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Immobilization of carbonylcobalt catalyst by poly (4-vinylpyridine) (P4VP) through N→Co coordination bonds: the promotional effect of pyridine and the reusability of polymer catalyst

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Abstract: A carbonylcobalt catalyst has been immobilized by poly (4-vinylpyridine) (P4VP) through N→Co coordination bonds has been prepared by solvothermal method. It has been revealed that the pyridine fragments in the polymer catalyst act not only as promoters to improve the catalytic performance of carbonylcobalt catalyst for alkoxy-carbonylation of ethylene oxide to methyl 3-hydroxypropanoate but also as stabilizers to enhance the reusability of polymer catalyst.

It is well known that carbonylcobalt coordination compounds like $Co_2(CO)_8$ and $Na[Co(CO)_4]$ are the key homogeneous catalysts and have been widely used in the alkoxy-carbonylation of epoxides as well as in the hydroformylation of olefins.[1] Recently, carbonylcobalt-catalyzed alkoxy-carbonylation of ethylene oxide (EO) to methyl 3-hydroxypropanoate (3-MHP) and subsequent hydrogenation of 3-MHP to 1,3-propanediol (1,3-PDO) have attracted much attention, because this route is an atom economic and environmentally benign process for production of 1,3-PDO intermediate to synthesize the advanced polypropylene terephthalate (PTT) fibers:[2]

$$\text{EO} + CH_3OH + CO = HO\text{-}CH_2CH_2COOCH_3 \ \text{(3-MHP)}$$
$$\text{3-MHP} + H_2 = CH_3OH + HO\text{-}CH_2CH_2CH_2\text{-}OH \ \text{(1,3-PDO)}$$

In fact, the carbonylcobalt catalysts with nitrogen heterocyclic compounds as promoters have been found to be the effective catalysts for alkoxy-carbonylation of EO in the homogeneous catalytic reaction system,[3,4] however, it is very difficult to separate the catalysts from mixture products and to reuse them. The most challenging problem in production of 1,3-PDO from EO is to explore a stable and reusable carbonylcobalt catalyst for alkoxy-carbonylation of EO. So far, great efforts have been made in preparation of reusable catalysts and in studying their catalytic properties for the alkoxy-carbonylation of epoxides.[4a, 5] As previously reported, the organometallic ionic liquids $[ILs]^+[Co(CO)_4]^-$ exhibited excellent catalytic performances and considerable reusability for the alkoxy-carbonylation of EO. However, the ion pairs in the ionic compound $[ILs]^+[Co(CO)_4]^-$ are combined by a relatively weak ionic bond, which probably makes the ions leach out especially in contact with water or some other strong polar solvents. Obviously, it is preferable that the carbonylcobalt catalysts are immobilized in solid polymer materials containing ligands through a relatively strong coordination bond because the polymer catalysts are easy to separate, and the catalysts stability are potentially enhanced by confinement and coordination effects.[6]

Herein, we report the synthesis, characterization and catalytic performance of a recyclable poly (4-vinylpyridine) - carbonylcobalt polymer catalyst.[7] The catalytic activity, selectivity and reusability of the polymer catalysts are satisfactory, and their structures have been well-defined by using various physico-chemical methods.

The carbonylcobalt polymer catalyst studied in this work was synthesized by solvothermal method, in which the synthesis procedures were described in detail in the supporting information (SI) section. Commercially available poly (4-vinylpyridine) (P4VP) and $Co_2(CO)_8$ were used as starting materials and reacted in a mixed solvent THF/CH_3OH (1:3 V/V) at 75 °C under 3 MPa CO atmosphere for 24 h. From Figure S1 (a,b), one can see that the solvothermal treatment results in swelling of P4VP polymer materials. Moreover, the swelling degree of $Co_2(CO)_8$ loaded sample is higher than that of bare P4VP sample (Figure S1 b,c), suggesting that $Co_2(CO)_8$ reacts with P4VP in the solvothermal system. As determined by an inductively coupled plasma optical emission spectroscopy (ICP-OES) method, the as-prepared catalyst contained 16.1 wt% Co, 8.1 wt% N, i.e., n(Co)/n(N) = 1/2 (molar ratio). The energy diffusion spectroscopy (EDS) image displayed a homogeneous distribution of Co and N in the solid polymer materials (Figure S2), and the X-ray diffraction (XRD) pattern indicated that the polymer materials were in an amorphous state (Figure S3).

The gas chromatography-mass spectrometer (GC-MS) analysis results indicated that methyl 3-hydroxypropanoate (3-MHP) was a main product of EO alkoxy-carbonylation reaction catalyzed by carbonylcobalt. Besides, ethylene glycol (EG), 2-methoxyethanol (EM) and ethylene glycol dimethylether (EGDME) were also formed as the by-products in the reaction (S1). Table 1 listed the EO conversion and product selectivity of $Co_2(CO)_8$ catalyst in a homogeneous reaction system with or without organic compound as promoters under the same reaction conditions. For $Co_2(CO)_8$ catalyst without any promoter, EO conversion was 87.5 % with 3-MHP selectivity of 37.2 %. In contrast, pyridine itself didn't show any catalytic activity for EO alkoxy-carbonylation to form 3-MHP. Interestingly, $Co_2(CO)_8$-pyridine gives both higher EO conversion and higher 3-MHP selectivity, suggesting that for the alkoxy-carbonylation of EO catalyzed by $Co_2(CO)_8$-pyridine, $Co_2(CO)_8$ acts as a main

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Table 1. The alkoxy-carbonylation of EO over $Co_2(CO)_8$ and $[Co_2(CO)_6]$P4VP catalysts.[a]

Catalyst	Promoter[d]	EO Conversion (%)[e]	Selectivity (%)[e]				
			3-MHP	EM	EG	EGDME	Other Products
-	pyridine	14.7	0	94.4	5.6	0	0
$Co_2(CO)_8$	-	87.5	37.2	10.8	1.4	5.4	45.2
	pyridine	98.1	77.6	1.8	11.7	7.2	1.7
	4-vinylpyridine	97.8	74.6	9.3	10.4	1.3	4.4
	4-ethylpyridine	97.3	76.5	8.3	11.1	1.4	2.7
	3-hydroxypyridine	98.9	80.3	5.7	12.3	0.5	1.2
	imidazole	97.6	78.4	3.7	14.9	0.5	2.5
	triphenyl phosphine	29.2	19.1	5.2	36.4	30.2	9.1
$[Co_2(CO)_6]$ P4VP	-	85.8	79.6	3.5	9.1	5.6	2.2
$[Co_2(CO)_6]$ P4VP[b]	-	74.3	73.1	10.9	5.3	6.6	4.1
$[Co_2(CO)_6]$ P4VP[c]	-	99.6	50.9	19.7	1.5	12.3	15.6

[a] n(Co):n(EO)=5.7:100, n(EO):n(CH_3OH)= 1:1.5, V(THF)=15 mL T=75 °C , t=15 h, P_{co} =3 MPa. [b] $[Co_2(CO)_6]$P4VP stored in air for a month at 0-4 °C. [c] Without using THF as a solvent. [d] n(Co):n(promoter)=1:2 [e] Determined by GC.

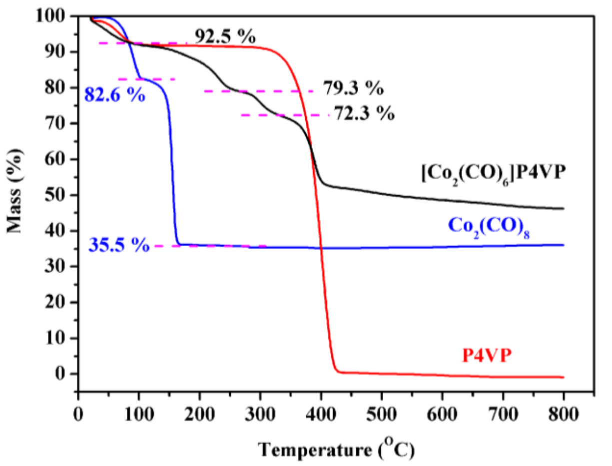

Figure 1. TG curves of $Co_2(CO)_8$, P4VP and $[Co_2(CO)_6]$P4VP.

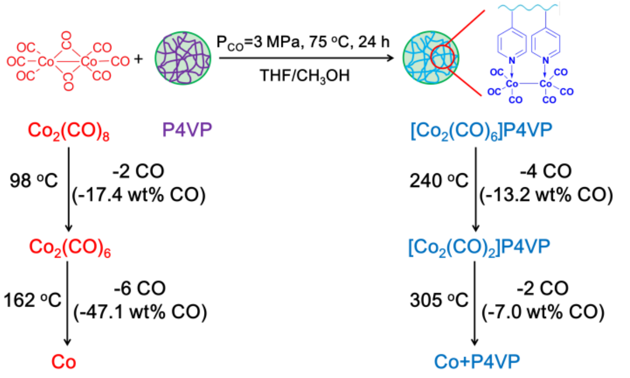

Figure 2. The structure and thermal decomposition of $Co_2(CO)_8$ and $[Co_2(CO)_6]$P4VP polymer catalyst.

catalytic component while pyridine acts as a promoter for the formation of 3-MHP. It can be seen from Table 1 that EO alkoxy-carbonylation reaction catalyzed by carbonylcobalt with different groups substituted-pyridine and imidazole as promoters exhibited very similar EO conversion and 3-MHP selectivity. In contrast, the alkoxy-carbonylation of EO catalyzed by $Co_2(CO)_8$-triphenylphosphine gave very lower EO conversion and 3-MHP selectivity. These results indicated that the carbonylcobalt catalysts with nitrogen heterocyclic compounds as promoters were the effective catalysts for alkoxy-carbonylation of EO. The promotional effect of pyridine on the $Co_2(CO)_8$ catalyst will be discussed in the later section of poly (4-vinylpyridine) - carbonylcobalt polymer catalyst.

To develop an easily separative and reusable carbonylcobalt catalyst for alkoxy-carbonylation of EO, the poly (4-vinylpyridine)-carbonylcobalt polymer catalyst containing both the $Co_2(CO)_8$ catalyst and pyridine promoter has been synthesized and characterized. Figure 1 and S4 showed the thermogravimetric (TG) and differential thermal analysis (DTA) results of samples. For $Co_2(CO)_8$ (34.5 wt% Co), three endothermic peaks can be observed in its DTA curve, the first of which not accompanied by mass loss, is attributed to melting of $Co_2(CO)_8$, while the second at 98 °C accompanied by mass loss of 17.4 wt% and the third at 162 °C accompanied by mass loss of 47.1 wt%, are attributed to decomposition of $Co_2(CO)_8 \rightarrow Co_2(CO)_6 \rightarrow Co$, respectively (Figure 2). For the P4VP sample pretreated by solvothermal method, two peaks appeared at 76 °C and 405 °C accompanied by mass loss, the first of which can be attributed to release of solvents absorbed and/or adsorbed in the polymer, and, the second to the complete decomposition of the polymer.[8] As for $Co_2(CO)_8$ uploaded P4VP sample, two endothermic peaks appeared at 67 °C and 392 °C, which were very similar to those of bare P4VP. In contrast with DTA curve of bare P4VP sample, two new endothermic peaks accompanied by mass loss of 13.2 wt% at 240 °C and 7.0 wt% at 305 °C can be observed (Figure

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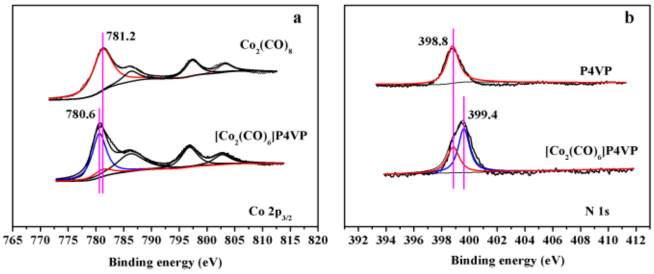

Figure 3. XPS results of $[Co_2(CO)_6]$P4VP, $Co_2(CO)_8$ and P4VP.

S4 c) in the TG/DTA curves of $Co_2(CO)_8$ uploaded P4VP sample, which are attributed to decomposition of carbonylcoblt in the sample. Considering that the as-prepared catalyst contained 16.1 wt% Co, it is estimated that total n(CO)/n(Co) molar ratio is ca. 3:1 (denoted as $[Co_2(CO)_6]$P4VP), and the above two new peaks can be attributed to decomposition of $[Co_2(CO)_6]$P4VP→ $[Co_2(CO)_2]$P4VP → [Co]P4VP (Figure 2). Compared with $Co_2(CO)_8$, $[Co_2(CO)_6]$P4VP decomposition shifts to higher temperatures, suggesting that there is a strong interaction between carbonylcobalt and P4VP, which stabilizes the structure of carbonylcobalt.

The interaction between carbonylcobalt and P4VP in the $[Co_2(CO)_6]$P4VP catalyst has been characterized by using various methods. X-ray photoelectron spectra (XPS) of the catalyst (Figure 3) demonstrated the binding energy of Co $2p_{3/2}$ in $[Co_2(CO)_6]$P4VP was 780.6 eV, which was lower than that of Co $2p_{3/2}$ (781.2 eV) in $Co_2(CO)_8$, and the N1s spectra of catalyst possessed a peak with higher binding energy of 399.4 eV than that of bare P4VP (398.8 eV), indicating that the electrons probably transfer from N atoms in part of pyridine rings of polymer to Co atoms in carbonylcobalt, resulting in formation of electron-riched Co species in the polymer catalyst.

The IR spectra of $Co_2(CO)_8$ (Figure 4) showed terminal and bridging C=O stretching vibrations v(CO) at 2003 cm^{-1} and 1825 cm^{-1}, respectively.[9] Compared with IR spectra of $Co_2(CO)_8$, the terminal CO stretching vibrations of the polymer catalyst exhibited a red shift from 2003 cm^{-1} to 1863 cm^{-1} and the bridging CO stretching vibration (1825 cm^{-1}) was almost disappeared, suggesting that there was only terminal CO groups in the polymer catalyst and their vibrational frequency decreased obviously. This is probably because the electron-riched Co transfers more electrons to CO π^* antibonding orbit, resulting in decrease of CO vibrational frequency. The IR absorption band at 1595 cm^{-1} attributable to the C=N characteristics vibration shifted to ca. 1603 cm^{-1} in the polymer catalyst, indicating that the C=N bonds in pyridine rings became stronger due to N → Co coordination.[10] From the raman spectra (Figure S5), the 1888 cm^{-1} of polymer catalyst was clearly assigned to carbonyl vibration in correspondence with IR spectra (1863 cm^{-1}). On the other hand, the raman bands in the region of 600-1600 cm^{-1} are originated from P4VP, as $[Co_2(CO)_6]$P4VP and P4VP have the same spectroscopic characteristics in this region. Figure 5 showed the UV-Vis spectra of $Co_2(CO)_8$ and $[Co_2(CO)_6]$P4VP polymer catalyst. For $Co_2(CO)_8$, the bands at 356 nm and 529 nm were assigned to the $\sigma \rightarrow \sigma^*$ transitions of Co-Co bond and the d-d transitions of Co, respectively,[11] and the band at 320 nm was ascribed to the metal to ligand charge transfer (MLCT) of Co-CO. For the polymer catalyst $[Co_2(CO)_6]$P4VP, the peak assigned to $\sigma \rightarrow \sigma^*$ transitions of Co-Co bond can also be observed at 356 nm, while Co d-d transitions shifted to higher wavelength (590 nm). These results clearly confirm that CO ligands in $Co_2(CO)_8$ were partly substituted by pyridine rings branched to polymer chains. The red shift of Co d-d transitions band was probably because of weaker ligand field strength of pyridine than that of CO.[12] Based on the above results, the composition and structure of poly (4-vinylpyridine) - carbonylcobalt polymer catalyst was proposed in Figure 2, which obeys the 18 electron rule. The formation of N→Co coordination bond not only stabilizes the carbonylcobalt species but also makes Co to be an electron-riched state.

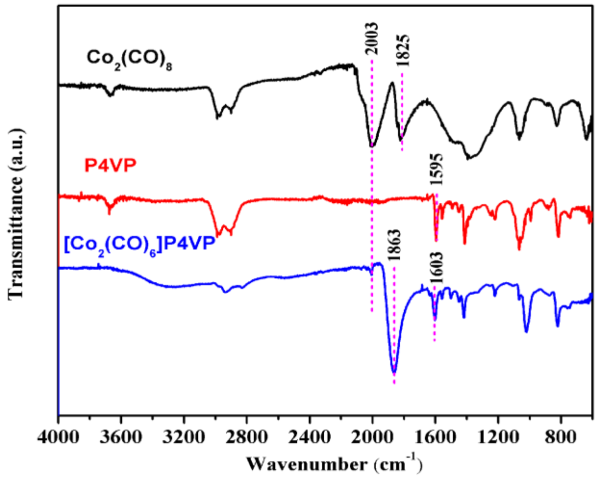

Figure 4. IR spectra of $[Co_2(CO)_6]$P4VP, $Co_2(CO)_8$ and P4VP.

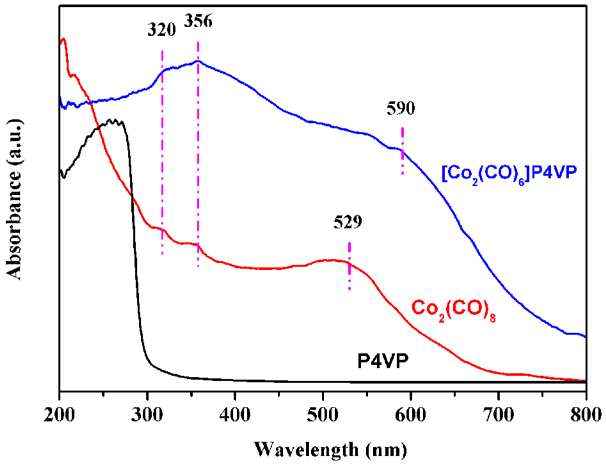

Figure 5. UV-Vis spectra of $[Co_2(CO)_6]$P4VP and $Co_2(CO)_8$.

The catalytic performance of above $[Co_2(CO)_6]$P4VP catalyst for alkoxy-carbonylation of EO has been investigated and the results are summarized in Table 1. It can be seen that the polymer catalyst presented high EO conversion (85.8 %) and 3-MHP selectivity (79.6 %). Even after exposure to air at 0-4 ^{o}C for

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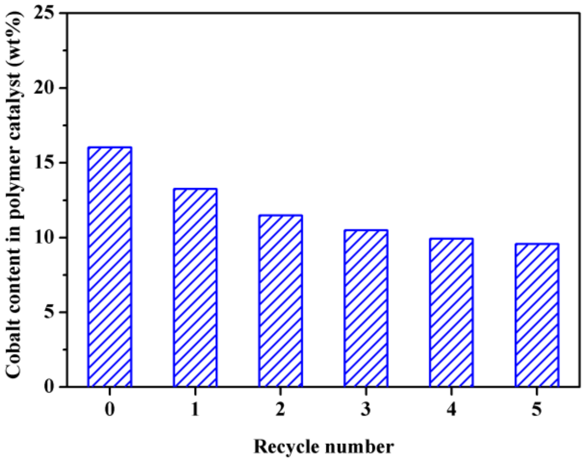


Figure 6. Cobalt content in the polymer catalyst after recycles.

a month, the $[Co_2(CO)_6]$P4VP catalyst showed a minor drop in EO conversion (74.3 %) and 3-MHP selectivity (73.1 %), indicating that the $[Co_2(CO)_6]$P4VP polymer catalyst had higher structure stability. For the polymer catalyst without using THF as a solvent, the EO conversion increased to 99.6 % and 3-MHP selectivity decreased to 50.9 %, indicating that THF solvent is beneficial to the formation of 3-MHP. It's worth noting that the 3-MHP selectivity of $[Co_2(CO)_6]$P4VP catalyst was much higher than $Co_2(CO)_8$ catalyst without any nitrogen heterocyclic compound as a promoter, suggesting that pyridine in the $[Co_2(CO)_6]$P4VP polymer catalyst acts not only as a ligand to coordinate and stabilize carbonylcobalt but also as a promoter for the alkoxy-carbonylation of EO. As revealed by the XPS results mentioned above, the N→Co coordination makes Co in the carbonylcobalt to be an electron-riched state, which is beneficial to nucleophilic attack of Co atoms in carbonylcobalt to carbon atoms in EO, [13] leading to remarkable increase of 3-MHP selectivity. As shown in Table 2, the polymer catalyst also showed excellent catalytic performance for the alkoxy-carbonylation of other terminal epoxides and alcohols with different carbon chain length.

Furthermore, the effects of amount of catalyst used and the reaction conditions on the catalytic properties of $[Co_2(CO)_6]$P4VP catalyst for alkoxy-carbonylation reaction of EO were investigated. As presented in Figure S6, both EO conversion and 3-MHP selectivity increased remarkably with increasing the amount of catalyst. On the contrary, the selectivity of by-products decreased obviously. Figure S7 depicted the influence of reaction temperature on the catalytic activity and selectivity. The EO conversion and 3-MHP selectivity increased remarkably with increase of reaction temperature to 75 °C, but further increasing temperature resulted in decrease of 3-MHP selectivity. The optimum reaction temperature of $[Co_2(CO)_6]$P4VP catalyst for alkoxy-carbonylation of EO was determined to be ca. 75 °C. As shown in Figure S8, the alkoxy-carbonylation of EO over $[Co_2(CO)_6]$P4VP catalyst proceeded rapidly within the first 8 h. After reaction for 15 h, EO conversion and 3-MHP selectivity reached 85.8 % and 79.6 %, respectively.

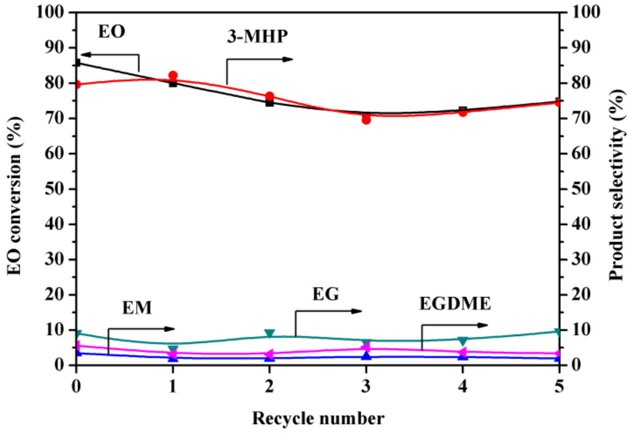
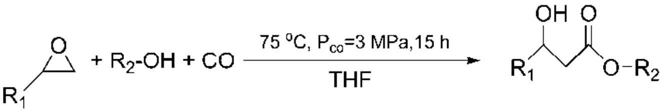
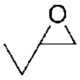


Figure 7. Reusability of the polymer catalyst. (n(Co):n(EO)=5.7:100, n(EO):n(CH_3OH)= 1:1.5, V(THF)=15 mL, T=75 °C , t=15 h, Pco =3 MPa).

Table 2. The alkoxy-carbonylation of various epoxides and alcohols over $[Co_2(CO)_6]$P4VP catalysts.[a]



Epoxides	Alcohols	Epoxides Conversion (%)[c]	β-hydroxy esters Selectivity (%)[c]
	CH_3-OH[b]	92.9	84.1
	CH_3CH_2-OH	90.4	71.1
	$CH_3CH_2CH_2$-OH	83.5	78.0
	CH_3-OH	73.6	85.3
	CH_3CH_2-OH	66.4	84.3
	CH_3CH_2-OH	54.9	82.7

[a] n(Co):n(epoxides)=11.4:100, n(epoxides):n(R_2-OH)= 1:1.5, V(THF)=15 mL T=75 °C, t=15 h, P_{co} =3 MPa. [b] n(Co):n(epoxides)=8.6:100. [c] Determined by GC.

Further prolonging reaction time resulted in a minor increase of EO conversion but obvious decrease of 3-MHP selectivity. Apparently, the optimum reaction time for alkoxy-carbonylation of EO catalysed by $[Co_2(CO)_6]$P4VP was ca 15 h. As shown in Figure S9, increasing CO pressure from 1.0 to 4.0 MPa, EO conversion increased greatly, while 3-MHP selectivity increased not obviously. It is noteworthy that alkoxy-carbonylation of EO over $[Co_2(CO)_6]$P4VP catalyst can be operated under CO pressure lower than 3.0 MPa. In comparison, for the $[ILs]^+[Co(CO)_4]^-$ catalyst, the reaction should be carried out under CO pressure higher than 3.7 MPa.[2, 3b, 3c]

The reusability of as-prepared polymer catalyst was investigated. After reaction for 15 h, the catalyst was readily separated just by filtration and washed with THF in air. The

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catalyst was reused in the following recycle experiments and its cobalt content was analysed by an inductively coupled plasma optical emission spectroscopy (ICP-OES) method after every cycle. As shown in Figure 6 and 7, the cobalt content in the polymer catalyst decreased within the first 2 recycles, accompanied by decreases of EO conversion and 3-MHP selectivity. This is probably because there is a part of carbonylcobalt species weakly adsorbed in the fresh polymer catalyst, which will be inevitably leached out in the first 2 recycles. Interestingly, the cobalt content in the polymer catalyst remained almost constant after 3 cycles and the EO conversion and 3-MHP selectivity kept stable, indicating that the carbonylcobalt species immobilized in the solid polymer materials through N→Co coordination bonds are very stable and thus reusable.

In summary, immobilization of carbonylcobalt catalyst by poly (4-vinylpyridine) (P4VP) through N→Co coordination bonds has been realized, and as a result, the polymer catalyst exhibited better catalytic properties and stability than $Co_2(CO)_8$ even after storage in air for a month. The polymer catalyst can be readily separated by filtration and reused 5 times with only slightly decreased in EO conversion and 3-MHP selectivity. The structure of polymer catalyst has been characterized and it has been proposed that pyridine fragments in the polymer catalysts act not only as promoters to enhance the catalytic activity and selectivity for alkoxy-carbonylation of ethylene oxide but also as stabilizers to increase the reusability of carbonylcobalt species through N→Co coordination bonds. Our results have revealed that immobilizing carbonyl-cobalt catalysts in the solid polymer materials by coordination bonds is a promising strategy to stabilize the homogeneous catalysts and to easily separate and reuse them.

Keywords: alkoxy-carbonylation of ethylene oxide • carbonylcobalt catalyst • pyridine promoter • polymer catalyst • reusability

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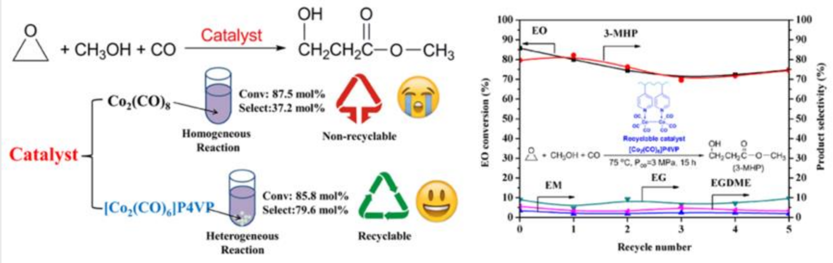

A recyclable $[Co_2(CO)_6]$P4VP polymer catalyst has been synthesized and its structure has been proposed. It has been demonstrated that the pyridine fragments in the polymer catalyst act not only as promoters to improve the catalytic performance for alkoxy-carbonylation of ethylene oxide but also as stabilizers to increase the reusability of polymer catalyst. Furthermore, the polymer catalyst could be easily separated by filtration and reused with only slightly loss of catalytic efficiency.

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Immobilization of carbonylcobalt catalyst by poly (4-vinylpyridine) (P4VP) through N→Co coordination bonds: the promotional effect of pyridine and the reusability of polymer catalyst

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