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The synthesis of diphenyl carbonate from dimethyl carbonate and phenol over mesoporous MoO_3/SiMCM-41

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ABSTRACT

The mesoporous catalyst activities of supported molybdenum oxide for diphenyl carbonate (DPC) synthesis in liquid-phase transesterification of dimethyl carbonate (DMC) and phenol were investigated. The yields of DPC and methyl phenyl carbonate (MPC) were greatly improved when MoO_3 was supported on SiMCM-41 to act as catalyst. MoO_3/SiMCM-41 catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption isotherms, and Fourier transform infrared (FT-IR) spectroscopy. Characterized results revealed that the high activity sites of MoO_3/SiMCM-41 were isolated MoO_4^{2-} tetrahedral species and polymerized octahedral molybdenum oxide species. MPC formation increased with reaction time up to 4 h and then decreased thereafter, and maximum MPC yield achieved 39.6%. The decrease of MPC yield after 4 h might be ascribed to MPC disproportionation into DPC and reversible transesterification reaction.
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1. Introduction

DPC is used to produce many organic compounds and polymer materials, particularly as an intermediate for synthesis of polycarbonate without using phosgene [1,2]. The synthesis routes of DPC include the phosgene processes [3], carbonylation of phenol and CO_2 [4,5], oxidative carbonylation of phenol [6–9] and transesterification of phenol with dimethyl oxalate (DMO) [10–13] or dimethyl carbonate (DMC) [14–26]. The transesterification between DMC and phenol is considered as a better green route to synthesize DPC, because DMC is nontoxic to human health and environment [27]. This route is a two-step process, which involving the transesterification of DMC and phenol to methyl phenyl carbonate (MPC) (Eq. (1)) and the further transesterification of MPC and phenol (Eq. (2)) or disproportion of MPC to DPC (Eq. (3)) (see Scheme 1).

For transesterification of DMC and phenol to DPC, most of catalysts were acidic, for example, homogeneous catalysts such as Lewis acids [14], samarium trifluoromethanesulfonate [15], titanium esters [16] and organotin compounds [17], and heterogeneous catalysts like MoO_3/SiO_2 [18], TiO_2/SiO_2 [19–21], V_2O_5/SiO_2 [22]. PbO/MgO [23], lead and zinc double oxide [24], Mg–Al–hydrotalcite catalyst [25] and 12-molybdophosphoric salts [26]. In homogeneous transesterification systems, the difficult separation of catalysts from products will cause problems. Therefore, the development of active solid catalysts is highly desirable.

Fu and Ono [18] reported that unsupported MoO_3 catalyst showed a very low activity because of low surface area. When molybdenum oxide was supported on SiO_2, ZrO_2, and TiO_2, high MPC yield was obtained. When MoO_3 was supported on SiO_2–Al_2O_3, Al_2O_3 and CaO, MPC yield was quite low but with high yields of anisole. The high yield of anisole was due to the decarboxylation of MPC into anisole when reaction was catalyzed by basic or acidic sites on supports [28–30]. Among the supports used, silica was found to be the best with respect to both the yield of and the selectivity for MPC.

The discovery of mesoporous MCM-41 materials [31,32] has given an enormous stimulus to research in heterogeneous catalysis, selective adsorption, and novel functional materials [33,34]. This is due to their outstanding advantages such as large exposed surface areas for interactions, large and defined pore sizes and enhanced surface reactivities due to their richness in reactive, coordinatively unsaturated sites, usually edges, corners, and kinks. The presence of a large number of SiOH groups on the inner surface provides the opportunity to support or anchor various functional groups by postsynthetic modification, such as chemical deposition and impregnation [35,36]. However, up to now, there were no reports on the use of mesoporous MCM-41 supported catalysts in transesterification.

Here, the effects of MoO_3/SiMCM-41 on DPC synthesis in liquid-phase transesterification of DMC and phenol were investigated.

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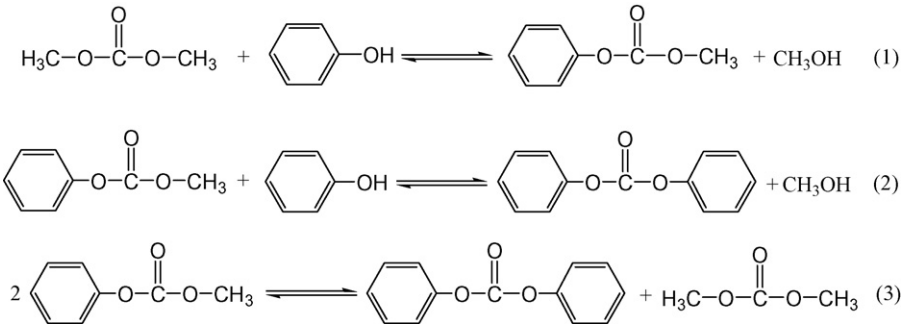

Scheme 1. DPC synthesis from transesterification of DMC and phenol.

It was found that DPC and MPC yields were greatly improved when MoO_3 was supported on SiMCM-41. The high activity sites on catalyst surface were the isolated tetrahedral molybdenum oxide species and polymerized octahedral molybdenum oxide species. In addition, effects of MoO_3 loading, time, temperature, the amount of catalyst usage and ratio of phenol to DMC on reactions were investigated.

2. Experimental

2.1. Chemical reagents

$ZrOCl_2{\cdot}8H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. with AR grade. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ was purchased from Tianjin Chemical Reagent Co. (IV) and used as received. Dimethyl carbonate (Tianjin Chemical Reagent Research Institute) was fractionally distilled and stored over molecular sieve (4A). Phenol (Tianjin Chemical Reagent Co. (III), China) was of analytic reagent (AR) grade and used without further purification. Other chemical reagents were analytical reagent (A.R.) grade and used as received from local manufactures without further purification.

2.2. Sample preparation

SiMCM-41 was prepared according to the documented procedure in Ref. [37]. 4.4 g hexadencyltrimethyl ammonium bromide (CTAB) and 1.1 g NaOH were dissolved in 200 mL distilled water, and the mixture was agitated to give a clear solution. 22.3 mL ethyl silicate was added into above clear solution with constant stirring to give a white precipitate gel solution which was stirred for 24 h at room temperature and heated in a sealed stainless steel autoclave at 90 °C for another 24 h. Product was recovered by filtration, washed thoroughly with distilled water and dried at 100 °C for 4 h. The removal of CTAB was carried out using alcoholic solutions of ammonium nitrate [38]. Typically, 1 g of the as-synthesized material was dispersed in 125 mL of ethanol (95%) containing 0.3 g of ammonium nitrate, and the mixture was stirred at 60 °C for 1 h. Powders were recovered by filtration and washed with ethanol and deionized water. The above treatment was repeated twice. The obtained sample was denoted as SiMCM-41.

ZrO_2 was prepared according to the following procedure. 4.4 g CTAB and 4.5 g NaOH were dissolved in 200 mL distilled water, and the mixture was agitated to give a clear solution. 32 g $ZrOCl_2{\cdot}8H_2O$ was dissolved in 100 mL distilled water, and then $ZrOCl_2$ solution was added drop-wise into above solution to give a white precipitate gel solution which was stirred for 24 h at room temperature and heated in a sealed stainless steel autoclave at 90 °C for another 24 h. The product was recovered by filtration, washed thoroughly with distilled water and dried at 100 °C for 4 h. The removal of CTAB was carried out using alcoholic solutions of ammonium nitrate.

γ-Al_2O_3 (BET = 161 m^2/g) was obtained from Shan Xi commodity chemistry institute, and SiO_2 (BET = 408 m^2/g) was purchased from Qing Dao Ocean Chemistry Corporation.

SiMCM-41, SiO_2, γ-Al_2O_3 and ZrO_2 were impregnated to incipient wetness with aqueous solutions of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ to give 10 wt% molybdenum oxide loading, and samples were dried in an oven at 110 °C for 8 h to remove moisture. At last, catalysts were activated at 500 °C for 4 h.

2.3. Characterization

N_2 adsorption–desorption isotherms of mesoporous samples were measured at 77 K on an ASAP2000 (Micromeritics Instrument Co., USA), prior to the measurement, all samples were outgassed at 200 °C and 10^{-6} Torr over night. The specific surface areas of mesoporous samples were calculated using the multiple-point Brunauer–Emmett–Teller (BET) method. The pore size distribution curves of samples were calculated from the adsorption branch of isotherms using the Barrett–Joyner–Halenda (BJH) method. Pore sizes were obtained from the peak positions of distribution curves.

Powder X-ray diffraction (XRD) pattern characterization of catalyst samples was measured on a Bruker AXS (Germany) diffractometer using Cu Kα radiation, and date were recorded from 10° to 45° (2θ). Fourier transform infrared (FT-IR) spectrum was obtained on a Nicolet Nexus 470 FT-IR analyzer using the KBr method.

Product structure was confirmed by GC–MS (HP5972) and compared with authentic samples. Quantitative analysis was carried on a gas chromatograph (Agilent 6890N GC with a FID detector, HP-5/DB-5 capillary column) with cetane as interior standard.

2.4. Reaction procedure

Reactions were carried out in a four-neck flask, equipped with a thermometer, nitrogen inlet, dropping funnel and fractionating column connected to a liquid dividing head. Phenol and catalyst were charged into flask under nitrogen atmosphere. When mixture was heated to 175 °C, DMC was added drop-wise, and reaction was continued for a certain period of time. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask. After reaction finished, mixture was cooled and analyzed.

3. Results and discussion

3.1. Catalytic activities of various catalysts

The effects of supports on catalytic activities were carefully studied, and results were summarized in Table 1. The yield of DPC and MPC was 0.3 and 14.1% over 0.25 g of MoO_3 alone. If 0.5 g MoO_3 was loaded in reaction system, DPC and MPC yields were improved to 0.9 and 36.2%. When 0.5 g MoO_3/SiO_2 was employed as catalyst, the