



## Effects of Pb dopant on structure and activity of Pd/K-OMS-2 catalysts for heterogeneous oxidative carbonylation of phenol

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### ABSTRACT

Palladium catalysts supported on Pb-cation-doped manganese oxide octahedral molecular sieves were prepared and used for heterogeneous oxidative carbonylation of phenol to diphenyl carbonate in the absence of homogeneous cocatalysts. The synthesized catalysts were characterized by ICP-AES, XRD and XPS techniques. The experimental results demonstrated that an enhanced activity was obtained when  $\text{Pb}^{2+}$  entered into the tunnels of cryptomelane by replacing  $\text{K}^+$  to form a new hollandite-type phase of  $\text{Pb}_{2-x}\text{Mn}_8\text{O}_{16}$ . The promotion effect of Pb dopant on activity was ascribed to the increase of low-valence  $\text{Mn}^{3+}$  and OH group, which was favor of reoxidation of  $\text{Pd}^0$  to active  $\text{Pd}^{2+}$  species.

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### 1. Introduction

Diphenyl carbonate (DPC) is an important starting material for producing polycarbonate. Several methods have been developed to synthesize DPC [1]. Among them, oxidative carbonylation of phenol with CO and O<sub>2</sub> is a simple and environmentally benign process that avoids the use of phosgene. In this catalytic reaction, two or more metallic and/or organic homogeneous cocatalysts should be added into the system in order to promote the reoxidation of reduced  $\text{Pd}^0$  because direct oxidation of  $\text{Pd}^0$  with gas oxygen to regenerate active  $\text{Pd}^{2+}$  species proved to be a slow process [2,3]. Although Pd complexes anchored on various supports have been developed to facilitate the recovery of homogeneous palladium catalysts [4–9], the problems in the separation and product refining still remain owing to the presence of homogeneous cocatalysts. Therefore, some researchers attempted to use metal oxides instead of homogeneous cocatalysts [2,4,5,10]. Insoluble metal oxides are easily separated and the function of reoxidation of  $\text{Pd}^0$  is performed simultaneously.

Takagi and his coworkers discovered that PbO effectively promoted the activity in the  $\text{Pd/C-N}(\text{C}_4\text{H}_9)_4\text{Br}$  system and 9.65% DPC yield was obtained in combination of CuO as a second cocatalyst [4]. But PbO was likely to react with phenol to form an organic lead compound, which meant it was a homogeneous cocatalyst

in fact [10]. Although other single metal oxides, such as CuO [5], CrO<sub>3</sub>, MoO<sub>3</sub>, OsO<sub>4</sub> and RuO<sub>3</sub> [2], were also chosen as redox cocatalysts, the activities were not satisfactory. The best yield was only 8.9% when using 5%Pd/C as catalyst and CuO as cocatalyst. Besides, both the Pd catalyst and the Co cocatalyst were heterogenized and proven to form an effective catalytic system using layered double hydroxides as a support. Preliminary test showed a promising result as far as activity and Pd leaching is less than 5% [7]. Our research group placed emphasis on manganese oxides because only MnO<sub>2</sub>/Mn<sup>2+</sup> pair with potentials of between the potentials of  $\text{Pd}^{2+}/\text{Pd}^0$  and O<sub>2</sub> + H<sup>+</sup>/H<sub>2</sub>O pairs can oxidize  $\text{Pd}^0$  and then be reoxidized by O<sub>2</sub>. The  $\text{Pd}^0$  formed was oxidized with Mn<sup>4+</sup> to form  $\text{Pd}^{2+}$  and Mn<sup>2+</sup>, and then Mn<sup>2+</sup> was reoxidized by O<sub>2</sub>. The dual role of manganese oxides as cocatalyst and support for the metallic parts of the catalytic system led to an easy separation process and the DPC yield achieved 10.7% [11].

As mentioned above, the activities of catalysts with metal oxides as cocatalysts are inferior to those using homogeneous cocatalysts; nevertheless the advantage of easy separation for metal oxide as cocatalysts is very attractive. Thus, an enhanced activity is essential in order to substitute for homogeneous cocatalysts, and introduction of other metal dopant into metal oxides is a powerful method. In this work, Pb was doped into potassium-containing manganese oxide octahedral molecular sieves (K-OMS-2), on which the active palladium species were loaded by a precipitation method. The supported catalysts were characterized to clarify the modification effects of Pb on structure and activity of heterogeneous catalysts.

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## 2. Experimental

### 2.1. Catalyst preparation

Hydrothermal, reflux, solvent free and high temperature calcination methods were used to synthesize K-OMS-2. The details of preparation were given in the literature [12]. To prepare lead-cation-doped K-OMS-2, 7000 g K-OMS-2 prepared by the reflux method was impregnated with 70.0 ml of  $\text{Pb}(\text{NO}_3)_2$  aqueous solutions with different concentrations. And then the mixture was stirred for 24 h, followed by evaporation. The lead modified supports (designed as Pb-OMS-2) were obtained by calcination in a muffle furnace at 400–900 °C for 6 h.

0.042 g  $\text{PdCl}_2$  was dissolved in 50.0 ml aqueous solution when the pH value was adjusted to 1.0 with concentrated hydrochloric acid. K-OMS-2 or Pb-OMS-2 was dipped into the  $\text{PdCl}_2$  solution. 5.0% NaOH solution as a precipitant was dropped slowly till the pH value was kept at 9.5. After stirred for 2 h, the solid was separated by filtration, then dried at 80 °C overnight and calcined at 300 °C for 3 h. The powdery catalysts prepared were labeled as Pd/K-OMS-2 or Pd/Pb-OMS-2, respectively.

### 2.2. Characterization

The phase identification and crystalline structure analysis were determined by X-ray diffraction (XRD) on a PANalytical X'Pert PRO X-ray diffractometer with high-intensity  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ). The chemical shift and valence of element on surface were studied by X-ray photoelectron spectra (XPS) in a Perkin-Elmer PHI 1600 ESCA system with  $\text{Mg K}\alpha$  X-ray radiation (1253.6 eV, 250 W). The bulk chemical composition of the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin Elmer ELAN DRC-e instrument. Samples were dissolved in the mixture of HCl and  $\text{HNO}_3$ , and then diluted with ultrapure water.

### 2.3. Activity test

The oxidative carbonylation reaction was performed in a 250 ml stainless steel autoclave equipped with a magnetic stirrer. A typical reaction condition was as follows: phenol 47 g (0.5 mol), 4A molecular sieves (MS) 2 g, tetrabutylammonium bromide (TBAB) 1 g (3 mmol) and Pd (in the catalyst) 0.09 mmol were introduced into the autoclave. Then the autoclave was sealed and heated to 65 °C. Subsequently, the gas mixture of CO and  $\text{O}_2$  ( $\text{CO}/\text{O}_2 = 12/1 \text{ M ratio}$ ) was charged. It must be noted that the conditions employed in this procedure fell within the explosion range of CO in  $\text{O}_2$ . After the reaction lasted for 4 h at the pressure of 4.8 MPa, the autoclave

was cooled and the products were taken out. The yields of final products were determined by a capillary gas chromatography with a FID detector and a SE-54 capillary column.

## 3. Results and discussion

### 3.1. Activity studies

Table 1 shows the catalytic activities of Pd/K-OMS-2 and Pd/Pb-OMS-2 catalysts for oxidative carbonylation of phenol. As listed in Table 1, the activities of Pd/K-OMS-2 catalysts prepared by different methods were almost the same (entries 1–4). The yields of DPC varied in a narrow range of 7.5%–9.2%.

It can be also observed from Table 1 that the DPC yields of Pd/Pb-OMS-2 catalysts changed with Pb/Mn mass ratios and calcination temperatures. When the Pb/Mn mass ratio was 3/10 and the calcination temperature of Pb-OMS-2 was 700 °C, the DPC yield was up to 18.1%, indicating the best catalytic activity. The yield of Pd/Pb-OMS-2(C) was almost twice as much as that of undoped Pd/K-OMS-2 catalysts.

### 3.2. XRD characterization

Fig. 1 illustrates the results of XRD analysis for Pb-OMS-2 with different Pb/Mn mass ratio at the calcination temperature of 400 °C. The reference pattern of K-OMS-2 synthesized by a reflux method was given in Fig. 1a, corresponding to cryptomelane [12]. K-OMS-2 has a one-dimensional tunnel structure formed by  $2 \times 2$  edge shared  $\text{MnO}_6$  octahedral chains and a general composition  $\text{KMn}_8\text{O}_{16}$ . After Pb was doped into K-OMS-2 with the Pb/Mn mass ratio at 1/10, diffraction pattern of Pb-OMS-2(A1) sample (Fig. 1b) was almost identical to that of K-OMS-2. When the Pb/Mn mass ratio increased to 3/10, however, the intensity of the peak at  $2\theta = 37.5^\circ$  was suppressed and the intensity at  $2\theta = 28.7^\circ$  was enhanced. Fig. 1c showed that the strongest peak appeared at  $2\theta = 28.7^\circ$ , not at  $37.5^\circ$ . It indicated that a new hollandite-type phase of  $\text{Pb}_{2-x}\text{Mn}_8\text{O}_{16}$  generated through ion exchange in tunnels. In the light of the results of activity studies shown in Table 1 (entry 6), the reason for increasing catalytic activity might be ascribed to the formation of  $\text{Pb}_{2-x}\text{Mn}_8\text{O}_{16}$  after the doping of Pb. When the Pb/Mn mass ratio was over 3/10, the crystalline phase of  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ , as shown in Fig. 1d, was found at  $2\theta = 35.6^\circ$ . The appearance of  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  was possibly due to the reaction of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in air with  $\text{Pb}^{2+}$ , which did not enter into tunnels. Combined with the activity of Pd catalyst supported on Pb-OMS-2(A3) (entry 7), it was found that the formation of  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  was detrimental to the catalytic activity.

**Table 1**  
Catalytic activities of palladium catalysts supported on K-OMS-2 and Pb-OMS-2.

	Support	Method of preparation	[Pb/Mn] <sup>b</sup>	Pd <sup>c</sup> %	DPC Yield <sup>d</sup> (%)
1	K-OMS-2	Solvent free		4.92	9.2
2		Reflux		4.88	8.7
3		High temperature		4.92	8.0
4		Hydrothermal		4.79	7.5
5	Pb-OMS-2(A1)	Calcine at 400 °C, Pb/Mn <sup>a</sup> = 1/10	0.106	4.99	10.0
6	Pb-OMS-2(A2)	Calcine at 400 °C, Pb/Mn = 3/10	0.321	4.87	13.2
7	Pb-OMS-2(A3)	Calcine at 400 °C, Pb/Mn = 5/10	0.546	5.00	10.3
8	Pb-OMS-2(B)	Calcine at 550 °C, Pb/Mn = 3/10	0.332	4.95	17.0
9	Pb-OMS-2(C)	Calcine at 700 °C, Pb/Mn = 3/10	0.311	4.95	18.1
10	Pb-OMS-2(D)	Calcine at 850 °C, Pb/Mn = 3/10	0.320	4.89	7.0

<sup>a</sup> Theoretical value of mass ratio of Pb to Mn.

<sup>b</sup> Mass ratio of Pb to Mn detected by ICP-AES.

<sup>c</sup> Actual loading of active Pd species in heterogeneous catalysts detected by ICP-AES.

<sup>d</sup> DPC yield based on the amount of charged phenol.

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