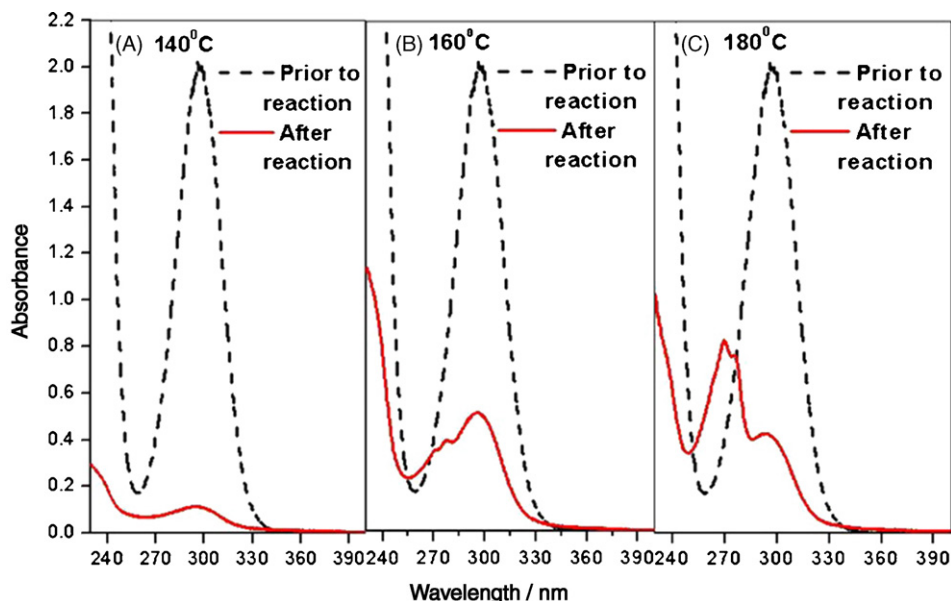


Fig. 3. UV-vis spectra of model wastewater of salicylic acid treated on the LaFeO_3 catalyst in the CWAO reaction at different temperatures. Reaction conditions: 0.5 MPa O_2 initial, 300 rpm, and 2000 ppm salicylic acid_(aq) initial.

when the reaction temperatures is more than 140°C , salicylic acid becomes unstable and is easy to be converted to some aromatic intermediates with the role of thermal decomposition. The aromatic compounds formed during the CWAO process at the higher temperature are the end intermediates because they are too stable to be oxidized further under the reaction condition. This is also accordable to the very low COD_{Cr} removal values and the low salicylic acid conversion values at 160 and 180°C . With the decomposition of salicylic acid at the temperature more than 140°C , the catalytic activity decreased significantly, implying the special structure of salicylic acid should play a crucial role in the CWAO process.

3.3. Effect of the acidities of different model pollutants on their degradations over LaFeO_3 in the CWAO process

In order to give a preliminary explanation of the role of the special structure of salicylic acid, the other three similar organic compounds, including phenol, benzoic acid and sulfonic salicylic acid, that have a benzene ring substituted by both (either) hydroxyl and (or) carboxylic groups, were employed as model pollutant to investigate the catalytic activity of LaFeO_3 .

Fig. 4 illustrates the reaction results obtained in the CWAO of phenol, benzoic acid, salicylic acid and sulfonic salicylic acid on LaFeO_3 catalyst at 140°C . As seen in Fig. 4, the catalytic activities for CWAO of salicylic acid and sulfonic salicylic acid are little higher than that of phenol and benzoic acid. Under the selected reaction condition, the COD_{Cr} removal values of phenol and benzoic acid are 13% and 2%, which are both much lower than that of salicylic acid (84%) and sulfonic salicylic acid (90%). Meanwhile, the conversion values of phenol and benzoic acid are 19% and 4%, which are also much lower than the values of salicylic acid (87%) and sulfonic salicylic acid (95%).

For all four the model pollutant compounds, although they have similar structure with a hydroxyl and (or) carboxyl on the benzene ring, the difference of them, especially compared salicylic acid and sulfonic salicylic acid with phenol and benzoic acid, is very obvious. For salicylic acid and sulfonic salicylic acid, both a hydroxyl and carboxyl substitute the two adjacent sites of benzene ring. On the contrary, for phenol and benzoic acid, either a hydroxyl or carboxyl substitutes only one site on benzene ring. Co-existence of adjacent hydroxyl and carboxyl on benzene ring can play a key role in catalytic wet oxidation of both salicylic acid and sulfonic salicylic acid. The crucial role may be ascribed to the formation of intramolecular H-bonding between carboxyl group and hydroxyl group, whose acidity is 15.9 times

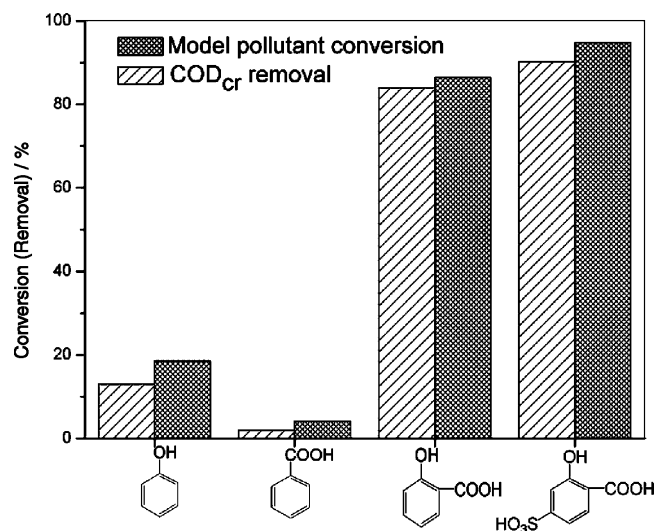
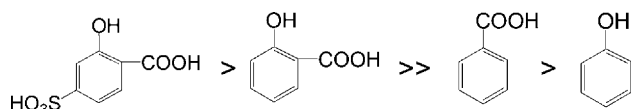


Fig. 4. Catalytic activity of LaFeO_3 in the CWAO of four organic model reactants. Reaction conditions: 140°C , 0.5 MPa O_2 initial, 300 rpm, 2200 ppm phenol_(aq) initial, 2000 ppm benzoic acid_(aq) initial, 2000 ppm salicylic acid_(aq) initial and 5000 ppm sulfonic salicylic acid_(aq) initial.



Scheme 1. The acidities of four model pollutant compounds.

stronger than the carboxyl group of benzoic acid [29]. With further comparison between salicylic acid and sulfonic salicylic acid, the strong electron absorbing para-substituent of sulfonic group on the benzene ring makes its acidity harder than salicylic acid. Taking this into account, the acidities of four model compounds are different and decreases in the order indicated in Scheme 1.

Expecting that the activity for CWAO of phenol is little higher than benzoic acid, the activities for CWAO of the four model compounds, as showed in Fig. 3, also decrease in the same order as described in Scheme 1.

3.4. Preliminary mechanism of degradation of salicylic acid on LaFeO_3 catalyst in the CWAO process

On the whole, the activities for the CWAO of four model pollutants on the LaFeO_3 catalyst increase simultaneously with the increase of their acidities. Especially, in comparison with phenol and benzoic acid, the activities of salicylic acid and sulfonic salicylic acid are enhanced greatly with the hard acidities of their intramolecular H-bondings. This implies that the acid strength of the model compound may play a key role in its degradation. Although further investigation is needed to clarify the effect of the acidity of the model compound on its removal, a possible mechanism of the CWAO of salicylic acid on LaFeO_3 catalyst at the lower reaction temperature of 140°C is described in Fig. 5.

It is concluded that the high activity for the total oxidation of salicylic acid over LaFeO_3 catalyst in CWAO may be attributed to its intramolecular H-bondings on benzene ring, whose strong acidity is favorable for it to form further an intermolecular H-bonding with a basic center of oxygen atom on the surface of LaFeO_3 catalyst. Lagier et al. [30] have characterized intermolecular hydrogen bond complexes of phenol with bases in liquid and solid state. The ^1H chemical shift of the hydroxyl proton and the ^{13}C chemical shift of the phenol carbons were found to be sensitive to the strength of the intermolecular H-bonding. The strength of intermolecular H-bonding was varied using

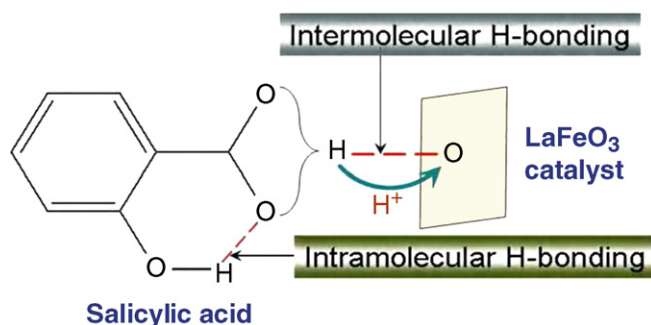


Fig. 5. Schematic diagram of catalytic wet oxidation of aqueous salicylic acid on LaFeO_3 .

either organic reactants of different acid strength or bases with different proton acceptor capability. As showed in Scheme 1, the acid strength of salicylic acid and sulfonic salicylic acid is greatly harder than phenol and benzoic acid, so the strength of intermolecular H-bondings of the former to basic oxygen atoms of the catalyst is greatly stronger than the latter. The strong strength of intermolecular H-bonding means the strong interaction with the catalyst, which suggests the strong adsorption of salicylic acid and sulfonic salicylic acid on the surface of catalyst. The too strong adsorption of salicylic acid and sulfonic salicylic acid will result in their too long contact time on the surface of catalyst with the corresponding increase of their total oxidation degree, which is well in accordance with their highly effective removals. With the decomposition of salicylic acid into some aromatic intermediates at the temperature more than 140°C , the intramolecular H-bonding structure is destroyed, which causes directly great decrease of COD_{cr} removal and the very low catalytic activities of LaFeO_3 at 160 and 180°C . This confirms further the beneficial role of the intramolecular H-bonding of salicylic acid in its total oxidation process.

To clarify clearly the above mechanism, it is necessary to distinguish which played a main key role in the CWAO of sulfonic salicylic acid between its sulfonic group and intramolecular H-bonding. Although the acidity of sulfonic group is much stronger than that of the intramolecular H-bonding on benzene ring, the H^+ of sulfonic group is easy to form the intermolecular H-bonding with H_2O . The hydrated H^+ of sulfonic group is difficult to act further with the basic center of LaFeO_3 catalyst. On the other hand, with the role of its weaker acidity, the intramolecular H-bonding on benzene ring is difficult to act with H_2O and easy to take action with the basic center of LaFeO_3 catalyst to form the intermolecular H-bonding. This conclusion is supported by the similar degradation behavior of sulfonic salicylic acid to that of salicylic acid on LaFeO_3 catalyst under the same reaction conditions, which is shown in Fig. 6. It is seen that for the two model pollutants, their COD_{cr} removals increase greatly with reaction

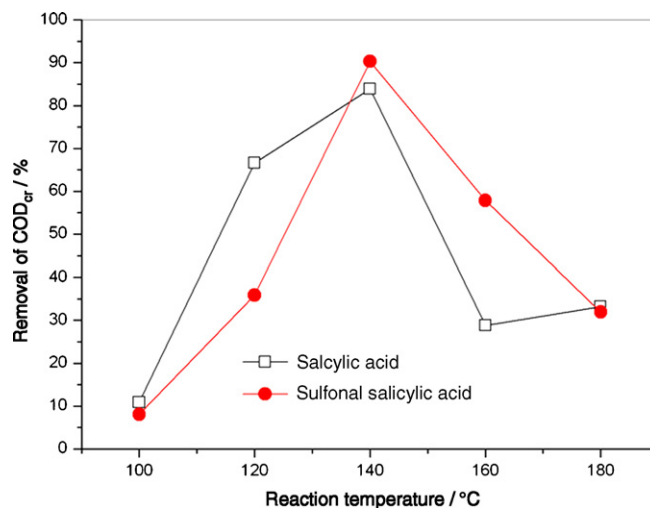


Fig. 6. Variation of the catalytic performances in the CWAO of salicylic acid and sulfonic salicylic acid as function of reaction temperature, respectively. Reaction conditions: 0.5 MPa O_2 initial, 300 rpm, and 2000 ppm salicylic acid $_{(\text{aq})}$ initial and 5000 ppm sulfonic salicylic acid $_{(\text{aq})}$ initial.

Table 1
The extent of leaching of different catalysts in the CWAO of salicylic acid

Catalyst	Leaching (ppm)	
	La	Fe
La ₂ O ₃	532	–
Fe ₂ O ₃	–	1.48
LaFeO ₃	49.5	15.6

Reaction conditions: 140 °C, 0.5 MPa O₂ initial, 300 rpm, and 2000 ppm salicylic acid_(aq) initial.

temperature increasing and reach their maximums at 140 °C in the interval of 100–140 °C, respectively. However, with temperature up to 160 and 180 °C, their COD_{cr} removal values decrease drastically because of the decomposition of their intramolecular H-bondings. The similar degradation behaviors of salicylic acid and sulfonic salicylic acid in the CWAO can only be interpreted by the fact that two model pollutants are degraded by the same reaction mechanism.

3.5. The stability of LaFeO₃

To test the stability of LaFeO₃ catalyst, the concentration of dissolved La and Fe metals were measured. For comparison, the leaching of La₂O₃ and Fe₂O₃ were also measured. Table 1 shows the extent of metal leaching on the La₂O₃, Fe₂O₃ and LaFeO₃ catalysts in the CWAO process. It can be seen that lanthanum of La₂O₃ catalyst leaches greatly and its leaching is 532 ppm. On the other hand, the rather low concentration of dissolved iron of Fe₂O₃ has been detected and its leaching is only 1.5 ppm under the same reaction conditions. The harder basic of La₂O₃ than that of Fe₂O₃ should be responsible for much more leaching of La₂O₃. As shown in Table 1, the Fe and La leaching of LaFeO₃ catalyst are 49.5 and 15.6 ppm, respectively. The La leaching of LaFeO₃ is much lower than that of La₂O₃, which may be attributed to the stable perovskite-type crystal structure of LaFeO₃. Taking no biologic toxicity of Fe into account, the Fe leaching value of 15.6 ppm is acceptable to a certain extent.

To investigate further the stability of LaFeO₃ catalyst, the activity of LaFeO₃ catalyst was evaluated with reaction cycle, which is shown in Fig. 7. As presented in Fig. 7, the COD_{cr} removal gradually decreases from the first cycle to the fourth cycle, which can be ascribed to the formation of polymer during reaction. However, the COD_{cr} removal rises to 81% after the 10th reaction cycle, in a level similar to the fresh catalyst. Moreover, it is needed to note that the high COD_{cr} removal does not decline even after the 12th reaction cycle. It can be explained that the polymers formed during reaction are oxidized and do not appear again on the surface of catalyst with reaction cycle.

The crystalline phases of the catalysts before and after the reaction were also determined by XRD (Fig. 8). The X-ray diffraction pattern of the fresh LaFeO₃ catalyst showed characteristic reflections for the perovskite-type oxide without other phases. Although the signals in sample after reaction were weaker than before reaction, both samples exhibited obvious spectra of the perovskite phase. The activity and perovskite-

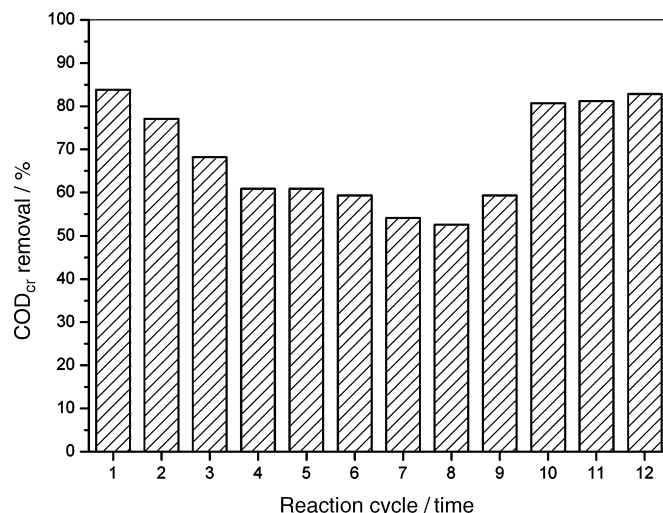


Fig. 7. COD_{cr} removal vs. reaction cycle over LaFeO₃ catalyst.

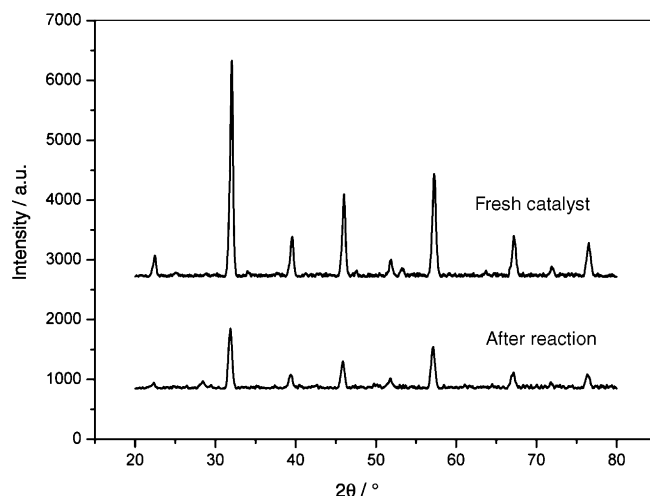


Fig. 8. XRD spectra of the two LaFeO₃ samples before and after the CWAO of salicylic acid.

type structure of LaFeO₃ catalyst did not almost change after the 12th reaction cycle, suggesting that the LaFeO₃ catalyst in the CWAO process is stable.

4. Conclusion

The perovskite-type LaFeO₃ catalyst prepared by sol–gel method exhibited high activity in the CWAO of salicylic acid model wastewater. At the lower reaction temperature of 140 °C, the conversion of salicylic acid and COD_{cr} removal of the model wastewater attained values of 87% and 84%, respectively. The intramolecular H-bonding structure of salicylic acid was likely responsible for its high degradation. The perovskite-type LaFeO₃ catalyst also possesses superior stability of activity and structure in the CWAO of salicylic acid. This indicates that the perovskite-type oxide LaFeO₃ is a novel and potential kind of CWAO catalyst.

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