Copolymerization of Carbon Dioxide and Propylene Oxide by DMC: Effect of Central Metal on Catalytic Performance

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Abstract: A series of double metal cyanide (DMC) complexes based on $Zn_a[M(CN)_b]_c$ (M= Fe^{2+}, Co^{3+}, Ni^{2+}, Co^{3+}, Mn^{3+}, Mo^{4+}, Cd^{2+} and Fe^{3+}) were prepared and employed as catalysts for copolymerization of propylene oxide and CO_2 to investigate the effect of central metal on catalytic performance. The results showed that the efficiency of catalysts and the composition of products varied significantly with change of central metal. The DMC based on Co^{3+}, Ni^{2+} exhibited highest efficiency among these catalysts, which was 2000 and 482 g/g whereas the DMC based on Cd^{2+}, Mn^{3+} nearly exhibited no catalytic activity towards copolymerization. The copolymer with molar fraction of CO_2 ($x(CO_2)$) greater than 0.3 could be obtained when DMC based on Co^{3+}, Ni^{2+}, Fe^{3+} were employed, in contrast copolymers with low $x(CO_2)$ (≤ 0.1) produced in most cases for other catalysts.

Key words: double metal cyanide complex; propylene oxide; carbon dioxide
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The production of aliphatic polycarbonate by the copolymerization of carbon dioxide and epoxides has received much attention and a number of catalysts were developed since Inoue discovered the catalytic system such as ZnEt$_2$-H$_2$O[1-2]. Double metal cyanide (DMC) complex is a kind of potential catalytic system[3-5], in which $Zn_a[M(CN)_b]_c$ is of main composition. However, the effect of central metal on copolymerization of epoxide and CO_2 has never been investigated. Herein DMC complexes with Cr^{3+}, Ni^{2+}, Mn^{3+}, Mo^{4+}, Cd^{2+}, Co^{3+}, Fe^{2+} and Fe^{3+} as central metal were prepared and their catalytic performance was examined.

1 Experiments

1.1 Materials

$K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ were analytical grade and recrystallized before use. Other potassium cyanometallate were prepared according to published literatures. CO_2 (> 99.9%) was used as received and other reagents were analytical grade.

1.2 Experiments and measurement

The preparation of catalyst was conducted as follows: 10 mL of $K_a[M(CN)_b]_c$ solution (0.2 mol/L) was added dropwise in $ZnCl_2$ solution (8 g $ZnCl_2$ in mixture of 30 mL water and 15 mL tert-butyl alcohol (TBA)) under vigorous stirring at 35 ℃, the resulting suspension was filtered to isolate precipitate of DMC catalyst. Then it was washed with TBA and water (v/v = 1∶1) and dry for further use. The composition of catalysts was analyzed by Hitachi 180-50 atomic absorption spectrophotometer and Flash EA1112 elemental analyzer; the molar fraction of CO_2 was calculated by ^{1}H NMR (AVANCE DMX 500).

2 Results and discussion

The reaction of propylene oxide and CO_2 catalyzed by these catalysts may result in copolymer as well as propylene carbonate, a byproduct via coupling reaction. The results of copolymerizations of propylene oxide (PO) and CO_2 (Table 1) showed that the efficiency of catalysts and the composition of products varied significantly with the change of central metal. DMC based on Co^{3+} and Ni^{2+} exhibited relatively higher efficiency among these catalysts; Cr^{3+} and Fe^{3+} exhibited moderate efficiency; whereas the DMC based on Mo^{4+}, Cd^{2+}, Mn^{3+} exhibited nearly no catalytic activity towards copolymerization. The copolymer with $x(CO_2)$ (molar fraction of CO_2) $\geq$ 0.3 could be obtained when DMC based on Fe^{3+}, Co^{3+}, Ni^{2+} were em-

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ployed. In contrast, copolymers with extremely low $x(CO_2)$ (0.02 or 0.06 for Cd^{2+} and Cr^{3+}, respectively) were produced by other catalysts. From viewpoint of percentage of propylene carbonate (W_{PC}), the products obtained by DMC based on Ni^{2+} had lowest W_{PC}, which was only 6.6% ~9.1% under these conditions, whereas the product obtained by DMC based on Fe^{2+} under 80 ℃ contained 72.3% propylene carbonate. Combining with their several aspects of catalytic features, Co^{3+} and Ni^{2+} were most suitable central metal of DMC catalysts for copolymerization of propylene oxide and CO_2.

Tab.1 The results of copolymerization catalyzed by DMC with various central metal

Central Metal	Temperature (T/°C)	W_{pc} (%)	Efficiency (g/g)	$x(CO_2)$
Cr^{3+}	120	31.3	29.3	0.06
	140	36.6	75.4	0.10
Mo^{6+}	100	11.9	10.8	0.06
	130	16.5	51.3	0.14
Mn^{3+}	130	50.4	5.2	/
Fe^{2+}	60	38.8	44.6	0.16
	80	72.3	18.6	0.05
Fe^{3+}	60	12.1	27.4	0.33
	80	25.9	127.7	0.30
Co^{3+}	80	12.2	1444	0.32
	110	14.2	2000	0.24
	130	17.2	2111	0.19
Ni^{2+}	110	6.6	74.3	0.30
	130	9.1	438.7	0.24
Cd^{2+}	110	3.6	5.0	0.08
	130	6.5	7.1	0.02

3 Conclusion

The double metal cyanide complexes with different central metals were prepared and employed as catalysts for copolymerization of PO and CO_2. The results revealed that the kind of central metal has significant impact on its catalytic performance. Among them, Fe^{2+}, Co^{3+} and Ni^{2+} were suitable candidates of central metal in DMC catalyst.

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双金属络合催化剂中心金属对环氧丙烷/二氧化碳共聚影响

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摘 要: 合成了一系列基于 $Zn_a[M(CN)_b]_c$(M= Fe^{2+}, Cr^{3+}, Ni^{2+}, Co^{3+}, Mn^{3+}, Mo^{6+}, Cd^{2+}和 Fe^{3+})的双金属络合催化剂, 并且用于催化环氧丙烷和二氧化碳的共聚反应, 以研究中心金属对催化剂催化性能的影响。实验结果表明中心金属对催化剂催化性能影响很大, 其中以 Co^{3+}, Ni^{2+}为中心金属的催化剂具有较高的催化效能, 分别达到 2000和 482 g/g, 而以 Cd^{2+}, Mn^{3+}为中心金属的催化剂几乎没有催化活性。以 Co^{3+}, Ni^{2+}, Fe^{3+}为中心金属的催化剂能得到 $x(CO_2)$ 大于 0.3的共聚物, 而其它催化剂的共聚产物的 $x(CO_2)$ 小于 0.1.

关键词: 双金属氰化络合物; 环氧丙烷; 二氧化碳

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