A new and efficient catalytic system for synthesis of diphenyl carbonate with W–Mo-heteropolyacids as a cocatalyst

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A new catalytic system, which consists of $Pd(OAc)_2$ as the catalyst and W–Mo-containing heteropolyacids (HPAs)/$Mn(OAc)_2$ as the bicomponent cocatalysts, has been found to be very efficient in the oxidative carbonylation of phenol to diphenyl carbonate at low pressure in the absence of solvent. The efficiency of the catalytic system is dependent on the ratio of W/Mo in the HPAs, being best in a ratio of 6/6. The synergistic effect between W–Mo-containing HPAs and $Mn(OAc)_2$ has been observed in the catalysis.

Keywords: diphenyl carbonate, phenol, bicomponent cocatalyst, synergistic effect, oxidative carbonylation

1. Introduction

Polycarbonates (PCs), as important engineering thermoplastics, are commercially produced by the interfacial polycondensation of biphenol with phosgene or the transesterification of biphenol with diaryl carbonate [1]. Diphenyl carbonate (DPC), industrially prepared by the reaction of phosgene and phenol, is usually used in the transesterification. In recent years, there have been increasing demands for a safer and environmentally benign process for PCs synthesis. Alternative approaches to DPC production are on the highlight in the PCs industry now [2].

Oxidative carbonylation of phenol with CO and O_2 in the presence of Pd catalysts in one step is one of the most attractive methods for manufacturing DPC [3–11], in that H_2O is the sole by-product and the use of highly toxic phosgene can be avoided. In this reaction, the efficient regeneration of Pd(II) species from Pd(0) is the crucial step for high yield of DPC and high turnover number of Pd. However, direct oxidation of Pd(0) to Pd(II) with oxygen has been proven to be very slow. Therefore, efficient cocatalysts are essential to achieve rapid reoxidation of Pd(0). In the Wacker process [12], copper salts were chosen to regenerate Pd(II) with high efficiency. In the DPC synthesis reaction, the turnover number of Pd was far lower than that in the Wacker process when copper salts were used as the redox cocatalyst [7]. Although many simple metal salts and complexes have also been investigated as good cocatalysts, it is still desirable to find efficient catalytic systems for the production of DPC from practical point of view. Heteropolyacids have been used as catalysts in the oxidation of organic compounds [13,14], and also as the redox cocatalysts to regenerate active Pd(II) species in the other catalytic reactions [14]. We report herein a new and efficient catalytic system with W–Mo-containing heteropolyacids plus $Mn(OAc)_2$ as the cocatalysts for the oxidative carbonylation of phenol to DPC under low pressure in the absence of solvent.

2. Experimental

All reagents were used as received. Molecular sieves (MS) were activated at 300 °C in air for 10 h before use. All the reactions are run in a flow system.

A typical reaction procedure was as follows: phenol 47 g (0.5 mol), $Pd(OAc)_2$ 0.036 g (0.16 mmol), $Mn(OAc)_2 \cdot 4H_2O$ 0.078 g (0.32 mmol), heteropolyacid 0.06 mmol, tetrabutylammonium bromide 1 g (3 mmol), benzoquinone 0.074 g (0.69 mmol) and MS 7 g were charged to a 100 ml stainless-steel autoclave. The autoclave was sealed and heated to 80 °C. With mechanical stirring at 800 rpm, a gas mixture (6.5 mol% O_2 and 93.5 mol% CO) was introduced at a flow rate of 535 ml/min. The pressure of the autocalve was kept at 8 atm with continuous gas flow for 3 h. Then, the reaction mixture was analyzed by GC with a capillary colomn (DB-1, 15 m × f0.53 mm, J&W Scientific). The products were identified by GC-MS spectra. The yield of DPC is based on charged phenol with diphenyl as the internal standard. The selectivity is based on DPC percentage in the products evaluated from the peak areas on GC.

3. Results and discussion

In the absence of solvent, some heteropolyacids are chosen as the redox cocatalysts for the oxidative carbonylation of phenol to DPC with $Pd(OAc)_2$ as the catalyst under low pressure and in a flow system. The results are summarized in table 1. From the table, one can see that, without cocatalyst, $Pd(OAc)_2$ is also slightly active for the oxidative carbonylation of phenol to DPC, although the yield of

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Table 1
Oxidative carbonylation of phenol to DPC with various heteropolyacids as cocatalysts.[a]

Entry	Cocatalyst	DPC yield[b] (%)	DPC selectivity[c] (%)
1	–	0.3	>99.9
2	$H_4PVMo_{11}O_{40}$	1.4	99
3	$H_5PV_2Mo_{10}O_{40}$	4.4	97.4
4	$H_3PW_6Mo_6O_{40}$	0.4	>99.9
5	$Mn(OAc)_2$	14.9	96.6
6	$H_3PW_{10}Mo_2O_{40} + Mn(OAc)_2$	18.6	97.8
7	$H_3PW_8Mo_4O_{40} + Mn(OAc)_2$	19.6	98.1
8	$H_3PW_6Mo_6O_{40} + Mn(OAc)_2$	21.6	98.5
9	$H_3PW_4Mo_8O_{40} + Mn(OAc)_2$	18.8	99.2
10	$H_3PW_{12}O_{40} + H_3PMo_{12}O_{40} + Mn(OAc)_2$	13.1[d]	98.0
11	$H_4SiW_4Mo_8O_{40} + Mn(OAc)_2$	17.8	97.7
12	$H_4SiW_6Mo_6O_{40} + Mn(OAc)_2$	22.0	98.0
13	$H_3PW_6Mo_6O_{40} + Mn(OAc)_2$	22.0[e]	98.9
14	$H_5PV_2Mo_{10}O_{40} + Mn(OAc)_2$	10.2	98.6
15	$H_5PV_2Mo_{10}O_{40} + Co(OAc)_2$	5.5	98.3
16	$H_5PV_2Mo_{10}O_{40} + Cu(OAc)_2$	10.3	98.2
17	$H_5PV_2Mo_{10}O_{40} + Cr(OAc)_2$	3.2	97.8
18	$H_5PV_2Mo_{10}O_{40} + Ce(OAc)_3$	7.4	99.9
19	$H_5PV_2Mo_{10}O_{40} + NaVO_3$	5.0	97.3

[a] Phenol 0.5 mol, $Pd(OAc)_2$ 0.16 mmol, $Mn(OAc)_2$ 0.32 mmol, heteropolyacid 0.06 mmol, benzoquinone 0.69 mmol, tetrabutylammonium bromide 3 mmol, MS 7 g, 8 atm, CO 500 ml/min, O_2 35 ml/min, 80 °C, 3 h.

[b] GC yield based on charged phenol.

[c] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC-MS spectroscopy.

[d] $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, 0.03 mmol, respectively.

[e] Without benzoquinone.

DPC is only 0.3% based on phenol with 99.9% selectivity (entry 1). This result shows that regeneration of the active Pd(II) species from Pd(0) with gaseous oxygen is a slow reaction under the present conditions and the Pd black aggregated from Pd(0) is also very difficult to reoxidize to Pd(II). The V-containing heteropolyacids have been reported as efficient cocatalysts to oxidize Pd(0) to Pd(II) [14]. In the present reaction, 1.4% yield is obtained with $H_4PVMo_{11}O_{40}$ as the cocatalyst (entry 2). $H_5PV_2Mo_{10}O_{40}$ is more active than $H_4PVMo_{11}O_{40}$; its yield can be improved to 4.4% with 97.4% selectivity (entry 3). $H_3PW_6Mo_6O_{40}$ is inactive as a cocatalyst (entry 4), which suggests that $H_3PW_6Mo_6O_{40}$ is incapable of reoxidizing Pd(0) to Pd(II). $Mn(OAc)_2$ is a good cocatalyst, and its yield can reach 14.9% although selectivity drops down to 96.6% (entry 5). The major byproducts are phenylsalicylate and 4-phenoxyphenol, which have been identified by GC-MS spectra.

Unexpectedly, the combination of P–W–Mo-containing heteropolyacids and $Mn(OAc)_2$ as the bicomponent cocatalysts, gives generally higher yields and selectivities than the case of $Mn(OAc)_2$ as the sole cocatalyst, despite that $H_3PW_6Mo_6O_{40}$ as the sole cocatalyst is inactive (entries 4 and 6–9). Especially, the yield can be improved to 21.6% with 98.5% selectivity when $H_3PW_6Mo_6O_{40}$ is combined with $Mn(OAc)_2$ as the cocatalyst (entry 8). However, low yield (13.1%) was obtained with $Mn(OAc)_2$ combined with $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ as the cocatalyst (entry 10). Furthermore, Si–W–Mo-containing heteropolyacids have shown the same activity as the P–W–Mo-containing heteropolyacids (entries 11 and 12). For example, 22% yield could be obtained with $H_4SiW_6Mo_6O_{40}/Mn(OAc)_2$ as the cocatalysts.

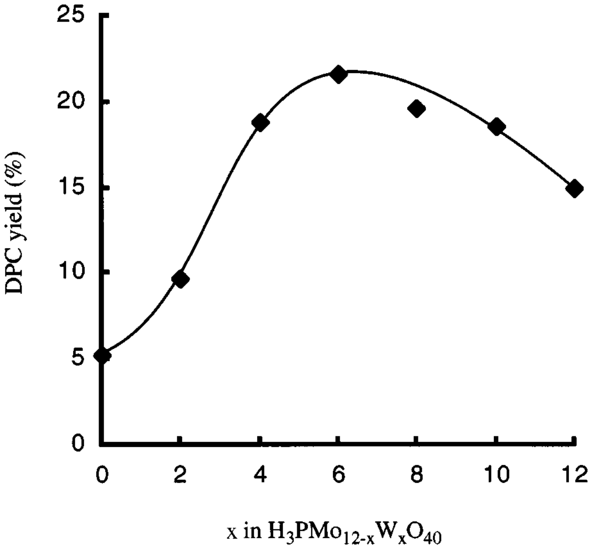
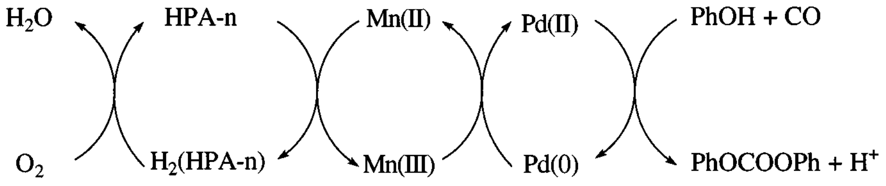


Figure 1. The influence of the ratio of W/Mo in heteropolyacids on the catalytic activity.

These results suggest that there is a synergistic effect existing between $Mn(OAc)_2$ and the W–Mo-containing heteropolyacids for regenerating Pd(II). The synergistic effect was observed only when the W and Mo atoms in one heteropolyacid, otherwise, no synergistic effect was observed in the reaction (entry 10). In addition, the central element (P or Si) of the heteropolyacids seems to have no influence on the synergistic effect, although it has been reported that the central element of heteropolyacids often has a great influence on the catalytic activity of the heteropolyacids [13]. In the same case, benzoquinone is unnecessary, which means the bicomponent cocatalyst is efficient enough to reoxidize Pd(0) (entry 13). In addition, the combination of $H_5PV_2Mo_{10}O_{40}$ and $Mn(OAc)_2$ as the cocatalysts, gives lower yield of DPC (10.2%) than the case of $Mn(OAc)_2$ as the only cocatalyst (entry 14), although $H_5PV_2Mo_{10}O_{40}$ and $Mn(OAc)_2$ are all active. $H_5PV_2Mo_{10}O_{40}$ plus other metal salts as the bicomponent cocatalyst also give inferior results (entries 16–19).

The influence of the ratio of W/Mo in heteropolyacids on the catalytic activity is shown in figure 1. From the figure, one can see that, with $H_3PMo_{12}O_{40} + Mn(OAc)_2$ as the cocatalysts, the yield of DPC is only 5%. Instead of $H_3PMo_{12}O_{40}$, with $H_3PMo_{10}W_2O_{40}$ ($x = 2$), the yield can go up to 9.7%. When $H_3PW_{12}O_{40}$ ($x = 0$) is chosen as one part of the cocatalyst, 15% yield could be obtained. And yield can be improved to 21.6% when $H_3PMo_6W_6O_{40}$ ($x = 6$) is used as one part of the cocatalyst. Judging from no synergistic effect of a simple mixture of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, as in table 1 (entry 10), the presence of



Scheme 1. A possible mechanism for the oxidative carbonylation of phenol.

polyanions with W–Mo mixed addenda atoms is responsible for the excellent yields. The best ratio of W/Mo is 6 to 6. It has been reported that the redox potential and catalytic performance can be changed by the W–Mo mixed coordination ($H_3PMo_{12-x}W_xO_{40}$) [15]. Therefore, the synergistic effect between W–Mo-containing heteropolyacids and $Mn(OAc)_2$ is likely to be associated with the change in the redox properties of polyanions.

A possible mechanism of multistep electron transfer is shown in scheme 1. Pd(II) would be reduced to Pd(0) during the DPC formation from phenol and CO. The Pd(0) thus formed would be then reoxidized by Mn(III) to form Pd(II) and Mn(II). Mn(II) would be reoxidized to Mn(III) with HPA-n which is thus reduced to H_2(HPA-n). Finally, H_2(HPA-n) would be oxidized to HPA-n by O_2.

4. Conclusions

V-containing heteropolyacids have been found to be active for regenerating the active Pd(II) species. Although W–Mo-containing heteropolyacids are inactive as the sole cocatalyst, the efficiently synergistic effects are observed when they are combined with $Mn(OAc)_2$ as the bicomponent cocatalyst for regenerating Pd(II). The central element (P or Si) of heteropolyacids has little influence on the synergistic effect. The best yield (22%) can be obtained with W/Mo ratio at 6/6 in the W–Mo-containing heteropolyacids at low pressure.

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