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Short Communication

Amorphous mesoporous aluminophosphate as highly efficient heterogeneous catalysts for transesterification of diethyl carbonate with dimethyl carbonate

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ABSTRACT

The catalytic performance of an amorphous mesoporous aluminophosphate (AlPO) was investigated for the transesterification of diethyl carbonate (DEC) with dimethyl carbonate (DMC) to synthesize ethyl methyl carbonate (EMC). Compared with other solid acid and/or base catalysts, the mesoporous AlPO showed remarkably high activity, stability and recoverability for the reaction. We proposed that the presence of suitable weak acid–base pairs on the surface of the mesoporous AlPO material should play a critical role in the activation of reactants to produce EMC.

1. Introduction

Recently, interest on developing novel and efficient ways to synthesize ethyl methyl carbonate (EMC) is growing since EMC can be utilized as a cosolvent in a nonaqueous electrolyte to improve the performance of the alkali metal ion cells [1–3]. Traditionally, EMC is synthesized by the esterification of methyl chloroformate with alcohol over base catalyst [4]. However, this route is not environmentally benign since methyl chloroformate is highly toxic. Another route to synthesize EMC is the transesterification of dimethyl carbonate (DMC) with ethanol [5–7]. However, the formation of three binary azeotropes during the reaction course brings a serious difficulty in the separation.

Alternatively, EMC can also be obtained by the transesterification of diethyl carbonate (DEC) with DMC. The main advantage of this approach is that the separation step after the reaction (to purify product) could be avoided since all the reaction mixtures (including DEC and DMC) can be used directly as solvent in a nonaqueous electrolyte [8–10]. For this process, compounds such as $Ti(OBu)_4$ and Bu_2SnO were found to be active homogeneous catalysts. However, the separation of the homogeneous catalysts from the reaction system is quite difficult [8]. Besides, several heterogeneous catalyst systems have also been investigated [4,9,10]. For example, Gan et al. [4] reported that lithium diethylamide and lithiated carbon are active heterogeneous catalysts for the reaction. However, these catalysts are quite expensive, thus limiting their application. Shen et al. [9] investigated the catalytic properties of several kinds of solid basic catalysts, and found that MgO is the most active catalyst. Chen et al. [11] reported that a kind of acid–base bifunctional mesoporous material, i.e., $MgO–Al_2O_3$–SBA-15, exhibits a moderate activity for the synthesis of EMC. In another work reported by Palani et al. [10], they found that Al–MCM-41 and Al–Zn–MCM-41 are active catalysts in the vapour-phase transesterification reaction of DEC with DMC. However, rapid deactivation could be observed due to the coke formation. In addition, metal–organic frameworks (MOFs) ($Zn_4O(BDC)_3$) [12] could also be used as an active solid acid catalyst for the transesterification of DEC with DMC. Relatively high yield of EMC was achieved. MOFs could be recovered by drying under vacuum and were reused three times with a slight decrease in its catalytic activity. Currently, it is still an attractive subject to search and to develop highly active, stable and easily recycled heterogeneous catalysts under mild conditions for the transesterification of DEC with DMC.

Very recently, our group reported that carbon-supported MgO materials (MgO/NC-2) [13] prepared by a wet impregnation technique, exhibit high activity in the transesterification reaction and the used catalyst can be recycled after heating activation at high temperature. Herein, the catalytic performance of a kind of mesoporous aluminophosphate (AlPO), prepared by using the so-called citric acid route [14–16], was investigated for the transesterification of DEC with DMC in comparison with other solid acid and/or base catalysts. It was found that mesoporous AlPO shows very high activity and stability, and can be easily recycled without any special treatment (e.g., heat-activation) on the used catalyst.

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2. Experimental

2.1. Catalyst preparation

The amorphous mesoporous AlPO was prepared as described previously [14–16]. Typically, H_3PO_4 (85%) is dropped into a mixed aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ and citric acid (CA) at ambient temperature, leading to a composition in molar ratio of $1.0{:}1.0{:}1.0{:}0.86 = Al(NO_3)_3/CA/H_3PO_4/H_2O$. After that, an aqueous ammonia (10 wt.%) solution was added dropwise until pH = 5.0. The mixture was heated at 363 K in air and then the resulting white solid was calcined at 873 K.

A reference sample of the MgO powder was prepared by a precipitation method using $Mg(NO_3)_2$ and NH_4OH [9]. A solution of NH_4OH (30%, 100 mL) was added dropwise to a solution of $Mg(NO_3)_2 \cdot 6H_2O$ (50 g) in 80 mL of distilled water under stirring at 313 K. Magnesium hydroxide was precipitated and digested in the mother liquor at 333 K for 4 h. The precipitate was washed with distilled water, and then calcinated at 873 K for 2 h in argon.

AlPO-5 was synthesized by the standard gel route in which aluminum isopropoxide, phosphoric acid, triethylamine (TEA) and distilled water were mixed. The molar ratio was $Al_2O_3/P_2O_5/TEA/H_2O = 1{:}1{:}1{:}1{:}40$. P_2O_5 (Beijing Chemical Works) and Al_2O_3 (Beijing Chemical Works) were commercial samples.

2.2. Catalyst characterization

N_2 adsorption–desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2010N analyzer. Pore volumes were estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the BJH model.

Temperature-programmed desorption (TPD) was carried out using CO_2 or NH_3 as probe molecules. In a standard procedure, 50 mg of fresh sample was first calcined at 873 K under Ar stream for 60 min and then cooled to 323 K. Carbon dioxide (99.99%) or ammonia (99.99%) was injected into the stream until saturation was reached, and the system was maintained at 323 K for 30 min. After the system was purged with flowing Ar for 1 h at 323 K, the sample was heated at a rate of 10 K min^{-1} in He (30 mL/min), and the concentration change of the desorbed CO_2 or NH_3 was monitored using an online thermal conductivity detector (TCD).

2.3. Catalyst tests

The liquid-phase transesterification of DEC with DMC was carried out as follows: 5.9 g (0.05 mol) of DEC, 4.5 g (0.05 mol) of DMC and 0.5 g of the catalyst were charged to a 50-mL two-neck flask. Then the mixture was heated up to 366 K with stirring to start the reaction. The reaction products were analyzed by gas chromatography (GC-8A) equipped with an HP-5 capillary column and FID.

3. Results and discussion

3.1. Catalytic performance

Fig. 1 shows the catalytic performance of the mesoporous AlPO and other solid catalysts for the transesterification of DEC with DMC. It should be mentioned first that a blank test (without addition of catalyst) was also carried out, and no obvious activity could be observed under the identical reaction condition.

In the presence of the above solid catalysts, the transesterification reaction could occur with nearly 100% selectivity to EMC. Among them, the mesoporous AlPO exhibited the highest activity, and a 47.7% conversion of DEC was achieved after 0.5 h reaction, which is very near from the equilibrium conversion of the reaction. The catalytic activity decreases in the order: $AlPO > MgO > Al_2O_3 > AlPO\text{-}5 > P_2O_5$. Previously, Shen et al. [9] have reported that MgO is one of the most active catalysts for the transesterification of DEC with DMC. Our results clearly show here that the mesoporous AlPO catalyst is even more active than the MgO catalyst.

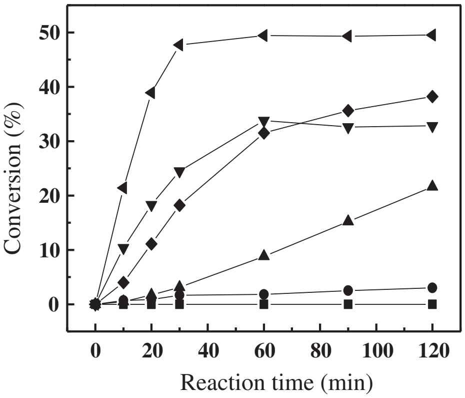

Fig. 1. Dependence of the DEC conversion on the reaction time with different catalysts: (■) blank; (●) P_2O_5; (▲) AlPO-5; (▼) Al_2O_3; (◆) MgO; and (◀) AlPO. Reaction conditions: catalyst 0.5 g, DMC 0.05 mol, DMC/DEC = 1, and reaction temperature 366 K.

The effect of the reaction temperature on the transesterification activity of the mesoporous AlPO catalyst was also investigated (Fig. 2). It was found that the conversion of DEC decreased with the decrease of the reaction temperature. However, the AlPO catalyst is still very active even at the reaction temperature of 336 K, a 43.8% conversion of DEC could be obtained after 2 h reaction. These results suggest that the mesoporous AlPO catalyst possesses very good activity under mild reaction conditions.

A hot leaching test (typically half way through every reaction in which the materials were tested) was performed to study whether the reaction takes place homogeneously or heterogeneously (Fig. 3). There is almost no detectable subsequent conversion in the filtrated solution at the reaction temperature, suggesting that the mesoporous AlPO catalyst behaves in a truly heterogeneous manner in the transesterification reaction.

In addition, the mesoporous AlPO material can be reused after being quantitatively recovered by simple centrifugation. The catalytic activity decreases slightly with the increase of recycle time, which might be attributed to the adsorption of a small amount of reactants and/or products on the surface of the AlPO catalyst (Fig. 4). In a recent work reported by our group [13], we found that carbon supported MgO catalyst (MgO/NC-2) is also quite active and reusable for the

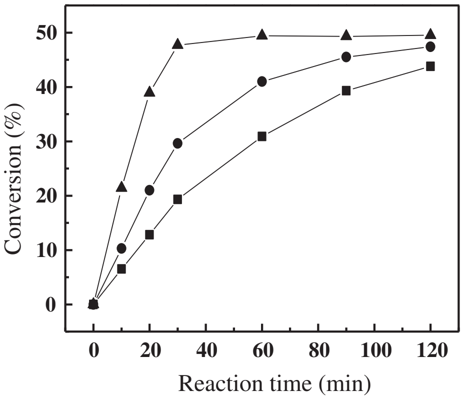

Fig. 2. Dependence of the DEC conversion on the reaction time of the AlPO catalysts with different reaction temperatures: (■) 336 K; (●) 353 K; and (▲) 366 K. Reaction conditions: catalyst 0.5 g, DMC 0.05 mol, and DMC/DEC = 1.

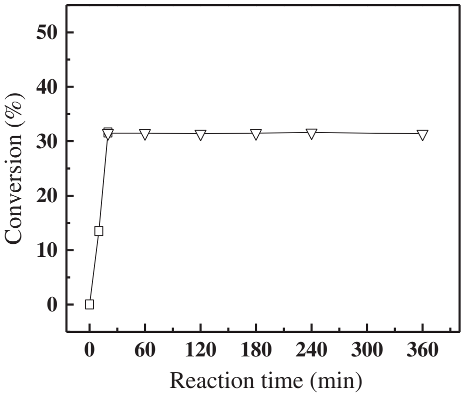

Fig. 3. Heterogeneous reaction check for AlPO (□) and continuation of the reaction after removing the catalysts by filtration (▽). Reaction conditions: catalyst 0.25 g, DMC 0.05 mol, DMC/DEC = 1, and reaction temperature 366 K.

transesterification of DEC with DMC to EMC. However, a heat-treatment (under an argon atmosphere at 1073 K) of the used catalyst is required in order to fully recover the catalytic activity of the MgO/NC-2 catalyst. Hence, it can be concluded that the mesoporous AlPO catalyst possesses much better recoverability compared with the carbon supported MgO catalyst.

3.2. Catalyst characterization

N_2 adsorption–desorption isotherms of mesoporous AlPO and microporous AlPO-5 materials are shown in Fig. 5. The AlPO and AlPO-5 samples present type IV and type II isotherms (definition by IUPAC), which are characteristic of mesoporous and microporous materials, respectively.

In general, relatively narrow pore size (e.g., for microporous materials) may bring serious constraint of the diffusion of reactants, thus decreasing the reaction rate of the catalyst. Some addition experiments and calculations were carried out in order to prove whether the relatively low reactivity in the small pore AlPO-5 is diffusion limited.

It was well known that the Weisz–Prater modulus [17] can be used to demonstrate that the pore diffusion is not important when the following inequality holds:

$$C_{wp} = \frac{R_p^2 \rho_p r_{A,app}}{D_{A,eff} C_{A,s}} < 1 \tag{1}$$

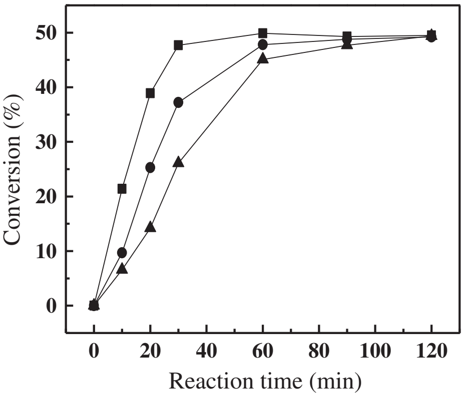

Fig. 4. Transesterification activities of AlPO during three reaction cycles: (■) 1st; (●) 2nd; and (▲) 3rd. Reaction conditions: catalyst 0.5 g, DMC 0.05 mol, DMC/DEC = 1, and reaction temperature 366 K.

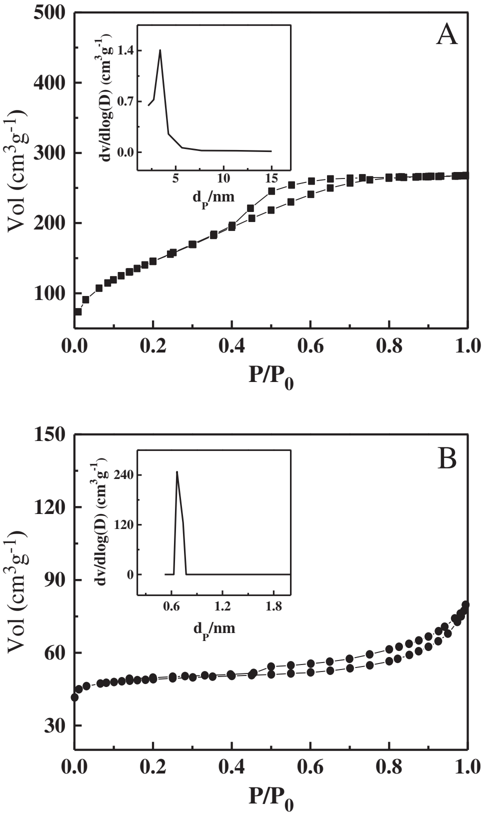

Fig. 5. N_2 adsorption–desorption isotherms and pore size distribution (inset) at 77 K of (A) the mesoporous AlPO and (B) the microporous AlPO-5.

where, R_p is the semidiameter of the particles; ρ_p is the particle density; $\gamma_{A,app}$ is the rate of reaction; and $D_{A,eff}$ is the effective diffusivity.

The effective diffusion coefficient ($D_{A,eff}$) is obtained from the molecular diffusion coefficient (D_{AB}), the catalyst particle porosity (ε_p) and tortuosity (τ_p):

$$D_{A,eff} = D_{AB}\left(\frac{\varepsilon_p}{\tau_p}\right). \tag{2}$$

In the present investigation in which the microporous AlPO-5 is the catalyst and DEC is the representative reagent (A), the average values for τ_p and ε_p can be assumed as 5 and 0.35, respectively on the basis of related literature [18–20]; and the diffusion coefficient D_{AB} is estimated to be 3.8×10^{-5} cm^2 s^{-1} according to a reference method [21]; $\gamma_{A,app}$ and $C_{A,S}$ are determined to be 9.2×10^{-6} mol s^{-1} g$^{-1}_{cat}$ and 5 mol L^{-1}, respectively, from the initial reaction rate (calculated from the reaction kinetic results); R_p is 15 μm according to SEM measurement, and ρ_p is 1.1 g cm^{-3} for the AlPO-5 catalyst. Substitution of the above quantities in equation, yielded the result of $Cwp = 1.7\times10^{-3}$. This value is much lower than 1, indicating that the pore diffusion limitation is not important (or can be neglected) for the transesterification reaction of DEC with DMC on the microporous AlPO-5 catalyst.

Moreover, the acidity and basicity of various materials are determined by means of CO_2-TPD and NH_3-TPD. The CO_2-TPD patterns of various samples are presented in Fig. 6A. Pure MgO shows a very broad CO_2 desorption peak, extended from 353 to 823 K, which could be assigned to the existence of weak and medium basic sites. Al_2O_3, AlPO-5 and mesoporous AlPO materials show a broad desorption peak at relatively low temperature, implying the existence of a certain amount of weak basic sites.

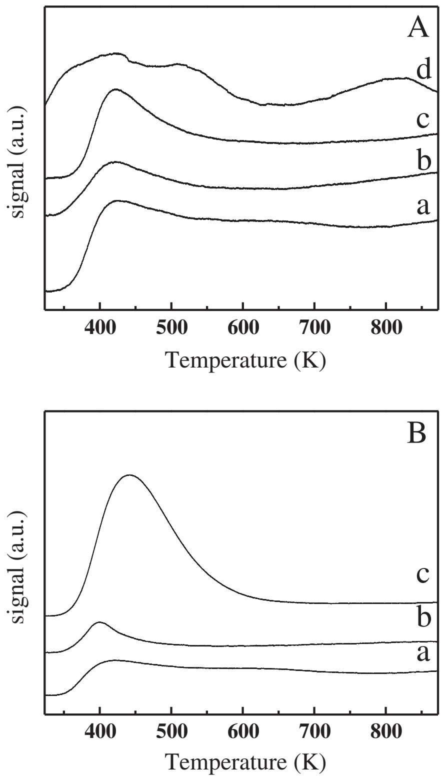

Fig. 6. CO_2-TPD (A) and NH_3-TPD (B) patterns of catalysts calcined at 873 K. (a) Al_2O_3, (b) AlPO-5, (c) AlPO, and (d) MgO.

NH_3-TPD profiles of Al_2O_3, AlPO-5 and mesoporous AlPO materials are shown in Fig. 6B. The desorption patterns of all the samples show similar shapes, with a broad NH_3 desorption peak centered at about 425–450 K, which indicates the presence of weak acid sites. Compared with Al_2O_3 and AlPO-5 samples, the mesoporous AlPO material contains a larger amount of acid sites. According to the related literatures [22–24], it was known that the acidity of the AlPO-5 originates from either Lewis acid sites or terminal P–OH groups, and the amount of acid sites in this microporous material is rather low due to its relatively high crystallinity. On the other hand, the mesoporous AlPO used in this work is amorphous essentially, and there are many structural defects in the material, thus resulting in the formation of relatively large numbers of weak acid sites on the surface of the material [15].

Previously, Shen et al. [9] have proposed a mechanism about the dissociative adsorption of DMC on the surface of the MgO catalyst to yield the methoxide ion species firstly, which could attack the carbon atom of the carbonyl group of DEC subsequently. The main product EMC could be formed after the removal of the ethoxide ion species from the intermediate. In another work reported by Zhou et al. [12], they proposed a similar mechanism concerning the transesterification reaction over the MOF ($Zn_4O(BDC)_3$) catalyst, in which the reagents (DEC and/or DMC) could be chemisorbed on the Lewis acid site of MOFs. In our case, it was known that the mesoporous AlPO catalyst contains a relatively large amount of weak acid and base sites, which may exist in the form of neighboring acid–base pairs on the surface of the mesoporous AlPO. Hence, it should be reasonable to assume that there might be a relationship between these acid–base pairs and the high catalytic activity of the mesoporous AlPO catalysts. Thus a mechanism for the transesterification of DMC with DEC catalyzed by AlPO materials may be proposed as shown in Scheme 1. First, chemisorption of DEC and DMC could occur on the neighboring acid–base pairs simultaneously (step 1). Then the two adjacent chemisorbed species (e.g., $^{+}COOC_2H_5$ and CH_3O^{-}) react directly to form EMC that desorbs easily (step 2).

4. Conclusions

The mesoporous AlPO material, prepared using the citrate acid route, is an efficient heterogeneous catalyst for EMC production by the transesterification of DEC with DMC. The presence of abundant weak acid–base pairs on the surface of the mesoporous AlPO material should play a critical role on the activation of the reactants in the transesterification reaction. Further detailed investigations are in progress in order to clarify the correlation of the physicochemical properties with the catalytic performance of the mesoporous AlPO materials.

Acknowledgements

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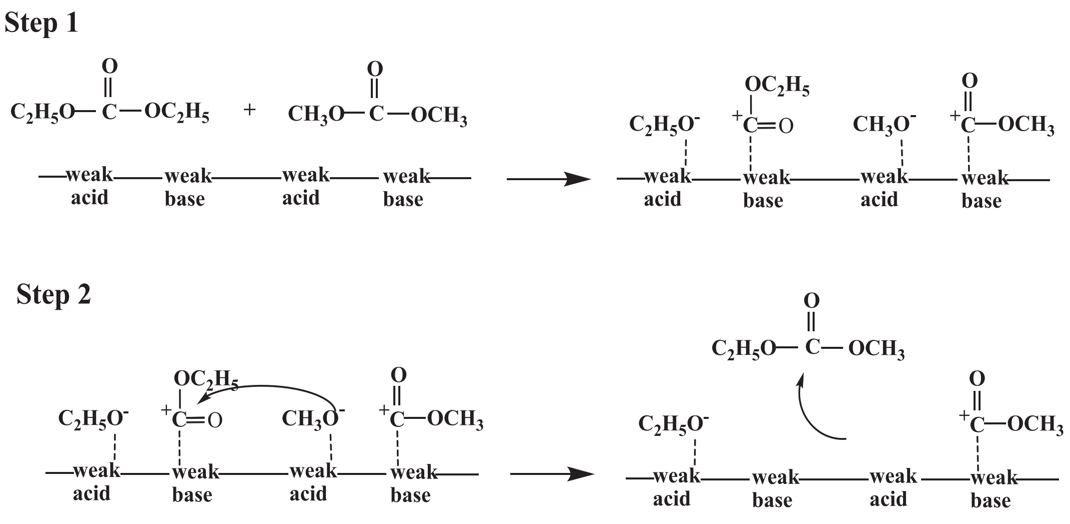

Scheme 1. Possible mechanism of transesterification of DMC with DEC on the AlPO catalyst.

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