



Oxidative carbonylation of phenol to diphenyl carbonate by Pd/MO–MnFe₂O₄ magnetic catalyst



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HIGHLIGHTS

- MnFe₂O₄ spinel ferrites were prepared by the co-precipitation method as the catalysts supporter.
- Pd/PbO–MnFe₂O₄ showed higher catalytic activity than other Pd/MO–MnFe₂O₄ catalysts.
- The oxygen deficiency and ion transference influences the catalytic activity.
- The catalyst showed well superparamagnetic behavior with high saturation magnetization.
- The Pd/10% PbO–MnFe₂O₄ catalyst may be applied to the magnetically stabilized bed reactor.

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ABSTRACT

In order to screen one suitable catalyst for magnetically stabilized fluidized bed (MSFB) reactor in the process of oxidative carbonylation of phenol to diphenyl carbonate (DPC), Pd/MnFe₂O₄ catalysts were chosen, then prepared and characterized by XRD, H₂-TPR, O₂-TPD and VSM. Compared to the other metal ion doped spinel ferrite catalysts, the catalytic activity of Pd/10% PbO–MnFe₂O₄ was much higher, which the single pass yield of DPC reached 33.12% with selectivity above 99%, and TOF (turnover frequency) reached 70.56 molDPC·(molPd h)⁻¹. The result showed that the formation of the ferrite oxygen-deficient and ion transference in the ferrites was in favor of the catalytic activity. When the support MnFe₂O₄ was calcinated at 500 °C, the saturation magnetization of the obtained catalyst Pd/10% PbO–MnFe₂O₄ came up to 37.81 Am² kg⁻¹. With good magnetic property and brilliant catalytic activity the catalyst Pd/PbO–MnFe₂O₄ may suite for industrial experiments in MSFB reactor in future.

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1. Introduction

Diphenyl carbonate (DPC) as an important green chemical intermediate, is commonly used to synthesize polyaryl carbonate, mono-isocyanate, hydroxybenzoic acid polyester and produce high quality polycarbonates (PC) with bisphenol A by the melt transesterification method [1]. There are several methods such as phosgene method, transesterification and oxidative carbonylation method to synthesize DPC. In the current search for environmentally benign and sustainable processes, the oxidative carbonylation method is a promising alternative in industrial application that avoids the use of phosgene in the one-step synthesis of DPC. Compared to the homogeneous catalysts, the advantage of easy separation for solid catalysts is very attractive. Thus, improving

catalytic activity and decreasing the intraparticle diffusion resistance are essential for heterogeneous catalysts to substitute homogeneous catalysts in DPC synthesis. However, the reaction device for synthesizing DPC by the oxidative carbonylation method is only limited in stirred tank reactor. Our group pioneer professor Wu [2] has reported synthesis of DPC in fixed bed as an engineering basic research, but the yield of DPC was low. Considering the intraparticle diffusion resistance, the MSFB reactor which can strengthen mass-transfer and reduce the inhibitory effect of diffusion resistance on the yield was considered [3]. In order to make a good magnetic response to the applied magnetic field in MSFB reactor, the catalyst loaded in it should have a good magnetic property besides a high catalytic activity. Spinel manganese ferrite is a kind of composite oxide mainly based on Fe, which have the crystal structure as spinel MgAl₂O₄ [4]. When metal ions with different radius and charges are doped into the lattice system, the distribution of the original cations in the crystal lattice is changed significantly, and then the redox capacity and magnetic properties

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of the material are largely affected [5,6]. Therefore using the Pd/MO–MnFe₂O₄ (M=Cu and Pb) as the magnetic catalyst to synthesis of DPC through oxidative carbonylation method was carried out.

2. Experimental

2.1. Preparation

The support and catalyst are prepared according to the reported literatures [7]. The supports are prepared by co-precipitation method with different amount of MO (0%, 10%, 20%, and 30%), using Mn(NO₃)₂ and Fe(NO₃)₃·9H₂O as precursors and 25 wt% NaOH as precipitator. The precipitated solids were collected by filtration and washed with deionized water, followed by drying at 110 °C for 12 h and subsequently calcination at 500 °C for 3 h in the static air atmosphere.

The active component PdCl₂ was loaded on the support by co-precipitation method. PdCl₂ was added into 50 ml distilled water of proper volume by using hydrochloric acid to make it dissolve completely. And then the 5 g support was dipped into the PdCl₂ solution as in order to have a palladium loading of 0.5 wt%. The NaOH solution as a precipitant was the added onto the solution to keep pH value at 9–10 with stirring. The product was filtrated, dried and finally calcined at 300 °C for 3 h to obtain the catalysts of Pd/MO–MnFe₂O₄. The catalyst was signed as Pd/aMO–MnFe₂O₄, where the a represented the mass ration of MO and M denoted Cu or Pb.

2.2. Characterization

The catalysts were characterized by the X-ray diffract meter (XRD, D8 ADVANCE, Germany) operating at 40 kV and 40 mA using Cu K α radiation and Ni filter. The scanning rate is 4° min⁻¹ in the 2 θ range from 10° to 80°. Temperature-programmed reduction (H₂-TPR) and temperature-programmed desorption (O₂-TPD) experiments were performed in a quartz reactor using a thermal conductivity detector (TCD) as detector on Micromeritics AutoChem2920 (USA) instrument. The magnetic properties of the samples were measured at room temperature using a HH-10 vibration sample magnetometer manufactured by Nanjing University.

2.3. Catalytic activity measurements

DPC synthesis by oxidative carbonylation of phenol was carried out in a 250 ml stainless steel autoclave equipped with a mechanical stirrer, which was pre-filled with 50 ml dichloromethane, 1.0 g catalyst (Pd in the catalyst = 0.046 mmol), 80 mmol phenol, 3.0 mmol tetrabutylammonium bromide (TBAB), 4 mmol hydroquinone, and 2.0 g of 4A molecular sieve used as drying agent. Then oxygen and carbon monoxide were introduced into the autoclave to the reaction pressure (5 Mpa) with the oxygen content was about 5.0%. The reaction was carried out for 4 h at 100 °C and the stirring speed was 750 r min⁻¹. At the end of the reaction the autoclave was cooled to room temperature and weighted. The reaction products were identified and quantified by gas chromatography with a flame ionization detector (FID) detector and a SE-54 capillary column (GC-2014, SHIMADZU, Japan).

3. Results and discussion

3.1. Activity studies

Table 1 shows the catalytic activities of Pd/CuO–MnFe₂O₄ and Pd/PbO–MnFe₂O₄ catalyst for oxidative carbonylation of phenol. As listed in Table 1, the activities of Pd/PbO–MnFe₂O₄ and Pd/

CuO–MnFe₂O₄ catalysts were much higher than that without oxides doping (entries 3–8). And then the activities of Pd/PbO–MnFe₂O₄ were well than the CuO doped catalysts. The yields of DPC varied in a wide range of 13–33% with different catalysts.

It can be also observed from Table 1 that the DPC yields of Pd/PbO–MnFe₂O₄ changed with the PbO mass ratios. When the PbO mass ratio was 10% with the calcination temperature of PbO–MnFe₂O₄ was 300 °C, the DPC yield was up to 33.12%, indicating the best catalytic activity. The yield of Pd/10% PbO–MnFe₂O₄ (300 °C) was almost twice as much as that of undoped Pd/MnFe₂O₄ catalyst.

3.2. XRD characterization

Fig. 1 illustrates the results of XRD analysis for CuO–MnFe₂O₄ and PbO–MnFe₂O₄ with different MO mass ratio at the calcination temperature of 300 °C. The reference pattern of MnFe₂O₄ synthesized by co-precipitation method was given in Figs. 1a and 2a, corresponding to MnFe₂O₄. After Cu was doped into MnFe₂O₄ with the CuO mass ratio at 10%, diffraction pattern of CuO in CuO–MnFe₂O₄ (b) sample (Fig. 1) was detected. When the CuO mass ratio increased, the intensity of CuO peak was enhanced, but the peak of MnFe₂O₄ was almost no changed. However, after Pb was doped into MnFe₂O₄ with the PbO mass ratio at 10%, diffraction pattern of PbO in PbO–MnFe₂O₄ (b) sample (Fig. 2) was detected. As the PbO mass ratio increasing, the new peaks belong to PbO₂ was detected. At the same time, the intensity of peaks belong to MnFe₂O₄ was weakened. This possible due to the Pb enter into MnFe₂O₄ lattice and cause the intense interaction of PbO and MnFe₂O₄. Combined with the activity of Pd catalyst supported on 10% PbO–MnFe₂O₄, it was found that the interaction of PbO and MnO_x was beneficial to the catalytic activity.

3.3. H₂-TPR and O₂-TPD characterization

The reducibility and oxidizability of the PbO–MnFe₂O₄ supporters was examined by H₂-TPR and O₂-TPD, the reduction and oxide desorption profiles being displayed in Figs. 3 and 4, respectively. There are three reduction peaks of ferrite MnFe₂O₄ in the H₂-TPR spectra and the reducing process may be inferred to be MnFe₂O₄ → MnFe₂O_{4- δ} → MnO–FeO solid solution → α -Fe [8,9]. When mass ratio of 10% PbO was doped, the initial reduction peak temperature ($T = 263$ °C) of the supporter was the lowest and the peak becomes much sharper. However, with the mass ratio of PbO increasing the low-temperature reduction peak weakening even disappeared. This may be because the redundant PbO was encapsulated on the surface of MnFe₂O₄ then prevent it to be reduced to MnFe₂O_{4- δ} .

The O₂-TPD patterns of PbO–MnFe₂O₄ supporters with different mass ratio PbO doped in are shown in Fig. 4. It is commonly believed that the peak temperature implied the ability of supplying oxygen centers, the peak area indicated the number of supplying oxygen centers [10]. In this work, two O₂ desorption peaks centered at 100 and 500 °C were observed in MnFe₂O₄. It is believed that the desorption peak centered at 100 °C was corresponding to the desorption of oxygen species named mobile oxygen. The desorption peak centered at the temperatures of higher than 500 °C could be attributed to the desorption of lattice oxygen [11]. As the PbO doped, the peaks belong to lattice oxygen was shifted toward to high temperature. Interestingly, between the two main desorption peaks, another little desorption peak close to the higher one was appeared. After identification, the new appeared peak could be attributed to the decompose process of PbO on the surfaces of MnFe₂O₄. From the figure, we could see that as the mass ratio of doped PbO increasing, the peak intensity of mobile oxygen was weakening which was especially shown in

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