Article

Ruthenium Supported on Ionically Cross-linked Chitosan-Carrageenan Hybrid MnFe$_2$O$_4$ Catalysts for 4-Nitrophenol Reduction

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Abstract: Herein, we report a facile procedure to synthesize the hybrid magnetic catalyst (Ru@CS-CR@Mn) using ruthenium (Ru) supported on ionically cross-linked chitosan-carrageenan (CS-CR) and manganese ferrite (MnFe$_2$O$_4$) nanoparticles with excellent catalytic activity. The ionic gelation of CS-CR is acting as a protecting layer to promote the encapsulation of MnFe$_2$O$_4$ and Ru nanoparticles by electrostatic interactions. The presence of an active metal and a CS-CR layer on the as-prepared Ru@CS-CR@Mn catalyst was well determined by a series of physicochemical analyses. Subsequently, the catalytic performances of the Ru@CS-CR@Mn catalysts were further examined in the 4-nitrophenol (4-NP) reduction reaction in the presence of sodium borohydride (reducing agent) at ambient temperature. The Ru@CS-CR@Mn catalyst performed excellent catalytic activity in the 4-NP reduction, with a turnover frequency (TOF) values of 925 h$^{-1}$ and rate constant ($k$) of 0.078 s$^{-1}$. It is worth to mentioning that the Ru@CS-CR@Mn catalyst can be recycled and reused up to at least ten consecutive cycles in the 4-NP reduction with consistency in catalytic performance. The Ru@CS-CR@Mn catalyst is particularly attractive as a catalyst due to its superior catalytic activity and superparamagnetic properties for easy separation. We foresee this catalyst having high potential to be extended in a wide range of chemistry applications.

Keywords: Ruthenium; chitosan; carrageenan; MnFe$_2$O$_4$; 4-nitrophenol reduction

1. Introduction

Phenols and nitrophenol derivatives are toxic organic wastes that are generated or released as wastewater during the manufacturing process of agriculture, dyes, and pharmaceuticals. [1]. Due to the environmental concerns related to water disposal, water scarcity and water pollution, there is a growing interest in the transformation of these harmful organic pollutants into non/toxic composite in aqueous solutions under mild conditions [2]. Several techniques have been employed for nitrophenol degradation in polluted water, including membrane filtration, photodegradation, adsorption and chemical reduction [3–7]. Among these techniques, chemical reduction of nitrophenol is one of the
most popular techniques to address this issue due to its high efficiency [8]. The transformation of nitrophenol to aminophenol compounds is of great industrial importance. Aminophenol is an important intermediate compound in the chemical industry, especially for pharmaceuticals and bulk chemical production [8,9]. Hence, numerous studies have been carried out to develop an ideal catalytic reaction to convert nitrophenol compounds into valuable amine derivatives. Furthermore, conversion of nitrophenol to aminophenol using a reducing agent (e.g., NaBH₄, H₂O₂, NH₃·NH₃) is presently considered as a benchmark reaction to evaluate the respective catalytic behavior for a newly-prepared catalyst [10].

Recently, the reduction of 4-NP to 4-aminophenol (4-AP) over metal catalysts has been broadly studied. Many literature studies have focused on the use of noble metal nanoparticles (NPs) such as Pd, Au, Pt, and Ru for the nitroarenes reductions [11–14]. For the nitrophenol reduction, Ru metal is one of the promising noble metals in this reaction, owing to its high efficiency. Different types of Ru catalysts have been successfully exploited for many chemical reactions. Although, the homogeneous Ru catalysts usually exhibited superior reaction rates towards the 4-NP reduction, it is difficult to recover and reuse in the next reaction. Furthermore, the performance of the catalyst degrades over time as a result of agglomeration and leaking during the reduction process [15,16]. To alleviate these problems, the development of a new heterogeneous supported catalyst with a larger surface area is needed. Thus, many studies have been conducted on Ru metals impregnated on various supports, which include metal oxide, activated carbon, and dendrimers [17–19].

The development of magnetic-supported catalyst that works on a wide range of application such as C–C coupling reaction, waste water treatment, and heavy metal removal has been extensively studied [20–22]. The magnetic-supported catalysts have a magnetic nature that allows for simple separation and recovery from the reaction medium by an external magnetic field [23]. Manganese(II) ferrite (MnFe₂O₄) is a magnetic material that showed high adsorption capacity, biocompatibility, exceptional chemical stability, and high magnetic susceptibility [24].

In the recent past, the coating of magnetic nanoparticles (MNP) with polymer and other materials was explored rapidly. The coating process can act as a protecting layer to prevent the degradation of MNP during the catalytic reactions [25]. The surface modification of MNP can be easily to achieve through coating it by natural or synthetic polymers [26]. Chitosan (CS), is a natural polyaminosaccharide that has a good biocompatibility, low toxicity, and low pH sensitivity as well as containing amino and hydroxyl functional groups that could promote metal ion chelation [27]. Based on the literature, the introduction of MNP into a CS network using a cross-linker, such as tripolyphosphate (TPP) and glutaraldehyde, allows the interaction of metal NPs with the cationic CS via electrostatic interactions [28]. Kappa carrageenan, denoted as CR, is another type of polysaccharide that can be found in red seaweeds. CR has a linear structure of sulfated polysaccharide of D-galactose and 3,6-anhydro-D-galactose [29]. The crosslinking of biopolymers, CS-CR can be formed via electrostatic interaction of −NH₃⁺ cations on CS with sulfate groups (−OSO₃⁻) on CR.

In this work, we fabricated a facile synthesis of Ru@CS-CR@Mn catalysts at ambient temperature by a simple wet-impregnation technique based on ionic gelation between CS and CR and the entrapped MnFe₂O₄ as the magnetic core for magnetic separation purpose (Scheme 1). The newly-prepared Ru@CS-CR@Mn catalysts exhibited magnetic properties of the MnFe₂O₄ together with the metal adsorption capabilities of CS that would promote the immobilization of Ru metal and magnetic core. This is the first article in the literature on the synthesis of Ru@CS-CR@Mn catalysts by entrapped of Ru metal onto MnFe₂O₄ with a CS-CR matrix by an ionic gelation method. The catalytic performance of the newly-prepared Ru@CS-CR@Mn catalysts was evaluated in 4-NP reduction in mild condition.
2. Results

2.1. Characterization of Ru@CS-CR@Mn Catalyst

Figure 1 illustrated the Fourier transform infrared (FTIR) spectra of MnFe$_2$O$_4$ and Ru@CS-CR@Mn catalyst. In the FTIR spectra of MnFe$_2$O$_4$, the absorption band at 3328, 1626, 1576 and 1420 cm$^{-1}$ are ascribed to O–H stretching vibration of hydroxyl group overlapped with the N–H stretching vibration, C=O stretching of amide I, C=O stretching of amide II and C–N bending of amide III, respectively of the protecting layer of isopropanolamine (MIPA) on the surface of MnFe$_2$O$_4$ [30]. After the formation of the Ru@CS-CR@Mn catalyst, the specific bands at 1655 and 1596 cm$^{-1}$ that related to the CS materials were shifted to 1647 and 1534 cm$^{-1}$ in the spectrum of Ru@CS-CR@Mn catalyst [31]. The absorption band at 1534 cm$^{-1}$ is attributed to –NH$_3^+$ groups formed during the fabrication process. Several identical bands of CR were observed in the FTIR spectra, which is including carbohydrate overtones of the –COH stretch at 2200-2000 cm$^{-1}$, sulfate groups at 1259 cm$^{-1}$, 3,6-anhydrogalactose at 930 cm$^{-1}$, and galactose-4-sulfate at 846 cm$^{-1}$. All the results indicated the formation of CS-CR complexes between –NH$_3^+$ groups of CS and sulfates groups of CR [32–34].
The X-ray diffraction (XRD) patterns of MnFe$_2$O$_4$ and Ru@CS-CR@Mn catalyst are shown in Figure 2. The diffraction patterns for MnFe$_2$O$_4$ and Ru@CS-CR@Mn catalyst displayed a similar pattern with seven characteristic peaks at 2 theta = 18.3°, 29.8°, 35.3°, 43.0°, 53.1°, 56.2° and 62.1°, which corresponded to the (111), (220), (311), (400), (422), (511) and (440) planes of the face centered-cubic (fcc) close packing structure of the MnFe$_2$O$_4$ nanoparticles (JCPDS No. 88-1965), respectively [31]. These results suggested that the spinel structure of the MnFe$_2$O$_4$ magnetic core remains unchanged after the ionic gelation of CS-CR complex on the surface of magnetic core. Overall, the intensity of peaks of Ru@CS-CR@Mn catalyst was slightly lower than MnFe$_2$O$_4$, which confirmed the protecting layer of CS-CR on the surface of MnFe$_2$O$_4$. The diffraction peak of Ru metal was not observed in the XRD pattern of Ru@CS-CR@Mn and this may due to the Ru NPs were in an amorphous state and with very low abundance of Ru content [35]. The average crystal size of the MnFe$_2$O$_4$ in Ru@CS-CR@Mn was determined to be 12.2 nm (calculated by Scherrer formula) and this size is similar to the raw MnFe$_2$O$_4$ MNPs (~12.0 nm).

The morphology of the Ru@CS-CR@Mn catalyst was carried out by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis and the micrographs of the catalyst are presented in Figure 3. The obtained SEM micrograph showed that the Ru@CS-CR@Mn catalyst is in nanosize and the chemical composition was identified by using energy-dispersive X-ray spectroscopy (EDX), which shows that it is constituted mainly elements of C, O, Mn, and Fe (Figure 3a). The existence of Ru peak in the EDX spectrum indicated the immobilization of Ru metal in the Ru@CS-CR@Mn catalyst. Additionally, the high resolution (HR)TEM image showed the average diameter of Ru@CS-CR@Mn catalyst was 15.6 ± 0.7 nm which is larger than the MnFe$_2$O$_4$ MNPs (~9.3 nm) that reported previously [30]. To identify the Ru content, ICP-MS was used. The ICP-MS analysis indicated that the Ru@CS-CR@Mn catalyst consists of 0.46 wt. % of Ru NPs.
The magnetic properties of MnFe$_2$O$_4$ and Ru@CS-CR@Mn catalyst were investigated further by using vibrating sample magnetometry (VSM) at room temperature. The magnetic field-dependent magnetization (M–H) curve of the samples at 300 K at a magnetic field up to H = 30 000 Oe is shown in Figure 4, and the magnetic detail data is summarized in Table 1. The saturation magnetization (Ms) values obtained for MnFe$_2$O$_4$ and Ru@CS-CR@Mn catalyst were 63.3 and 38.7 emu/g, respectively. The Ms value of Ru@CS-CR@Mn was reduced compared to that of MnFe$_2$O$_4$ MNPs because of the coating layer of CS-CR complexes, which is a nonmagnetic material [36]. The coercivity ($H_C$) and remnant magnetization ($M_r$) values of MnFe$_2$O$_4$ are 15.0 Oe and 1.7 emu/g, respectively. By contrast, the $H_C$ and $M_r$ values for Ru@CS-CR@Mn are 15.9 Oe and 1.7 emu/g, respectively. Both of the samples showed a very low squareness ratio ($M_r/M_s$) (0.027 and 0.044 for MnFe$_2$O$_4$ and Ru@CS-CR@Mn, respectively) which confirms the superparamagnetic behavior of samples [37].

**Figure 3.** (a) Scanning electron microscopy (SEM) image (inset: energy-dispersive X-ray spectroscopy (EDX) spectrum) and (b) high resolution transmission electron microscopy (HRTEM) image of Ru@CS-CR@Mn catalyst.

**Figure 4.** Applied magnetic field-dependent magnetization (M–H) curve of the samples at 300 K in the magnetic field range of −30000 to 30,000 Oe (insert image: separation and re-dispersion of Ru@CS-CR@Mn).
Table 1. Magnetic properties of samples.

| Materials   | $M_S^{300\,\text{K}}$ (emu/g) | $M_r^{300\,\text{K}}$ (emu/g) | $H_c$ (Oe) | $M_r/M_S$ Ratio |
|-------------|-------------------------------|-------------------------------|------------|-----------------|
| MnFe$_2$O$_4$ | 63.3                          | 1.7                           | 15.0       | 0.027           |
| Ru@CS-CR@Mn | 38.5                          | 1.7                           | 15.9       | 0.047           |

2.2. Catalytic Performance Test of Ru@CS-CR@Mn Catalyst

The reduction of 4-NP to 4-AP is an ideal model catalytic reaction to determine the catalytic activity of metal nanoparticles in aqueous solution [10]. Thus, the catalytic activity of the as-prepared Ru@CS-CR@Mn catalyst was evaluated in the 4-NP reduction reaction in aqueous solution with NaBH$_4$ as a reducing agent. Because of the highly excess amount of NaBH$_4$ that was used, the reduction rate can be assumed to be independent of the concentration of NaBH$_4$ and thus, the reduction rate can be calculated based on pseudo-first-order kinetics [31]. The rate constant of the catalyst ($k$) was calculated from the slopes of the linear ranges of the $\ln(A_t/A_0) = -kt$ plots, where $A_t$ and $A_0$ are refer to the 4-NP concentrations at time $t$ and 0, respectively (Figure 5) [38] For a better comparison, the turnover frequencies (TOF) value was also calculated from the rate constant, $k$ according to the equation: $\text{TOF} = k \frac{n_0\text{4-NP}}{n_{Ru}}$, where $n_0\text{4-NP}$ is the starting concentration of 4-NP substrate and $n_{Ru}$ is the amount of Ru in the nanocatalyst (Based on the Ru content obtained from ICP-MS analysis).

![Figure 5. (a) UV-Vis spectra of the 4-NP with and without the presence of NaBH$_4$. (b) UV-Vis spectra of the 4-NP reduction catalyzed by the 1.0 mg of Ru@CS-CR@Mn catalyst and (c) plot of $\ln(A/A_0)$ against the completion time ($t$) for the reduction of 4-NP.](image-url)
The 4-NP reduction reaction progress was monitored by UV-Vis spectroscopy. As can see in Figure 5a, the strong absorption peak at 400 nm is belonged to 4-nitrophenolate ion, which formed after addition of NaBH₄ into the 4-NP solution. In the absence of Ru@CS-CR@Mn catalysts, the peak at 400 nm remains unchanged for over two hours (not show). The intensity of absorption peak at 400 nm was progressively decreased upon increase of the reaction time. Meanwhile, a small new peak was gradually increased in intensity at 300 nm, which indicated the 4-NP was reduced to 4-AP [39]. Furthermore, the 4-NP reduction reaction progress can be monitored visually based on the color changes from yellowish solution (4-NP) to colorless solution (4-AP).

In Figure 5b, the 4-NP reduction reaction took approximately 60 s to complete after addition of 1.0 mg of Ru@CS-CR@Mn catalyst with a rate of constant of 0.078 s⁻¹. The kinetic profile of Ru@CS-CR@Mn-catalyzed 4-NP reduction confirmed the reduction showed a good linear relationship with the first-order kinetics as mention previously (Figure 5c). In a control experiment, MnFe₂O₄ exhibited very low catalytic activity (k = 0.00055 s⁻¹) toward 4-NP reduction [31]. The control experiment in the absence of catalyst has been carried out and the results showed that the intensity of 4-NP absorption remains unchanged (data not shown). These findings indicated that the 4-NP reduction reaction is strongly depended on the active metal used.

Besides, the TOF value is one of the parameter used for comparing the catalyst performance [40]. The TOF value of the Ru@CS-CR@Mn catalyst in the 4-NP reduction was 925 h⁻¹. The TOF values of the Ru@CS-CR@Mn catalyst and other noble catalysts are listed in Table 2. The result shows that the TOF value of Ru@CS-CR@Mn catalyst is superior to some other noble catalyst (Pd, Ag, Au) in 4-NP reduction reaction except for Ru colloidal solutions that reported previously [15,41–46]. Thus, these data proved that Ru@CS-CR@Mn has superior catalytic activity in a reduction reaction of 4-NP.

| Catalyst            | Metal Loading | Completion Time (s) | Rate Constant (s⁻¹) | TOF (h⁻¹) | Reference |
|---------------------|---------------|---------------------|---------------------|-----------|-----------|
| Ru colloidal solution | -             | 840                 | 16.8                | 4800      | [15]      |
| Pd/PdO             | 9.5 wt. %     | 240                 | 0.01                | 750       | [41]      |
| Pd-CeO₂            | 2.15 wt. %    | 120                 | -                   | 335       | [42]      |
| Pd NP/CNT-220      | 1.69 wt. %    | 300                 | 0.01                | 18        | [43]      |
| Ag@micelle-2       | 5.0 mg mL⁻¹   | 80                  | 0.02                | 48.7      | [44]      |
| Ag-OMS-C           | 3.86 wt. %    | 150                 | 0.03                | 91.2      | [45]      |
| AuNPs-SPEG         | -             | -                   | 0.035               | 1.14      | [46]      |
| Ru@CS-CR@Mn       | 0.46 wt. %    | 60                  | 0.078               | 925       | This work |

The reusability performance of Ru@CS-CR@Mn catalyst for the 4-NP reduction under the same conditions was evaluated. The results revealed that Ru@CS-CR@Mn catalyst could be reused for 10 cycles with almost 100% 4-NP conversion (Figure 6). The reaction rate for the reduction reactions gradually decreased whereas the completion time was slightly increased. This may probably occur due to the catalyst loss or aggregation of the catalysts during the reusability test [33]. Nevertheless, the results confirmed the Ru@CS-CR@Mn catalyst possesses robust stability not less than 10 consecutive cycles in the 4-NP reduction process.
Figure 6. Reusability of Ru@CS-CR@Mn catalyst for 10 consecutive cycles: (a) rate constant, (b) 4-NP conversion and (c) completion time.

After the reusability test, the used Ru@CS-CR@Mn nanocatalyst was denoted as Ru@CS-CR@Mn_4NP was characterized by XRD analysis. The XRD diffractogram of Ru@CS-CR@Mn_4NP did not show obvious changes compared with the fresh Ru@CS-CR@Mn catalyst, which indicated the high stability performance of the catalyst during the reusability test (Figure 7).

Figure 7. XRD patterns of Ru@CS-CR@Mn and Ru@CS-CR@Mn_4NP catalyst.
3. Materials and Methods

3.1. Materials

k-carrageenan was commercially obtained from Takara Corporation Sdn. Bhd. (Sabah, Malaysia). Chitosan, CS (medium molecular weight, 75–85% deacetylated), manganese(II) chloride tetrahydrate (98%), ruthenium(III) chloride hydrate (ReagentPlus), isopropanolamine (93%), 4-nitrophenol, 4-NP (+99.5%), sodium borohydride (98%), were obtained from Sigma Aldrich. Iron(III) chloride hexahydrate (for analysis) and HCl (37%, analytical grade) were purchased from Merck (Darmstadt, Germany). Acetone (analytical grade) was obtained from Fisher Chemical (Loughborough, UK). Deionized water was used throughout the experiments. All reagents were of analytical reagent grade and used without further purification.

3.2. Preparation of MnFe\textsubscript{2}O\textsubscript{4} Nanoparticles

MnFe\textsubscript{2}O\textsubscript{4} magnetic nanoparticles were prepared by the coprecipitation method that developed by Pereira et al [30]. Generally, MnCl\textsubscript{2}·4H\textsubscript{2}O (10 mmol) were mixed with 5 ml of HCl (0.1 M, 1:4 v/v), and FeCl\textsubscript{3}·6H\textsubscript{2}O (20 mmol) were dissolved in 40 ml of water. Both solutions were heated to 50 °C and then quickly added into 200 ml of MIPA (3.0 M) solution. The reaction mixture was then heated to 100 °C and continued stirring for 2 h. The freshly as-prepared MnFe\textsubscript{2}O\textsubscript{4} nanoparticles, denoted as Mn, were isolated by external magnet and dried under vacuum at room temperature overnight.

3.3. Preparation of Ru@CS-CR@Mn Catalyst

The Ru@CS-CR@Mn was synthesized according to a modification of a method described by Grenha et al. and Calvo et al. by ionic complexation of chitosan-carrageenan (CS-CR) materials [32,47]. The CS-CR matrix was formed by an electrostatic interaction of CS with CR, in which the amino groups (–NH\textsuperscript{3+}) of CS will interact with the sulfate groups (–OSO\textsubscript{3}–) of CR (Scheme 1). Generally, RuCl\textsubscript{3} (20 mg) was added in acetic acid solution (25 mL, 0.5%, v/v) and then the Mn (100 mg) was dispersed in the acetic acid solution by ultrasonication for 1 min. CS (5 mg/mL) was dissolved in the same acetic acid solution and kept under stirring at ambient temperature for 1 h. 10 mL of CR solution (1 mg/mL) was added dropwise into the CS solution. The formed product was collected, washed and dried under vacuum at 40 °C overnight. The product was expressed as Ru(III)@CS-CR@Mn. Afterward, the Ru(III)@CS-CR@Mn was dispersed in a fresh NaBH\textsubscript{4} solution (0.1 M, 10 mL) under continuous stirring for 3 h at room temperature (28 ± 2 °C). The material was separated, washed and dried under vacuum for overnight. The final reduced catalyst was represented as Ru@CS-CR@Mn and subjected to further analysis.

3.4. Characterization

The X-ray power diffraction patterns were examined with a Bruker D8-Advanced diffractometer in the range of 2 theta = 10° to 80°. Inductively coupled plasma mass spectrometry (ICP-MS) was examined by using a Perkin Elmer ELAN 9000 ICP mass spectrometer. Fourier transform infrared spectra were collected with Agilent Technologies Cary 630 FTIR spectrometer in the range of 650–4000 cm\textsuperscript{-1}. High-resolution transmission electron microscopy (HRTEM) images were obtained from FEI TECNAI G2 F20 X_Twin High-resolution transmission electron microscope at 200 kV. Field emission scanning electron microscopy (FESEM) was performed with a Merlin Compact Zeiss scanning electron microscope and VSM analysis was examined with LakeShore 7404 series vibration sample magnetometer. UV-Vis spectra were collected with a Shimadzu UV-2450 UV-Vis spectrophotometer.

3.5. Reduction of 4-NP to 4-AP

Catalytic activity of Ru@CS-CR@Mn was examined in the reduction of 4-nitrophenol (4-NP) in the presence of NaBH\textsubscript{4} (reducing agent) at ambient temperature. Briefly, 5.67 mg of NaBH\textsubscript{4} (0.15 mmol)
was added to 3 mL of 0.05 mM 4-NP solution, resulting in a yellow-green solution of 4-nitrophenolate. Then, 1.0 mg of Ru@CS-CR@Mn was then added to the solution and the conversion of 4-NP to 4-AP was started immediately. The reduction of 4-NP was monitored by UV-Vis spectrometer.

4. Conclusions

In summary, we have successfully developed a simple and efficient procedure for the synthesis of the hybrid magnetic catalyst (Ru@CS-CR@Mn) using Ru supported on ionically cross-linked CS-CR and MnFe$_2$O$_4$ nanoparticles, which displayed superior catalytic activities toward 4-NP reduction. The reduction of 4-NP only took 60 s to achieve a ~100% conversion with the TOF value of 925 h$^{-1}$. Furthermore, Ru@CS-CR@Mn exhibited superparamagnetic properties that allow the catalyst easy separated from the reaction medium. The Ru@CS-CR@Mn catalyst demonstrated a very consistent catalytic performance in the 4-NP reduction and was capable for at least 10 cycles, probably because of the highly active of Ru metal in the catalyst. Hence, the newly-prepared catalyst is a very efficient and stable catalyst, and thereby shows potential it could be extended for other catalytic applications.

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