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Selective Catalysis for Synthesis of Benzaldehyde by Magnetic Ag/Fe_2O_3

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Magnetic Ag/Fe_2O_3 was prepared by the solvent thermal reduction method. The magnetic Ag/Fe_2O_3 was characterized by powder X-ray diffraction, scanning electron microscope and transmission electron microscopy, which suggested that the particle size was about 20 nm. The composite was used to synthesize benzaldehyde *via* the catalytic oxidation of benzyl alcohol by hydrogen peroxide. It was found that composite showed higher catalytic activity. The effects of reaction time, reaction temperature and the amount of silver in the catalyst on the reaction were investigated. The results showed that when benzyl alcohol and hydrogen peroxide was reacted for 12 h at 80 °C, silver content of 2 % mol in the catalyst, the yield of benzaldehyde was up to 61.3 %.

Keywords: Magnetic Ag/Fe_2O_3, Hydrogen peroxide, Benzyl alcohol, Benzaldehyde, Catalytic oxidation.

INTRODUCTION

Selective oxidation of alcohols to aldehydes is one of the pivotal reactions in organic synthesis. Benzaldehyde is an important intermediate for the production of perfumes, pharmaceuticals, dyestuffs and agrochemicals[1]. It can be produced by the hydrolysis of benzal chloride[2]. However, organic chlorine or benzoic acid contamination are limiting factors in high demanding uses of benzaldehyde. So it is preferable to produce benzaldehyde more selectively by catalytic liquid phase oxidation of benzyl alcohol. Hydrogen peroxide is widely used in liquid oxidation of organic compounds due to its clean and environmentally friendly nature[3-5]. But nowadays most of the catalysts for oxidation by hydrogen peroxide still have drawbacks such as uneasy separation of the reaction mixture, complicated synthesis methods, or contain polluted metals as the catalytically active site. As a result, it is a challenging subject to find magnetic separable heterogeneous catalyst which is easy prepared, environmentally benign and of low cost for the synthesis of benzaldehyde[6-7]. Herein, we reported that magnetic Ag/Fe_2O_3 can be an effective and magnetic separable catalyst of benzaldehyde from oxidation of benzyl alcohol.

EXPERIMENTAL

Ferric nitrate nonahydrate, silver nitrate, ethanol, ethylene glycol, dimethylformamide, hydrogen peroxide, benzyl alcohol were of analytical grade and obtained from the Shanghai Lingfeng Chemical Reagent Company. All chemical reagents were used as received without further purification. Deionized water was used throughout all the experiments.

Preparation of Ag/Fe_2O_3: The magnetic Fe_2O_3 was prepared by the sol-gel method[8]. Ethylene glycol was used as reductants and dispersant. Briefly, 8.08 g ferric nitrate and 30 mL ethylene glycol were added into 100 mL three-neck flask and then stirred for 3 h and then washed several times with deionized water and ethanol, respectively. Finally, the product was dried at 80 °C for 10 h and subsequently calcined at 350 °C for 2 h.

The magnetic Ag/Fe_2O_3 was prepared by the solvent thermal reduction method[9]. 30 mL ethylene glycol and 5 mL dimethylformamide were added into 100 mL three-neck flask, then 0.32 g magnetic Fe_2O_3 and a certain amount of silver nitrate were also added and dispersed. Subsequently the solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL for solvothermal treatment at 160 °C for 8 h. After the autoclave was cooled down to room temperature, the precipitates were separated by using magnet and then washed several times with deionized water and ethanol, respectively. As a result, the brown Ag/Fe_2O_3 was prepared.

Catalytic oxidation of benzyl alcohol: The magnetic Ag/Fe_2O_3 was used for the catalytic oxidation of benzyl alcohol to synthesize benzaldehyde and the process was as follow: 10 mL of benzyl alcohol, 1 % wt. catalyst and 10 mL H_2O_2 was added into 100 mL three-neck flask, was heated to certain temperature for several hours. Finally, At the end of the reaction, the resulting products and unreacted substrate benzyl alcohol were extracted by benzene three times. The extracted liquid mixture was analyzed by gas chromatograph (SP-6800A) and then the conversion rate of benzyl alcohol, the yield and selectivity of benzaldehyde were calculated.

Characterization of catalyst: In this study, XRD patterns were obtained on a DX2700 diffract meter using CuK_α radiation at 40 kV and 35 mA in the range of 2θ value between 10° and 85°. Scanning electron microscope (SEM) observations were carried out using a QuanTa200 scanning electron microscope. Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2200FS transmission electron microscope. EDX patterns were taken from a JEM-3010 high resolution transmission electron microscope at 300 kV.

RESULTS AND DISCUSSION

X-ray diffraction analysis: The powder X-ray diffraction patterns of Fe_2O_3 and Ag/Fe_2O_3 prepared by solvothermal method are shown in Fig. 1. It can be found that the crystal of Fe_2O_3 can not change ultimately during the process of solvothermal reduction by the comparison of Fig. 1a and 1b. The peaks of Fe_2O_3 and Ag/Fe_2O_3 at 2θ = 24.299°, 33.279°, 49.496°, are corresponding to the characteristic peaks reflections of α-Fe_2O_3 and γ-Fe_2O_3[6]. Meanwhile, the diffraction peaks of Ag/γ-Fe_2O_3 at 2θ = 37.933°, 44.141° are corresponding to the characteristic peaks reflections of silve.

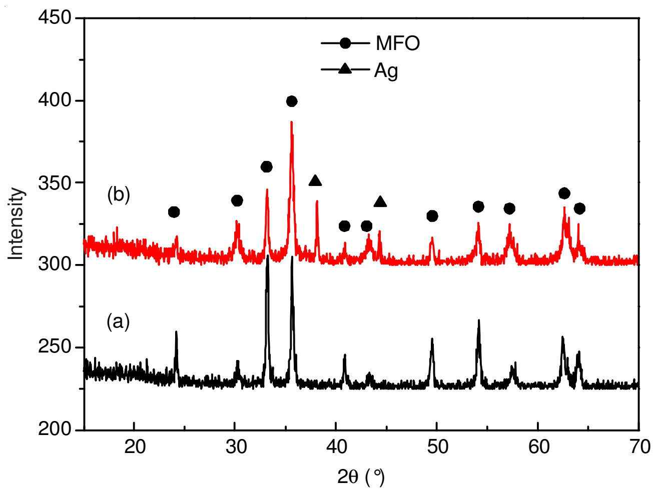

Fig. 1. X-ray diffraction patterns of magnetic Fe_2O_3 (sample-a) and magnetic Ag/Fe_2O_3 (sample-b)

Scanning electron microscope and TEM-EDX characterization: The scanning electron microscope, TEM-EDX images of the prepared Ag/Fe_2O_3 are shown in Fig. 2. By comparison of Fig. 2a and Fig. 2b, it can be found that the structure of prepared Ag/Fe_2O_3 is not specific shape and the particle size of Fe_2O_3 in Ag/Fe_2O_3 is about 20 nm. The particle size of the prepared Ag/Fe_2O_3 with strong magnetism is small. As a result, the particles with high surface energy are reunited[10]. Silver nanoparticles cannot be found from the images of Ag/Fe_2O_3 due to the smaller particle size and lower content of silver, but the element of silver can be identified by EDX as shown in Fig. 2c. Elements of iron and oxygen are contained from Fig. 2c.

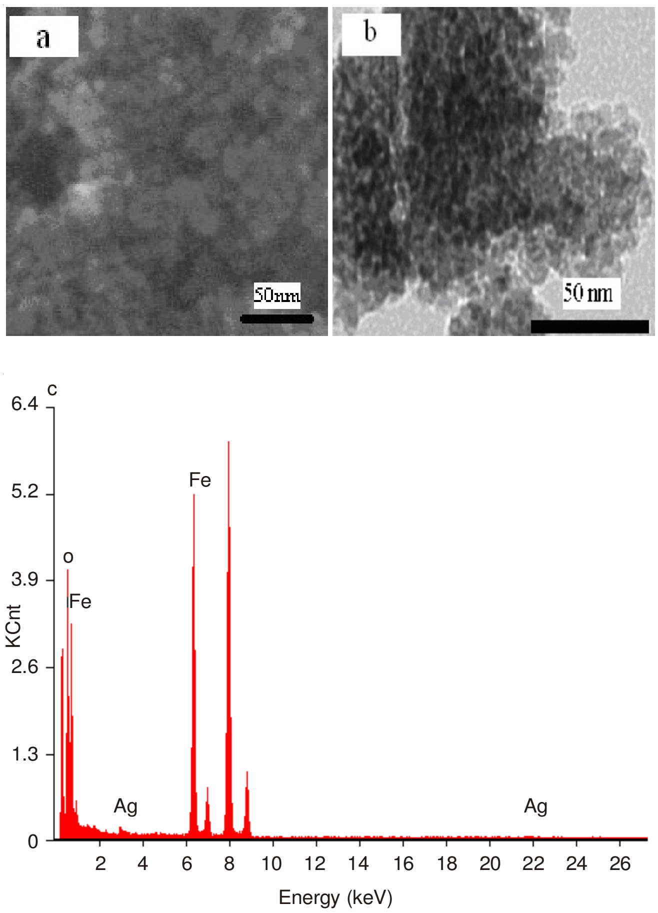

Fig. 2. Scanning electron microscope (a), transmission electron microscopy (b) and EDX (c) images of the prepared magnetic Ag/Fe_2O_3

Catalytic application

Silver contents in the catalyst: The effects of silver content in the catalyst on the oxidation are shown in Fig. 3. As we can see from Fig. 3, magnetic Fe_2O_3 has lower catalytic activity, while the yield of benzaldehyde is improved significantly by doping nanometer silver. As the silver content reaches 2 % mol, the yield of benzaldehyde can reach 61.3 %. The silver nanoparticles with high dispersion can increase the active

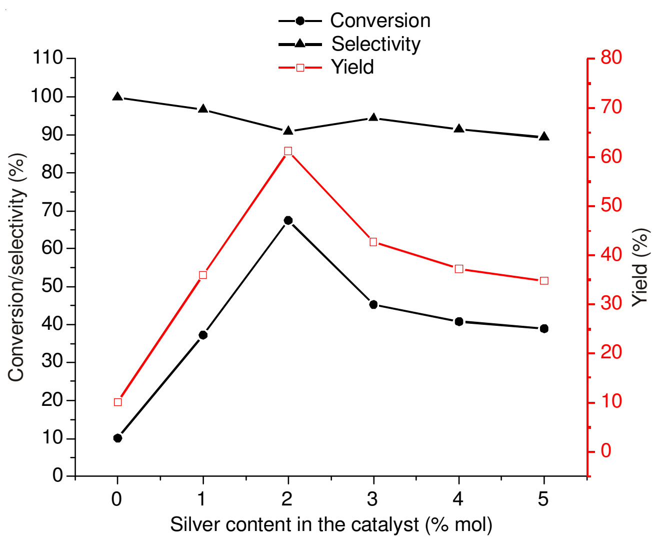

Fig. 3. Effects of silver content in the catalyst for the synthetic benzaldehyde

sites of H_2O_2 decomposed to hydroxyl radical and accelerate the oxidation of benzyl alcohol[11]. However, the yield of benzaldehyde appears to decrease with the increase of silver content subsequently, which may be because the increase of nanometer silver content causes the agglomeration of particles and the increase of particle size[12].

Reaction time: The effects of reaction time on the oxidation by magnetic Ag/Fe_2O_3 are shown in Fig. 4. As we can see from Fig. 4, with the increasing of the reaction time, while the yield of benzaldehyde increases firstly and then decreases. When the reaction time is 12 h, the yield of benzaldehyde can reach 61.3 %. The conversation of benzyl alcohol increases gradually with the increasing of the reaction time, but the amplitude decreases for producing benzoic acid. Therefore, as the reaction time is 12 h, the appropriate reaction time for the oxidation by Ag/Fe_2O_3, the yield of benzaldehyde is up to the maximum.

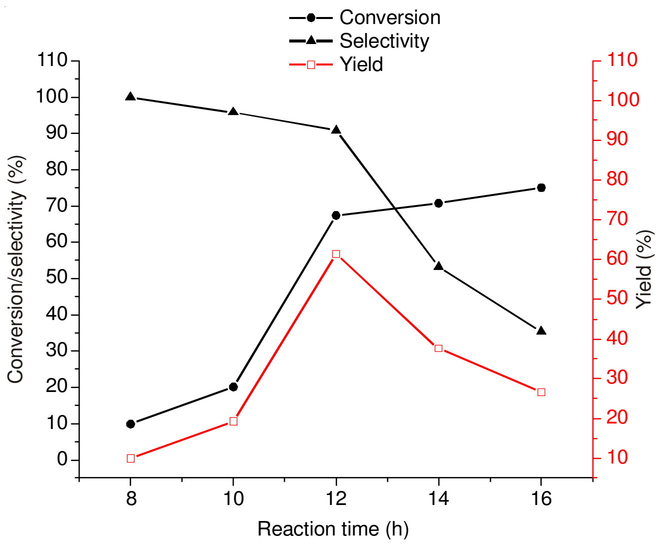

Fig. 4. Effects of reaction time for the synthetic benzaldehyde

Reaction temperature: The effects of reaction temperature on the oxidation by magnetic Ag/Fe_2O_3 are shown in Fig. 5. Fig. 5 suggests that with the increase of reaction temperature, the yield of benzaldehyde increases firstly and then decreases. Meanwhile, when the reaction temperature reaches 80 °C, the yield of benzaldehyde is up to the maximum. For the same reason, benzoic acid is produced more and more with inceasing temperature above 80 °C, the yield and selectivity of benzaldehyde are also decreased.

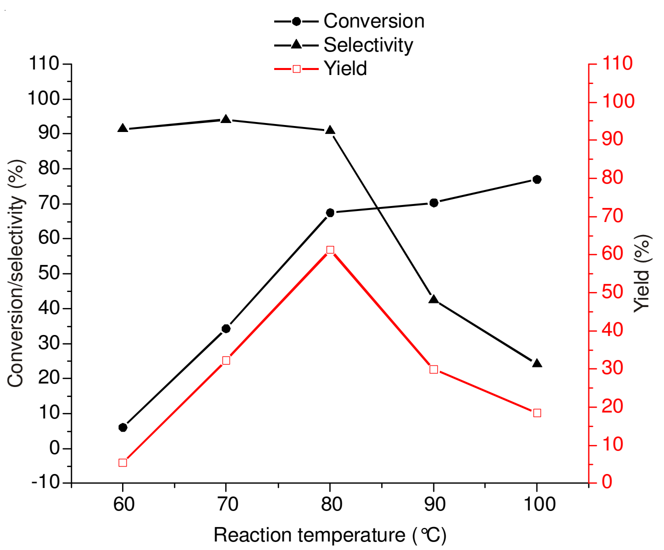

Fig. 5. Effects of reaction temperature for synthetic benzaldehyde

Regeneration of catalyst: The regeneration of magnetic Ag/Fe_2O_3 and the yield of benzaldehyde by several cycles are illustrated in Fig. 6. It can be discovered that the catalytic activity of Ag/Fe_2O_3 for the oxidation is kept effective, but tends to reduce gradually. The catalytic activity of Ag/Fe_2O_3 is largely dependent on the content of silver in the Ag/Fe_2O_3, so the loss of silver drops off during the recycling process. However, the whole process is facile to operate with low cost. Therefore, Ag/Fe_2O_3 is competent to be one of the most desired catalysts for oxidation of benzyl alcohol to benzaldehyde.

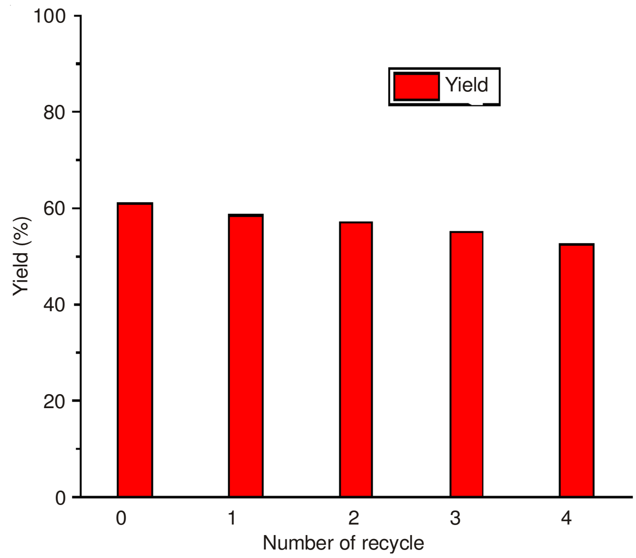

Fig. 6. Recycle study of synthetic benzaldehyde by magnetic Ag/Fe_2O_3

Conclusion

Magnetic Ag/Fe_2O_3 was prepared by solvothermal reduction method, which showed high catalytic activity in the oxidation of benzyl alcohol to benzaldehyde by H_2O_2. The prepared magnetic Ag/Fe_2O_3 was characterized by XRD, scanning electron microscope, TEM, EDX and VSM, which show that the particle size of Fe_2O_3 in the Ag/Fe_2O_3 with high dispersion is about 20 nm. It can be found that magnetic Ag/Fe_2O_3 shows higher catalytic activity than the same conditions of Fe_2O_3. The yield of benzaldehyde can reach 61.3 % for the oxidation of benzyl alcohol 12 h at 80 °C when the silver content in the catalyst is 2 % mol. Meanwhile, the Ag/Fe_2O_3 can also be recycled for several times with high catalytic activity by magnetic recovery.

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