

Oxidative carbonylation of phenol to diphenyl carbonate by the Pd load manganese oxide catalyst

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Highlights

- MnO_x oxides were prepared by co-precipitation method in the ISR as the catalysts supporter.
- Pd/MO- MnO_x catalysts were obtained with the supporters modified by Pb and Cu oxides.
- The catalysts showed high activity in the phenol oxidative carbonylation process.
- The oxygen deficiency and ion transference influences the catalytic activity.

1. Introduction

Diphenyl carbonate (DPC) is an important green chemical intermediate, which was commonly used to synthesize polyaryl carbonate, high quality polycarbonates (PC), mono-isocyanate, hydroxybenzoic acid polyester et. al. [1]. There are several methods to synthesize DPC. There are the phosgene method, transesterification and oxidative carbonylation methods. However, in the current search for environmentally benign and sustainable processes, producing DPC through the oxidative carbonylation method is a promising alternative in industrial application. Because during the one-step process to synthesize DPC, phosgene was avoided to be used. 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. Usually, the oxides was thought to be the well catalyst supporters and promoters. In the large family of metal oxides, manganese oxides (MnO_x) are typically thought to be one of the most attractive multifunctional materials which have been applied in multidisciplinary areas of catalysis and electrochemical supercapacitors as well as adsorption [2, 3]. Furthermore when metal ions with different radius and charges are doped into the MnO_x lattice system, the distribution of the original cations in the crystal lattice is changed significantly, and then the redox capacity properties of the supporters are largely affected [4]. Therefore using the Pd/MO- MnO_x (M=Cu and Pb) as the magnetic catalyst to synthesis of DPC through oxidative carbonylation method was carried out.

2. Methods

MnO_x oxide was prepared by coprecipitation method in the impinging stream reactor (ISR). NaOH solution was uniformly added to $Mn(NO_3)_2 \cdot 50\%$ and stirred continuously. The obtained solid was calcined at to obtain the MnO_x oxide supports. Then 5.0 g MnO_x was added to the deionized water with mixing with the ultrasonic shock for 10 min, and then the mass fraction (5%, 10%, 15% $(NO_3)_2$ or $Cu(NO_3)_2$) were stirred for 30 min and then steamed to dryness. After calcination, the modified MnO_x carrier was obtained. The active component $PdCl_2$ was loaded on the support by co-precipitation method. The 5.0 g supports was dipped into the $PdCl_2$ 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- MnO_x . DPC synthesis by oxidative carbonylation of phenol in the dichloromethane was carried out in a 250 ml stainless steel autoclave. The reaction conditions were control at 100 °C, with P=5 MPa, P_{O_2} = 5% and 4 h. XRD patterns of the samples were obtained with a Bruker diffractomete (D8 Advance). The reducibility of supporters was examined by the temperature-programmed reduction (H_2 -TPR). The morphologies of the catalysts were characterized by FE-SEM (SU8000).

3. Results and discussion

From the catalytic results, it was found that the activity and selectivity of the catalyst of the Pd/PbO-MnO_x were much higher than the in Cu oxide doping or without doping. When the mass ratios of 15% Pb(NO₃)₂ was doped on MnO_x supporter, the activity of the catalyst was the highest as the DPC yield was 7.76% with the selectivity was 95.45%. Through the fig1, we could see that the catalyst exhibited several spheres with uniform scales. At the same time, we could also found that each the spheres was next to the other, but not tight fit together, which makes the catalysts have a large interior pore volume.

Tab.1 Catalytic performance of different catalysts

Catalysts	Selectivity	DPC yield/%
Pd/400°C MnO _x	93.99	0.55
Pd/500°C MnO _x	97.39	1.99
Pd/600°C MnO _x	92.36	0.68
Pd/5%PbO-MnO _x	86.06	1.89
Pd/10%PbO-MnO _x	90.55	6.49
Pd/15%PbO-MnO _x	95.45	7.55
Pd/5%CuO-MnO _x	94.27	6.69
Pd/10%CuO-MnO _x	89.77	3.88
Pd/15%CuO-MnO _x	90.93	1.76

Fig.1 SEM images of the Pd/MnO_x catalyst

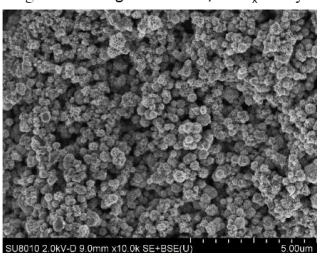


Fig.2 H₂-TPR profiles of Pd/Cu-MnO_x

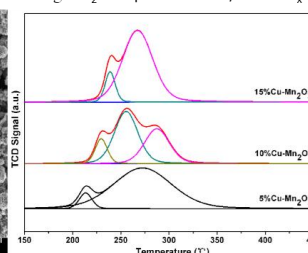
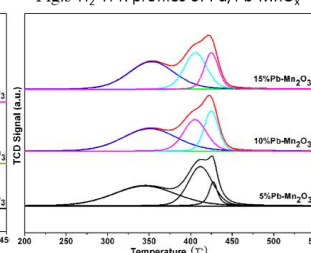


Fig.3 H₂-TPR profiles of Pd/Pb-MnO_x



In fig.2 there are three reduction peaks in the spectra of different CuO doped catalysts. The smaller reduction peak (peak temperature $T < 250^{\circ}\text{C}$) occurs at lower temperatures, may be due to the reduction of the consumption of H₂ due to the accumulation of Cu oxides. When the doping CuO mass ratio increased, the intensity of CuO peak was enhanced. The peak area of Cu (2+) increases with the increase of amount Cu oxide doping. It can be seen from the fig.3 that there are three reduction peaks in the PbO-MnO_x oxide carrier with different amount of PbO doping, with the low-temperature reduction peak located near 350°C. 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 [5, 6]. The increase crystal lattice oxygen are beneficial to the re-oxygen of reduced compounds. Otherwise, PbO doping promotes the dispersion of active compounds on the surface of catalyst. Both the two effects could improve the performance of the catalyst. Meanwhile, the introduction of PbO promotes the synergistic effect between metals [7]. When the PbO content is 15%, the effect is most obvious. The synergistic effect could make the increasing amount of lattice oxygen and produce more oxygen vacancies that improve the redox ability of active component Pd.

4. Conclusions

The MnO_x oxide carrier was prepared by coprecipitation method in the ISR. The MnO_x oxide was modified by doping Pd and Cu oxides with different mass ration. The carrier was subjected to oxidative carbonylation of phenol after loading 0.5% Pd. The results of H₂-TPR analysis showed that the surface oxidation of MnO_x catalyst modified by different metal oxides was different. The decrease of the temperature of the low temperature reduction peak of the MnO_x oxide support increases with the increase of the doping ration. Then supportes contributed to the redox cycle efficiency of the active species Pd, and the yield of the final DPC increased. When the catalysts with the PbO ratio doping was 15%, the best catalytic activit of Pb/PbO-MnO_x was best, with the yield of DPC was 7.76% and the selectivity was 94.27%.

References

- [1] Gong J, Ma X, Wang S. *J. Appl Catal A*, 316(2007) 1-21.
- [2] Zhang L, He Y, Yang X, *J. Chem. Eng. J.*, 278(2015):129-133.
- [3] Hu Y, Yang X, Cao S, *J. Appl Surf. Sci.*, 400(2017):148-153.
- [4] Yin C, Zhou J, Chen Q, *J. J. Mol. Cat. A Chem.*, 424(2016):377-383.
- [5] Spivack J L, Cawse J N, Whisenhunt D W, *Appl. Catal., A*, 254(2003) 5-25
- [6] Katsaounis A, Nikopoulou Z, Verykios X E, Vayenas C G. *J Catal*, 226(2004) 197-209.
- [7] G.W. Wu, Y.X. Wu, P.S. Ma, *Front. Chem. Eng. China* 1(2007) 59-64.

Keywords

Diphenyl carbonate, Oxidative carbonylation, impinging stream reactor, oxygen deficiency