

# Schiff-base Complexes Immobilized on the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> for Selective Oxidation of Benzyl Alcohol

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**Abstract.** Efficient and highly selective heterogeneous catalysts were prepared through grafting the metal-salen on the modified magnetic nanoparticles. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by hydrothermal synthesis, after the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was amino-functionalized using 3-aminopropyltriethoxysilane and then Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> was obtained by the reaction. Finally, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>[(EtO)<sub>3</sub>Si-L<sup>2</sup>]/Mn were successfully synthesized. These surface-modified nanoparticles were using various characterize techniques such as XRD, FT-IR and SEM. The heterogeneous catalyst showed high conversion and selectivity in the reaction of oxidation of benzyl alcohol. Furthermore, the catalysts were easily separated by the external magnetic field after the reaction, reused at least 8 consecutive cycles without significant loss catalysis activity.

## 1. Introduction

Metal Schiff-base complexes have a wide range of applications in catalysis. Schiff-base complexes coordinate with transition metal easily, and form steadily metal Schiff-base complexes with different valence state. The metal Schiff-base complexes could catalysis a lot kinds of chemical reactions, and prepare essential chemical intermediates, such as polymerization reaction [1], oxidation reaction [2-3], epoxidation reaction [4], reduction reaction [5], Michael addition reaction [6], cyclopropane reaction [7-8], ring opening reaction [9]. Homogeneous metal Schiff-base complexes have high catalytic activity. However it is difficult to separate them from the products, they are not conducive to reuse, which greatly limits the catalyst of reuse. In addition, in the process of the catalysis reaction, polymerization phenomenon can also lead to deactivation of catalyst. So the heterogenization of the homogeneous catalyst research increasingly draws people attention. Heterogenization not only can keep the structure of the homogeneous catalyst and the excellent properties, but also can avoid the disadvantage of recycling hard. At the same time, Heterogenization could show some synergistic effect, which can improve the catalyst of performance.

At present, the supporting according to their material can be divided into inorganic supporting, organic synthetic polymer supporting, natural high polymer supporting. Inorganic supports mainly including carbon nanotubes, carbon nanofibers, SiO<sub>2</sub> particles, zeolites. These supports with high specific surface area to disperse the metal Schiff-base complex greatly improve the catalytic performance. Guangxing Li encapsulated Co(salen) in NaY type molecular sieve to catalyze the oxidative carbonylation reaction of benzene ammonia under the condition of 170 °C, and high conversion and selectivity were obtained [10]. Priti Sharma grafted Mn Schiff-base complexes on the modified SBA-15 to catalyze the oxidation of sulfide [11]. Organic synthetic polymer carrier contains

polyacrylic acid polymer material, polypropylene, polyvinyl alcohol and polyethylene imine. Kim et al. prepared heteropoly nuclear complexes by inserting the metal Schiff-base complexes into the structure of the polymer to catalyze ring-opening reaction of epoxide. Alan J. McCue reported [12] epoxidation reaction catalyzed by one kind of chiral metal Schiff- base immobilized onto PAMAM polymer.

Ferroferric with the spinel structure oxide belongs to the cubic crystal system. It has good magnetic properties that make it useful in the field of magnetic storage, microwave absorbing materials, coatings with special function, drug targeting, magnetic multifunctional composite materials, biological engineering [13]. The catalyst immobilized on the magnetic materials can be recycled by the extra magnetic field, which can reduce the cost of reaction and avoid the organic solvents pollution to the environment. Magnetic nanoparticles may be synthesized by several typical methods, including coprecipitation [14], microemulsion synthesis [15], hydrothermal synthesis [16], thermal decomposition [17], sol-gel [18], and others [19]. The morphology and properties of the product vary from preparation process. People can select the suitable preparation methods to achieve the desired goal according to the need.

## 2. Experiments

### 2.1. Materials and characterization

Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), 3-Aminopropyltriethoxysilane, tetraethyl orthosilicate (TEOS), ethylene glycol, 3,5-Dinitro-2-hydroxybenzaldehyde, metal acetate, ammonia (25 wt.%) were purchased from commercial sources and used for the reaction without further purification. Thermo scientific Nicolet Magna 750 Research FT-IR Spectrophotometer. X-Ray power diffraction (XRD) pattern were carried out utilizing a Bruker D8 Advance diffractor meter equipped with Cu-K $\alpha$  radiation ( $\lambda=0.15418\text{nm}$ ) at 40 kV and 40 mA. The diffraction data were revealed under  $2\theta$  between  $10\sim 70^\circ$ . The surface morphology and microstructure of these samples was exhibited utilizing a Scanning Electron Microscope (SEM).

*2.1.1. Preparation of ligand and magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ).* The ligand was prepared according to the reported method [20-21]. The preparation of magnetic nanoparticles specific experimental steps: 1.35 g of ferric chloride hexahydrate was dissolved in 60 ml of ethylene glycol with stirring to form a clear solution. Then surface active agent and anhydrous sodium acetate (6.12 g) was added under magnetic stirring to form a uniform system. Next transferred into a Teflon-lined stainless-steel autoclave with a capacity of 100 ml, heated to  $200^\circ\text{C}$  for 10h. After cooling to room temperature the resultant solid was filtered, and the black solid products were collected and washed with ethanol and distilled water some times, respectively. Finally the products were dried in vacuum for 10 h at  $60^\circ\text{C}$ .

*2.1.2. Preparation of magnetic  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles.* Ferroferric oxide nanoparticles (1 g) were dispersed and ultrasonic in the mixture of ethanol 35 ml and deionized water 10 ml for 15 min. TEOS 1.5 ml was added slowly to the dispersion and ultrasonic for another 10 min. Then aqueous ammonia (10 %, 1.4 ml) was added slowly over 10 min under mechanical stirrer. The reaction continued for 12 h at  $40^\circ\text{C}$ . After the reaction, the silica coated magnetic nanoparticles was separated from the mixture using the extra magnetic field and washed several times with distilled water and ethanol. The products were vacuum dried for 10 h at  $60^\circ\text{C}$ . At last obtained the silica coated ferroferric oxide nanoparticles  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ .

*2.1.3. Preparation of  $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 [(\text{EtO})_3\text{Si-L}^2]/\text{Mn}$ .* For the modification step: 2 g of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  were dispersed in 100 ml of toluene. After 15 min ultrasonic processing 2 ml 3-Aminopropyltriethoxysilane were added into the suspension under nitrogen atmosphere. Then the

mixture was refluxed for 12 h. After the result solid cooled to room temperature, the products were separated by the magnetic field, and washed with a certain volume of ethanol and deionized water several times, respectively. Last the products were vacuum dried for 10 h at 100 °C. For the grafting step: The modified material was dispersed into 100 ml of acetonitrile ultrasonic for 10 min. Added 3.2 mmol 3,5-Dinitro-2-hydroxybenzaldehyde and 0.5 ml triethylamine into the suspension, then the resulted mixture was refluxed for 12 h. When it cooled room temperature, the products were removed by the extra magnetic field, washed with a certain volume of ethanol several times. The final products dried vacuum 100 °C for 10 h. The above products dispersed into the solution of 50 ml of ethanol solution containing 1.5 mmol of metal acetate. After ultrasonic for 10 min, the resulted mixture was refluxed for 10 h. While the reaction cooled room temperature, the final products were removed by the extra magnetic field, and then washed with ethanol several times and vacuum dried for 10 h at 100 °C.

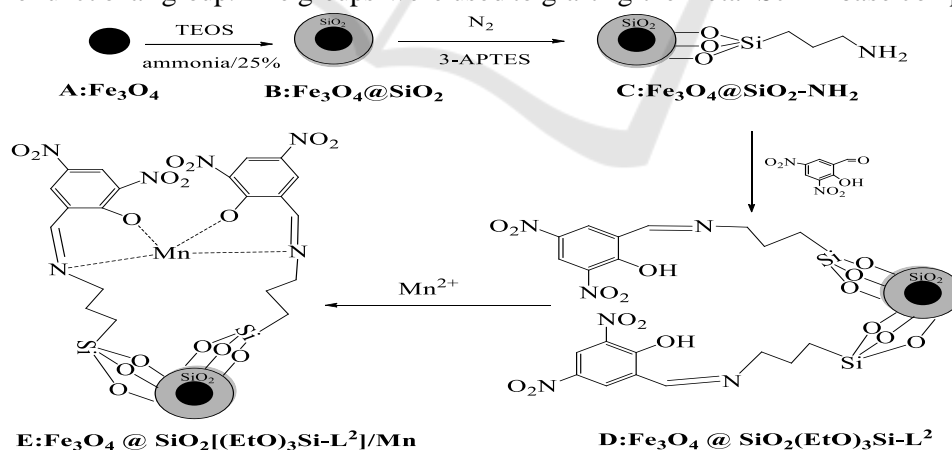
### 2.2. Test the catalytic performance

The oxidation reaction was carried out in a 50 ml round bottomed flask equipped with a condenser and a stirrer. H<sub>2</sub>O<sub>2</sub> was used as oxidation. Benzyl alcohol 0.28 mmol and 30 ml toluene, catalyst 100 mg was added into the flask. The flask was immersed into an oil bath to keep the reaction temperature at 60 °C. The reaction continued for 4 h. Then use the gen GC 800 to detect the reaction conversion and selectivity.

## 3. Results and discussion

### 3.1. Preparation and characterization of the modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> catalyst.

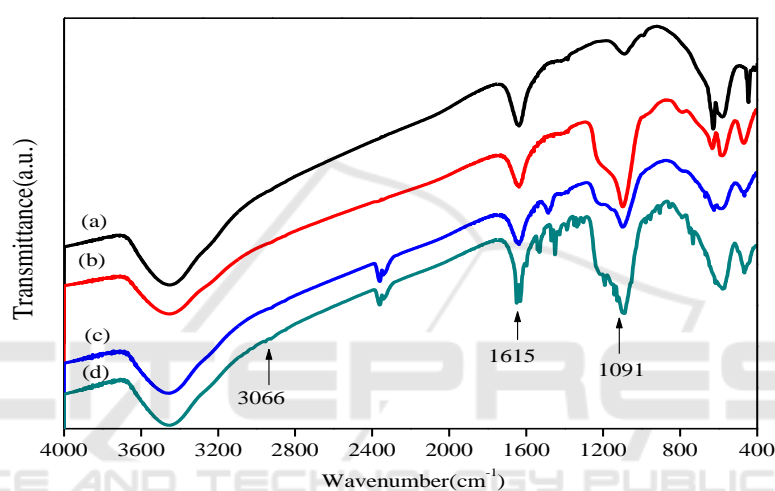
As illustrated in Figure 1 the overall procedure for the preparation of the catalyst contains three steps. Firstly, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized via a solvothermal method according to the previous report [22-23]. Secondly, a thin silica layer was coated on the surface of the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles to form Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composites through adding TEOS and aqueous ammonia (10 %). Thirdly, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composites were modified with ammonia propyl triethoxy silane to increase the functional group. The groups were used to grafting the metal Schiff-base complexes.



**Figure 1.** Catalyst preparation process: (A) Fe<sub>3</sub>O<sub>4</sub> (B) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (C) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (D) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>(EtO)<sub>3</sub>Si-L<sup>2</sup> (E) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>[(EtO)<sub>3</sub>Si-L<sup>2</sup>]/Mn.

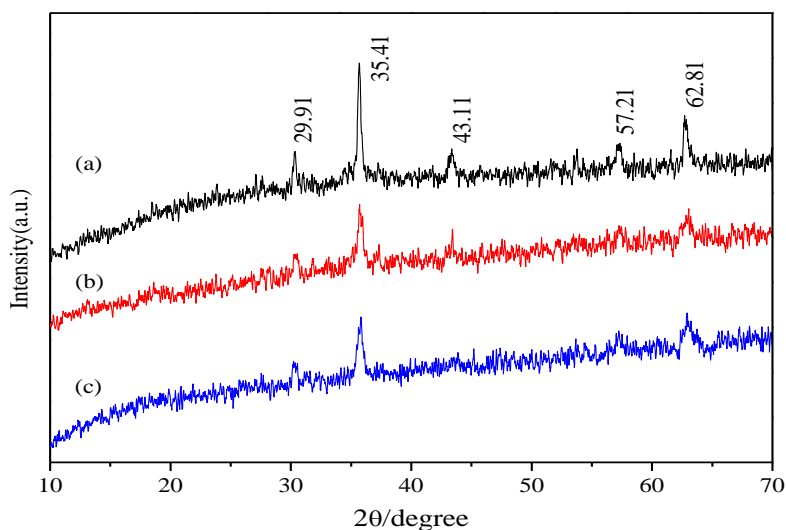
### 3.2. Characterization of the catalyst

**3.2.1. FT-IR.** The strong absorb bands related to Si–O–Si stretching vibrations was observed in all spectra at  $1000\text{--}1100\text{ cm}^{-1}$  shown in Figure 2. It is suggest that silica shell is successfully formed on the magnetic nanoparticles surface. The spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (Figure 1c) showed several signals appeared in the area of  $1450\text{--}1560\text{ cm}^{-1}$  and  $2250\text{--}2345\text{ cm}^{-1}$  which are related to C–H stretching modes of the propyl groups. These bands conformed that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was by 3-Aminopropyltriethoxysilane successfully modified. In the spectrum a band at  $1630\text{ cm}^{-1}$  associated to C=N stretching vibration [24], and some weak bands at  $3066\text{--}3040\text{ cm}^{-1}$  and  $1400\text{--}1500\text{ cm}^{-1}$  assigned to stretching vibrations of aromatic rings were observed in Figure1(d). These bands confirmed the successful anchoring of Schiff base ligand. The band at  $1615\text{ cm}^{-1}$  (Figure 1d) indicated the coordination of C=N group of complexes with Mn. Also, a new absorption band at  $529\text{ cm}^{-1}$  was assigned to Mn–N band [25].



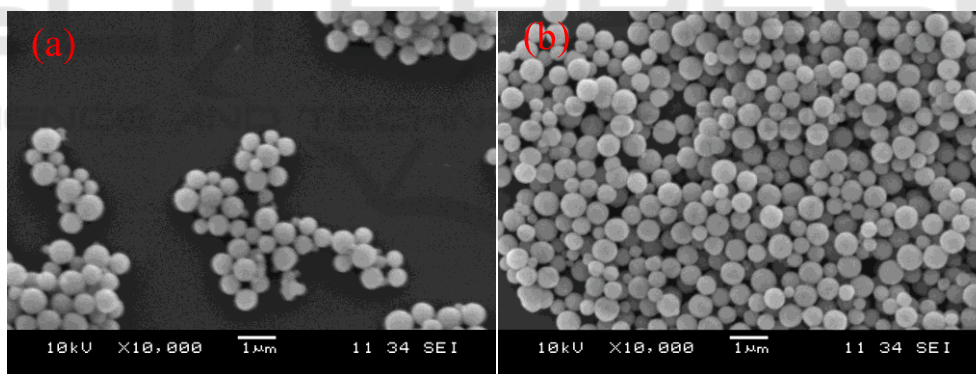
**Figure 2.** The FT-IR spectrum of (a) $\text{Fe}_3\text{O}_4$  (b) $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$  (c) $\text{Fe}_3\text{O}_4 @ \text{SiO}_2\text{-NH}_2$  and (d)  $\text{Fe}_3\text{O}_4 @ \text{SiO}_2[(\text{EtO})_3\text{Si-L}^2]/\text{Mn}$ .

**3.2.2. XRD.** From the XRD spectra of the samples in Figure 3, the characteristic diffraction peaks of the  $\text{Fe}_3\text{O}_4$  nanoparticles could be observed at  $2\theta=29.91, 35.41, 43.11, 57.21,$  and  $62.81^\circ$ , which can be assigned to cubic spinel phase of  $\text{Fe}_3\text{O}_4$  [26]. However the main peaks of  $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$  and  $\text{Fe}_3\text{O}_4 @ \text{SiO}_2[(\text{EtO})_3\text{Si-L}^2]/\text{Mn}$  exhibit no obvious changes compared to  $\text{Fe}_3\text{O}_4$ , which confirmed that the coating and grafting process didn't induce any phase change of the  $\text{Fe}_3\text{O}_4$ .



**Figure 3.** The X-ray diffraction patterns of (a) Fe<sub>3</sub>O<sub>4</sub> (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>[(EtO)<sub>3</sub>Si-L<sup>2</sup>]/Mn.

3.2.3. *SEM.* The image in Figure 4 showed the morphology change in the modification process. The image of the production after coating showed less smoothing than before, which may cause by the coating process. This could confirm the coating modification process might be successful. And after coating showed some agglomeration piece that might be the SiO<sub>2</sub>.



**Figure 4.** SEM images of Fe<sub>3</sub>O<sub>4</sub> before (a) and after coating modification (b).

### 3.3. Catalyst activity tests

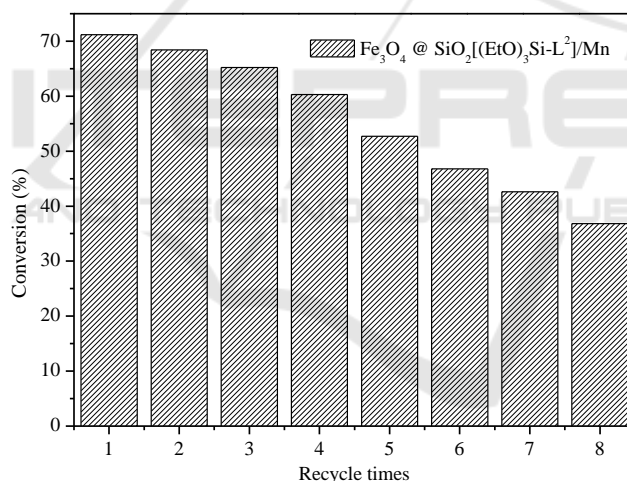
Table 1 showed performance of homogeneous catalyst and heterogeneous catalyst in selectivity oxidation of benzene methanol. From the blank experiment, the influence of the 1, 2, 3 to the catalyst could be excluded. Through comparing the entries 4 with 5, the little reduction of performance happened, which might be related with the loading amount of homogeneous catalyst. In the modification process, the loading amount was limited, so the catalysis effect decreased. Compared with other reports literature, The reaction conversion rate relatively lower. We will continue to study the catalyst performance.

**Table 1.** Test of catalysis performance.

| Entry | Catalyst                            | Conversion (%) | Selectivity (%) |
|-------|-------------------------------------|----------------|-----------------|
| 1     | $L^2$                               | 0.78           | 96.0            |
| 2     | $Fe_3O_4@SiO_2$                     | 1.2            | 97.2            |
| 3     | Mn-acetate                          | 7.5            | 95.3            |
| 4     | $Mn-L^2$                            | 74.1           | 98.6            |
| 5     | $Fe_3O_4 @ SiO_2[(EtO)_3Si-L^2]/Mn$ | 71.2           | 97.5            |

### 3.4. Catalyst life tests

Figure 5 shows the catalyst life in the recycle process. In the experiment, the recovered heterogeneous catalyst can be reused for at least 5 times at the same reaction conditions without great loss of activity. After 5 times reused, the damage of coating layer and the small part of polymerization of the Schiff base complexes may cause the decrease gradually. However the performance of the homogeneous catalyst reduced apparently in the recycle process, and they almost deactivated after the 4 times. So the immobilization can efficiently enhance the recycle capacity of the catalyst. Although catalyst can be reused eight times, and closed to reported literature, but the catalytic performance of falling fast, we will continue to further research.

**Figure 5.** Catalyst life test.

## 4. Conclusions

In this work we have shown that heterogeneous catalyst made by anchoring the metal Schiff-base on the magnetic nanoparticles coated by silica have excellent performance in the reaction of selective oxidation of benzyl alcohol. The catalyst can be reused for at least 8 times without great loss of activity. Due to the magnetic nature of the support, the catalyst was separated simply by applying an external magnet. It is not only reduced the pollution of organic solvent used in the recycle process, also is good to the practical application in industry.

## Acknowledgement

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