



Synthesis of methyl propyl carbonate via gas-phase transesterification over $\text{TiO}_2/\text{Al}_2\text{O}_3$

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ABSTRACT

A heterogeneous catalyst, TiO_2 supported on Al_2O_3 was used for the synthesis methyl propyl carbonate (MPC) by the transesterification of dimethyl carbonate (DMC) and propanol. The morphological and chemical states of titanium species in $\text{TiO}_2/\text{Al}_2\text{O}_3$ were characterized by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and CO_2 -TPD, respectively. The effect of reaction conditions, such as temperature, gaseous hourly space velocity (GHSV), and the molar ratio of propanol/DMC on the reaction were discussed. The results showed that under the optimized reaction conditions, the reaction temperature 403 K, the molar ratio of propanol/DMC of 0.5:1, and a GHSV 360 h^{-1} , the conversion of DMC was 62%, the yields of MPC was 51%.

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1. Introduction

Methyl propyl carbonate (MPC), which contains methyl, propyl and carbonyl groups, could be served as an important precursor for methylation as well as a useful propylating and carbonylation agent for the syntheses of numerous organic products. Owing to its larger molecular weight, higher flash point and stronger antioxidation than that of dimethyl carbonate (DMC) and diethyl carbonate (DEC), MPC is a more stable and safe electrolyte for lithium batteries [1].

At present, the esterification of methyl chloroformate with alcohol is the main synthesis method for methyl alkyl carbonate [2,3]. However, the esterification route is a not environmentally benign process since the highly toxic methyl chloroformate is used and the process brings about co-production of HCl. DMC is a non-toxic building block that can be used in organic syntheses as a green substitute for toxic and corrosive reagents such as dimethyl sulfate, methyl chloroformate, and phosgene [4–6]. Therefore, DMC may act as a methylation agent reacting with dipropyl carbonate or propanol to form MPC. In the transesterification of DMC with dipropyl carbonate, the reaction system is a not economic route since dipropyl carbonate is quite expensive. In addition, it is a critical thermodynamic limitation. Therefore, a new approach of

transesterification of DMC and propanol becomes more attractive to us.

In general, transesterification reactions are carried out in the liquid phase using homogeneous catalysts such as acids and bases, organic Pb, Sn or Ti compounds, and so on [7–9]. However, there is an obvious disadvantage due to the difficulty of catalyst-product separation. Therefore, the development of active solid catalysts is highly desirable. As a few reports on the development of active solid catalysts indicate, $\text{TiO}_2/\text{SiO}_2$ and $\text{MoO}_3/\text{SiO}_2$ were found to be effective in the synthesis of methyl phenyl carbonate and diphenyl carbonate from DMC and phenol [9–12]. However, there are very few reports on the synthesis of MPC.

In the previous report, 5 wt% Ti loadings of $\text{TiO}_2/\text{Al}_2\text{O}_3$ showed higher activity to synthesis of MPC [13]. In the present paper, the morphological and chemical states of titanium species of catalyst were recorded by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption of CO_2 analysis (CO_2 -TPD), respectively. Furthermore, the effects of reaction temperature, molar ratio of DMC/propanol and gaseous hourly space velocity (GHSV) on the reaction profile were studied in detail and suitable reaction conditions for MPC synthesis were worked out.

2. Experimental

2.1. Catalysts preparation

$\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts were prepared by the impregnation method using Al_2O_3 as a support. Al_2O_3 and other chemical reagent

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used for catalyst preparation were commercial products with C.P. grade. Al_2O_3 particles were impregnated with a solution of tetrabutyl titanate dissolved in ethanol. Samples of metal loadings given in weight percent by metal were dried in an oven at 383 K for 6 h to remove the organic solvent and calcined in a muffle furnace at 773 K for 3 h.

2.2. Gas-phase transesterification of DMC and propanol

The transesterification of DMC and propanol was carried out in a continuous flow system with a fixed bed reactor. The reactor was made of a stainless-steel tube, with a diameter of 12 mm and a length of 450 mm [13]. A 5.0 g catalyst sample (20–40 mesh) was packed in the middle of the reactor and placed between two layers of glass bead beds. The temperature of the catalyst bed in the reactor was measured by a thermocouple and controlled with a precision of 1 °C by a temperature controller. The reaction pressure was measured by a digital pressure indicator and maintained constant by a back- and pre-pressure regulator. The reactant mixture composed of DMC and propanol, with a ratio of 1 mol of DMC to 1 mol of propanol, was introduced using a syringe pump (SZB-2) to the pre-heater, where it was vaporized and then entered the reactor together with nitrogen. The flow rate of nitrogen was controlled by a mass flow controller (D07-12A/ZM). The products were analyzed using the gas chromatograph (SP2100) equipped with a flame ionization detector (FID). A PEG20M (3 mm × 2.5 m) column was used for the analysis of liquid products.

2.3. Characterization of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts

XRD patterns were recorded over a 2θ range of 5–80° with a scanning rate of 10° min⁻¹ on a SA-HF3 of Rigaku diffractometer using a nickel-filtered $\text{Cu K}\alpha$ (0.15418 nm) radiation source, and the operation voltage and operation current are 40 kV and 30 mA, respectively.

XPS analysis was performed with an AXIS Ultra spectrometer (Kratos, UK) equipped with a focused monochromatised X-ray source ($\text{Al K}\alpha$, $h\nu = 1486.6$ eV) operated at 225 W with a corresponding voltage of 15 kV. To compensate for surface charges effects, binding energies were calibrated using C1s hydrocarbon peak at 284.8 eV.

CO_2 -TPD spectra were recorded using a TP-5000 chemical adsorption spectrometer. The catalysts were heated to 423 K in flowing He for 1 h, and then cooled to room temperature. The gases adsorption (CO_2) was carried out at room temperature to saturation. CO_2 was replaced with argon and the sample was heated to 873 K at a rate of 10 K min⁻¹.

3. Results and discussion

3.1. Catalyst characterization and its catalytic activity

3.1.1. X-ray diffraction

Fig. 1 showed the XRD patterns of different $\text{TiO}_2/\text{Al}_2\text{O}_3$ samples calcined at 500 °C for 3 h. Diffraction characteristic peaks of pure TiO_2 and the crystal phase of new species could not be observed by XRD in the samples when dopant TiO_2 concentration was less than 3 wt%. It suggested that TiO_2 was uniformly dispersed on the surface or intruded into the body phase of Al_2O_3 , thus resulting in decrement of the specific surface area of the doped catalysts. However, characteristic peaks at Bragg angle 2θ of 25.34 ascribed to the crystal phase of TiO_2 in anatase could be detected in XRD patterns when the TiO_2 concentration was higher than 5 wt%, suggesting that the amount of dopant exceeded the largest capacity of the single layer distribution on the Al_2O_3 surface.

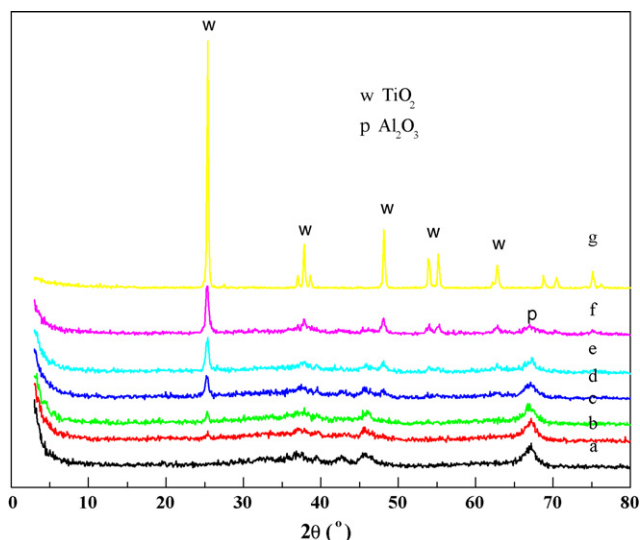


Fig. 1. X-ray diffraction patterns of $\text{TiO}_2/\text{Al}_2\text{O}_3$ with different Ti loading. (a) Al_2O_3 , (b) 1%, (c) 3%, (d) 5%, (e) 10%, (f) 20% and (g) TiO_2 .

3.1.2. X-ray photoelectron spectroscopy (XPS) analysis

Because of its high surface sensitivity (probing depth ca. 2 nm), XPS had been considered as one of the best techniques for studying the dispersion of metal oxides on various supports and to gain knowledge on the type of interaction involved.

Fig. 2(a) and (b) showed the high resolution XPS spectra of the Ti2p and O1s region of $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst with Ti loadings of 5 wt% corresponding to the surface. The Ti2p (see Fig. 2(a)) region was composed of two symmetric peaks situated at $E_b(\text{Ti}2p_{3/2}) = 458.4$ eV and $E_b(\text{Ti}2p_{1/2}) = 464.2$ eV, in agreement with the literature [14,15], as means that the valences of titania species stayed in 4+. As presented in Fig. 2(b), the O1s peak was, in general, broad and complicated due to non-equivalence of surface oxygen ions. It was due to the overlapping contribution of oxygen from titania and alumina in the case of $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst, as indicated that at least two oxygen species were present in the near-surface region [16]. The peak at about $E_b = 530.0$ –530.4 eV was due to oxygen in the TiO_2 lattice, while the peak at about $E_b = 531.1$ –531.7 eV was due to oxygen in the Al_2O_3 lattice. This assignment was easily possible judging from the difference in the electronegativity of the elements involved [17] and also from the literature [18].

3.1.3. CO_2 -TPD analysis

Solid base-catalysts were effective for selective synthesis of unsymmetrical organic carbonates via direct condensation of diethyl carbonate [19,20]. In order to investigate the effect of the basic property of the catalysts on the transesterification of DMC with propanol, CO_2 -TPD characterization was conducted.

CO_2 -TPD was used to characterize the basic sites on catalyst. The peaks in the high temperature region above about 673 K can be attributed to the desorption of CO_2 from strong basic sites, the peaks in the temperature range between 450 and 673 K can be attributed to the desorption of CO_2 from intermediate basic sites, and the peaks in the temperature region below 450 K can be assigned to the desorption of CO_2 from weak basic sites, respectively. Ma reported that adding TiO_2 to Al_2O_3 decreased the amount of basic sites while the relative basic strength was hardly changed [21]. Fig. 3 showed CO_2 -TPD patterns of $\text{TiO}_2/\text{Al}_2\text{O}_3$ with different Ti loadings.

From the result shown in Fig. 3, two peaks appeared in the 423 and 483 K temperature regions simultaneously. Therefore, there must exist both weak and intermediate basic sites on catalysts,

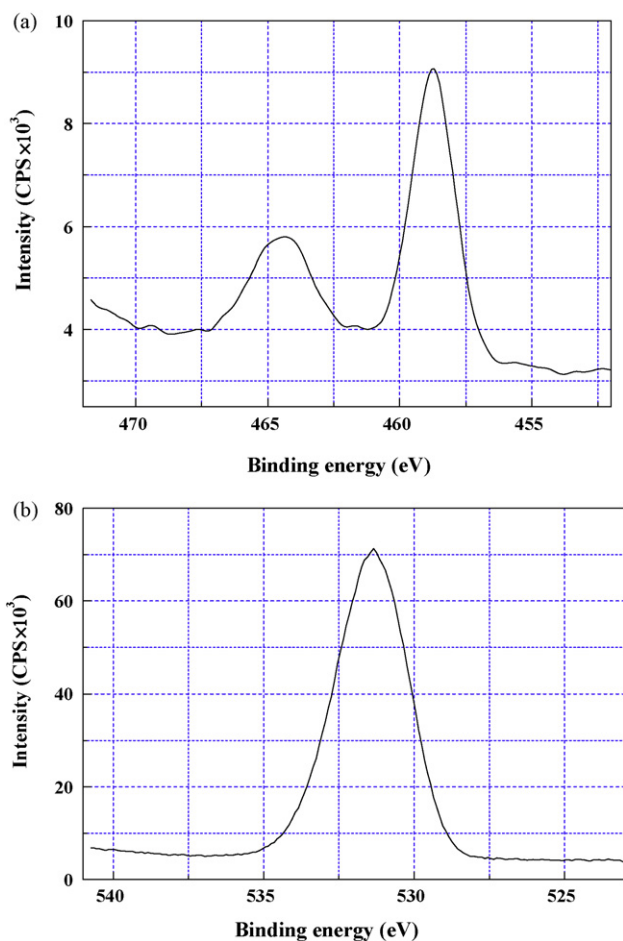


Fig. 2. XPS spectra of Ti2p and O1s of TiO₂/Al₂O₃ catalyst. (a) XPS spectra of Ti2p and (b) XPS spectra of O1s.

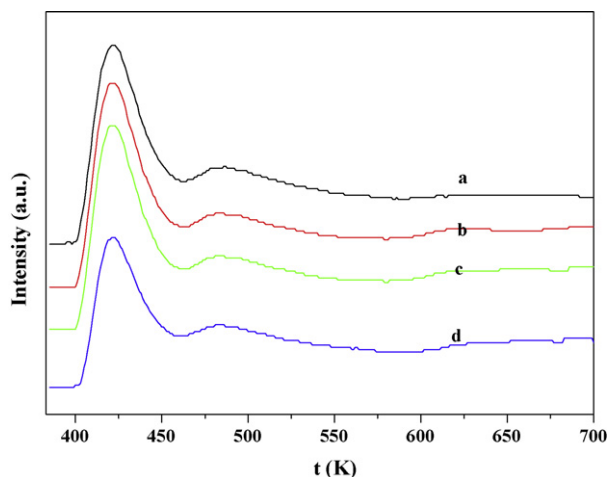


Fig. 3. CO₂-TPD patterns of TiO₂/Al₂O₃ with different Ti loadings. (a) 1%, (b) 3%, (c) 5% and (d) 10%.

Table 1
Relation between $\Delta_r G$ of reaction (1) and temperature.

Temperature (K)	300	400	500	600	700	800
$\Delta_r G$ (kJ/mol)	-1.36	-3.23	-5.00	-6.71	-8.26	-9.60

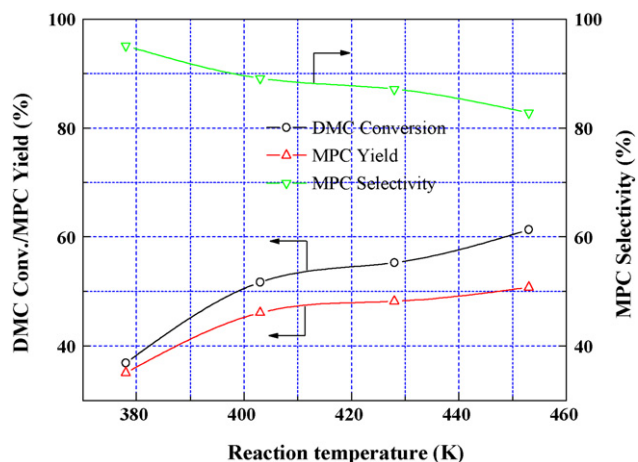


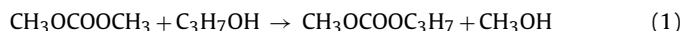
Fig. 4. The effect of reaction temperature on transesterification. Reaction conditions: reactant mixture feeding rate = 5 ml/h, the mole ratio of DMC to propanol = 1, N₂ flow rate = 30 ml/min, reaction pressure = 1.1 MPa.

while there were no strong base sites. And amount of weak basic sites were more than that of intermediate basic sites. It could also be noted that the characteristics of basic sites varied slightly with different Ti loadings on Al₂O₃, except that the amount of basic sites decreased on 10 wt% TiO₂/Al₂O₃, which might be due to the formation of the anatase phase. We also observed the conversions of DMC decreased when TiO₂ reached 10 wt% [13]. This indicated that the base sites were responsible for activity during the transesterification reaction.

3.2. Influence of the process parameters

3.2.1. Effect of the reaction temperature on transesterification

The synthesis of MPC from DMC and propanol proceeds was shown in reaction (1).



We investigated the thermodynamic properties of the reaction (1) in the gas phase over the temperature range of 298–800 K at atmospheric pressure with an assumption of the ideal gas state. Since there was no available thermodynamic data of DMC and MPC, we applied the Benson group contribution method [22,23]. The enthalpies of formation at 298 K were estimated to be -602.48, -657.02, -200.70 and -255.51 kJ/mol for DMC, MPC, methanol and propanol, respectively. Consequently, the standard heat of reaction (1) in the gas phase was estimated to be 0.27 kJ/mol. And the relation between the Gibbs energy ($\Delta_r G$) of the reaction (1) and temperature was shown in Table 1. $\Delta_r G$ of reaction (1) decreased with the temperature increased, as suggested that the endothermic reaction should be more favorable for a high yield of MPC at relatively high temperature.

The effect of reaction temperature on the conversion of DMC, the selectivity of MPC, and the yield of MPC over catalysts were shown in Fig. 4. The results indicated that the DMC conversion and MPC yield increased with temperature rising from 373 to 453 K, as indicated that the reaction was slightly activation energy demanding. This result was similar to $\Delta_r G$ of reaction (1) shown in Table 1. However, the selective of MPC decreased with increasing temperature, as was due to the production of undesired ethers, such as methyl

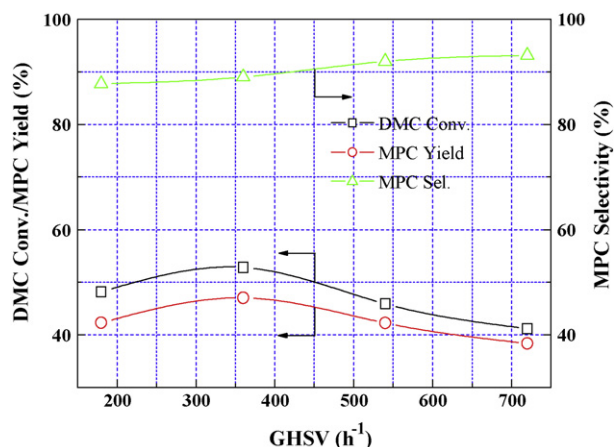


Fig. 5. The effect of GHSV on transesterification. Reaction conditions: the mole ratio of DMC to propanol = 1, reaction temperature = 403 K, reaction pressure = 1.1 MPa.

propyl ether, and propyl ether. The yield of MPC increased from 46.6% to 50.3% as the temperature increased from 403 to 453 K, as showed that yield increased slightly with increasing temperature. On the other hand, Fu thought that DMC might be decomposed readily on $\gamma\text{-Al}_2\text{O}_3$ at relatively low temperatures (for instance 423 K) and cause catalyst deactivation because of carbon deposition [24]. So the optimum reaction temperature lies around 403 K.

3.2.2. Effect of GHSV on transesterification

Fig. 5 showed the variation of DMC conversion and MPC yields as a function of reaction GHSV. It was seen that the conversion of DMC and the yield of MPC increased with GHSV increasing from 200 to 360 h^{-1} , and reached 53.3% and 47.6%, respectively. By further increase of the GHSV beyond 360 h^{-1} , DMC conversion and MPC yields decreased markedly. In addition, the selectivity of MPC slightly increased with GHSV increasing, because the increase of space velocity could make the products leave the catalytic surface in time to avoid deep reaction. Therefore, higher GHSV was advantageous to the MPC selectivity, but was disadvantageous to the DMC conversion. So the favorable GHSV was 360 h^{-1} for getting a better MPC yields.

3.2.3. Effect of propanol/DMC molar ratio

The effects of propanol/DMC molar ratio on transesterification were investigated, and results were shown in Fig. 6. As could be

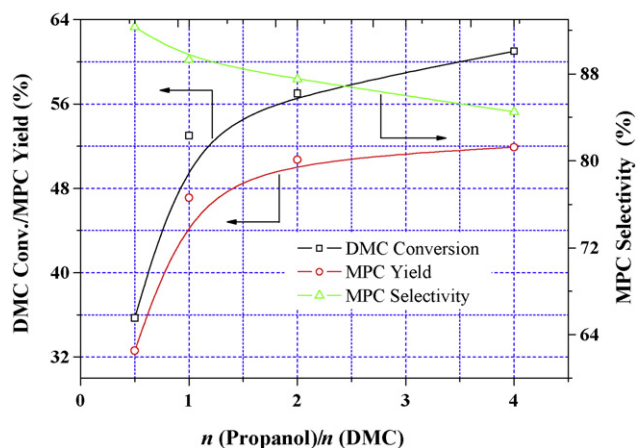


Fig. 6. The effect of DMC/propanol molar ratio on transesterification. Reaction conditions: reactant mixture feeding rate = 5 ml/h, N_2 flow rate = 30 ml/min, reaction temperature = 403 K, reaction pressure = 1.1 MPa.

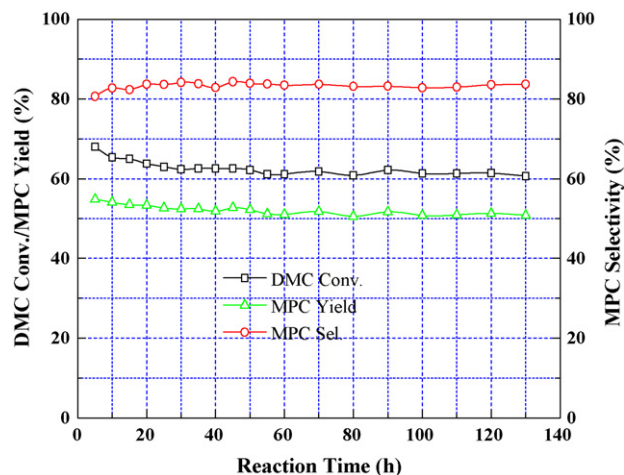


Fig. 7. Stability of $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst on transesterification. Reaction conditions: reactant mixture feeding rate = 5 ml/h, the mole ratio of DMC to propanol = 2, GHSV = 360 h^{-1} , reaction temperature = 403 K, reaction pressure = 1.1 MPa.

observed from Fig. 6, there were distinct increasing trends in DMC conversion and MPC yields as molar ratio of propanol/DMC. The DMC conversion was increased from 35.9% to 56.8%, and MPC yields was enhanced from 32.4% to 50.3% with an increase of molar ratio of propanol/DMC from 0.5 to 2. Hereafter, the DMC conversion and the MPC yields increased slightly by increasing molar ratio of propanol/DMC. In addition, with the increase of the molar ratio of propanol/DMC, the MPC selectivity kept decreasing. So we could conclude that an optimum molar ratio of propanol/DMC existed for the transesterification of DMC and propanol, which was about 1:1.

3.3. The stability of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst

Under conditions (403 K, $n(\text{DMC})/n(\text{propanol}) = 0.5$, GHSV = 360 h^{-1}), the stability of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst was examined as shown in Fig. 7. During the 130 h stability test, DMC conversion slightly decreased from 64% to 62% within 50 h, and remained constant at longer reaction times. The selectivity of MPC did not change with the time on stream. MPC was the most predominant product and the main by-product was dipropyl carbonate. The selectivity of MPC was no less than 83%. This result clearly demonstrated that $\text{TiO}_2/\text{Al}_2\text{O}_3$ showed a stable activity and high MPC selectivity.

4. Conclusions

Alumina-supported titania was the active catalyst for the synthesis MPC from DMC and propanol in a continuous flow system with a fixed bed reactor. The surface Ti(IV) species form crystal phase because the amount of dopant exceeded the largest capacity of the single layer distribution on the Al_2O_3 surface when the Ti concentration was higher than 3 wt%. The CO_2 -TPD characterization indicated that the base sites were responsible for activity during the transesterification reaction.

When the reaction was carried 403 K, with a molar ratio of propanol to DMC 1:1, a GHSV 360 h^{-1} , the conversion of DMC was 62%, and selectivity and yields of MPC was 81% and 51%, respectively.

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