

THE ENHANCED ACTIVITY OF PALLADIUM/ MIXED OXIDE Pb-Mn-O CATALYSTS FOR DIRECT SYNTHESIS OF DIPHENYL CARBONATE

Xiaojun Yang,^{†,‡} Yuanxin Wu,^{†,‡,*} Zhiguo Yan,[†] Suqun Wu,[†] and Youqing Yu[†]

[†]*School of Chemical and Pharmaceutical Engineering, Wuhan Institute of Technology, Wuhan 430073, P R China*

[‡]*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China*

Summary

Palladium catalysts supported on mixed oxide Pb-Mn-O were prepared by two different methods--impregnation and solid-phase pyrolysis method. And then the catalysts were characterized by SEM, XRD and XPS to investigate the effects of lead species on activity. The activity studies indicate that the strong interaction between Pb and Mn in the mixed oxide improves the yield of DPC, regardless of a great discrepancy in the textural and morphology of the two catalysts. The increase of yield may be related to the change of mixed valent Mn ions.

Keywords diphenyl carbonate; oxidative carbonylation; mixed oxide Pb-Mn-O

Introduction

The oxidative carbonylation of phenol to diphenyl carbonate (DPC) catalyzed by Pd-based systems, instead of conventional phosgene method, has received considerable attention with an increasing awareness of environmental protection. The high value-added product DPC is synthesized from cheap raw materials--phenol, CO and O₂ and generally employed as an important precursor for producing polycarbonate. The main emphasis of the related research is placed on the developing of heterogeneous catalysts for the synthesis of DPC because the recovery of homogeneous catalysts remains a critical item. Up to now, a number of heterogeneous palladium catalysts anchored on supports including activated carbon, polystyrene, silicon dioxide, zeolites, organic-inorganic hybrid materials and mixed metal oxides have been reported to be effective. However, the low yield of DPC limits its industrialization.

It was pointed out in an earlier study that heterogeneous lead oxides and homogeneous Pb(acac)₂ were both good promoters of Pd-based catalytic systems, which provided some directions for further developing high-efficiency heterogeneous catalysts^{1,2}. In this work, two different methods--impregnation and solid-phase pyrolysis method were adopted to prepare heterogeneous catalysts Pd/mixed oxide Pb-Mn-O. A series of characterization techniques were used to examine the chemical and texture properties of the catalysts aiming at understanding the promotion effect of Pb species on catalytic activity.

Experimental

The impregnation method was described as follows: 7g manganese oxide octahedral molecular sieves (OMS-2) prepared by a reflux method was impregnated with 70ml Pb(NO₃)₂ aqueous solutions. And then the mixture was stirred for 24h, followed by evaporation of the water and calcination at 400°C in a muffle furnace. For the solid-phase pyrolysis method, Pb(CO₃)₂ and Mn(CO₃)₂ were mixed and then calcined at 400°C. The two catalysts have the same loadings of Pb (30 wt %). Hereafter, Pd/Pb-Mn-O(I) denotes the catalyst prepared by impregnation method, and Pd/Pb-Mn-O(SP) stands for the catalyst prepared by solid-phase pyrolysis method.

The active palladium species were supported on mixed oxide Pb-Mn-O by the precipitation method with NaOH as a precipitation agent. The activity studies of catalysts were performed in a 250ml autoclave equipped with a magnetic stirrer.

The corresponding lead-free catalysts were prepared according to the previous paper³. The physical mixture of lead oxides and OMS-2 was prepared by manual milling in an agate mortar, denoted as PbO_x+MnO_x.

Results and Discussion

* To whom all correspondence should be addressed.

Email: vyx@mail.wit.edu.cn.

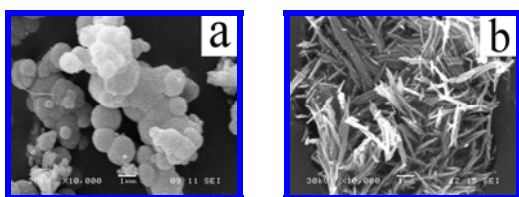


Figure 1. Scanning electron microscope (SEM) images of (a) Pd/Pb-Mn-O(SP) and (b) Pd/Pb-Mn-O(I)

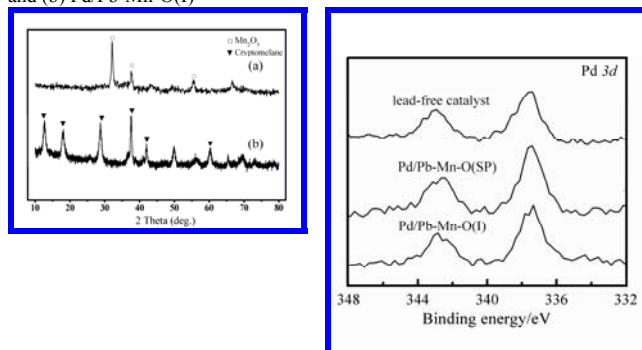


Figure 2. X-ray diffraction (XRD) patterns of (a) Pd/Pb-Mn-O(SP) and (b) Pd/Pb-Mn-O(I)

Figure 3. Pd_{3d} spectrums of lead-free catalysts, Pd/Pb-Mn-O(SP) and Pd/Pb-Mn-O(I)

XRD pattern of Pd/Pb-Mn-O(SP) corresponds to bixbyite(Mn₂O₃) with poor crystallinity, while a pure cryptomelane-type MnO₂ is observed for the sample Pd/Pb-Mn-O(I). The absence of other peaks in Figure 2(a) and (b) suggests that lead species are well dispersed. Compared with the corresponding lead-free catalysts, however, two catalysts both enhance the catalytic activity (Figure 4), regardless of a great discrepancy in the textural and morphology of the mixed oxide Pb-Mn-O catalysts.

Pd_{3d} spectrums show that the binding energy of Pd_{3d} for Pd/Pb-Mn-O(I) and Pd/Pb-Mn-O(SP) are almost the same as that of lead-free catalysts at 337.5eV, exhibiting no interaction of Pb with active Pd species. It is because the element Pb has an identical electronegative value to Pd(11.0). The XPS analysis shows that the function of lead species to regenerate active Pd²⁺ sites is performed indirectly.

In order to investigate the existing form of lead species in the mixed oxide that are beneficial to the activity, the activities of palladium catalysts supported on single lead oxides and a physical mixture of lead oxides and OMS-2 were evaluated for comparison and displayed in Figure 4. No promotion effect was observed when these materials were used. Homogeneous Pb₄O(OC₆H₅)₆ was also added into the lead-free catalysts but there was a slight decrease in activity. The above results exclude the possibility that the presence of homogeneous Pb species and single lead oxides is the reason for the promotion of activity for the Pd/mixed oxide Pb-Mn-O catalysts. Moreover, PbO₂ reacted with phenol violently and the lowest DPC yield was obtained, which was not consistent with the results in an earlier study that Pb⁴⁺ had an ability to improve the activity through direct oxidizing of Pd⁰.

Therefore, we deduce that the enhanced activity is ascribed to the strong interaction between Pb and Mn combined with the earlier study of our group³, for example, the Pb species exert an influence on the valence of Mn. Mn⁴⁺/Mn²⁺ pairs in the mixed oxide Pb-Mn-O (which contains mixed valent manganese ions) can oxidize Pd⁰ to Pd²⁺ and then be reoxidized by gas oxygen.

Conclusions

Palladium catalysts supported on mixed oxide Pb-Mn-O, which are prepared by two different methods, are the only one group that improves the activity for direct synthesis of DPC when various supporters involving lead oxides, a physical mixture of lead oxides and OMS-2 and mixed oxides Pb-Mn-O are screened out. The promotion effect of lead species of this catalyst is ascribed to the strong interaction between Pb and Mn.

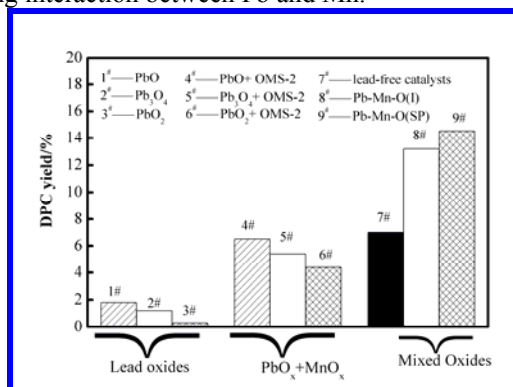


Figure 4. Catalytic activities of palladium catalysts supported on various supporters

Reaction conditions: Phenol 47g, 4A molecular sieves 2g, tetrabutylammonium bromide 1g and Pd (in the catalyst) 0.09mmol, temperature 65□, total pressure 4.8MPa, CO/O₂ = 12/1 (molar ratio)

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