

Homogeneous Mo-based Catalysts for Transesterification between Dimethyl carbonate and Phenol

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Introduction

The Polycarbonate (PC) is one of important engineering thermoplastics because of its good mechanical and optical properties as well as its electrical and heat resistance. The PC has been produced traditionally via the phosgene process, the interfacial polymerization between bisphenol-A and phosgene. As the need for environmental-friendly processes increases recently, the substitution of the phosgene process with the non-phosgene process has come to be welcomed. The most practical non-phosgene process for manufacturing polycarbonates is the melt transesterification of diphenyl carbonate (DPC) and bisphenol-A [1]. For this process, the efficient synthesis of DPC is essential. Among various synthetic routes, DPC is prepared commercially by the transesterification of DMC with phenol. Because the transesterification between DMC with phenol into DPC is not thermodynamically favorable ($K_p = 3 \times 10^{-4}$ at 453 K) [2], the two-step process, in which methylphenyl carbonate (MPC) was formed and transformed into DPC through the disproportionation reaction, is proposed to give us high yields of DPC. Until now, several catalytic systems for the non-phosgene DPC synthesis have been disclosed including homogeneous and heterogeneous catalysts. In our previous study [3], $\text{MoO}_3/\text{SiO}_2$, most active catalyst in liquid- and gas- phase reaction as a heterogeneous catalyst, could be deactivated by strong adsorption of reactant and products. Furthermore, some Mo species were leached from $\text{MoO}_3/\text{SiO}_2$ during a reaction and these dissolved metal species took part in this reaction as a homogeneous catalyst. Therefore, we go back to the homogeneous catalyst to find out the most active one for this reaction. In this work, we focused on the catalytic activity of ammonium molybdate as a homogeneous catalyst for the transesterification between DMC and phenol to production of MPC in the liquid-phase reaction. Among them, $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ showed the most active catalytic activity for this reaction.

Materials and Methods

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Daejung Chemical) were purchased and utilized as a catalyst or a parent material. The modified forms were prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ through calcinations in He or in air at 393 K, 423 K, 473 K and 523 K for 1 hr before a reaction. The catalysts were characterized by XRD, FT-IR, TGA, TPD & mass. The transesterification of phenol and DMC was carried out in a batch reactor. Phenol, DMC and a catalyst were introduced into an autoclave (100 ml, DMC / PhOH = 5, phenol = 55 mmol). The reactor was filled with nitrogen and the pressure was fixed to 300 psig. After the reaction, the autoclave was cooled to room temperature, and the products were filtered with 0.2 μm membrane filter and analyzed with a gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector (FID). The participation of the homogeneous catalyst leached from the solid catalyst was examined by using the filtered solution. The amount of metal species in a solution was measured with an ICP-AES and the solution was used as a homogeneous catalyst for the transesterification of DMC with phenol.

Results and Discussion

The catalytic activity for the transesterification between DMC and phenol was compared over Sn-, Pb- and Mo-based catalysts. The amount of MPC decreased in the following order: $\text{PbO} > (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} > \text{SnCl}_4 \cdot 5\text{H}_2\text{O} > (\text{C}_2\text{H}_3\text{O}_2)_2\text{Sn} > \text{Sn}(\text{CH}_3\text{COCHCOCH}_3)_2 > (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot n\text{H}_2\text{O} \sim \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} > \text{MoO}_3 \sim \text{CaMoO}_4 \sim \text{SnO} \sim \text{SnO}_2$. In the case of Mo-based catalysts, only $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ showed the noticeable catalytic activity. The effect of pretreatment condition $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was further examined. $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ through calcinations at ~ 423 K showed the highest MPC yield among various Mo-based catalysts.

The role of dissolved Mo and Pb species as a homogeneous catalyst was examined as shown in Table. 1. The turnover number based on the amount of homogeneous metal complexes decreased in the following order: $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34} > \text{PbO} > (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. This suggests that $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ can be a promising catalyst precursor to replace the commercial catalyst precursor such as PbO.

Table 1. The activity comparison among homogeneous catalysts leached from PbO, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$.

Catalyst	Reaction temperature /K	TOF ($\text{mol}_{\text{MPC}}\text{mol}_{\text{Metal}}^{-1}\text{min}^{-1}$)
PbO	413	3.9
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	413	1.8
$(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$	413	12.9
PbO	453	55.0
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	453	3.5
$(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$	453	119.7

^aReaction condition: Pressure = 300 psig; DMC/phenol=5, phenol=55 mmol.

Significance

Based on the comparison work for the transesterification between DMC and phenol over various homogeneous catalysts, $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ can be selected to show the highest MPC yields. The dissolved Mo species from $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ appeared to mainly take part in this reaction. This homogeneous catalyst showed the superior turnover frequency to the homogeneous lead complexes from PbO.

References

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