

## Catalytic wet air oxidation of phenol over CeO<sub>2</sub>-TiO<sub>2</sub> catalyst in the batch reactor and the packed-bed reactor

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### Abstract

CeO<sub>2</sub>-TiO<sub>2</sub> catalysts are prepared by coprecipitation method, and the activity and stability in the catalytic wet air oxidation (CWAO) of phenol are investigated in a batch reactor and packed-bed reactor. CeO<sub>2</sub>-TiO<sub>2</sub> mixed oxides show the higher activity than pure CeO<sub>2</sub> and TiO<sub>2</sub>, and CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst displays the highest activity in the CWAO of phenol. In a batch reactor, COD and TOC removals are about 100% and 77% after 120 min in the CWAO of phenol over CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst at reaction temperature of 150 °C, the total pressure of 3 MPa, phenol concentration of 1000 mg/L, and catalyst dosage of 4 g/L. In a packed-bed reactor using CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst, over 91% COD and 80% TOC removals are obtained at the reaction temperature of 140 °C, the air total pressure of 3.5 MPa, the phenol concentration of 1000 mg/L for 100 h continue reaction. Leaching of metal ions of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst is very low during the continuous reaction. CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst exhibits the excellent activity and stability in the CWAO of phenol.

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**Keywords:** Catalytic wet air oxidation (CWAO); CeO<sub>2</sub>; TiO<sub>2</sub>; Phenol; Wastewater treatment

### 1. Introduction

Phenol and its derivatives are widely used as raw materials in many chemical, petrochemical, pharmaceutical, textile and agricultural industries. They generate large quantities of the wastewater including highly concentrated phenol and its derivatives. If discharged into the environment, the wastewater damages the water bodies and human health, and has disagreeable taste and odor under the low concentration. According to the 80/778/EEC Directive, the admissible concentration of phenol in drinking water should not exceed 0.5 µg/L [1]. Consequently, the development of effective technologies for treating the industrial wastewater is crucial. The biological technologies are the most common methods to treat the wastewater, while they are suitable for the wastewater with the low phenol concentration due to the toxicity of organic compounds present in the effluent to the microorganisms. Other technologies, such as incineration,

electrochemical oxidation, the Fenton process, photocatalysis and ozonation, have been used to treat the wastewater including phenol [2,3]. However, the concentration and loading of the wastewater, energy consumption and the operating cost prevent them from the application for treating the wastewater.

Wet air oxidation (WAO) is an effective technology for the treatment of hazardous, toxic and highly concentrated organic compounds. In the WAO process, organic compounds are oxidized into CO<sub>2</sub>, H<sub>2</sub>O and other innocuous end products under high temperature (125–320 °C) and pressure (0.5–20 MPa) using oxygen as the oxidant [4,5]. WAO has shown good potential to treat the industrial wastewater, while its application is limited due to the severe operation conditions and the high operating costs. Using catalysts in the WAO could effectively decrease the operating conditions, shorten reaction time and enhance the oxidation efficiency of organic compounds [6,7]. In the last decades, various catalysts have been developed. Homogenous catalysts were proved to have good catalytic activity, but it was necessary to remove and recover metal ions in the effluents. To overcome the drawback, heterogeneous catalysts were developed and seemed to be more promising for wastewater

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treatment [8–12]. Transition metal oxides catalysts showed good activity, while leaching metal ions from the solid catalysts could lead to the deactivation of the catalysts [13–16]. Noble metal catalysts with the high cost were studied, and showed excellent activity and stability [17–20].

CeO<sub>2</sub>, the most reactive rare earth oxides, is studied and employed in various applications, including catalysts, supports, oxygen storage capacitors, ion conductors, UV blockers and polishing materials [21,22]. Among the applications, it shows the most important use in the catalysis fields. CeO<sub>2</sub> is used as both the support and catalyst in the CWAO of organic compounds [23–27]. However, the thermostability of pure CeO<sub>2</sub> under high-temperature conditions is poor. This could severely affect its activity and physical structure in the oxidation reaction. One approach to solving the problem is the synthesis of CeO<sub>2</sub> complex metal oxides, such as CeO<sub>2</sub>-CuO, CeO<sub>2</sub>-ZrO<sub>2</sub>-CuO, and CeO<sub>2</sub>-ZrO<sub>2</sub>-MnO<sub>x</sub> [28–31]. The oxides showed the higher activities and better physical structure than that of pure CeO<sub>2</sub> in the CWAO of organic compounds, while leaching metal ions from the mixed oxides was observed.

TiO<sub>2</sub> is a promising material both as an active material and a support for some catalytic reaction [3,32]. In the CWAO, TiO<sub>2</sub> with the good stability do not display the activity, and was often used as the support of metals [33–35]. On the other hand, the fact that Ti<sup>4+</sup> has the lower ionic radius than Ce<sup>4+</sup> indicates that Ce<sup>4+</sup> in the CeO<sub>2</sub> lattice could be replaced by Ti<sup>4+</sup>, so that a fluorite structure solid solution could be formed, and improve the properties of pure CeO<sub>2</sub>. In the paper, a novel catalyst, CeO<sub>2</sub>-TiO<sub>2</sub>, was prepared with the coprecipitation method. The activity and stability of the catalyst were investigated in a batch reactor and continuous packed-bed reactor. In a batch reactor, the effect of the Ce/Ti mol ratio, the reaction temperature and phenol concentration on the catalytic activity was tested in the CWAO of phenol. In a packed-bed reactor, a continuous reaction for 100 h was performed to evaluate the stability of CeO<sub>2</sub>-TiO<sub>2</sub> catalyst.

## 2. Materials and methods

### 2.1. Catalyst preparation and characterization

CeO<sub>2</sub>-TiO<sub>2</sub> oxides were prepared with the coprecipitation method. The molecular ratio of Ce and Ti was 3/1, 1/1 and 1/3, respectively. The hydrolysis of TiCl<sub>4</sub> was performed at 0 °C to get Ti aqueous solution. The mixture solution of the aqueous Ti and Ce(NO<sub>3</sub>)<sub>3</sub> was added dropwise to excess ammonia solution at room temperature under stirring, and then aged in the 40–80 °C for 6 h. The precipitate was washed with distilled water to remove Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, and then dried at 100 °C overnight to obtain the precursor of the mixed oxides. The precursor was calcinated in the air at 450 °C for 5 h to obtain CeO<sub>2</sub>-TiO<sub>2</sub> powder catalyst. CeO<sub>2</sub>-TiO<sub>2</sub> catalyst used in a continuous packed-bed reactor was prepared as followed: the powder precursor mixed with pseudoboehmite solution was pressed to get 20-mesh particle, dried at 100 °C overnight, and then calcinated in the air at 450 °C for 5 h to obtain CeO<sub>2</sub>-TiO<sub>2</sub> particle catalyst. Pure CeO<sub>2</sub> or TiO<sub>2</sub> catalysts were prepared with coprecipitation by adding Ce(NO<sub>3</sub>)<sub>3</sub> or Ti aqueous solution to excess

ammonia solution. The precipitate was dried and calcinated at 450 °C for 5 h in the air to get pure CeO<sub>2</sub> or TiO<sub>2</sub> powder catalyst.

X-ray powder diffractometer (XRD) analysis was carried out in D/max-III A powder diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a scanning range of  $2\theta = 10^\circ - 70^\circ$  under a speed of  $4^\circ/\text{min}$ . The average crystallite size of catalysts was estimated using the Debye–Scherrer equation:

$$D = \frac{0.90\lambda}{\beta \cos \theta}$$

where  $D$  is the crystallite size (nm),  $\lambda$  is the wavelength (nm),  $\beta$  is the corrected full width at half maximum (radian) and  $\theta$  is the Bragg angle (radian).

The surface areas of the samples were estimated at 77 K by N<sub>2</sub> adsorption using a Quantachrome Autosorb Automated Gas Sorption System. Before each measurement, samples were out-gassed at 573 K for 3 h. C elements of the used CeO<sub>2</sub>-TiO<sub>2</sub> catalysts were measured with means of a scanning electron microscope (SEM) with JEOL JSM-6301F equipped with energy-dispersion microanalysis system.

### 2.2. CWAO test

#### 2.2.1. Batch reactor: experimental set-up and procedures

A batch reactor for the CWAO of phenol was shown in our study [29]. The experiments in the CWAO of phenol were carried out in a 1 L autoclave equipped with a magnetically driven stirrer ensuring desirable mass transfer. First, the catalyst and 500 mL phenol aqueous solution were loaded into the reactor, and the mixture was purged with N<sub>2</sub> to remove air in the reactor. After the reactor was heated with heating tape to reach the desirable temperatures, pure oxygen was added into the reactor under stirring. The time was defined as the “zero” time. The reaction was performed for 150 min. The samples in the effluent were taken, and the chemical oxygen demand (COD<sub>Cr</sub>) and total organic carbon (TOC) were analyzed. COD of the effluent was measured following the standard determination technique. Total organic carbon (TOC) of the effluents was measured with a TOC 5000A analyzer.

#### 2.2.2. Packed-bed reactor: experimental set-up and procedures

The stability of CeO<sub>2</sub>-TiO<sub>2</sub> catalyst was tested in a packed-bed reactor. The configuration of the reactor system is shown in Fig. 1. The phenol aqueous solution was mixed with air from a high-pressured air cylinder, and then up-flowed through the packed bed consisting of  $\varnothing 20 \times 200$  mm Ti steel tube. 15 mL CeO<sub>2</sub>-TiO<sub>2</sub> particle catalyst was loaded into the reaction bed. The ceramic beads were packed on the top and bottom sections of the bed in the reactor. The reaction temperature was measured by two thermocouples inserted into the packed bed and the heating tapes wrapped around the reactor. The effluent from the reactor entered into a high-pressured separator. The bottom of the separator was a liquid tank. The samples were taken from the liquid tank by a micrometric valve. The pressure of the tank was adjusted to maintain the constant pressure in the reaction

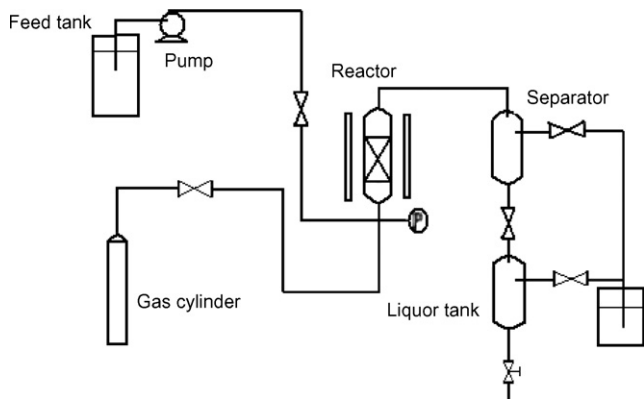


Fig. 1. Experimental setup of the packed-bed reactor in the CWAO of phenol.

process by the valve that was contacted with air cylinder. The flow rate of gas and liquor was measured and controlled by a flow meter. The gas flow rate was 60 mL/min, and the liquor flow rate was 0.5 mL/min at  $0.5 \text{ h}^{-1}$  of WHSV (weight hourly space velocity). After the continuous experiment start in 4 h, the operating system (reaction temperature, pressure, the liquid and gas flow) trends to the stability. Then, the first sample was taken from the liquid tank. Samples in the effluents were periodically taken, and analyzed to determine COD and TOC of the effluent. The metal ions leaching for the solid catalyst were measured with ICP of IRIS intrepid.

### 3. Results and discussion

#### 3.1. The structure characteristics of the catalysts

Table 1 lists the BET surface areas of the catalysts. For pure  $\text{CeO}_2$ , the surface area is  $92.8 \text{ m}^2/\text{g}$ . For doped- $\text{CeO}_2$  catalysts, the surface areas of  $\text{CeO}_2\text{-TiO}_2$  catalysts are higher than that of pure  $\text{CeO}_2$  or  $\text{TiO}_2$  catalyst. Moreover, the BET surface areas of  $\text{CeO}_2\text{-TiO}_2$  catalysts increase from 92.8 to  $198.6 \text{ m}^2/\text{g}$  with the increase of Ti content.

Fig. 2 shows XRD patterns of the different catalysts. For pure  $\text{TiO}_2$  catalyst (in Fig. 2A), the peaks of anatase titania ( $2\theta = 25.28^\circ, 37.80^\circ, 48.05^\circ$ ) and rutile titania ( $2\theta = 27.45^\circ, 41.23^\circ$ ) are detected in the patterns, and the anatase titania is the dominating structure. For pure  $\text{CeO}_2$  (in Fig. 2B), the strong diffraction peaks attributed to cubic  $\text{CeO}_2$  ( $2\theta = 28.57^\circ, 33.10^\circ, 47.53^\circ, 56.38^\circ$ ) are observed in the pattern. In the patterns of  $\text{CeO}_2\text{-TiO}_2$  catalysts (in Fig. 2C–E), no relevant Ti peaks is observed, and the peaks of cubic  $\text{CeO}_2$  phase are observed.

Table 1  
The BET surface area and the particle size of the different catalysts

Samples	The surface area ( $\text{m}^2/\text{g}$ )	The size of the particles (nm)
$\text{TiO}_2$	22.1	19
$\text{CeO}_2$	92.8	11
$\text{CeO}_2\text{-TiO}_2$ 3/1	104.8	7
$\text{CeO}_2\text{-TiO}_2$ 1/1	160.9	5
$\text{CeO}_2\text{-TiO}_2$ 1/3	198.6	–

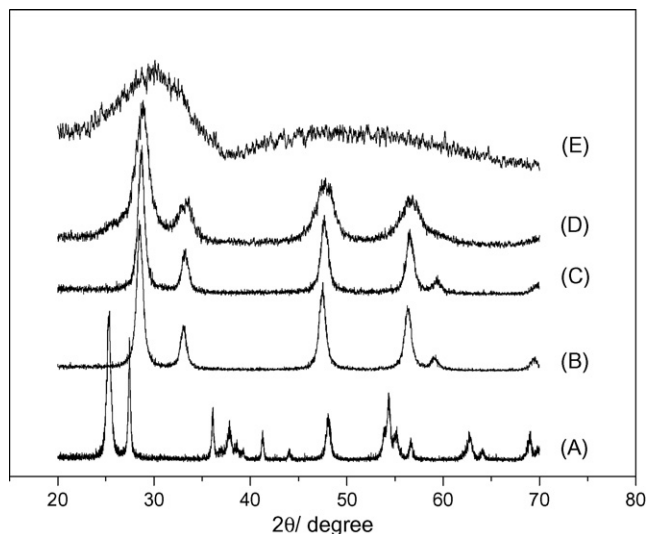


Fig. 2. XRD pattern of the different catalysts. ((A)  $\text{TiO}_2$ ; (B)  $\text{CeO}_2$ ; (C)  $\text{CeO}_2\text{-TiO}_2$  3/1; (D)  $\text{CeO}_2\text{-TiO}_2$  1/1; (E)  $\text{CeO}_2\text{-TiO}_2$  1/3.)

Moreover, the intensity of  $\text{CeO}_2$  peaks becomes very weaker with increasing Ti content. When the mol ratio of Ce/Ti is 1/3 (in Fig. 2E), the peaks become very faint scattering, indicating that  $\text{CeO}_2$  exists as amorphous phase in the  $\text{CeO}_2\text{-TiO}_2$  1/3 catalyst. This could be due to the insertion of Ti ions into the  $\text{CeO}_2$  lattice and replacement of Ce ions. It makes the long-range order structure of  $\text{CeO}_2$  crystal particles destroyed, and restrain  $\text{CeO}_2$  particles to increase. It is found that that the surface areas of  $\text{CeO}_2\text{-TiO}_2$  catalysts increase and the particle size decreases. Through the Scherrer equation, it is found that the crystal size of  $\text{CeO}_2$  decreases from 11 to 5 nm with increasing Ti content (Table 1). The result is in agreement with previous study [36].

#### 3.2. CWAO of phenol in the batch reactor

##### 3.2.1. The effect of the ratio of Ce and Ti

Fig. 3 shows the activity of the different catalysts in the CWAO of phenol under the reaction temperature of  $150^\circ\text{C}$ , the total pressure of 3 MPa, a catalyst dosage of 4 g/L and the initial phenol concentration of 2100 mg/L.  $\text{CeO}_2\text{-TiO}_2$  catalysts exhibit the better activities in the CWAO of phenol. Without catalysts, about 6% COD removal is obtained after 150 min reaction. About 15% COD conversion is obtained in the CWAO of phenol over pure  $\text{CeO}_2$  and  $\text{TiO}_2$ , indicating that pure  $\text{CeO}_2$  and  $\text{TiO}_2$  have very low activity. Using  $\text{CeO}_2\text{-TiO}_2$  catalysts, COD removals are much higher than that of pure  $\text{CeO}_2$  or  $\text{TiO}_2$  catalyst. The activity order is observed:  $\text{CeO}_2\text{-TiO}_2$  1/1 >  $\text{CeO}_2\text{-TiO}_2$  3/1 >  $\text{CeO}_2\text{-TiO}_2$  1/3 >  $\text{CeO}_2$  >  $\text{TiO}_2$  > without catalysts.  $\text{CeO}_2\text{-TiO}_2$  1/1 catalyst has the best catalytic activity, and 100% COD and 77% TOC was removed after 120 min reaction. It is noticed that the active order is not in agreement with that of the surface areas of the catalysts (in Table 1). With the addition of Ti content in the  $\text{CeO}_2\text{-TiO}_2$  catalysts, Ce content on the surface of the catalyst decreases and a fraction of  $\text{Ti}^{4+}$  with

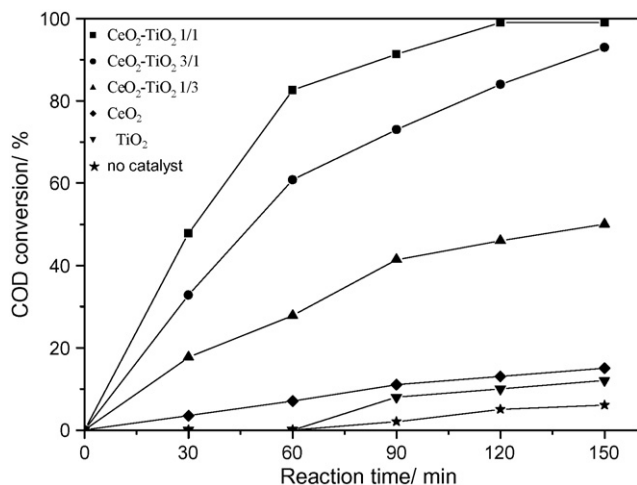


Fig. 3. COD conversion in the WAO of phenol over the different CeO<sub>2</sub>-TiO<sub>2</sub> catalysts. Reaction temperature of 150 °C; the total pressure of 3 MPa; catalyst dosage of 4 g/L; the phenol concentration of 2100 mg/L.

low ion radius can enter the CeO<sub>2</sub> lattice. Those could result in the concentration of the chemisorbed oxygen decrease on the surface of the catalyst [36]. The chemisorbed oxygen is the most active oxygen specie, and plays an important role in the CWAO of organic compounds. This could lead to the lower activity of CeO<sub>2</sub>-TiO<sub>2</sub> 3/1 catalyst with the higher surface area.

### 3.2.2. The effect of the reaction temperature

The effect of reaction temperature on the activity of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst in the range of 120–180 °C is investigated in the CWAO of phenol under the catalyst dosage of 4 g/L and the initial phenol concentration of 2100 mg/L (in Fig. 4). When reaction temperature increases to 180 °C without catalysts, COD removals enhance to 63% after 150 min reaction

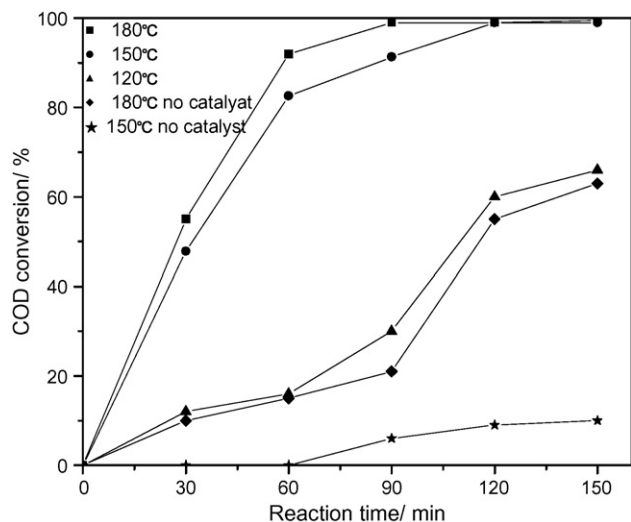


Fig. 4. COD conversion of the different reaction temperatures in the WAO of phenol. The total pressure of 3 MPa; catalyst dosage of 4 g/L; the initial phenol concentration of 2100 mg/L.

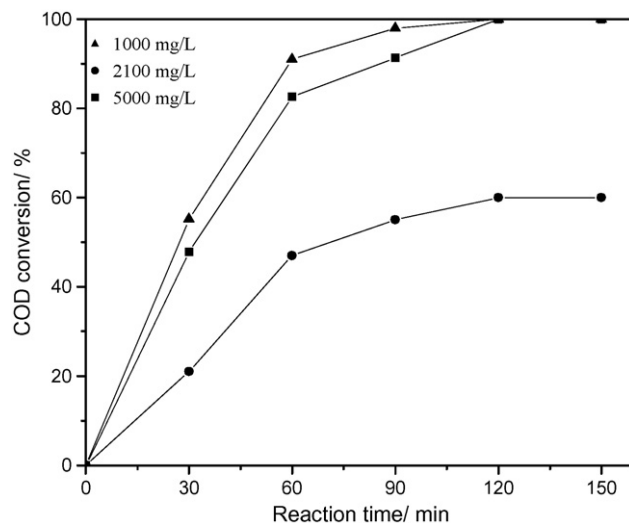


Fig. 5. COD conversion of the different phenol concentration in the WAO with CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst. Reaction temperature of 150 °C; Catalyst dosage of 4 g/L.

time. Using the CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst, COD removal obviously increases. For example, almost 100% COD and 85% TOC removals are obtained after 90 min in the CWAO of phenol using CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst at 180 °C. This indicates that the higher reaction temperature and CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst could effectively improve the oxidation rate of phenol, and make COD and TOC removals increase corresponding to the shorter reaction time.

### 3.2.3. The effect of the initial phenol concentration

Fig. 5 shows the effect of the initial phenol concentration on the activity of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst at 150 °C and the catalyst dosage of 4 g/L. It is observed that COD removal decreases with increasing the phenol concentration from 1000 to 5000 mg/L. At the concentration of 1000 mg/L, almost 100% COD and 83% TOC are removed after 120 min reaction. Increasing the initial phenol concentration to 5000 mg/L, only 60% COD and 51% TOC removals are obtained after 150 min reaction. COD conversion slows at the high initial phenol concentration. Very same result was observed in the CWAO of phenol over catalysts of carbon and MnO<sub>2</sub>/CeO<sub>2</sub> [37]. At the reaction temperature of 150 °C, the total pressure of 3 MPa, a catalyst dosage of 4 g/L and the initial phenol concentration of 1000 mg/L, CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst was reused for three time cycles. COD and TOC removals (87% and 65%, respectively) obviously decrease at 120 min reaction. The color of the catalyst changes from yellow to brown after the CWAO reaction. Furthermore, the used CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst was measured with SEM-EDX, and C element peak was found. The result is consistent with these reports [36], indicating that the intermediates in the CWAO of phenol deposited on the surface of the catalyst. The activity lost of the catalyst could be due to the deposition of carbonaceous polymers, lead to the irreversible adsorption of organic compounds on the catalyst, and make the lower activity of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst after three time cycles in the batch reactor for the CWAO of phenol.



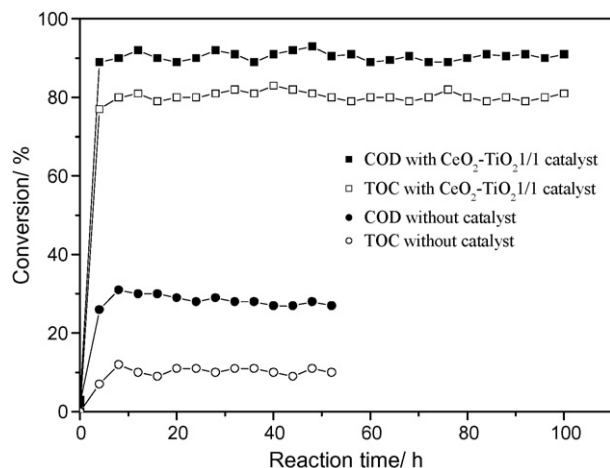


Fig. 6. COD and TOC conversions in the WAO of phenol in the packed-bed reactor. Reaction temperature of 140 °C; The phenol concentration of 1000 mg/L; The total pressure of 3.5 MPa.

### 3.3. CWAO of phenol in the packed-bed reactor

The stability of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst in the CWAO of phenol (1000 mg/L) was performed in the packed-bed reactor. To decrease the operating cost, the operating temperature is set to 140 °C, and the oxidant is air (air pressure of 3.5 MPa). Fig. 6 reveals the activity for CWAO of phenol over CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst. Without catalysts, about 28% COD and 10% TOC removals are observed for the continued reaction 52 h in the packed-bed reactor. With CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst, the catalyst displays the higher activity in the CWAO of phenol, and 91% COD and 80% TOC removals are obtained during 100 h reaction. Furthermore, leaching concentrations of Ce and Ti ions for CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst in the oxidation reaction for 100 h are very low, less than 0.2 and 0.04 mg/L, respectively. From the experimental results in the packed-bed reactor, it is indicated that CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst is the excellent activity and stability in the CWAO of phenol.

Compared with the activity of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst performed in the batch reactor and the packed-bed reactor, it is obviously different under the long reaction run. COD and TOC removals obviously decrease in the bath reactor after three time cycles, while the conversion of organic compounds preserves highly stable COD and TOC removals in the packed-bed reactor for 100 h reaction run. Moreover, the structure of the catalyst used in the different reactors is also changed. In the batch reactor, the high ratio of organic compound to solid catalyst enhances the formation of heavy polymer, occurs to irreversibly adsorb on the surface of the catalyst, and affects the surface property of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 powder catalyst. Moreover, the deposition of organic compounds leads to the lower activity in the batch reactor. In the packed-bed reactor, the low ratio of the liquid to solid catalyst could accelerate the oxidation of organic compounds adsorbing on the catalyst, and restrain the deposition of carbonaceous compounds. It is observed that the color of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst does not change during 100 h reaction in the packed-bed reactor. Furthermore, the used CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst was measured with SEM-EDX to analyze the

deposition of carbonaceous compounds on the surface of the catalyst. It is observed that no significant carbon polymers adsorb on the surface and the surface structure keeps the same as the fresh catalyst. These results indicate that the deposition of carbonaceous compounds obviously decreases in the continuous packed-bed reactor. This makes good activity of CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst obtained in the continuous reactor.

## 4. Conclusions

In the paper, CWAO of phenol over CeO<sub>2</sub>-TiO<sub>2</sub> catalysts was investigated in a batch reactor and packed-bed reactor. The following results were obtained:

- (1) CeO<sub>2</sub>-TiO<sub>2</sub> powder catalysts show the higher activity than pure CeO<sub>2</sub> and TiO<sub>2</sub> catalysts, and CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 is the most active catalyst, and COD and TOC removal is about 100% and 77% after 120 min under the reaction temperature of 150 °C, the total pressure of 3 MPa, phenol concentration of 1000 mg/L and catalyst dosage of 4 g/L. Under the same reaction conditions, COD and TOC removals obviously decrease, and are 87% and 65% after 120 min at third cycle.
- (2) The higher reaction temperature using CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst could effectively improve the oxidation rate of phenol. COD and TOC removals decrease with increasing the phenol concentration from 1000 to 5000 mg/L. This result could be due to the irreversible adsorption of organic compounds on the catalyst, leads to the low activity for CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 catalyst in the CWAO of phenol.
- (3) In a packed-bed reactor, CeO<sub>2</sub>-TiO<sub>2</sub> 1/1 particle catalyst shows the excellent activity and stability in CWAO of phenol. Around 91% COD and 80% TOC removals can be obtained for 100 h reaction at the reaction temperature of 140 °C, the air total pressure of 3.5 MPa, the gas flow rate of 60 mL/min, the liquor flow rate of 0.5 mL/min.

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