Active carbon–ceramic sphere as support of ruthenium catalysts for catalytic wet air oxidation (CWAO) of resin effluent

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ABSTRACT

Active carbon–ceramic sphere as support of ruthenium catalysts were evaluated through the catalytic wet air oxidation (CWAO) of resin effluent in a packed-bed reactor. Active carbon–ceramic sphere and ruthenium catalysts were characterized by N_2 adsorption and chemisorption measurements. BET surface area and total pore volume of active carbon (AC) in the active carbon–ceramic sphere increase with increasing KOH-to-carbon ratio, and AC in the sample KC-120 possesses values as high as $1100 \, m^2 \, g^{-1}$ and $0.69 \, cm^3 \, g^{-1}$ (carbon percentage: 4.73 wt.%), especially. Active carbon–ceramic sphere supported ruthenium catalysts were prepared using the $RuCl_3$ solution impregnation onto these supports, the ruthenium loading was fixed at 1–5 wt.% of AC in the support. The catalytic activity varies according to the following order: Ru/KC-120 > Ru/KC-80 > Ru/KC-60 > KC-120 > without catalysts. It is found that the 3 wt.% Ru/KC-120 catalyst displays highest stability in the CWAO of resin effluent during 30 days. Chemical oxygen demand (COD) and phenol removal were about 92% and 96%, respectively at the reaction temperature of 200 °C, oxygen pressure of 1.5 MPa, the water flow rate of $0.75 \, L \, h^{-1}$ and the oxygen flow rate of $13.5 \, L \, h^{-1}$.

1. Introduction

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_2, H_2O and other innocuous end products under high temperature (125–320 °C) and pressure (0.5–20 MPa) using oxygen as the oxidant [1,2]. WAO has shown good potential to treat the industrial wastewater, while its application is limited due to the high capital investment and operating costs. Using catalysts in the WAO could effectively decrease the operating conditions, shorten reaction time and enhance the oxidation efficiency of organic compounds [3,4]. Unfortunately, the lack of stable and active catalysts is a serious drawback, which prevents further industrial implementation [5].

Historically, AC has been extensively used not only as an adsorbent but also as a catalyst support or even as a direct catalyst [6]. In particular, AC has often been used to support active metals for CWAO [7]. Ruthenium supported on high surface area carbon is shown to be a very active CWAO catalyst. Gallezot et al. [8] showed

that ruthenium catalysts prepared by ion exchange of AC and high surface area graphite were active for WAO of acetic acid. AC was successfully used by Eftaxias et al. [9] for wet oxidation of phenol waste water. The AC catalyst employed was stable and performed phenol and COD conversions over 99% and 85% with a low residual content of bio-toxic aromatic compounds.

However, AC has some disadvantages that limit their application in CWAO system. Due to the low mechanical strength (i.e., mechanical and abrasion), wet air oxidation has been used to regenerate the spent AC with simultaneous destruction of the adsorbed pollutants and small carbon loss (1–5%) [5]. Moreover, in order to meet the requirement of internal mass transfer, carbon-based material needs to be ground and sieved, which causes an excessively large pressure drop across the fixed bed system [10,11].

As a group of innovative materials, porous ceramics show high mechanical strength, low-pressure drop, low heat exchange, good thermal stability, high porosity and a relatively uniform porosity with an open, three-dimensional structure [12]. Phenolic resins-based AC has structural features similar to those in coal-based AC. However, it contains much fewer mineral impurities. The preparation of carbon–ceramic composite materials makes it possible to obtain a functional material, which combines the properties of ceramic materials (i.e., high mechanical strength, three-dimensional structure, etc) with those of carbonaceous materials (i.e., adjustable surface properties). These materials are abrasion resistant and have a high crushing strength, a low-

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pressure drop and a good textural development, therefore, it increases the reaction rate while reducing pressure losses and plugging of the catalyst.

The formation of pores in carbon is generally achieved through carbonization of the precursors followed by etching of the resulting char with oxidizing agents. In the present work, the creation of porosity in the carbon derived from phenol–formaldehyde resins was conducted by treating the resins with potassium hydroxide. The key mechanisms in porosity development by KOH etching are presumed to be associated with carbon gasification by oxygen contained in the alkali [13,14]. Carbon etching with KOH has been reported to be more effective in porosity development than etching approaches involving physical methods [15].

The aim of this work is to evaluate active carbon–ceramic sphere as the support of Ru-based catalyst and investigate the performances of the active carbon–ceramic sphere supported ruthenium catalysts for the CWAO of real phenol wastewater. In this work, AC in the carbonized monoliths was prepared by KOH etching. Therefore, the effect of the KOH etching on the properties of the active carbon–ceramic composite material was investigated. In a packed-bed reactor, ceramic sphere, active carbon–ceramic sphere and active carbon–ceramic sphere supported ruthenium catalysts were tested in the CWAO of real phenol wastewater. Life test was carried out for 30 days in order to check the evolution of the catalytic activity and stability.

2. Experimental

2.1. Material

The spherical porous ceramic was provided by Huansheng catalyst Co. Ltd. The apparent porosity of ceramic sphere is 35%, the sphere diameter is 6 mm, and its average pore size is 200 μm. The crushing strength of ceramic samples tested is 20 MPa.

The carbon precursor chosen for this work was a thermoset phenolic resin from Huaqiang resin Co. Ltd. Because the inexpensive phenolic resins have very high carbon yield (∼70% of the cured weight), thus reducing the cost of the carbon produced. This phenolic resin's viscosity is 0.750 Pa s (25 °C).

2.2. Catalyst preparation

Active carbon–ceramic spheres were prepared by coating a porous ceramic sphere with a phenolic resin (carbon precursor). The following procedure was adopted [16]: (a) impregnation of the ceramic substrate with phenolic resin (40 °C, 24 h); (b) curing (130 °C, 1 h); (c) carbonization (800 °C, 1 h); (d) activation with KOH etching (800 °C, 20 min); (e) washing and drying (120 °C, 4 h). Carbon deposited throughout ceramic substrate is distributed in a relatively uniform manner on the ceramic substrate, inside the pores and coating the walls. It is difficult to see the boundary between the carbon and the ceramic. In the activation procedure, the carbonized monoliths were impregnated with the different concentrations of KOH solution at KOH-to-carbon ratios of 0.6 (KC-60), 0.8 (KC-80) and 1.2 (KC-120) by weight. According to the various KOH-to-carbon ratios, three kinds of active carbon–ceramic spheres were obtained, respectively.

These active carbon–ceramic spheres were used as the catalyst supports. The ruthenium metal loading was fixed at 1–5 wt.% of AC in the active carbon–ceramic sphere. After the impregnation, the preparation was dried for 24 h at room temperature, introduced in a quartz tube cell and reduced in flowing hydrogen at 400 °C for 5 h (temperature ramp rate: 4 °C min^{-1}). After cooling down to room temperature under H$_2$, the cell was purged with nitrogen and the catalyst was further passivated at room temperature under flowing 1% O$_2$/N$_2$ for 12 h.

Table 1
Initial characterization of the resin effluent.

Species in solution[a]	Resin effluent
Color	Dark yellow
Initial pH	2.0
COD	19,500
Phenol	6200
Formaldehyde	2000
Methanol	320
Cl$^-$	560
SO$_4^{2-}$	1600

[a] Concentration in mg L^{-1}.

2.3. Characterization

2.3.1. Pore structure of active carbon–ceramic sphere

The pore structure of active carbon–ceramic sphere was determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2010 apparatus. Before each measurement, the sample is evacuated at 300 °C for 3 h.

2.3.2. Chemisorption

Hydrogen and carbon monoxide chemisorption isotherms were determined in a glass-vacuum system with a capacitance manometer MKS for pressure measurements. Extrapolation of the hydrogen isotherm to zero pressure and the two isotherms method for carbon monoxide were applied in order to determine the uptake of these gases.

2.3.3. Induced coupling plasma (ICP) spectra

An ICP spectrometer (Optima, 2000DV) was used to determine concentrations of metal species leached from the catalysts.

2.4. Analysis of phenol concentration, COD

Phenol concentration was analyzed using a high-performance liquid chromatograph equipped with a Hypersil ODS2 column (250 mm × 4.6 mm) and a UV detector at 210 nm. COD of the solution was measured by the standard method using potassium dichromate as the oxidant.

2.5. CWAO test

2.5.1. Resin effluent

The crude resin effluent used in this work, a highly acidic aqueous stream which produced by the synthesis of resin used in this study, was obtained from Huaqiang resin Co. Ltd. The wastewater contains numerous organic compounds such as phenol, formaldehyde, and methanol. The characteristic of the resin effluent is summarized in Table 1. In order to reduce the cauterization of reactor, the pH of resin effluent was adjusted to 8.0 by adding KOH, resulting in the color change of effluent from dark yellow to dark red.

2.5.2. Packed-bed reactor: experimental set-up and procedures

The activity and stability of active carbon–ceramic sphere supported ruthenium catalyst were tested in a packed-bed reactor. The configuration of the reactor system is shown in Fig. 1, which consists mainly of a high-pressure pump, a high-pressured air cylinder, a heat exchanger as well as a reactor with a relief valve and a downstream separator. The resin effluent was mixed with pure oxygen from a high-pressured air cylinder, and then up-flowed through the packed-bed consisting of ϕ 54 mm × 1000 mm 316 L steel tube. The temperature of the catalyst bed was monitored and controlled via three thermocouples which placed into a thermowell inserted in the reactor tube, respectively. The effluent from the
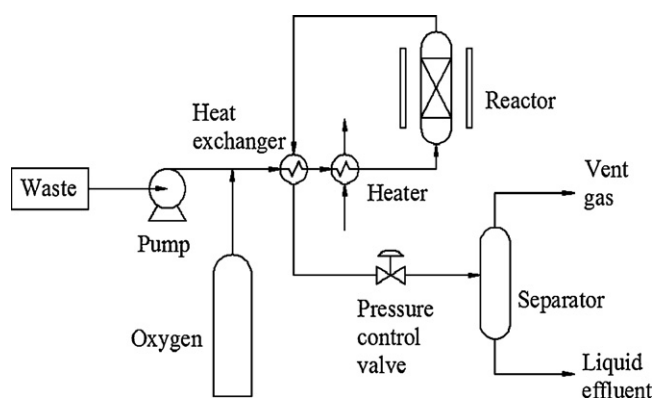
Fig. 1. Experimental setup of the packed-bed reactor in the CWAO of resin effluent.

reactor entered into separator through a relief valve. The oxygen pressure (1.5 MPa, P_{O_2}), the water flow (0.75 L h^{-1}) and the oxygen flow (13.5 L h^{-1}) at 1 h^{-1} of WHSV (weight hourly space velocity) were set at the desired values. Upon entering the reactor, the resin effluent and oxygen were mixed and heated before contacting the catalyst. After the continuous experiment start in 4 h, the operating system (reaction temperature, pressure, the liquid and gas flow) trends to the stability. The effluent at the outlet of packed-bed reactor was collected. Liquid product samples were periodically drawn and analyzed as mentioned above.

3. Results and discussion

3.1. Characterizations

3.1.1. Active carbon–ceramic sphere

3.1.1.1. Nitrogen adsorption isotherms. It is well known that the KOH-to-carbon ratio is the most important parameter in the preparation of AC using the KOH activation method [17]. The nitrogen adsorption isotherms on the AC studied at different KOH-to-carbon ratios are shown in Fig. 2. It can be seen that the shape of the adsorption isotherms and the adsorption capacity significantly change as the KOH-to-carbon ratio increases. The adsorption isotherms of KC-60 and KC-80 are approximately the Type I isotherm according to BET classification [18], in which the knees of the isotherms about $P/P_0 = 0.01$ ar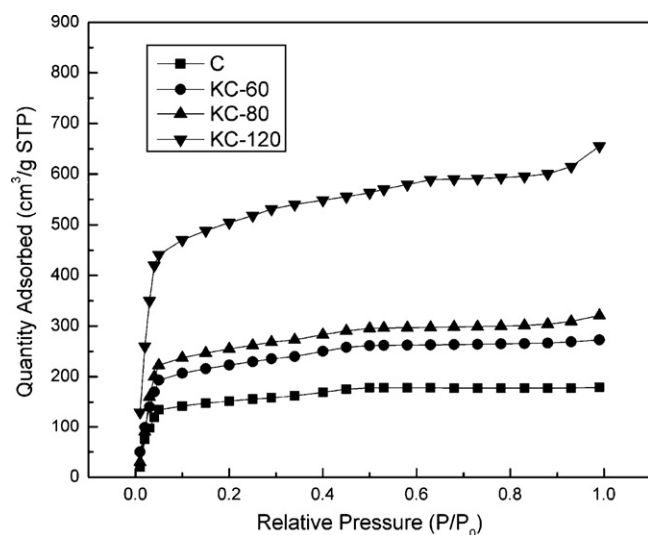e sharp and the plateaus are fairly horizontal. It has been known that adsorption on the microporous materials leads to an isotherm of the Type I at a lower P/P_0 [19].

Meanwhile, the nitrogen adsorption isotherm of the sample KC-120 significantly differs from that of KC-60 and KC-80, which is approximately the isotherm of the Type IV. As shown in Fig. 2, the sample KC-120 exhibits a more significant increase in adsorption at higher relative pressure, where the knee comes to be more open and round and the slope of the plateau increases. And also, the nitrogen uptake significantly occurs at high relative pressure ($P/P_0 > 0.9$). It indicates that the meso- or macropore structure in the sample is significantly developed with an increase in the KOH-to-carbon ratio due to the occurrence of the widening of the existing micropores [20].

3.1.1.2. Pore structure analysis. Table 2 summarizes the structural parameters at different KOH-to-carbon ratios determined from nitrogen adsorption isotherms according to the BET and Dubinin–Radushkevich equations. The data shows, as expected, that both BET surface area and total pore volume of AC in the active carbon–ceramic sphere increase with the increasing of KOH-to-Carbon ratio. Especially, AC in the sample KC-120 possesses values as high as 1100 m^2 g^{-1} and 0.69 cm^3 g^{-1} (carbon percentage: 4.73 wt.%), which is the same as those of conventional AC. It implies that AC with excellent porosity could be prepared from KOH-impregnated carbon–ceramic sphere and the increase in the KOH-to-carbon ratio results in the production of AC with high BET surface area and total pore volume.

Meanwhile, carbon in the composite material without activation to be discussed is the influence of KOH on the development of porosity. As shown in Fig. 2 and Table 2, the resulting sample carbon possesses a BET surface area of 471 m^2 g^{-1} and a low nitrogen adsorption capacity of 0.276 cm^3 g^{-1}, suggesting that KOH plays an important role in the preparation process of AC.

As shown in Table 2, it can be seen that the micropore and mesopore volumes and the average pore diameter increase with the increase in the KOH-to-carbon ratio. These behaviors obviously suggest that the pore evolution can be due to the creation of new pores and widening of existing pores with increasing KOH-to-carbon ratio [20]. However, it is noted that although micro- and mesopore volumes concurrently increase with the KOH-to-carbon ratio, there is a difference between the volume fractions of the resultant AC. As shown in Table 2, the percentage of micropore volume in the total pore volume decreases as the KOH-to-carbon ratio increased, and the percentage of mesopore volume increase. It is known that the new pore creation is involved in the creation of new micropore and pore widening of pore concurrently. It is shown that the rate of the pore widening and external surface decomposition results in the creation of mesopore exceeding new micropore creation. AC as the support of Ru-based catalyst, mesoporous carbon is better support than microporous carbon [21].

3.1.2. Active carbon–ceramic sphere supported ruthenium catalysts

The porous structure of these ruthenium catalysts is listed in Table 3. The BET surface areas of these catalysts without significant change were observed compared to the bare supports, after the impregnation of the support with ruthenium. Consequently, the porous structure of these catalysts was not changed obviously after impregnation and reduction. This can be explained by a strong interaction between the ruthenium metal and the AC support [22].

Table 3 also presents the metallic dispersion and the average particle size determined by H$_2$ and CO chemisorption for the Ru/AC catalysts. Seen from Table 3, the amount of adsorbed hydrogen is lower than that of adsorbed CO. The differences may be due to the non-complete removal of H$_2$ on ruthenium during the activation process and to the presence of residual chloride species which poi-

Fig. 2. Nitrogen adsorption isotherms at 77 K for the ACs of the carbon–ceramic sphere studied: (■) carbon without activation; (●) KC-60; (▲) KC-80; (▼) KC-120.

Table 2
Structural parameters of the AC in the carbon–ceramic sphere.

Samples	S_{BET} [a] (m^2 g^{-1})	V_t [b] (cm^3 g^{-1})	V_{micro} [c] (cm^3 g^{-1})	V_{meso} [d] (cm^3 g^{-1})	V_{micro}/V_t (%)	D_p [e] (nm)	Yc [f] (wt.%)
C	471	0.276	0.178	0.098	64.5	2.35	5.3
KC-60	712	0.421	0.27	0.15	64	2.37	5.10
KC-80	792	0.486	0.307	0.179	63	2.46	5.01
KC-120	1100	0.69	0.395	0.296	57	2.51	4.73

[a] Specific surface area determined from the BET equation.
[b] Total pore volume.
[c] Micropore volume determined from the DR equation.
[d] Mesopore volume.
[e] Mean pore diameter.
[f] Carbon percentage of active carbon–ceramic sphere.

son the metal ruthenium surface, with a subsequent decrease of H$_2$ chemisorption capacity.

3.1.3. Ruthenium leaching

The possible leaching of ruthenium from the catalyst is an important aspect regarding to its stability and performance. The ruthenium concentration in the effluent at the outlet of packed-bed reactor after 24 h reaction was repeatedly measured by ICP. The ruthenium concentration in the solution was systematically lower than 0.5 ppm which is the detection limit of the ICP analytical equipment we used. In conclusion, ruthenium catalysts are chemically stable under the applied reaction conditions.

3.2. CWAO treatment of resin effluent

3.2.1. Effect of the active carbon–ceramic sphere supports

Fig. 3 shows the activity of different Ru/KC catalysts in the CWAO of resin effluent under the reaction temperature of 200 °C. As seen from Fig. 3, Ru/KC catalysts exhibit the better activities in the CWAO of resin effluent. In our previous work, we had compared the performances of the bare ceramic and pure KC-120 in the CWAO of resin effluent. Without catalyst, COD and phenol removal were about 65% and 89%, respectively. Approximately 82% and 93% of COD and phenol removal, respectively, were obtained in the CWAO of resin effluent over pure KC-120, indicating that pure KC-120 has a certain extent activity. AC as catalyst in wet air oxidation of phenol has shown high catalytic activity and stability [23]. Moreover, KC-120 has the best effect on the color removal. The color of the effluent at the outlet of reactor is transparent.

After preparation of the ruthenium catalysts with the RuCl$_3 \cdot x$H$_2$O precursor by excess solution impregnation onto the supports KC-60, KC-80 and KC-120, the ruthenium loading was fixed at 3 wt.% of AC in the active carbon–ceramic sphere. Using Ru/KC catalysts, COD removal was more efficient than that of bare ceramic and pure KC-120. The catalytic activity varies according to the following order: Ru/KC-120 > Ru/KC-80 > Ru/KC-60 > KC-120 > without catalysts. Although these catalysts have similar metal

dispersions (Table 3) and the initial ruthenium load, Ru/KC-120 catalyst shows the best catalytic activity, and 92% COD and 96% phenol was removed after CWAO reaction at the reaction temperature of 200 °C. It is noticed that the active order is in agreement with that of the surface areas and pore structure of the supports, which can be explained by the more strong interaction and better dispersion of ruthenium metal on the KC-120 support than KC-60 and KC-80.

3.2.2. Effect of the ruthenium loading

It is often assumed that wet air oxidation of organic compounds, such as phenol [24], occurs by means of a free-radical chain reaction. That is, during the free-radical chain reaction, the rate of free radical formation is assumed to be equivalent to the rate of free radical destruction, hence maintaining the free radical concentration at a critical value. The rate of free radical formation is dependent on the amount of active sites on the catalyst, and the amount of active sites varies with ruthenium loading.

Having concluded that Ru/KC-120 is the most active supported ruthenium catalyst, we evaluated the effect of altering the ruthenium loading of this catalyst on its catalytic performance in the CWAO of resin effluent. Since the dispersion of ruthenium particles may be a function of the ruthenium loading on the support, catalysts containing 1, 2, 3 and 5 wt.% ruthenium were prepared on KC-120. Fig. 4 shows COD and phenol removal profiles over the Ru/KC-120 catalysts with different ruthenium loading in the CWAO of resin effluent under the reaction temperature of 200 °C.

Seen from Fig. 4, the activity of the Ru/KC-120 catalysts for wet air oxidation of resin effluent increased as the ruthenium loading increased up to 3 wt.%. Because ruthenium is the active species in the Ru/KC-120 catalyst, it might be expected that increasing amounts of ruthenium would lead to increasing activity of the catalyst, and hence an increasing CWAO rate of resin effluent. However, at the ruthenium loading above 3 wt.%, both COD and phenol removal increased slightly. This phenomenon probably occurred because at ruthenium loading exceeding 3 wt.%, the ruthenium on the support formed larger crystals, restricting the amount of active sites. Such formation of larger ruthenium crystals at higher ruthe-

Table 3
Characterization of Ru/KC catalysts using N$_2$ adsorption and chemisorption.

Samples	S_{BET} [a] (m^2 g^{-1})	D_p [b] (nm)	Ru dispersion[c] (%)		Crystallite sizes (nm)		Uptake[d] (μmol g^{-1})	
			CO	H$_2$	CO	H$_2$	CO	H$_2$
3 wt.% Ru/KC-60	588	2.17	31.1	19.1	4.18	6.75	75	21.4
3 wt.% Ru/KC-80	675	2.32	35.65	19.7	3.73	6.58	86	23.1
3 wt.% Ru/KC-120	980	2.47	46.9	22.4	2.86	5.96	118	26.8
1 wt.% Ru/KC-120	1040	2.49	51.2	28.2	2.05	3.72	83.2	22.8
2 wt.% Ru/KC-120	1015	2.47	48.2	24.2	2.64	5.25	108.6	25.1
5 wt.% Ru/KC-120	940	2.42	44.7	21.3	3.02	6.34	125.6	27.8

[a] Specific surface area determined from the BET equation.
[b] Mean pore diameter.
[c] The Ru dispersion for the Ru/AC catalysts in the carbon–ceramic sphere.
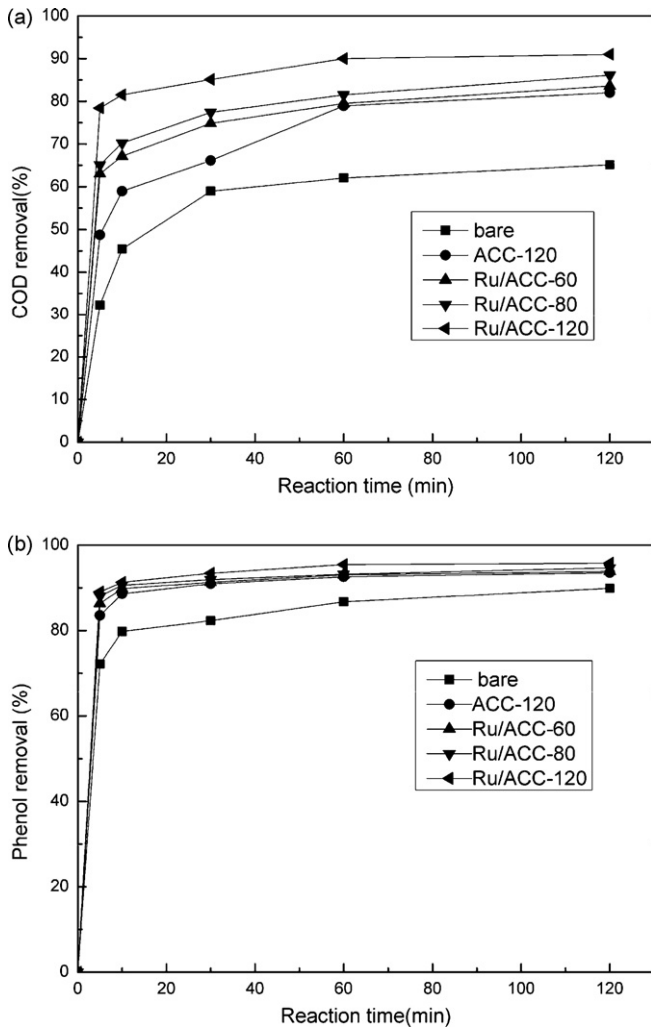[d] The uptake of the Ru/AC catalysts in the carbon–ceramic sphere.

Fig. 3. Effect of the active carbon–ceramic sphere supports on COD (a) and phenol (b) removal.

Fig. 5. Effect of the reaction temperatures on COD (a) and phenol (b) removal.

nium content can be verified via CO chemisorption of Ru/KC-120 catalysts. As shown in Table 3, the 1 wt.% Ru/KC-120 catalyst contained very small ruthenium particles with an average particle size of 2.05 nm, compared to the 3 wt.% Ru/KC-120 catalyst, which average particle sizes was 2.86 nm. Moreover, the ruthenium particles
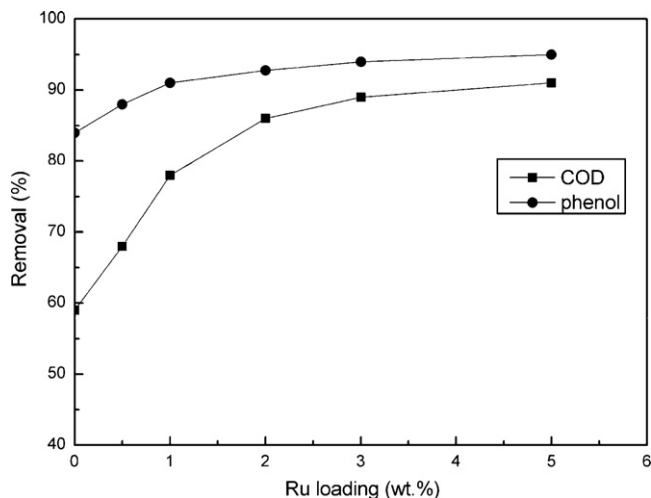

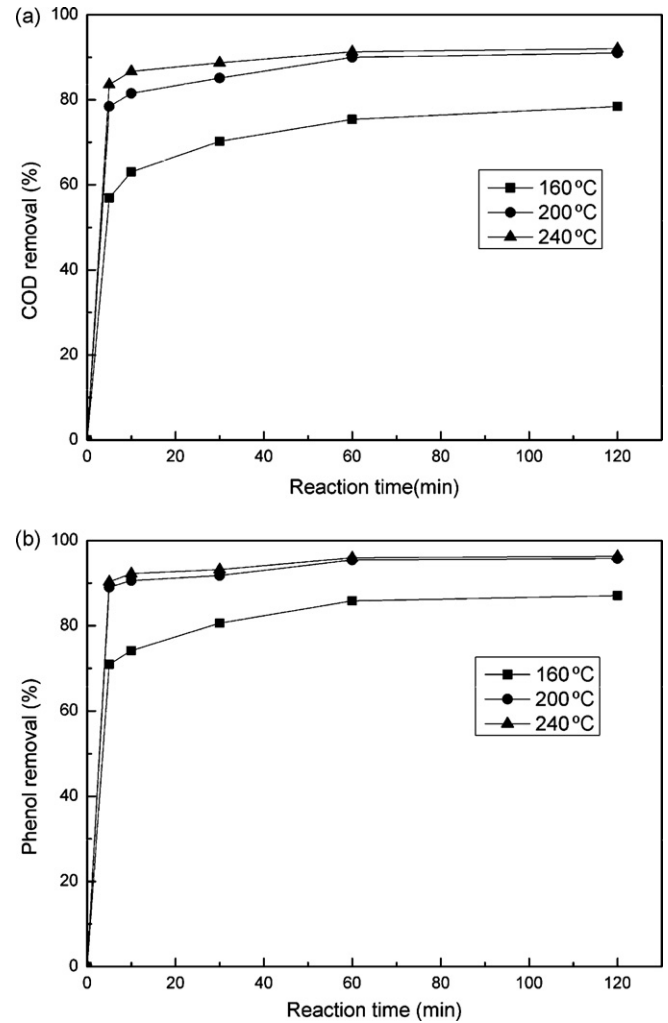**Fig. 4.** Effect of ruthenium loading on COD and phenol removal.

of the 3 wt.% Ru/KC-120 catalyst was distributed in a more homogeneous way, without agglomeration of individual particles. The average particle size of the 5 wt.% Ru/KC-120 catalyst, higher than other catalysts, was 3.02 nm. However, the dispersion of ruthenium particles is lower than the 3 wt.% Ru/KC-120 catalyst. These differences may be at the origin of the specific activity of catalyst.

Considering the activity of the Ru/KC-120 catalysts, the optimum loading of ruthenium was 3 wt.% in this work.

3.2.3. Effect of the reaction temperature

Temperature is also a very important parameter in the CWAO of organic compounds. A combination of beneficial effects due to the increase in temperature may affect the reaction. Firstly, according to Arrhenius' law the higher the reaction temperature, the faster the reaction is. Secondly, above 100 °C, the oxygen solubility in water increases with temperature [25]. But, from a practical point of view, one must keep in mind that the higher the reaction temperature, the more stringent the corrosion problems.

The influence of the reaction temperature was studied in the range 160–240 °C. Fig. 5 shows the evolution of the COD and phenol removal of resin effluent over the 3 wt.% Ru/KC-120 catalyst at different temperatures. Just as we anticipated, the COD and phenol removal increase with temperature. The effect of temperature in the CWAO of resin effluent was remarkable, when reaction temperature increases from 160 to 200 °C, COD and phenol removal increases 12.5% and 18%, respectively. Almost 92% of COD and 96%
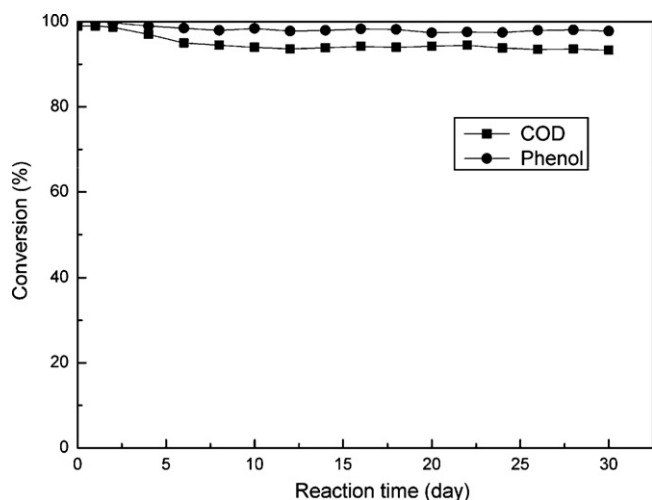
Fig. 6. Stability of the 3 wt.% Ru/KC-120 catalyst in the CWAO of resin effluent during 30 days.

of phenol removals were obtained in the CWAO of resin effluent using the 3 wt.% Ru/KC-120 catalyst at 200 °C. The effect of the temperature became weaker when reaction temperature increases from 200 to 240 °C, both COD and phenol removal increases less than 2%. This phenomenon can be interpreted that the removal of the smaller organic acids, which are refractory to the oxidation, are higher, when reaction temperature above 200 °C.

As a conclusion, the higher temperatures are favorable for the CWAO of resin effluent. However, higher temperatures practically translate into higher operating costs and severe corrosion problems due to the presence of by-products such as low molecular weight carboxylic acids generated during the reaction. Additionally, from a fundamental point of view, one has to make sure that the reaction is operated under chemical control, that is, not too fast. In order to observe the effects of other operating parameters, the reaction should not be too fast either. Taking into consideration the above-mentioned multisided reasons, we chose 200 °C as the optimum temperature for the study of the CWAO of resin effluent over the 3 wt.% Ru/KC-120 catalyst.

3.3. Stability of the Ru/KC-120 catalyst

Among the important problems of commercialization of CWAO catalysts is their resistance to the oxidative reaction medium under operation conditions. Another important problem is the catalyst stability in aggressive aqueous solutions. Leaching of the active component is the major factor that restricts application of solid catalysts of complex compositions in CWAO processes. Stability of the 3 wt.% Ru/KC-120 catalyst in the CWAO of resin effluent was performed in the packed-bed reactor during 30 days. The temperature (200 °C), oxygen pressure (1.5 MPa, P_{O_2}), a water flow (0.75 L h^{-1}) and oxygen flow (13.5 L h^{-1}) at 1 h^{-1} of WHSV (weight hourly space velocity) were set at the desired values.

Fig. 6 reveals the activity for CWAO of resin effluent over the 3 wt.% Ru/KC-120 catalyst. With the 3 wt.% Ru/KC-120 catalyst, the catalyst displays higher activity in the CWAO of resin effluent, and 99% COD and 100% phenol removal was obtained during 24 h reaction, then decreased slowly and stabilized around 92% and 96%. In addition, liquid samples were collected every 12 h at the reactor exit and analyzed by ICP. The analysis revealed that the ruthenium concentration in the solution was lower than 0.5 ppm. The pH of the feed solution was alkaline (pH = 8), and the most prevalent oxidation products were low molecular weight acid, which decreased pH to 4.8. It is observed that the color of effluent at the outlet of

the packed-bed reactor does not change obviously during 30 days of reaction. However, the physical blockage of active sites exhibited no considerable influence on the catalytic activity for COD and phenol removal. From the experimental results in the packed-bed reactor, it was indicated that the 3 wt.% Ru/KC-120 catalyst is the excellent activity and stability in the CWAO of resin effluent.

In the CWAO reaction process, there is competition between the classical oxidation reaction and the condensation reaction that forms polymers. The polymers, if formed, could irreversibly adsorb on the catalyst surface and progressively block the active site, thereby lowering the rate of organic compound removal. 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. Furthermore, the Ru/KC-120 catalyst has been regenerated by WAO during CWAO of resin effluent in the packed-bed reactor, which decrease the deposition of carbonaceous compounds some extent and maintain the stability of the Ru/KC-120 catalyst in the CWAO of resin effluent.

4. Conclusions

The studies reported in this paper indicate that the active carbon–ceramic sphere is a very promising support to promote the activity of the ruthenium catalysts in the CWAO of resin effluent. In the paper, CWAO of resin effluent over Ru/KC catalysts was investigated in a packed-bed reactor. The following results were obtained:

(1) According to the characterization of N$_2$ adsorption, BET surface area and total pore volume of AC in the active carbon–ceramic sphere increase with increasing KOH-to-carbon ratio, AC in the sample KC-120 possesses values as high as 1100 m^2 g^{-1} and 0.69 cm^3 g^{-1} (carbon percentage: 4.73 wt.%), respectively.

(2) Supported ruthenium catalysts were prepared using the RuCl$_3$ solution impregnation onto active carbon–ceramic sphere supports, which show the high catalytic activity in the CWAO of resin effluent. The catalytic activity varies according to the following order: Ru/KC-120 > Ru/KC-80 > Ru/KC-60 > KC-120 > without catalysts. The 3 wt.% Ru/KC-120 catalyst was the optimum active catalyst, and the ruthenium particles were distributed in a more homogeneous way than other catalysts.

(3) The effect of temperature in the CWAO of resin effluent over the 3 wt.% Ru/KC-120 catalyst was remarkable. When reaction temperature increases from 160 to 200 °C, COD and phenol removal increases by 12.5% and 18%, respectively. The effect of the temperature became weaker when reaction temperature above 200 °C.

(4) As the optimum catalyst, the 3 wt.% Ru/KC-120 catalyst displays highest stability in the CWAO of resin effluent during 30 days. COD and phenol removals were about 92% and 96% at the reaction temperature of 200 °C, oxygen pressure of 1.5 MPa, the water flow rate of 0.75 L h^{-1} and the oxygen flow rate of 13.5 L h^{-1}.

Acknowledgement

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