

Synthesis and Characterization of Cobalt(II) Salicylalimine Complex Supported on Silica Covered Magnetite

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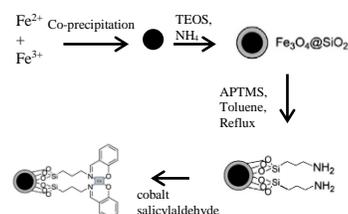
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Graphical abstract



Abstract

Cobalt Schiff base complex is widely used in many reactions such as reduction process, carbonylation of alcohol and oxidation of alkenes. Generally, this catalyst is in the powder form. It is difficult to separate the catalyst from the reaction mixture due to the small particles size of the catalyst. One way to easily separate the catalyst is by applying external magnetic field. However these catalysts would have to possess magnetic properties for this method to work on. One of the strategies to solve this problem is by adding magnetic material into the catalysts. Magnetite is a common magnetic material used as a support material which can be synthesized by the co-precipitation method of Fe²⁺ and Fe³⁺. Normally, magnetite is covered by silica in order to stabilize and reduce its toxicity. This can be done by using the sol-gel approach. Silica coated magnetite is widely used as a support material because of its high surface area and easy catalyst separation after the reaction simply by applying an external magnetic field. In this research, cobalt Schiff base complex/silica@magnetite was synthesized from the condensation of cobalt (II) salicylaldehyde with 3-aminopropyltrimethoxy silane on the surface of silica@magnetite. The catalysts were characterized using Fourier transform infrared spectrometer, scanning electron microscopy and diffuse reflectance ultra-violet visible spectrometry.

Keywords: Schiff base complex/silica@magnetite

Abstrak

Kompleks bes Kobalt Schiff digunakan secara meluas dalam sebilangan besar tindak balas seperti proses penurunan, karbonilasi alkohol dan pengoksidaan alkena. Secara praktikalnya, mangkin ini adalah dalam bentuk serbuk. Ini menyukarkan pemisahan mangkin dari campuran tindak balas disebabkan oleh saiz zarahnya yang kecil. Salah satu cara untuk memudahkan pemisahan mangkin ini adalah dengan menggunakan medan magnet luar. Akan tetapi masalahnya ialah mangkin ini tidak mempunyai sifat magnet. Salah satu strategi untuk menyelesaikan masalah ini adalah dengan menambah bahan magnet ke dalam mangkin ini. Magnetit adalah bahan magnet yang biasa digunakan sebagai bahan sokongan yang boleh disintesis dengan menggunakan kaedah sepemendakan Fe²⁺ dan Fe³⁺. Biasanya, magnetit akan disaluti oleh silika untuk menstabilkan dan mengurangkan ketoksikan. Ia boleh dilakukan dengan menggunakan pendekatan sol-gel. Magnet bersalut silika digunakan secara meluas sebagai bahan sokongan kerana kawasan permukaan yang tinggi dan mudah dipisahkan selepas tindak balas dengan hanya menggunakan medan magnet luar. Dalam kajian ini, kompleks bes kobalt Schiff /silika@magnetit telah disintesis daripada pemeluwapan kobalt(II) salisilaldehida dengan 3-aminopropiltrimetoksilana di permukaan silika@magnetit. Mangkin ini telah disifatkan dengan menggunakan spektroskopi infra-merah transformasi Fourier, mikroskopi pengimbasan elektron dan spektroskopi pantulan serakan ultralembayung-cahaya nampak.

Kata kunci: Kompleks bes kobalt Schiff/silika@magnetit

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1.0 INTRODUCTION

Transition metal complexes are widely used as a catalyst in oxidation reaction especially in chemical industry. Among all of the transition metals, cobalt complexes are particularly good in oxidizing olefin. The reason is because cobalt(II) is a good oxygen transfer agent [1]. Recently, there are many reports on synthesizing transition metal with Schiff base ligand because of their high catalytic activity [1]. Cobalt(II) bis(salicylalimine) is also commonly known as cobalt Schiff base complex. This complex is a stable as the ligand is a chelating ligand, which contains two donor atoms within one structure [2]. Since it shows high catalytic activity, Schiff base complexes can act as catalyst in many reactions for example in ring opening of the large cycloalkenes. It can easily catalyze this reaction with considerable enantioselectivity. These types of complexes also had been applied in reduction process in which ketones are converted to alcohols and for alkylation of allylic substrate. Moreover, many researchers have also reported that cobalt-salen complexes immobilized on mesoporous MCM-41 produced a very active and stable heterogeneous catalyst [3-4].

Many researchers have reported strategies to tune the hydrophobic properties of complex such as transition metal schiff-base complexes chemically anchored on Y-zeolite [3]. The partial modification by chemically anchoring Y-zeolite with Schiff-base transition metal compounds makes these catalysts amphiphilic and facilitated its accommodation at the phase boundary of aqueous H_2O_2 (hydrophilic phase) and organic substrate (hydrophobic phase) [3].

In this paper, we reported the synthesis and characterization of cobalt (II) salicylalimine complex supported on silica covered magnetite.

2.0 EXPERIMENTAL

2.1 Synthesis of Magnetite (Fe_3O_4)

The magnetic nanoparticles were synthesized by using chemical co-precipitation method of Fe^{3+} and Fe^{2+} in the presence of NaOH. 5.6026 g of $FeSO_4 \cdot 7H_2O$ and 8.2063 g of $FeCl_3 \cdot 6H_2O$ were weighed and dissolved in 40 mL of deionized water in a beaker. This solution was then stirred, followed by addition of 3M NaOH solution dropwise at $30^\circ C$ until the pH of the mixture reached 11. Then the mixture was heated at $80^\circ C$ for 30 minutes. The product was stored in the liquid form in order to be used in next reaction

2.2 Synthesis of Silica Covered Magnetite ($SiO_2@Fe_3O_4$)

Silica coated magnetite nanoparticle were synthesized by using sol-gel/Stober method. In this method, silica was formed on colloidal magnetic nanoparticles in a basic alcohol and water mixture. 2 g of magnetite solution was diluted with 30 mL of deionized water, ethanol 96% and ammonia solution. 10 mL of tetraethylorthosilicate (TEOS) was added drop wise to the mixture under stirring. The mixture was continuously stirred overnight. The product was collected by applying an external magnetic field and washed with ethanol, before leaving to dry at room temperature.

2.3 Preparation of 3-APTMS Functionalized Silica Covered Magnetite

0.2g of $SiO_2@Fe_3O_4$ was disperse in 20 mL of toluene and sonicated for 5 minutes. After that, 0.002mol of 3-APTMS was

added drop-wise into the mixture and refluxed for overnight. The mixture was left for 1 day before removing the solvent. The solid was then washed with ethanol.

2.4 Preparation of Cobalt (II) Salicylaldehyde

Cobalt(II) chloride hexahydrate (0.001 mol) was dissolved in 15 mL of ethanol. Then the cobalt salt was added drop-wise to salicylaldehyde (0.002 mol) in 20 mL of ethanol. The reaction mixture was stirred for 24 hours.

2.5 Synthesis of cobalt (II) salicylalimine complex/ $SiO_2@Fe_3O_4$

3-APTMS/ $SiO_2@Fe_3O_4$ was dispersed in 10 mL of ethanol. Then, the solution was added dropwise into the cobalt(II) salicylaldehyde (0.002 mol) containing molecular sieve. This reaction was carried out in an ultrasonic bath. The reaction mixture was sonicated for 30 minutes and left at room temperature for 1-2 days. Then the molecular sieve was removed and the product was washed using ethanol followed by hexane. The product was dried at temperature of $50-60^\circ C$ for 1 hour in the oven.

3.0 RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) images of magnetite (Fe_3O_4), silica covered magnetite ($SiO_2@Fe_3O_4$) and cobalt Schiff base complex coated silica magnetite (cobalt complex/ $SiO_2@Fe_3O_4$) are shown in Figure 1. The morphology of these three samples is quite similar. The shape of the samples is spherical and they tend to agglomerate. The size of the particle is in the nano range. Since they are in nanosize, they should have a high surface area, which can increase the interaction between the reactant with the active sites at the surface of the catalyst.

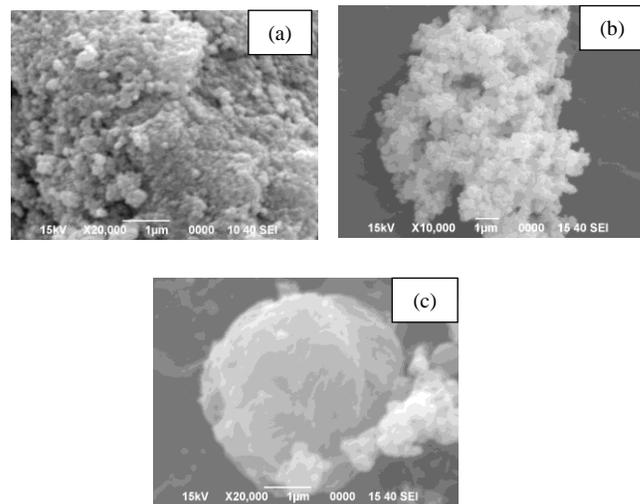


Figure 1 SEM images of (a) Fe_3O_4 , (b) $SiO_2@Fe_3O_4$ and (c) Cobalt complex/ $SiO_2@Fe_3O_4$

Figure 2 shows the FTIR of (a) Fe_3O_4 (b) silica covered magnetite ($SiO_2@Fe_3O_4$), (c) APTMS/ $SiO_2@Fe_3O_4$ and (d) cobalt complex/ $SiO_2@Fe_3O_4$. The FTIR spectrum of magnetite (Figure 2a) presented a band at $576cm^{-1}$, which is attributed to Fe-O bond. Meanwhile, for sample silica magnetite (Figure 2b) the peak at

1000 cm^{-1} is related to the Si–O–Si, besides a peak at 576 cm^{-1} associated with the Fe–O bonds [9].

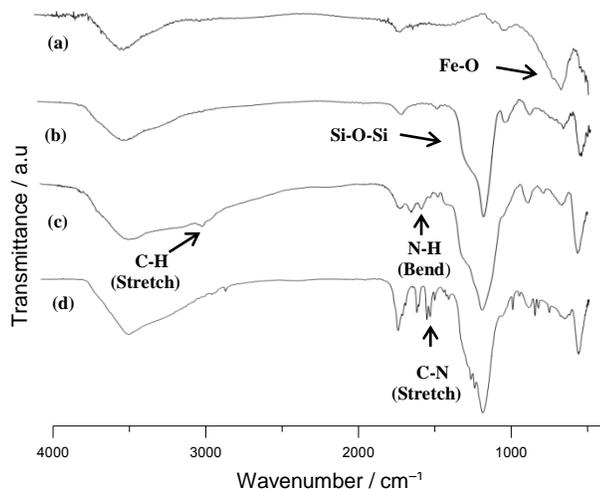


Figure 2 FTIR spectra of (a) Fe_3O_4 , (b) $\text{SiO}_2@\text{Fe}_3\text{O}_4$ (c) APTMS/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and (d) Cobalt complex/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$

The FTIR spectrum of APTMS/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$ (Figure 2c) shows the peaks of the Si–O–Si bond and Fe–O bond at $1200\text{--}900$ and 570 cm^{-1} , respectively. Besides that, a peak at $2800\text{--}2900\text{ cm}^{-1}$ is associated with the C–H alkane stretching. The peaks around 1600 and 1450 cm^{-1} are contributed by the N–H bending vibration and $-\text{CH}_2$ (bend) of alkane. As for the FTIR spectrum of the complex (Figure 2d), the characteristic peaks of Si–O–Si bond (1000 cm^{-1}) and Fe–O bond (570 cm^{-1}) can be observed.

In addition, the peaks for C–H alkane (stretching), $-\text{CH}_2$ (bend) of alkane and C–O bond at $2800\text{--}2900$, 1450 and 1300 cm^{-1} , respectively can also be observed (Figure 2d). The sharp band at 1650 cm^{-1} is assigned to $-\text{C}=\text{N}$ stretching vibration of the imine group of the ligand. This band is shifted to a higher region due to the coordination of imine moiety through nitrogen atom to cobalt metal [10].

Water absorption testing was conducted in order to investigate the ability of the catalyst in absorbing water (water capacity). Figure 3 shows the water capacity versus time for cobalt catalyst, $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and Fe_3O_4 . From this figure, it can be seen that Fe_3O_4 has the highest capacity in absorbing water with rapid increment. This indicates that Fe_3O_4 is hydrophilic and can easily adsorb water. For $\text{SiO}_2@\text{Fe}_3\text{O}_4$, the water capacity is very low. This shows that their ability to adsorb water decreased and proved that the surface of this material changed to hydrophobic. As for $\text{SiO}_2@\text{Fe}_3\text{O}_4$ functionalized with complex, the water capacity increased, indicating the surface become more hydrophilic as compared to $\text{SiO}_2@\text{Fe}_3\text{O}_4$ alone.

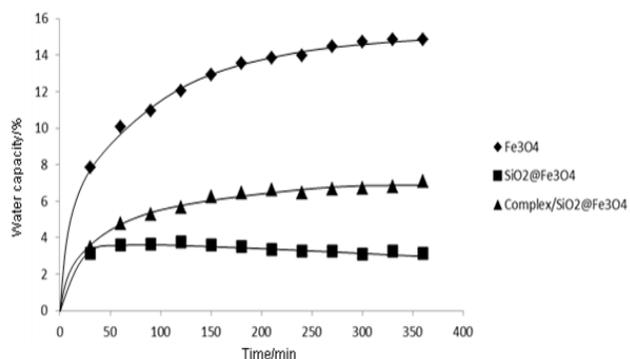


Figure 3 Graph of water capacity versus time of the catalysts

Figure 4 shows the DR-UV vis spectra of Fe_3O_4 , $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and cobalt complex/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$. The existence of cobalt complex species was proven by DR UV-Vis spectra. The spectrum of complex (Figure 4c) shows additional shoulder peak at higher wavelength at around 480 nm and 520 nm . These shoulder bands are associated with the $\pi\text{--}\pi^*$ transition of the (C=C) aromatic ring and imine (C=N) group.

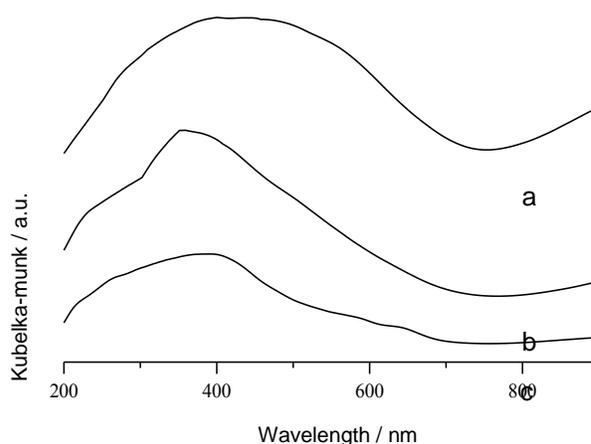


Figure 4 DR-UV vis spectra of the (a) Fe_3O_4 , (b) $\text{SiO}_2@\text{Fe}_3\text{O}_4$ (c) APTMS/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and (d) Cobalt complex/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$

4.0 CONCLUSION

Based on the FTIR and DR-UV vis spectra, magnetite, silica covered magnetite and cobalt(II) bis(salicylaldehyde) supported on silica covered magnetite were successfully synthesized. In addition, the hydrophobicity/hydrophilicity testing was conducted to compare the hydrophilicity between the catalysts. From the results, magnetite proved to be most hydrophilic followed by cobalt complex and silica covered magnetite.

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