Synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by K₂CO₃/MgO

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Abstract A series of M/MgO (M = CaO, KNO₃, KOH, K₂CO₃) catalysts were prepared by a dry impregnation method and used for synthesis of glycerol carbonate from glycerol and dimethyl carbonate. It was found that K₂CO₃/MgO was the most efficient catalyst, with a glycerol carbonate yield of approximately 99% under the conditions: DMC/glycerol molar ratio 2.5:1, catalyst/raw material weight ratio 1%, reaction time 2 h, and reaction temperature 80 °C. FTIR, BET, TEM, and XRD were used for characterization of the catalyst and showed that the active sites seemed to be K₂O formed on the K₂CO₃/MgO catalyst. Finally, a recycling experiment showed that the catalyst was relatively stable and could be reused up to four times, at least, by regeneration.

Keywords Glycerol carbonate · Transesterification · Supported catalyst · Dimethyl carbonate

Introduction

Glycerol is becoming an abundant and inexpensive natural resource since the rapid growth of global biodiesel industry, so exploration of its further processing has attracted much attention [1–4]. Among all the derivatives of glycerol, glycerol carbonate (GC), with many potential applications, is the most attractive. It can be widely used as an adhesive, surfactant, and elastomer, and is also an excellent solvent in the paint industry. In addition, its high reactivity enables its use as an intermediate in the synthesis of many valuable chemicals [5–8].

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W. Dong Shanghai Fine Chemical Co. Ltd, Shanghai 201505, China Several methods have been described for synthesis of GC, including reaction of glycerol with carbon dioxide using an Sn catalyst, which was found to be both directly and environmentally friendly but of high cost, and the catalyst is of low activity [9, 10]. Carbonylation of glycerol with carbon monoxide and oxygen or hazardous phosgene has also been reported, but these methods have the drawbacks of rigorous reaction conditions and the toxicity of the starting materials [11, 12].

Synthesis of glycerol carbonate from glycerol and dimethyl carbonate (DMC), an environmentally benign material, is an alternative means of producing glycerol carbonate under much milder conditions without the production of problematic side products, so it has aroused much interest [13]. Seeking highly efficient catalysts is the keystone of this base-catalyzed reaction. Compared with homogeneous alkaline catalysts, for example NaOH or KOH, heterogeneous catalysts are preferred because they are less corrosive, safer, less expensive, and more environmentally friendly [14-19]. Several heterogeneous alkaline catalysts have been investigated for synthesis of glycerol carbonate by transesterification of glycerol with DMC. CaO, the traditional solid base catalyst was found to be a good catalyst for production of glycerol carbonate, because its basicity is as high as that of traditional homogeneous catalysts and its sources such as calcium carbonate and calcium acetate are less expensive and less toxic; CaO is, however, very prone to deactivation in air and readily forms suspensions in the reaction mixture, resulting in poor reusability [14]. Other catalysts, for example lipase, hydrotalcite, and ionic liquids have also been investigated [15-17], but they either required long reaction times or needed an additional solvent environment. Recently, Bai et al. [18] reported KF-modified hydroxyapatite as a highly active catalyst for the synthesis of GC from glycerol and DMC. The yield of GC reached nearly 99%, but KF is a very toxic substance and its safety should be carefully considered in industrial applications. Mg/Al/Zr mixed oxide catalysts have also been investigated recently [19], but reactions catalyzed by these catalysts must be conducted in a large excess of DMC. Development of suitable non-toxic solid alkaline catalytic systems with high activity which are easily recoverable and recyclable is therefore of great importance.

To the best of our knowledge, there is no report of the application of MgO as a catalyst support for glycerol carbonate production. In work discussed in this paper, a series of M/MgO (M = CaO, KNO₃, KOH, K₂CO₃) catalysts were prepared and used for synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate. IR, BET, TEM, and XRD were used for characterization of the catalyst. The activity of the catalysts was investigated and compared with that of the conventional catalysts CaO, K₂CO₃, and KOH. The stability of the synthesized K₂CO₃/MgO catalyst was also evaluated.

Experimental

Catalyst preparation

All catalysts were prepared by a dry impregnation method. In all cases, a specific amount of MgO carrier was first preheated at 500 °C for 5 h to remove physisorbed

water and then impregnated with 20 wt% $Ca(CH_3COOH)_2$, KNO₃, KOH, and K_2CO_3 solutions, dried at 110 °C for 10 h, and then calcined at 600 °C in air for 3 h.

Catalyst characterization

FTIR spectra were recorded with a Hitachi (Japan) model 273-30 spectrometer over the wavenumber range $4,000-400 \text{ cm}^{-1}$. The KBr pellet technique was used to prepare samples. All measurements were conducted at room temperature.

Nitrogen adsorption-desorption isotherms were determined by use of a Micromeritics ASAP 2010 at 77 K. Before the measurements, all samples were degassed at 473 K under high vacuum (10^{-4}) for 2 h. The specific surface area of samples was calculated by use of the Brunauer-Emmett-Teller (BET) method. The pore volume was given at $p/p_0 = 0.990$. The pore size distribution was calculated by use of the Barrett-Joyner-Halenda (BJH) method.

Microstructure characterization was carried out by use of a Jeol JEM-1011 transmission electron microscope (TEM) with an accelerating potential of 100 kV.

X-ray diffraction (XRD) patterns of the catalysts were recorded with a Rigaku MiniFlex II using Cu K α radiation (1.5418 Å) at 30 kV and 15 mA. The measurements were obtained over a 2θ range of 20–70° with a step size of 0.01° at a scanning speed of 8°/min.

Synthesis of glycerol carbonate

Glycerol carbonate was synthesized in a 100-mL round-bottomed four-neck jacketed glass reactor fitted with a mechanical stirrer, a reflux condenser, and a thermometer. In a typical experiment, 0.1 mol glycerol (99%, AR grade), 0.25 mol DMC (99.5%, AR grade), and the catalyst (1 wt%, based on the mass of raw material) were successively added into the reactor. Transesterification was performed at a stirring speed of 250 rpm at 80 °C for 2 h. After the reaction, the catalyst was isolated by filtration and collected for reuse. To test the leakage of K from the catalyst in the reaction, the K content in the reaction mixture was analyzed by ICP using an iCAP6300 (Thermo Scientific, USA).

Product analysis

After separating the catalyst, the products were analyzed by gas chromatography (Agilent GC-6890) with flame ionization detection (FID) using an HP1701 (30 m × 0.32 mm × 0.25 µm) capillary column. Injector and detector temperatures were 280 and 300 °C, respectively. Oven temperature started at 80 °C and was increased at 12 ° min⁻¹ to 250 °C which was held 2 min. Tetraethylene glycol was used as the internal standard. Conversion of glycerol (X_G), and yield of glycerol carbonate (Y_{GC}) were expressed as:

$$X_{\rm G} = \frac{\text{Consumed amount of glycerol (mol)}}{\text{Charged amount of glycerol (mol)}}$$
$$Y_{\rm GC} = \frac{\text{Amount of glycerol carbonate (mol)}}{\text{Charged amount of glycerol (mol)}}$$

Results and discussion

Catalyst characterization

FTIR spectroscopy, an effective tool for obtaining semi-quantitative structural information about complex solids [20], was used to investigate the functional groups of the K_2CO_3/MgO catalyst, and of K_2CO_3 and the carrier MgO. All three samples were calcined at 600 °C for 3 h. The FTIR spectra are shown in Fig. 1. Two strong bands at 1,457 and 1,385 cm⁻¹ were obtained from K_2CO_3 ; these bands, which were attributed to carbonate species [21–23], were also observed in the spectrum of the synthesized K_2CO_3/MgO catalyst, indicating that the K_2CO_3 was successfully loaded on to the surface of the MgO.

The measured BET surface area, pore volume, and pore diameter are shown in Table 1. The BET surface areas and the pore volumes and pore diameters decreased with loading of CaO, KNO₃ and KOH, indicating these active sites were well dispersed on MgO. In contrast, BET surface areas increased on loading with K_2CO_3 . This might be because of chemical reaction between absorbed K_2CO_3 and MgO, it seems that the K⁺ ions of the K_2CO_3 could become inserted into the vacant sites of



Fig. 1 FTIR spectra of K₂CO₃, MgO, and K₂CO₃/MgO

Table 1 BET surface areas, pore volumes, and pore diameters of the prepared catalysts diameters	Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
	MgO	19.16	0.0690	14.7
	CaO/MgO	16.85	0.0391	9.4
	KNO ₃ /MgO	8.74	0.0175	7.1
	KOH/MgO	3.21	0.0058	7.6
	K ₂ CO ₃ /MgO	25.74	0.1073	24.3



Fig. 2 TEM images of a MgO and b K2CO3/MgO

MgO, accelerating dispersion and decomposition of K_2CO_3 to form strong basic sites of K_2O either during the impregnation process or later [24]. These processes induced recrystallization and the formation of more new small crystals in the large pores or on the MgO surface, which might mainly contribute to the higher BET surface area, pore volume, and pore size.

TEM of MgO and K_2CO_3/MgO is shown in Fig. 2a, b. It can be seen that after impregnation with K_2CO_3 followed by calcination at 600 °C, agglomeration of MgO particles is obvious, and formation of new small crystals on the surface of the MgO can also be observed. This result agrees well with that of BET.

XRD analysis (Fig. 3) of the synthesized K₂CO₃/MgO catalyst was also carried out. The results showed that the difference between the catalyst and the carrier MgO was obvious, as shown by the appearance of new peaks. In addition to the typical diffraction peaks of K₂CO₃ at $2\theta = 25$, 32, 38, and 41° [23], the new phase of K₂O could also be observed clearly at $2\theta = 31^{\circ}$ [25, 26]. Accordingly, it is reasonable to suppose that part of the loaded K₂CO₃ should be decomposed under the activation conditions, depending on whether or not the K₂CO₃ interacts with the MgO support, which further confirms the results of BET and TEM.

Screening of highly active supported catalysts for synthesis of glycerol carbonate

Magnesium oxide has been widely used as a basic carrier in industrial processes, with excellent catalytic activity [24, 27–29]. In this work, MgO supported by CaO



Fig. 3 X-ray diffraction patterns of MgO and K₂CO₃/MgO

Entry	Catalyst	Conversion of glycerol (%)	Yield of glycerol carbonate (%)
1	CaO	97.4	96.5
2	MgO	20.3	15.2
3	CaO/MgO	67.5	64.4
4	CaO/MgO ^a	68.0	64.7
5	KNO ₃ /MgO ^b	98.5	94.7
6	KOH/MgO	97.8	95.2
7	K ₂ CO ₃ /MgO	99.0	98.6
8	KOH ^c	98.7	98.3
9	$K_2CO_3^c$	96.8	96.3

Table 2 Screening of highly active supported catalysts for synthesis of glycerol carbonate

Reaction conditions: temperature, 80 °C; molar ratio of DMC to glycerol, 2.5; glycerol, 0.1 mol; reaction time, 2 h; amount of catalyst, 1 wt% (on the basis of the mass of raw material)

 $^{\rm a}$ The amount of catalyst: 2.0 wt%

^b Reaction time 3 h

^c Reaction time 40 min

and potassium compounds (KNO₃, KOH, and K_2CO_3) was prepared and used for the synthesis of glycerol carbonate from glycerol and DMC.

As shown in Table 2, the catalytic performance of MgO was affected by the nature of the active component. Although it has been reported that CaO/MgO can be used as an efficient catalyst for production of biodiesel by transesterification [27], this supported catalyst had poor activity in the synthesis of glycerol carbonate. Considering that the low catalytic activity may be because of the low CaO loading, we increased the amount of the catalyst to 2 wt% (on the basis of the mass of raw

material), however, both the conversion of glycerol and the yield of glycerol carbonate remained unchanged.

We then used MgO loaded with a series of potassium salts (KNO₃, KOH, and K_2CO_3) to catalyze the reaction; surprisingly, high conversion and yield were obtained. From Table 2, one can observe that, in the presence of supported catalysts KNO₃/MgO, KOH/MgO and K_2CO_3 /MgO, the glycol conversions are all higher than 97%, comparable with that of the traditional catalyst CaO. Under the same reaction conditions, using MgO, we obtained conversions of only 20.3%, indicating that these basic active components KNO₃, KOH, and K_2CO_3 had a positive effect on the MgO after impregnation or calcination, resulting in excellent catalytic activity.

Because KNO₃/MgO needed more time to reach the equilibrium state and KOH/ MgO was almost as active as CaO, K_2CO_3 /MgO was the best and most active catalyst for high glycerol conversion (99.0%) and good selectivity for glycerol carbonate (almost 100%). For comparison, the catalytic activity of the homogenous catalysts, KOH and K_2CO_3 , were also examined in the transesterification of glycerol and DMC (Table 2, entries 8 and 9), and conversion of glycerol reached 98.7 and 96.8%, respectively. This showed that the catalytic performance of K_2CO_3 /MgO was almost the same as the homogenous catalyst of KOH and K_2CO_3 .

The effect of the amount of K_2CO_3/MgO catalyst on the reaction was also investigated; the results are shown in Fig. 4. It is apparent that the yield of glycerol carbonate increased gently with increasing amount of catalyst; this may be attributed to the availability of more active sites for the reaction when the amount of catalyst is increased. However, even when the amount of catalyst was as low as 0.2 wt%, the yield of glycerol carbonate reached approximately 95%. This result



Fig. 4 Effect of the amount of K_2CO_3/MgO catalyst on activity in glycerol transesterification. (Reaction conditions: temperature, 80 °C; molar ratio of DMC to glycerol, 2.5; glycerol, 0.1 mol; reaction time, 2 h)

reiterates the high activity of the K_2CO_3/MgO catalyst for transesterification of glycerol with dimethyl carbonate to yield glycerol carbonate.

Recycling of the catalyst

Recycling experiments were carried out to investigate the stability of the prepared K_2CO_3/MgO catalyst. At first, used catalyst was directly reused after washing with DMC and drying at 110 °C for 5 h. However, a remarkable reduction in activity occurred and the yield of glycerol carbonate achieved was only 45.7% in the second run.

Because deactivation of the catalyst may have been caused by products adhering during the reaction, the K_2CO_3/MgO was calcined at 600 °C for 3 h after each run and then reused. After this treatment, the yield of glycerol carbonate slowly decreased with increasing number of times reused (Fig. 5).

To discover the reason for the decrease in catalytic activity despite the regeneration procedure, the potassium content of the product mixture after the 1st run was investigated by ICP, and the result was 0.048% (mass concentration), which indicated leakage of K from the catalyst during the reaction. The very small amount leaching accorded with the slow decrease of glycerol carbonate yield (one can observe from Fig. 5 that the yield of glycerol carbonate was still >83% in the 4th run). However, because yield decrease continuously from run to run, it is reasonable that potassium leaching is another important reason for the catalyst's deactivation.

The results discussed above suggest the K_2CO_3/MgO catalyst was probably acting as a homogeneous–heterogeneous catalytic system [23]. Although not as good as a purely heterogeneous catalyst, it was of relatively good stability, because it retained its high activity when reused at least four times when calcined again after reaction.



Fig. 5 Recycle test of catalysts (reaction conditions: temperature, 80 $^{\circ}$ C; molar ratio of DMC to glycerol, 2.5; glycerol, 0.1 mol; reaction time, 2 h; amount of catalyst, 1 wt%)

Conclusion

MgO supported by CaO and a series of potassium compounds (KNO₃, KOH, and K_2CO_3) was adopted as alkaline catalyst for synthesis of glycerol carbonate from glycerol and DMC. It was found that MgO loaded with potassium salts, especially K_2CO_3/MgO , had high catalytic activity, with a glycerol carbonate yield of approximately 99% under mild reaction conditions. The catalyst was reasonably stable and could be reused at least four times after re-activation. One can expect its use as an alternative to conventional alkaline catalysts for synthesis of glycerol carbonate by transesterification of glycerol with DMC.

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