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12-Molybdophosphoric acid supported on titania: A highly active and selective heterogeneous catalyst for the transesterification of dimethyl carbonate and phenol



Songlin Wang^{a,b}, Rongzhi Tang^{a,b}, Yuanzhuo Zhang^{a,b}, Tong Chen^{a,*}, Gongying Wang^a

^a Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

HIGHLIGHTS

- HPMo/TiO₂ was first prepared by one-step in situ method.
- HPMo/TiO₂ revealed superior catalytic activity to other heterogeneous catalysts reported.
- Highly dispersed HPMo and Keggin structure played significant role for the excellent catalytic performance.
- The transformation of Mo⁶⁺ to Mo⁵⁺ decreased the catalytic activity.

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ABSTRACT

12-Molybdophosphoric acid supported on titania (HPMo/TiO₂) was prepared by one-step in situ method and first used to catalyze the transesterification of dimethyl carbonate and phenol to diphenyl carbonate, which exhibited excellent catalytic activity. The highly dispersed HPMo and stable Keggin structure played a significant role for the excellent catalytic performance of HPMo/TiO₂. With the conditions of weight ratio of HPMo to TiO₂ of 1:1, calcined temperature of 300 °C, catalyst amount of 0.6 g and reaction time 10 h, the phenol conversion and transesterification selectivity reached 50.4% and 99.4%, respectively. Moreover, after four consecutive runs, the phenol conversion slowly decreased from 44.7% to 29.5%, and the transesterification selectivity maintained at 99%. The characterization of XPS and FT-IR presented that the transformation of Mo⁶⁺ to Mo⁵⁺ and the adsorption of reaction intermediate were the key factors for the decrease of catalytic activity.

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1. Introduction

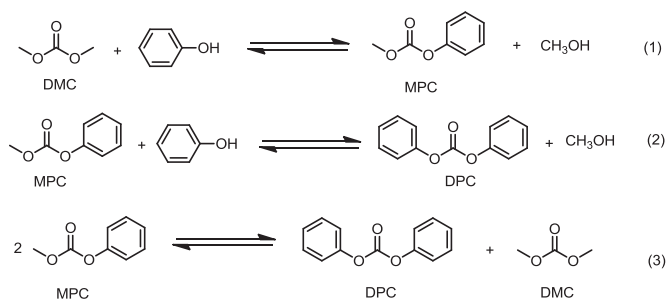
Polycarbonates (PC) was one of the most important engineering thermoplastics with high transparency, good mechanical property and heat resistance, which was useful in many applications such as office equipment, automobiles, construction glazing, household objects and medical devices (Kanega and Yamanaka, 2014; Fukuoka et al., 2003). Diphenyl carbonate (DPC) was extensively employed in the syntheses of various organic compounds and polymer materials (Park et al., 2014; Andraos, 2012; Bernini et al., 2007), especially utilized as an important building block for the non-phosgene preparation of PC by a melt polymerization process (Gong et al., 2007; Kim et al., 2004). The transesterification of dimethyl carbonate (DMC) and phenol was the most

prospective route to synthesize DPC with non-phosgene (Cheng et al., 2013; Kotbagi et al., 2012; Haubrock et al., 2008). This route was a two-step process consisting of the transesterification of phenol and DMC into methyl phenyl carbonate (MPC) (Scheme 1, Eq. (1)), followed by the further transesterification of phenol and MPC (Scheme 1, Eq. (2)) or the disproportionation of MPC to DPC (Scheme 1, Eq. (3)).

The transesterification reaction suffered from low yield and selectivity even at elevated temperature due to a critical thermodynamic limitation in the formation of MPC (3×10^{-4} , 180 °C) and the slow reaction rate (Wang et al., 2015; Mei et al., 2004). Therefore, the highly active catalysts played an important role for the transesterification of DMC and phenol. The liquid-phase transesterification of DMC and phenol was usually catalyzed by homogeneous catalysts, including Lewis acids (Deshmukh et al., 2010), organo-titanium (Niu et al., 2007) and organo-tin compounds (Wang et al., 2014; Lee et al., 2003, 2004), which were unstable and difficult to be separated from the products and

* Corresponding author. Tel.: +86 28 85250005; fax: +86 28 85220713.

E-mail address: chentongw@sina.com.cn (T. Chen).



further purified. Recently, more attention was paid to develop novel solid catalysts, and several heterogeneous catalysts had been explored like $\text{MoO}_3/\text{SiO}_2$ (Fu and Ono, 1997), $\text{MoO}_3/\text{SiMCM-41}$ (Li et al., 2008), $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ (Kim and Park, 2009b), $\text{TiO}_2/\text{SiO}_2$ (Kim and Park, 2009a; Kim et al., 2000), PbO/MgO (Cao et al., 2005), Pb-Zn composite oxide (Zhou et al., 2004), hydrotalcite (Wang et al., 2009), Ti-HMS (Luo et al., 2007), TiO_2/CNT (Zhou et al., 2014) and cerium-based binary and ternary oxides (Dibenedetto et al., 2014).

Our group was devoted to developing homogeneous and heterogeneous catalysts for the transesterification of DMC and phenol (Niu et al., 2005; Du et al., 2006; Tong et al., 2007; Ge et al., 2011; Li et al., 2012; Tang et al., 2014). Heteropoly compounds (HPCs) as environmentally-benign catalysts were widely used in homogeneous and heterogeneous catalysis due to their special hierarchical structure and physicochemical properties (Zhou et al., 2006). Recently, we found the catalytic potential of 12-molybdophosphoric acid mixed with TiO_2 promoter as heterogeneous catalyst for the transesterification of DMC and phenol (Chen et al., 2006, 2007), while the activity was not high enough for industrial purpose. In the present work, 12-molybdophosphoric acid supported on TiO_2 (HPMo/TiO_2) was prepared by one-step in situ method, and first used to catalyze the transesterification of DMC and phenol. The HPMo/TiO_2 revealed superior catalytic activity comparing with other heterogeneous catalysts reported. The effect of structural properties to catalytic performance was researched.

2. Experimental

2.1. Catalyst preparation

12-Molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, abbreviated as HPMo , $\geq 99\%$), titanium chloride (TiCl_4 , $\geq 99\%$) and ethanol absolute ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.7\%$) were purchased from Sigma-Aldrich. 12-Molybdophosphoric acid supported on titania (HPMo/TiO_2) was prepared by one-step in situ method. TiCl_4 was quickly added into 85% ethanol with rigorous stirring. The ethanol solution of HPMo was added dropwise into the above precursor solution. Afterwards, the resulting mixture was heated at 80–100 °C until that the solvent was completely evaporated. The resulting solid was dried at 110 °C overnight and then calcined in air for 5 h. HPMo contents were denoted by the weight ratio of HPMo to TiO_2 . For comparison, pure TiO_2 was prepared by the same method.

2.2. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 400 spectrophotometer using the KBr wafer technique in the range of 4000–400 cm^{-1} and the resolution was 4 cm^{-1} .

Powder X-ray diffraction (XRD) pattern was performed on Philip X'Pert PRO MPD diffractometer using Cu target (Cu $K\alpha$,

$\lambda = 1.54056 \text{ \AA}$) at 45 kV and 40 mA. The samples were scanned in the 2θ ranges from 5 to 70° with step time count of 1 s and step size of 0.02°.

X-ray photoelectron spectroscopy (XPS) was carried on a Kratos Model XSAM 800 apparatus with an Al $K\alpha = 1486.6 \text{ eV}$ exciting source (15 kV, 12 mA). The lines were recorded with a narrow sweep width in the range of 5–7 eV and an energy pass of 50 eV. The binding energy was corrected using the C1s peak (284.6 eV) as the reference to reduce the charge effect of samples.

The element contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an IRIS 1000 instrument (Thermo Electron, USA).

2.3. Activity tests

The transesterification of DMC and phenol was carried out in three-necked round-bottom flask (100 mL), equipped with nitrogen inlet, magnetic stirring bar, dropping funnel and fractionating column connected to a liquid dividing head. Typically, under nitrogen atmosphere, phenol and the desired catalyst were added into the flask. When the mixture was heated to 175 °C, DMC was added dropwise and the reaction temperature was kept at 150–180 °C under refluxing condition. During the reaction procedure, an azeotrope of DMC and methanol was slowly collected in a receiver flask.

Identification analysis of the products was detected by GC-MS on a HP-6890/5973 system. The products were quantitatively analyzed by gas chromatograph (Agilent Technologies 7820 A) equipped with a DB-35 capillary column (30 m \times 320 μm \times 0.25 μm) and a flame ionization detector (FID). The conversion and selectivity were calculated by GC results using a correction factor normalization method.

3. Results and discussion

3.1. Characterization

The FT-IR spectrum of HPMo/TiO_2 with different weight ratios of HPMo to TiO_2 are displayed in Fig. 1. For all samples, the peaks of Keggin structure were clearly observed at approximately 1065 cm^{-1} (P–O in the central PO_4 tetrahedron), 960 cm^{-1} (terminal Mo=O in the MoO_6 octahedron), 860 cm^{-1} and 780 cm^{-1} (Mo– O_b –Mo and Mo– O_c –Mo bridge) (Miao et al., 2009) (O_b : corner-sharing oxygen, O_c : edge-sharing oxygen). With the weight ratio of HPMo to TiO_2 decreasing from 5:1 to 1:3, the characteristic peaks of HPMo with Keggin structure weakened. When weight ratio of HPMo to TiO_2 was below 1:1, the characteristic peaks at 860 cm^{-1} and 780 cm^{-1} were overlapped by the peaks attributed

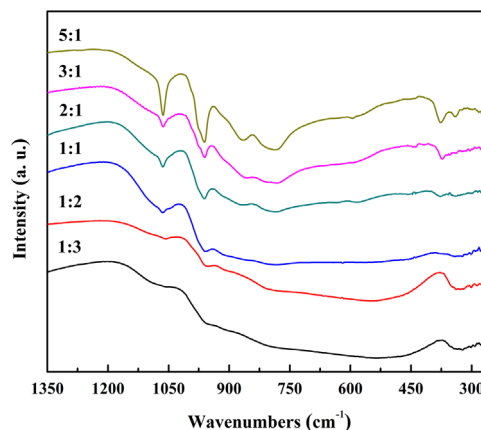


Fig. 1. FT-IR spectrum of HPMo/TiO_2 with different weight ratios of HPMo to TiO_2 .

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