



# Heterogeneous activation of peroxymonosulphate by supported ruthenium catalysts for phenol degradation in water

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## ABSTRACT

Activated carbon (AC) and Zeolite Socony Mobil-5 (ZSM5) supported ruthenium oxide catalysts were prepared and tested to degrade aqueous phenol in the presence of peroxymonosulphate. The physico-chemical properties of ruthenium oxide based catalysts were characterised by several techniques such as XRD (X-ray diffraction), SEM-EDS (scanning electron microscopy–energy dispersive X-ray spectroscopy), and N<sub>2</sub> adsorption. It was found that RuO<sub>2</sub>/AC was highly effective in heterogeneous activation of peroxymonosulphate to produce sulphate radicals, presenting higher reaction rate in phenol degradation compared with RuO<sub>2</sub>/ZSM-5. Degradation efficiency of phenol could be achieved at 100% of phenol decomposition and 60% of total organic carbon (TOC) removal in 1 h at the conditions of 50 ppm phenol, 0.2 g catalyst, 1 g Oxone<sup>®</sup> in 500 mL solution at 25 °C using the two catalysts. It was also found that phenol degradation was strongly influenced by catalyst loading, phenol concentration, Oxone<sup>®</sup> concentration and temperature. Kinetic studies proved that a pseudo first order kinetics would fit to phenol decomposition and the activation energies for RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5 were obtained to be 61.4 and 42.2 kJ/mol, respectively.

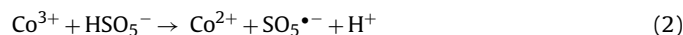
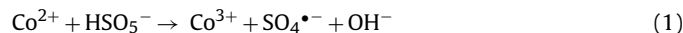
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## 1. Introduction

Phenol is one of the important pollutants in wastewater due to its toxic effect on the environment even at very low concentration. Phenol is widely used as a raw material in many industries such as chemical, petrochemical, and pharmaceutical industries [1]. Moreover, phenol is a water pollutant which can not be easily degraded with primary and secondary treatment processes so that a tertiary treatment of wastewater has to be adopted. These tertiary treatments include thermal oxidation, chemical oxidation, wet air oxidation, catalytic oxidation etc., which are generally known as advanced oxidation processes (AOPs). In principle, a tertiary treatment process is used to reduce the contaminants to harmless products such as CO<sub>2</sub> and H<sub>2</sub>O [2]. Among the methods, heterogeneous catalytic oxidation usually has some advantages such as operation at room temperature and normal pressure with high energy efficiency. Furthermore, heterogeneous catalysts can be synthesised using cheap materials as supports such as activated carbon, zeolite, silica, alumina etc., and can be regenerated for reuse in treatment processes [3].

Generally, the most popular method to degrade organic compounds in wastewater is Fenton oxidation, which involves

hydrogen peroxide and Fe ions (Fenton reagent) to generate hydroxyl radicals in solutions [4,5]. Nowadays, this principle has been developed with some other oxidants such as peroxymonosulphate (PMS) and persulphate, which are found effective in chemically mineralising various organic pollutants [6]. Many researchers have proved that some heavy metals such as cobalt and iron can activate PMS to produce sulphate radicals for oxidation of organic pollutants to harmless end products. The following reactions show the formation of sulphate radicals in Co activation [7].



It was reported, in comparison with the conventional Fenton reagent, the rate of organic oxidation by sulphate radicals is faster. Moreover, the oxidation by sulphate radicals is less dependent on pH of solution, providing an alternative route to efficiently degrade organic contaminants [7,8]. However, a major issue in using heavy metal ions as catalysts is the toxicity of the heavy metals in the treatment system. The metal ions can cause many health problems to humans such as asthma and pneumonia. Therefore, heterogeneous catalytic oxidation has to be conducted. For this purpose, the heavy metals should be loaded into solid supports such as activated carbon (AC), zeolite (ZSM5), silica, alumina etc., via different methods including impregnation and ion exchange. In the past few years, several investigations have been attempted for supported Co

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catalysts in activation of PMS for the degradation of organic compounds [9–17].

Ruthenium (Ru) is one of the popular noble metals and it can also be used as a catalyst in chemical degradation of organic compounds. Pirkanniemi and Sillanpaa [18] reported that ruthenium has traditionally been used as a heterogeneous catalyst for water treatment. Oliviero et al. [19] used activated carbon supported Ru as a catalyst in catalytic wet air oxidation of phenol and acrylic acid. They found that the catalyst was very reactive to oxidise phenol. Further, Cybulski and Trawczynski [20] studied a ruthenium catalyst loaded on carbon black in catalytic wet air oxidation to degrade phenol solution and also concluded that this catalyst was very reactive for phenol removal. Similar studies in mineralising organic contaminants by using ruthenium based catalysts in wet air oxidation have been reported [21–26]. All of them reported that this heavy metal had very good performance. However, the use of ruthenium based catalysts with the presence of PMS to generate sulphate radicals for phenol oxidation is less developed.

In this research we investigate the use of ruthenium catalysts supported on AC and ZSM5 in heterogeneous catalytic oxidation process with the presence of peroxymonosulphate (using Oxone<sup>®</sup>) to generate sulphate radicals for chemical mineralising of phenol in aqueous solution. Several key parameters in the kinetic study such as phenol concentration, catalyst loading, Oxone<sup>®</sup> concentration and temperature were also investigated.

## 2. Experimental

### 2.1. Synthesis of ruthenium based catalysts

Catalyst synthesis was carried out following a general impregnation method. For ruthenium (RuO<sub>2</sub>)/AC, a fixed amount of ruthenium chloride (Sigma–Aldrich) was added into 200 mL ultrapure water until the ruthenium compound was dissolved. Next, AC (Picactif) with particle size of 60–100 μm was added into the solution and kept stirring for 24 h. After that, the suspension was evaporated in a rotary evaporator at temperature of 50 °C under vacuum. The solid was then recovered and dried in an oven at 120 °C for 6 h. Calcination of the catalyst was conducted in a tube furnace at 550 °C for 6 h in nitrogen. For RuO<sub>2</sub>/ZSM5, the same method was also implemented but with a different calcination process. The RuO<sub>2</sub>/ZSM5 was calcined in air. The loading of Ru on the two supports was maintained at 5 wt%.

### 2.2. Characterisation of catalysts

The synthesised catalysts were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), and N<sub>2</sub> adsorption. The XRD (Siemen, D501 diffractometer) was used to identify the structural features and the mineralogy of the catalysts. The XRD pattern was obtained using filtered Cu Kα radiation with accelerating voltage of 40 kV and current of 30 mA. The samples were scanned at 2θ from 5–100°. SEM (Philips XL30) with secondary and backscatter electron detectors was used to obtain a visual image of the samples to show the texture and morphology of the catalysts with magnification more than 20,000. EDS was also used to detect Ru particles on supported catalysts. The catalysts were also characterised by nitrogen adsorption–desorption (Autosorb-1) to identify the BET surface area and pore volume. Prior to the analysis, the catalyst samples were degassed under vacuum at 200 °C for 12 h.

### 2.3. Kinetic study of phenol oxidation

Catalytic oxidation of phenol was conducted in 500 mL phenol solutions at concentrations of 25, 50, 75 and 100 ppm. A reactor

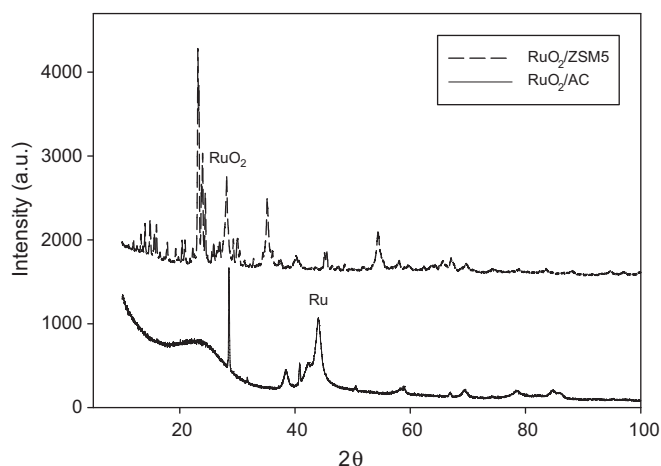


Fig. 1. XRD profiles of RuO<sub>2</sub>/ZSM5 and RuO<sub>2</sub>/AC.

attached to a stand was dipped into a water bath with a temperature controller. The solution was stirred constantly at 400 rpm to maintain homogeneous solution. Next, a fixed amount of peroxymonosulphate (Oxone<sup>®</sup>, DuPont's triple salt 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>, Aldrich) was added to the mixture until completely dissolved. Then, a fixed amount of catalysts (Ru/AC or Ru/ZSM5) was added into the reactor to start the oxidation of phenol. The reaction was run for 2 h and at the fixed time interval, 0.5 mL of a sample was withdrawn from the solution and filtered using HPLC standard filter of 0.45 μm and mixed with 0.5 mL methanol as a quenching reagent to stop the reaction. Phenol was then analysed on a HPLC with a UV detector at wavelength of 270 nm. The column is C18 with mobile phase of 80% acetonitrile and 20% ultrapure water. For some selected samples, total organic carbon (TOC) was determined by a Shimadzu TOX-5000 CE analyser where 0.5 mL sample was withdrawn, quenched with 3 M sodium nitrite solution, and diluted to 20 mL by ultrapure water and examined within 1 h.

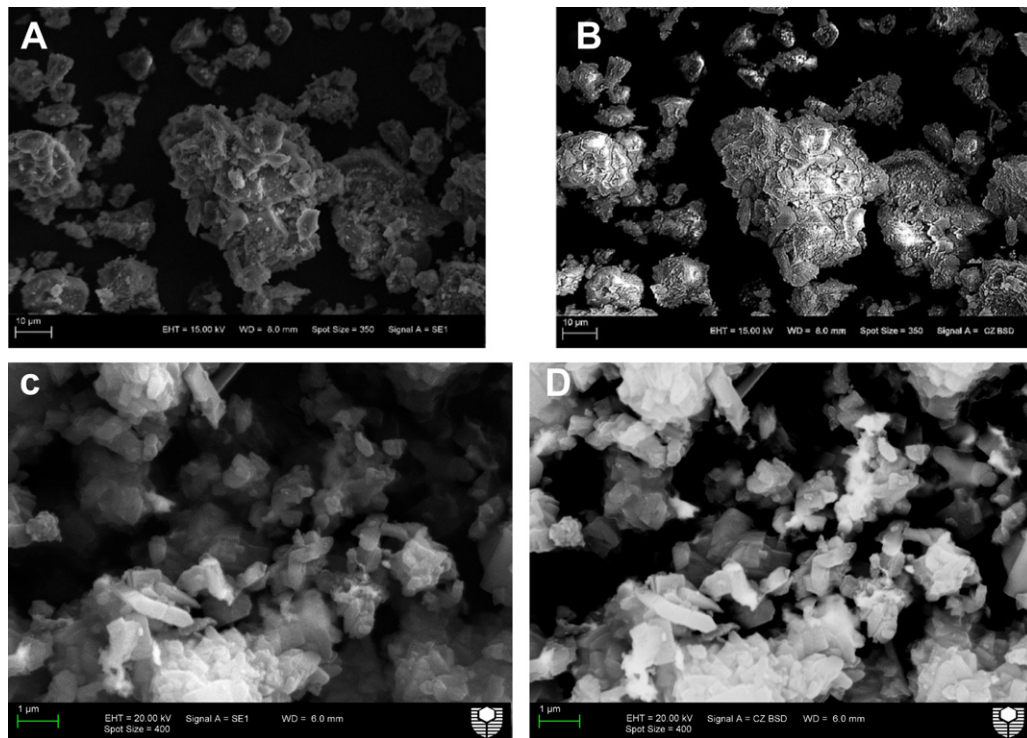
In recycling of catalysts for multiple round tests, the spent catalyst was recovered after each run from the reaction mixture by filtration and washed thoroughly with distilled water and dried at 70 °C for reuse.

## 3. Result and discussion

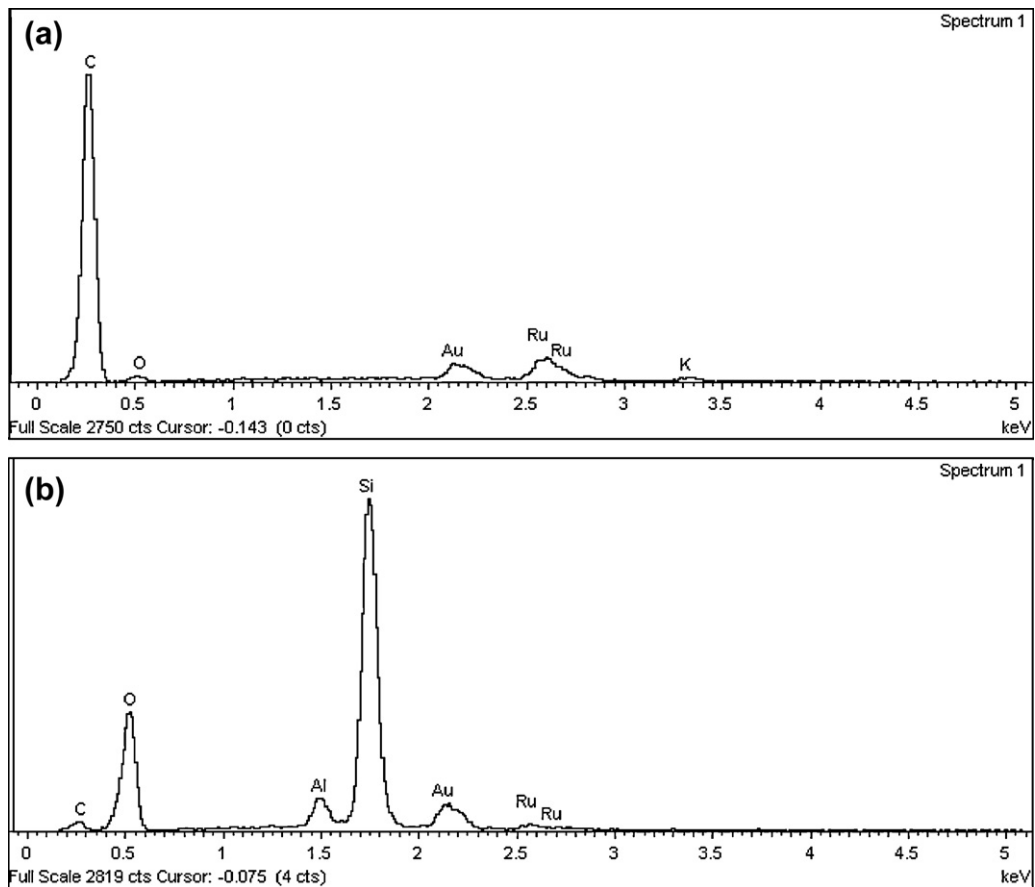
### 3.1. Characterisation of ruthenium impregnated activated carbon and ZSM5 catalysts

XRD patterns of RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5 are presented in Fig. 1. It can be seen, ruthenium species were found in the form of RuO<sub>2</sub> on RuO<sub>2</sub>/ZSM5 at 2θ coordinate of 28, 35, 40 and 54.3°. On the other hand, ruthenium oxide was found at 2θ angle of 28° and Ru at 38.4, 42.2, 44 and 69.4° on RuO<sub>2</sub>/AC. The differences in ruthenium species on the two catalysts were due to the different calcination processes. For RuO<sub>2</sub>/ZSM5, the calcination was done in air, whereas the calcination of RuO<sub>2</sub>/AC was carried out in nitrogen gas. Ru ions would be reduced by carbon in an inert gas to form Ru metal [27].

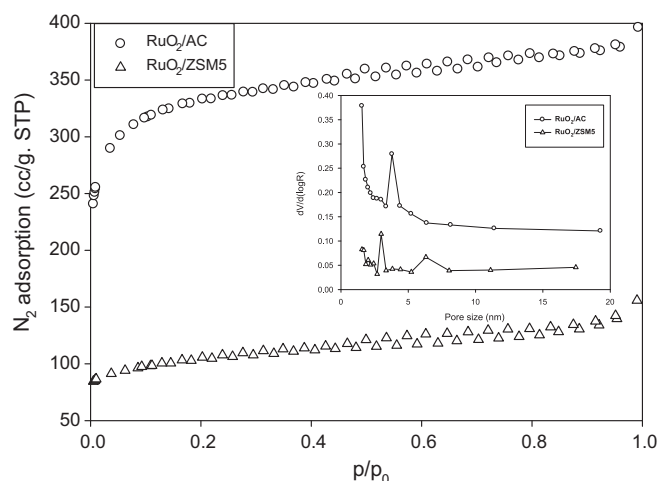
The texture and morphology of RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5 are shown in Fig. 2. Fig. 2A and B shows a SEM image of RuO<sub>2</sub>/AC analysed by a secondary electron detector (SE) and backscattered detector (BSE), respectively. It can be seen that the milled sample has different particle shape and size in a range of 5–60 μm. At the same area, the catalyst sample was also analysed using the BSE analysis and the presence of ruthenium specks is seen at the brighter area in the catalyst particles. It implies that ruthenium is well coated in the activated carbon samples. Further, in the SEM images, no small individual bright particles spread out around the



**Fig. 2.** SEM images of RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5, (A) SE Detector, RuO<sub>2</sub>/AC, (B) BSE Detector, RuO<sub>2</sub>/AC (C) SE Detector, RuO<sub>2</sub>/ZSM5, and (D) BSE Detector, RuO<sub>2</sub>/ZSM5.



**Fig. 3.** EDS spectra of RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5. (A) RuO<sub>2</sub>/AC (B) RuO<sub>2</sub>/ZSM5.



**Fig. 4.**  $N_2$  adsorption isotherm and pore size distribution of  $RuO_2/AC$  and  $RuO_2/ZSM5$ .

AC particles was observed suggesting that the assimilated ruthenium in the AC is not in the form of isolated  $RuO_2$ . This is also confirmed by XRD examination that  $RuO_2$  is the major species in the  $RuO_2/AC$  catalyst sample.

Fig. 2C and D presents SEM photos of  $RuO_2/ZSM5$  with SE and BSE measurements, respectively. As seen,  $RuO_2/ZSM5$  presents in smaller particle size. BSE showed brighter area than the image in SE, suggesting a good dispersion of Ru on ZSM5.

Fig. 3 displays EDS spectra of  $RuO_2/AC$  and  $RuO_2/ZSM5$ . C, Ru, O and K were found on  $RuO_2/AC$ . The presence of K may be due to the chemical activation process of carbon support using KOH. However, K does not affect catalyst activities in reducing phenol. For  $RuO_2/ZSM5$ , Si, Al, Ru, and O are the major elements. Thus the EDS spectra suggest the presence of Ru on both catalysts, confirming XRD and SEM results.

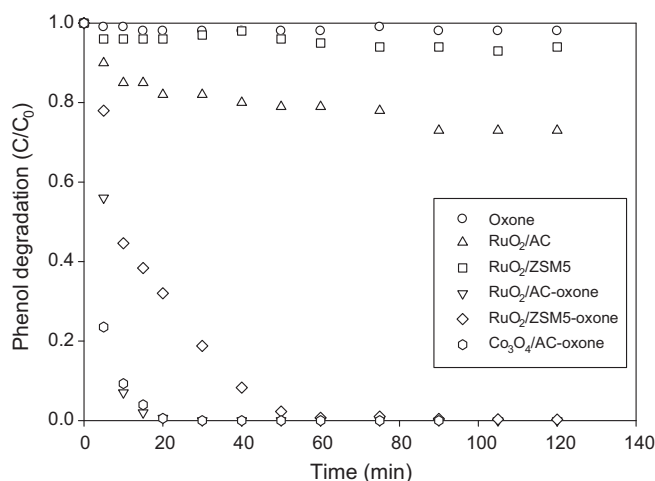
The catalyst samples were also characterised by  $N_2$  adsorption to identify pore size distribution and specific surface area ( $S_{BET}$ ). Fig. 4 shows  $N_2$  adsorption/desorption isotherms and pore size distributions of  $RuO_2/AC$  and  $RuO_2/ZSM5$ . As seen in Table 1,  $RuO_2/AC$  has a higher surface area ( $1178 \text{ m}^2/\text{g}$ ) than  $RuO_2/ZSM5$  ( $386 \text{ m}^2/\text{g}$ ).  $RuO_2/AC$  also has a higher pore volume ( $0.108 \text{ cm}^3/\text{g}$ ) than  $RuO_2/ZSM5$  ( $0.085 \text{ cm}^3/\text{g}$ ). However, both  $RuO_2/AC$  and  $RuO_2/ZSM5$  have a similar pore radius of  $15.6 \text{ \AA}$  and  $15.7 \text{ \AA}$ , less than  $20 \text{ \AA}$ , which means they are microporous materials. The pore size distribution of  $RuO_2/AC$  presented two peaks, centred at 1.5 and 3.9 nm, respectively.  $RuO_2/ZSM5$ , however, showed a different profile with three peaks, which are centred at 1.5, 2.9 and 6.3 nm, respectively.

### 3.2. Preliminary study of phenol oxidation

Preliminary tests including adsorption and phenol degradation in aqueous solution on  $RuO_2/AC$  and  $RuO_2/ZSM5$  are presented in Fig. 5. Generally, all the samples, AC, ZSM5,  $RuO_2/AC$  and  $RuO_2/ZSM5$ , can adsorb phenol compound despite of at low efficiency. Among them, AC has the highest efficiency in phenol adsorption with 34% removal in 2 h prior to reaching equilibrium.

**Table 1**  
Surface area, pore volume and pore radius of  $RuO_2/AC$  and  $RuO_2/ZSM5$ .

Catalyst	Surface area ( $S_{BET}$ , $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Average pore radius ( $\text{\AA}$ )
$RuO_2/AC$	1178	0.108	15.6
$RuO_2/ZSM5$	386	0.085	15.7

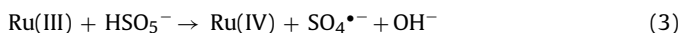


**Fig. 5.** Phenol reduction with time in adsorption and catalytic oxidation. Reaction conditions: 0.2 g catalyst loading, 1 g Oxone<sup>®</sup> in 500 mL phenol solution of 50 ppm,  $25^\circ\text{C}$  and stirring speed of 400 rpm.

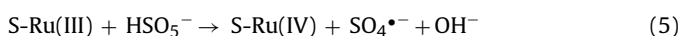
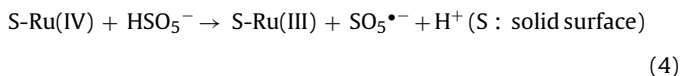
Lower adsorption efficiency of 10% in 2 h can be seen on ZSM5. AC has much higher surface area and pore volume than ZSM5, resulting in higher phenol adsorption. However, phenol adsorption on AC and ZSM5 was decreased when the materials were loaded by ruthenium. The phenol removal efficiencies on  $RuO_2/AC$  and  $RuO_2/ZSM5$  were reduced to 27% and 6% in 2 h, respectively. The decrease in removal efficiency of both catalysts is caused by the decrease of surface area and pore volume when ruthenium was loaded covering the support surfaces.

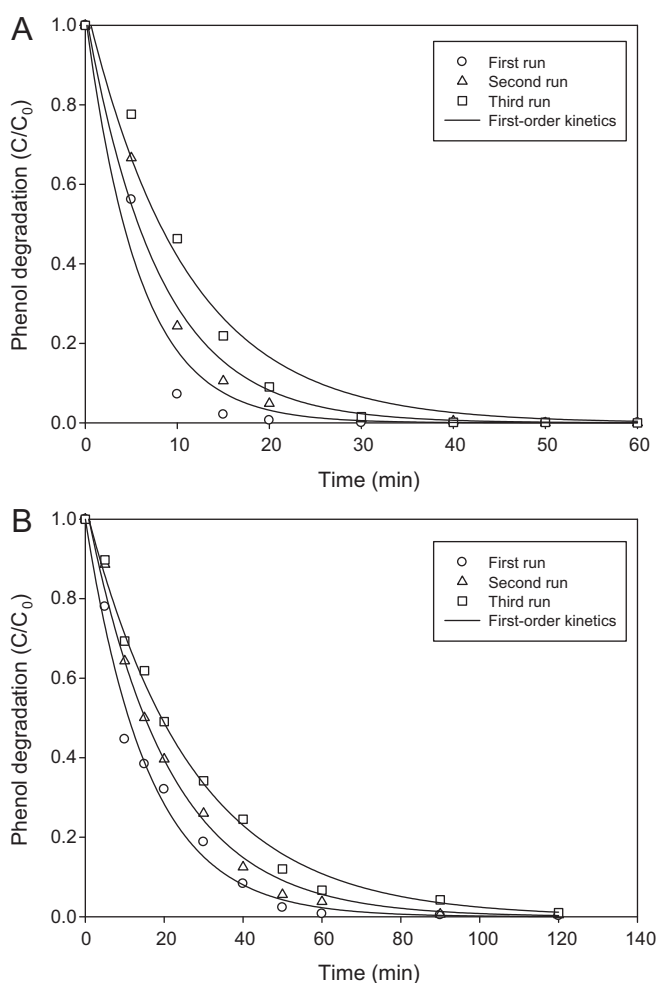
In oxidation tests, addition of PMS without a catalyst did not induce phenol oxidation reaction. Phenol removal would occur when catalysts ( $RuO_2/AC$  and  $RuO_2/ZSM5$ ) and oxidant (PMS) simultaneously were presented in the solution. In comparison of  $RuO_2/AC$ -Oxone<sup>®</sup> and  $RuO_2/ZSM5$ -Oxone<sup>®</sup> systems for phenol oxidation,  $RuO_2/AC$ -Oxone<sup>®</sup> exhibited much better performance producing complete removal of phenol in 20 min while  $RuO_2/ZSM5$ -Oxone<sup>®</sup> could completely remove phenol in 50 min. For a comparison,  $Co_3O_4/AC$  was also prepared and tested. It can be seen that  $Co_3O_4/AC$  catalyst exhibited faster initial rate in phenol degradation, however, the efficiency was the same as  $RuO_2/AC$ . The complete removal of phenol could be reached in 20 min.

TOC removal in  $RuO_2/AC$ -Oxone<sup>®</sup> and  $RuO_2/ZSM5$ -Oxone<sup>®</sup> systems was also examined and the results showed that about 70% and 60% of TOC reductions were obtained for  $RuO_2/AC$ -Oxone<sup>®</sup> and  $RuO_2/ZSM5$ -Oxone<sup>®</sup>, respectively, within 1 h. Anipsitakis and Dionysiou [28] investigated several transition metals for activation of  $H_2O_2$  and Oxone<sup>®</sup> and found that Co(II) and Ru(III) are the best metal catalysts for the activation of peroxymonosulphate. The reaction of Ru(III) with PMS can proceed as below.



According to XRD examination, the major species of ruthenium in  $RuO_2/AC$  are Ru and  $RuO_2$ . Meanwhile, the ruthenium species in ZSM5 is mainly  $RuO_2$ . Thus, it is believed that they are the active sites for activation of PMS to produce sulphate radicals in phenol oxidation system. The heterogeneous activation process is proposed as below.





**Fig. 6.** Phenol removal in multiple uses of (A) RuO<sub>2</sub>/AC and (B) RuO<sub>2</sub>/ZSM5. Reaction conditions: 50 ppm, 1 g Oxone<sup>®</sup>, 0.2 g catalyst, 25 °C.

RuO<sub>2</sub>/AC exhibited higher activity than RuO<sub>2</sub>/ZSM5, which can be attributed to several factors. Fig. 5 shows that RuO<sub>2</sub>/AC presented much high adsorption of phenol than RuO<sub>2</sub>/ZSM5. This will promote surface reaction of phenol with sulfate radicals. Our previous investigation showed that AC could induce activation of PMS to produce SO<sub>5</sub><sup>•-</sup> [11], which can result in more reduction of phenol. In addition, the multi-valent Ru species (Ru and RuO<sub>2</sub>) on AC could induce fast transformation of Ru and promote redox reactions of Ru (Ru–RuO<sub>2</sub>) with PMS for formation of sulfate radicals.

Both RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5 catalysts were also tested after their regeneration by water washing for multiple uses. It can be seen in Fig. 6 that, both catalysts showed somewhat deactivation in the second and third runs. However, the deactivation was not so significant. Complete removal of phenol could still be achieved within 1 h for RuO<sub>2</sub>/AC and 2 h for RuO<sub>2</sub>/ZSM5, respectively. The deactivation occurs presumably due to adsorption of intermediates and a small portion of loose ruthenium leaching from the supports of AC and ZSM5. Our previous investigations also showed that Co<sub>3</sub>O<sub>4</sub>/AC and Co<sub>3</sub>O<sub>4</sub>/ZSM5 presented strong stability in activation of PMS for phenol degradation, which is attributed to strong chemical binding of metal with the supports [5,10].

For the reaction kinetics, a general equation of the pseudo first order kinetics was used, as shown in the following equation.

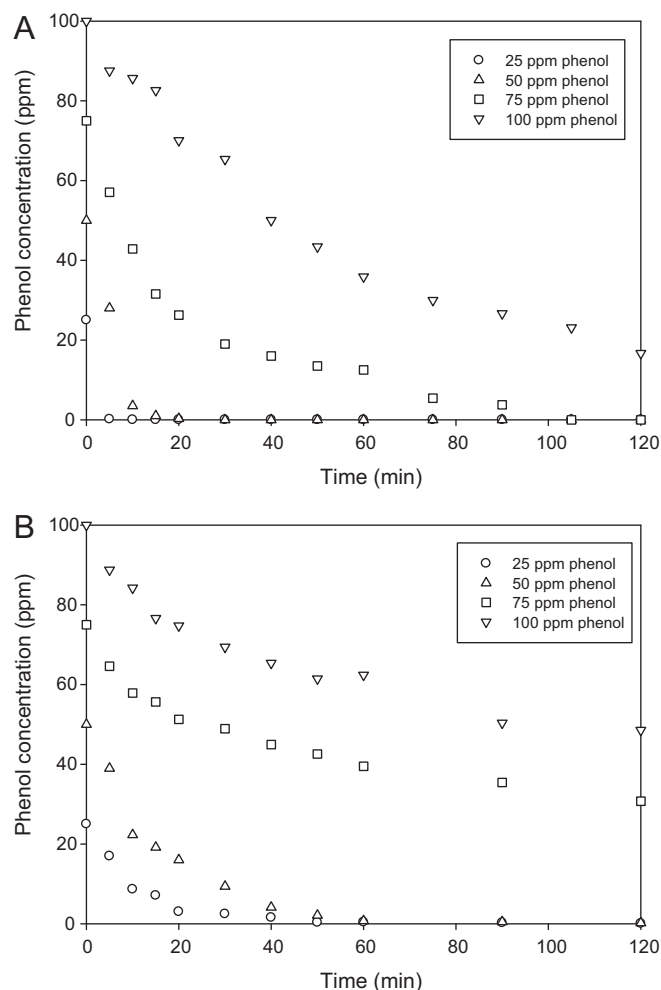
$$C = C_0 \cdot e^{-k \cdot t} \quad (7)$$

**Table 2**  
Kinetic constants of phenol degradation at different runs.

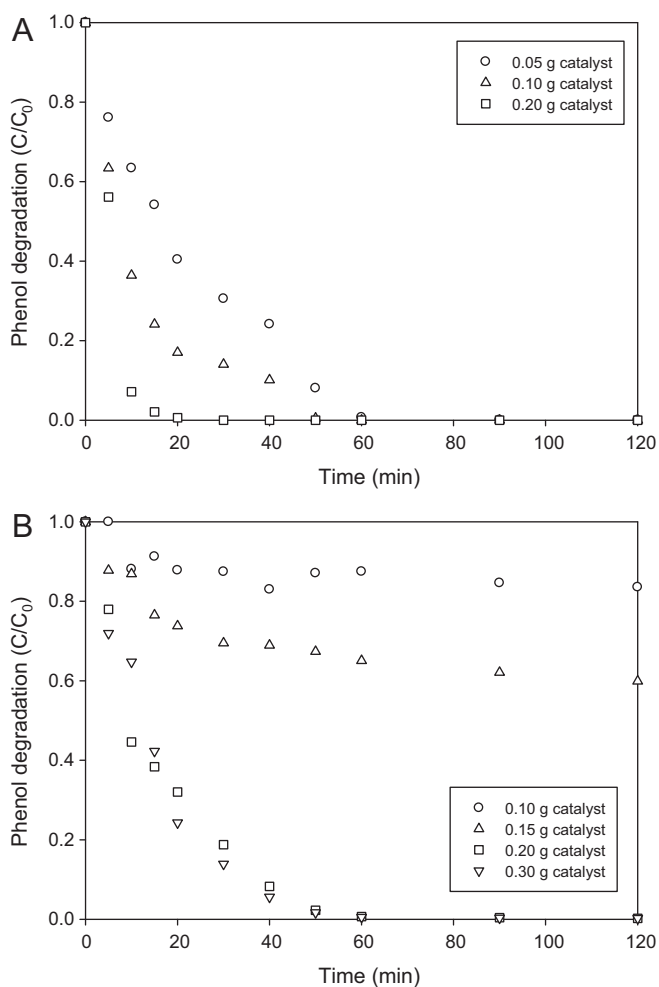
Catalyst	Test	K (min <sup>-1</sup> )	R
RuO <sub>2</sub> /AC	1st run	0.174	0.983
	2nd run	0.130	0.990
	3rd run	0.0928	0.987
RuO <sub>2</sub> /ZSM5	1st run	0.0631	0.994
	2nd run	0.0487	0.993
	3rd run	0.0376	0.997

Where  $K$  is the first order rate constant of phenol removal,  $C$  is the concentration of phenol at various time ( $t$ ),  $C_0$  is the initial concentration of phenol.

Fig. 6 also shows the first order kinetics fitting to experimental data and the kinetic constants are presented in Table 2. As seen, the experimental data were well fitted by the first-order kinetics with regression coefficients higher than 0.980. The rate constants ( $K$ ) for RuO<sub>2</sub>/AC are higher than those of RuO<sub>2</sub>/ZSM5, which means RuO<sub>2</sub>/AC is able to degrade phenol more rapidly. Several heterogeneous Co catalysts have been tested in PMS activation for phenol degradation. It was found that phenol degradation on Co/SiO<sub>2</sub> [15] and Co/ZSM5 [10] presented zero order kinetics while Co/AC showed the first order kinetics [11].



**Fig. 7.** Effect of phenol concentration on phenol removal. (A) RuO<sub>2</sub>/AC and (B) RuO<sub>2</sub>/ZSM5. Reaction conditions: 1 g Oxone<sup>®</sup>, 0.2 g catalyst, 25 °C.



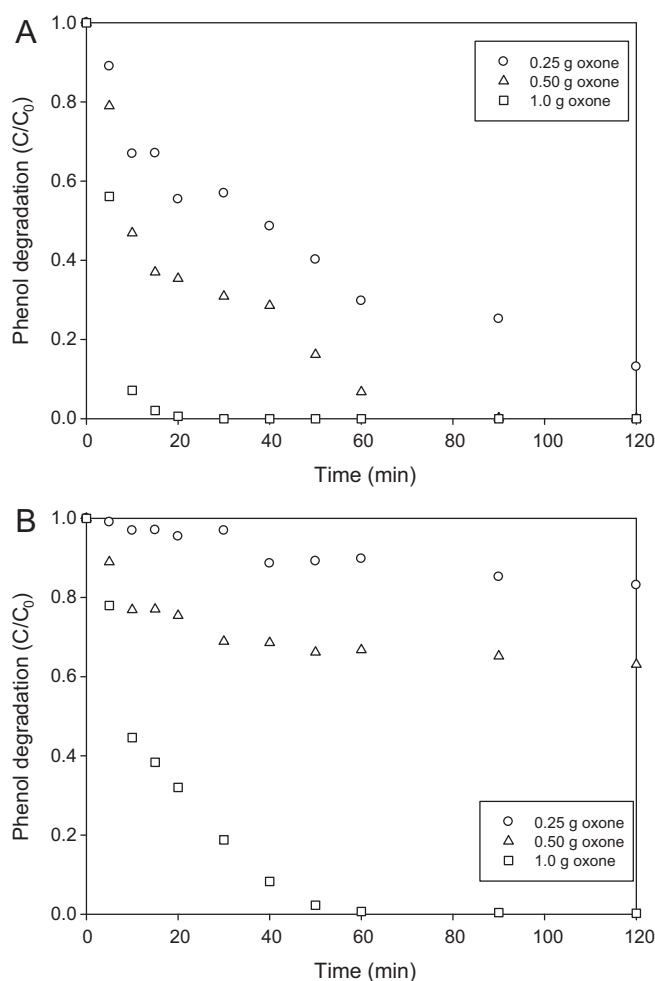
**Fig. 8.** Effect of catalyst loading on phenol removal, (A) RuO<sub>2</sub>/AC and (B) RuO<sub>2</sub>/ZSM5. Reaction conditions: 50 ppm, 1 g Oxone<sup>®</sup>, 25 °C.

### 3.3. Effects of reaction parameters on phenol removal

The first parameter measured in this study was phenol concentration which was maintained between 25–100 ppm. Fig. 7 shows variation of phenol concentration with time at different initial concentrations. Removal efficiency of phenol decreased with increasing phenol concentration. For RuO<sub>2</sub>/AC, 100% removal of phenol could be achieved within 20 min at low phenol concentrations (25–50 ppm). However, phenol removal was reduced at about 83% in 2 h for 100 ppm phenol. A similar trend can also be seen in Fig. 7B using RuO<sub>2</sub>/ZSM5. At phenol concentration of 25–50 ppm, complete removal occurred within 60 min, but for phenol concentration of 100 ppm, removal efficiency was only 52% within 2 h.

In phenol degradation, production of sulfate radicals is the key reaction, which depends on Ru catalysts and PMS (Eqs. (4) and (5)). Under the same loading of catalyst and PMS, high phenol concentration would take more time to be degraded, resulting in lower removal efficiency of phenol.

Fig. 8 shows the effect of catalyst loading on phenol degradation. High catalyst loading in solution would result in higher phenol reduction. This phenomenon is reasonable, because increasing the amount of catalyst will increase the adsorption and also the available catalyst sites to activate PMS. Therefore, the addition of catalysts will increase reaction rate significantly. For RuO<sub>2</sub>/AC at 0.1–0.4 g/L, complete removal could be achieved within 60 min. For RuO<sub>2</sub>/ZSM5, phenol removal was much lower at 0.2–0.3 g/L, but it increased significantly at 0.4–0.6 g/L. At the loading of 0.4–0.6 g/L

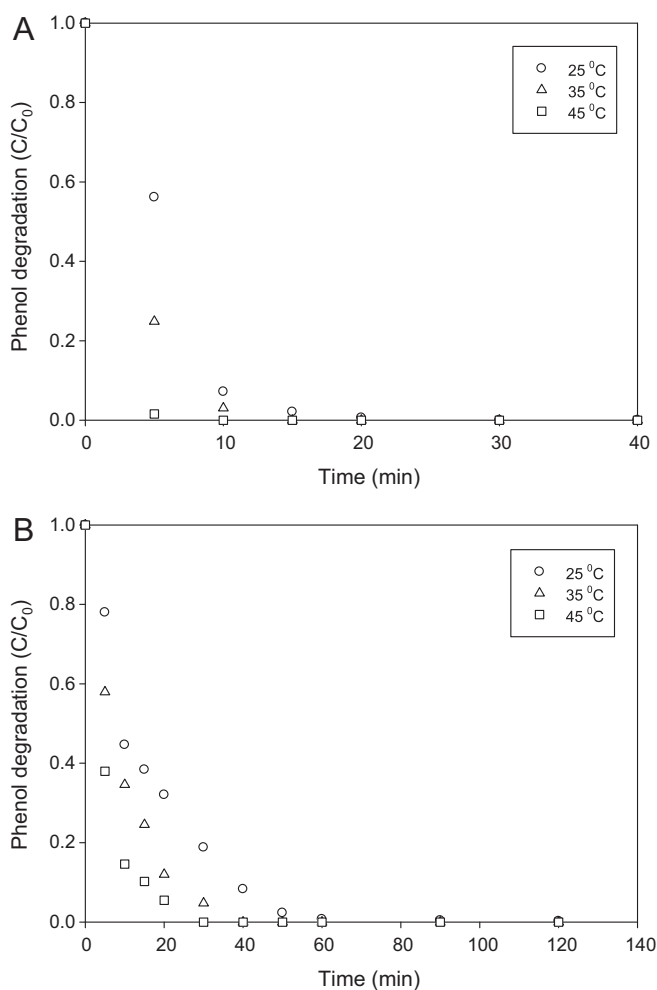


**Fig. 9.** Effect of Oxone<sup>®</sup> concentration on phenol removal, (A) Ru/AC and (B) Ru/ZSM5. Reaction conditions: 50 ppm, 0.2 g catalyst, 25 °C.

RuO<sub>2</sub>/ZSM5 in solution, phenol removal was similar and complete removal could happen in 60 min suggesting an optimal loading of RuO<sub>2</sub>/ZSM5 to be 0.4 g/L.

Fig. 9 shows that increased concentration of PMS in a solution will accelerate phenol removal significantly on RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5. For example, at 0.5 g Oxone<sup>®</sup>, complete removal of phenol could be achieved in about 90 min. However, an increase in phenol degradation would be very fast when 1 g Oxone<sup>®</sup> was used where the complete removal occurred within 20 min, an increase of phenol removal rate as high as 4 times. A similar change was seen in Fig. 9B for RuO<sub>2</sub>/ZSM5. Complete removal was not obtained within 2 h at 0.25 and 0.5 g Oxone<sup>®</sup> in solution. In contrast, at 1 g Oxone<sup>®</sup> in solution, complete removal of phenol could occur in about 60 min. The increase of reaction rate at the increased Oxone<sup>®</sup> concentration is attributed to higher production rate of sulphate radicals for reducing phenol concentration.

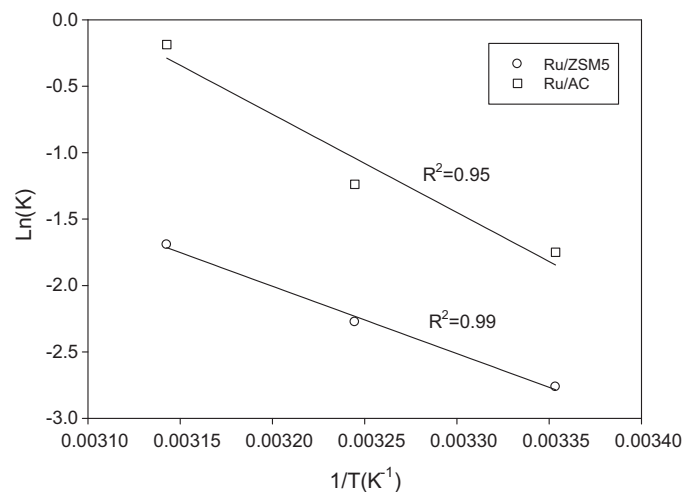
Effect of reaction temperature on phenol degradation is shown in Fig. 10. As can be seen, temperature showed quite significant impact on phenol oxidation process using either RuO<sub>2</sub>/AC or RuO<sub>2</sub>/ZSM5. An increase in temperature of 10 °C would enhance the reaction rate and phenol degradation efficiency by about two times. For example, a complete removal of phenol with Ru/AC–Oxone<sup>®</sup> at temperature of 25 °C was achieved in about 20 min. When the temperature was raised to 35 °C, complete removal of phenol would be achieved in about 10 min. Similarly, at temperatures of 45 °C, complete removal could be achieved in about 5 min. A same trend



**Fig. 10.** Effect of temperature on phenol removal, (A) RuO<sub>2</sub>/AC and (B) RuO<sub>2</sub>/ZSM5. Reaction conditions: 50 ppm, 1 g Oxone®, 0.2 g catalyst.

also occurred on Ru/ZSM5 as shown in Fig. 10B. At 45 °C, phenol degradation would reach 100% at 30 min.

Fig. 11 displays the Arrhenius plots of rate constants with temperature for RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5. As shown, the plots presented a good linear correlation and the activation energies for RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5 were derived as 61.4 and 42.2 kJ/mol,



**Fig. 11.** Arrhenius plots of phenol degradation on RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5.

**Table 3**

Activation energies of heterogeneous Co catalysts with PMS for phenol degradation.

Catalyst	Activation energy (kJ/mol)	Reference
Co/SiO <sub>2</sub>	61.7–75.5	[15]
Co/SBA-15	67.4	[29]
Co/ZSM5	69.7	[10]
Co/AC	59.7	[11]
Co/CX	48.3–62.9	[30]
RuO <sub>2</sub> /AC	61.4	This work
RuO <sub>2</sub> /ZSM5	42.2	This work

respectively. Previously, we have investigated several heterogeneous Co catalysts, Co/AC, Co/CX(carbon-xerogel), Co-exchanged ZSM5 (Co-ZSM5), and Co/SiO<sub>2</sub> in phenol degradation by Oxone®. Table 3 lists the activation energies of those catalysts. It is shown that Ru/AC has the similar activation energy as Co/AC while Ru/ZSM5 presents lower activation energy than that of Co-ZSM5.

#### 4. Conclusions

RuO<sub>2</sub>/AC and RuO<sub>2</sub>/ZSM5 are effective catalysts for activation of PMS for the production of sulphate radicals for phenol degradation. RuO<sub>2</sub>/AC has better performance of removing phenols than RuO<sub>2</sub>/ZSM5. Phenol removal on RuO<sub>2</sub>/AC is a combination of oxidation and adsorption. Both catalysts also showed good performance in the second and third runs after regeneration for multiple uses. The concentration of phenol, catalyst loading, concentration of Oxone®, and temperature are important parameters that affect the reaction rate in removing phenol. Kinetic studies showed that phenol oxidation on the catalysts, RuO<sub>2</sub>/AC or RuO<sub>2</sub>/ZSM5, follows the first order reaction with activation energies of 61.4 and 42.2 kJ/mol, respectively.

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