



## Short Communication

## Efficient synthesis of glycerol carbonate from glycerol and urea with lanthanum oxide as a solid base catalyst

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## ABSTRACT

Lanthanum oxide catalyst prepared by precipitation method and calcined at 600 °C exhibited better catalytic activity in the catalytic synthesis of glycerol carbonate from glycerol and urea with TOF up to 1506 mmol/g·h. It was proposed that the lanthanum oxide catalyst with more strong basic sites ( $T_d > 400$  °C) exhibited higher catalytic activity. Accordingly, the catalyst containing appropriate amount of  $\text{La}_2\text{O}_2\text{CO}_3$  phase exhibited higher catalytic activity. Moreover, the recycling experiments demonstrated that the catalytic activity can be essentially preserved during the recycling tests investigated.

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## 1. Introduction

Glycerol carbonate (GC) is a new and interesting material in the chemical industry. It has been investigated as a novel component of gas separation membranes, polyurethane foams, a component in coatings, paints and detergents, etc. [1,2]. In particular, inexpensive GC can be used to synthesize the high-value glycidol, a source of new polymeric material for production a number of polymers.

The production of GC from different pathways was well summarized in the literature [3]. Among the different carbonyl sources studied, urea has drawn specific attention due to the significance of indirect  $\text{CO}_2$  chemical utilization. Previously, several catalytic systems were reported for this reaction, including  $\gamma$ -zirconium phosphate [4], hydrotalcite [5], hierarchical  $\text{Co}_3\text{O}_4/\text{ZnO}$  [6]. Recently, gold-based catalyst was also found to promote the reaction effectively [7]. It should be noted that there were two different modes chosen to remove the  $\text{NH}_3$  formed during the reaction, under reduced pressure [4,5] or passing gas [6,7]. Among them, the  $\text{Co}_3\text{O}_4/\text{ZnO}$  exhibited good GC yield of 69% with 100% excellent selectivity using air as passing gas at atmospheric pressure. Though these catalytic systems can catalyze the title reaction to some extent, the development of more effective, reusable and inexpensive heterogeneous catalyst is highly desirable.

In many scientific reports, rare earth oxides was usually used as supports [8], catalytic promoters [9] and they also received increasing attention in base catalyzed reactions [10,11]. The basic properties of rare

earth oxides are essentially attributed to the low polarizing power of the cations with large size and relatively low charge. Therefore, the development of rare earth oxides as base catalysts is highly attractive.

Additionally, the conventional preparation of lanthanum oxide mainly focused on the sol-gel, combustion or gas-condensation methods [12]. Furthermore, the lanthanum oxide used as base catalyst was less well studied than alkaline earth metal oxides [13]. It is well known that the preparation method has great influence on the catalytic activity. Therefore, pure lanthanum oxide was prepared via precipitation method using sodium carbonate as precipitant and used for the first time as a solid base catalyst for the synthesis of glycerol carbonate from glycerol and urea.

In this work, a series of rare earth oxides, such as  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Pr}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ , which was prepared by precipitation method using sodium carbonate as precipitant, tested as catalysts in carbonylation of glycerol with urea under reduced pressure, and lanthanum oxide was found to exhibit better catalytic activity for GC synthesis. The relationship between the structure or basicity of catalyst and its catalytic activity was also discussed. Moreover, the catalytic activity can be essentially preserved during the recycling tests investigated.

## 2. Experimental

## 2.1. Materials

Glycerol and urea were analytical grade and purchased from Tianjin Chemical Reagent Co., Ltd.  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,

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$Y(NO_3)_3 \cdot 6H_2O$ ,  $Pr_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Eu_2O_3$  were purchased from Sinopharm Chemical Reagent Co., Ltd.

## 2.2. Catalyst preparation

In a typical procedure, lanthanum oxide was prepared by precipitation method. 1 M  $Na_2CO_3$  aqueous solution was added dropwise to an aqueous solution containing 0.5 mol/L lanthanum nitrate until  $pH=10-11$ . The resulting  $La(OH)_3$  precipitate was filtrated, washed with distilled water, dried, and calcined at 600 °C. The obtained white powdery solid was denoted as  $La_2O_3-600$ . The abbreviations represent as follows:  $La_2O_3-com$  (commercially obtained),  $La_2O_3-decom$  (thermal decomposition of lanthanum nitrate). Other rare earth oxides, were also prepared by similar precipitation method aforementioned, except for the  $Pr_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Eu_2O_3$  were firstly dissolved in diluted nitric acid to obtain the corresponding precursors of nitrate.

## 2.3. Catalyst characterization

$N_2$  adsorption and desorption isotherms at 77 K were measured on a Micromeritics ASAP 2010 surface analyzer.

X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffract meter. Diffraction patterns were recorded with  $Cu K\alpha$  radiation (40 mA, 40 kV) over a  $2\theta$  range of 10° to 80°.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB210 instrument.  $Mg K\alpha$  radiation at an energy scale calibrated versus adventitious C1s peak at 285.00 eV was used.

Fourier transform infrared spectroscopy (FT-IR) transmission data were collected for pressed catalyst disk made with KBr in the range of 4000–400  $cm^{-1}$  with a Nicolet 5700 FT-IR.

The surface acid-base properties of the catalysts were measured by temperature programmed desorption of  $CO_2$  and carried out on TPD flow system equipped with an MS detector (DM300, AMETEK, USA). The quantitative analysis for  $CO_2$  desorption is calculated based on the integration of the corresponding TPD traces.

## 2.4. Catalytic testing

In a typical catalytic test, 6 g urea (100 mmol), 18.4 g (200 mmol) glycerol and 0.06 g  $La_2O_3-600$  catalyst was added to a round-bottom flask (50 ml) equipped with a condenser. The reaction was conducted at 140 °C under pressure of ca. 3 KPa. After the reaction was completed, the product mixture was diluted by ethanol due to its relative high viscosity. The quantitative analysis of the product was determined by Agilent 6820 GC (FTD detector) using 1, 4-dioxane as internal standard. Qualitative analysis was conducted on a HP 6890/5973 GC-MS with a capillary column.

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. Characterizations of $N_2$ adsorption

The textural properties of the lanthanum oxides are given in Table 1. The BET surface area increased monotonically from 2.3 to 8.0  $m^2g^{-1}$  with the calcination temperature elevated from 400 to 800 °C. In parallel, the pore diameter decreased from 56.9 to 16.1 nm,

**Table 1**  
Textural properties of various lanthanum oxides.

Sample	Pore volume ( $cm^3/g$ )	BET area ( $m^2/g$ )	Pore diameter (nm)
$La_2O_3-400$	0.033	2.3	56.9
$La_2O_3-600$	0.021	5.0	21.7
$La_2O_3-800$	0.032	8.0	16.1
$La_2O_3-com$	0.027	5.5	19.8

suggesting that the calcination temperature has a great influence on the texture of lanthanum oxide. The texture of  $La_2O_3-com$  was also measured, and similar results as that of  $La_2O_3-600$  were obtained.

#### 3.1.2. Structural characterization studies

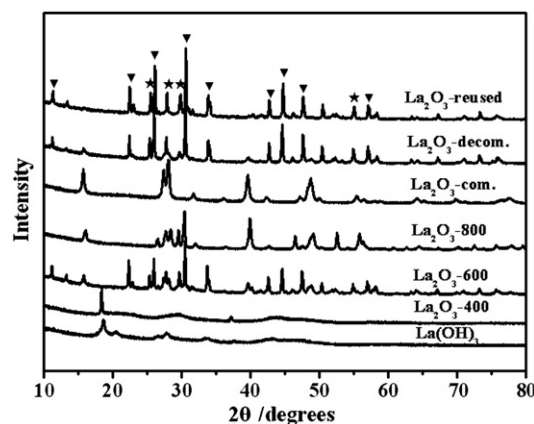
XRD patterns of various lanthanum oxides are shown in Fig. 1. The  $La_2O_3-600$  sample exhibited two distinct crystalline phases, hexagonal phase of  $La_2O_2CO_3$  (JCPDS 84-1963) and  $La_2O_3$  (JCPDS 24-0554), and the former was the dominant phase. The  $La_2O_3-decom$  and  $La_2O_3-800$  exhibited similar crystalline phases as compared to  $La_2O_3-600$ , though the relative intensities of diffraction lines related to  $La_2O_2CO_3$  were obviously lower. Whereas, for the  $La_2O_3-com$ , only the diffraction lines related to hexagonal structure of  $La_2O_3$  crystalline phase was observed. Poor crystalline phase of orthorhombic structure of  $La_2(CO_3)_3(H_2O)_8$  was observed for  $La(OH)_3$  precipitate and  $La_2O_3-400$ . The XRD patterns of the catalyst reused for six times basically matched with that of fresh one, though the peak at lower  $2\theta$  was slightly less intense.

#### 3.1.3. Surface compositions analyzed by XPS

The influence of the calcination temperature on the chemical states of  $La_2O_3$  has also been investigated by means of XPS, as shown in Fig. 2a. The binding energy (BE) of  $La3d_{5/2}$  varied slightly around  $833.5 \pm 0.2$  eV. Two distinct oxygen species for O1s can be well resolved. The BE around 528.7 eV was attributed to oxygen ions in the crystal lattice ( $O_{lat}$ ), while the line located at 531.2 eV can be ascribed to the adsorbed oxygen ( $O_{ads}$ ). Actually, the position of O1s BE value was considered to be correlated to the surface basicity [14,15]. The  $O_{lat}$  with higher electron density was considered to act as Lewis base site and shows stronger basicity than the  $O_{ads}$  species.

#### 3.1.4. Basicity characterized by $CO_2$ TPD

Fig. 3 shows the  $CO_2$  TPD profiles over various lanthanum oxides. According to carbon dioxide desorption temperature ( $T_d$ ), weak (<200 °C), medium (200–400 °C), strong (>400 °C) basic sites can be roughly classified, as shown in Table 2. In all the samples, the amounts of weak basic sites are <8  $\mu mol CO_2 g^{-1}$ .  $La_2O_3-com$  exhibited small basic sites (4 and 33  $\mu mol CO_2 g^{-1}$ , respectively) in the region of medium and strong strength. By contrast, the trace for  $La_2O_3-decom$  consists of four desorption peaks, especially dominant in the region of medium and strong strength. Accordingly, the basic sites with weak strength mostly correspond to  $OH^-$  groups on the catalyst surface, while those with medium and strong strength are related to the oxygen of  $M^{n+}-O^{2-}$  ion pairs and isolated  $O^{2-}$  anions, which are generally considered as Lewis basic sites for metal oxides [16]. In particular, the contribution of strong basicity for  $La_2O_3-600$  reaches



**Fig. 1.** Powder XRD patterns of lanthanum oxide catalysts. (▼) Features corresponding to hexagonal  $La_2O_2CO_3$  phase. (★) Features corresponding to hexagonal  $La_2O_3$  phase.

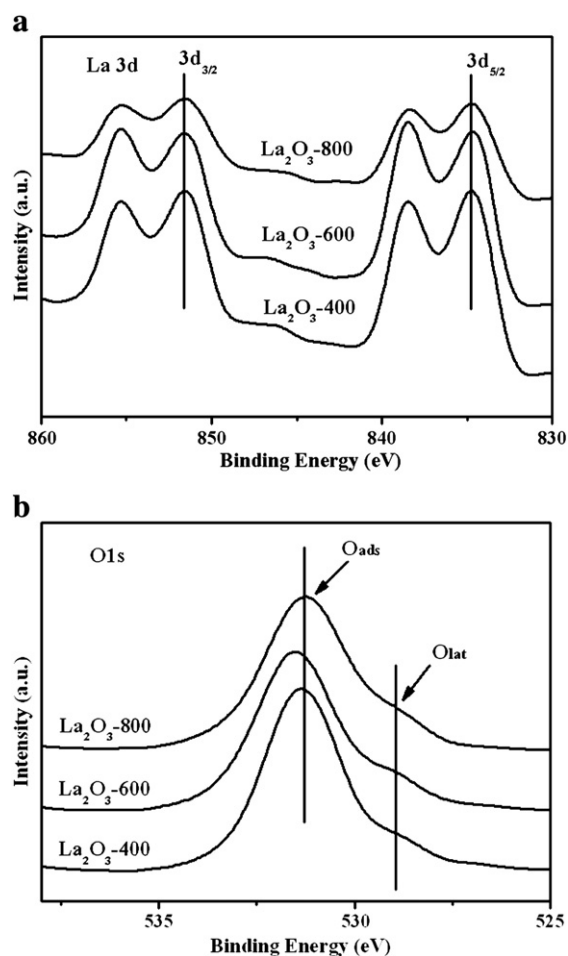


Fig. 2. XPS spectra recorded at the La3d (a), O1s (b) cores of surface atoms in lanthanum oxides calcined at different temperatures.

74% and has the maximum value of  $80 \mu\text{mol CO}_2 \text{ g}^{-1}$ . The total basicities of the samples follow the sequence: La-600 > La-400 > La-decom > La-com > La-800. As shown in Table 2, it also should be noteworthy that the basicity in strong region follows the order: La-600 > La-decom > La-com > La-800 > La-400. For La-com, the desorption of  $\text{CO}_2$  for La-com mainly located at higher temperature region, indicating it possessed very strong basicity. In association of the phase

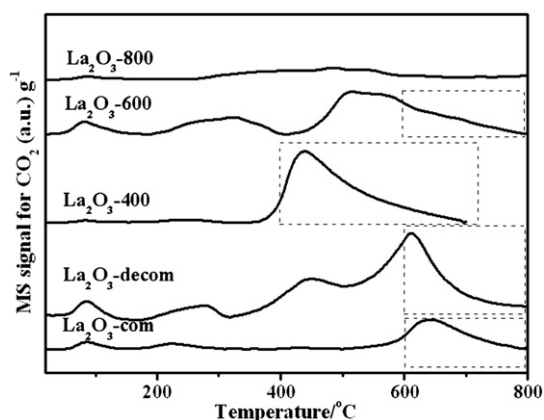


Fig. 3. TPD study of  $\text{CO}_2$  for lanthanum oxide samples (the rectangles with dash pattern represent the isothermal region).

Table 2  
Basic sites distribution evaluated on the basis of  $\text{CO}_2$ -TPD profiles.

Catalyst	Basic sites ( $\mu\text{mol CO}_2 \text{ g}^{-1}$ )			Total	Contribution of strong basic sites (%)
	Weak	Medium	Strong		
La-com	3	4	33	40	83
La-decom	8	10	65	83	78
La-400	–	99	–	99	–
La-600	7	21	80	108	74
La-800	2	–	22	24	92

composition determined by XRD, it indicated that the  $\text{La}_2\text{O}_2\text{CO}_3$  crystalline phase probably modified the surface basicity in strong region (but not very strong basicity) to some extent.

### 3.2. Catalytic performance

#### 3.2.1. Optimization of the reaction conditions

A series of rare earth oxides has been prepared and investigated for the GC synthesis, as shown in Table 3. Low to moderate glycerol conversions of 11.7–55.6% with GC selectivities of 88.9–97.4% were observed over  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{Pr}_2\text{O}_3$  as catalysts, entries 1–6. (2-Oxo-1, 3-dioxolan-4-yl) methyl carbamate as the byproduct was observed, which was formed due to the residual hydroxyl group belonged to GC over-reacted with urea. Among the catalysts examined, higher glycerol conversion of 68.9% with 98.1% selectivity of GC can be achieved over  $\text{La}_2\text{O}_3$ -600 catalyst, entry 7. The reaction was also tested with  $\text{La}_2\text{O}_3$ -600 as catalyst at atmospheric pressure and an equimolar solution of reactants, entry 8. Unfortunately, poor GC yield of 2.6% with 4.4% selectivity was observed, which is much lower than the result obtained when the reaction was conducted under the reduced pressure mode (entry 7). Therefore, the reaction was investigated under reduced pressure. When the reaction was carried out at molar ratio of glycerol/urea increased to 2, entry 9, GC yield of 89.1% with 98.6% selectivity was achieved, corresponding to higher TOF of  $1506 \text{ mmol/g}_{\text{cat}} \cdot \text{h}$  compared to the results previously reported [4,5]. 90.8% of slightly higher GC yield with 97.9% selectivity was obtained when further increasing the glycerol/urea to 3, entry 10, corresponding to TOF of  $1545 \text{ mmol/g}_{\text{cat}} \cdot \text{h}$ . It is apparent that the molar ratio of glycerol/urea increased to 3 has not resulted in remarkable increase of GC yield. From a practical view, the glycerol/urea of 2 may be a more favorable choice to ensure obtaining a satisfactory GC yield with acceptable selectivity.

Various lanthanum oxides were tested in GC synthesis, and the results are shown in Fig. 4a. It is obvious that the catalytic activity follows the order:  $\text{La}_2\text{O}_3$ -600 >  $\text{La}_2\text{O}_3$ -decom >  $\text{La}_2\text{O}_3$ -800 >  $\text{La}_2\text{O}_3$ -400 >  $\text{La}_2\text{O}_3$ -com >  $\text{La}(\text{OH})_3$ . In association with the result of  $\text{N}_2$  adsorption, the

Table 3  
Catalytic performance of various catalysts on the synthesis of GC from glycerol and urea.

Entry	Catalyst	Glycerol con./%	GC sel./%	GC yield/%	TOF ( $\text{mmol/g}_{\text{cat}} \cdot \text{h}$ )
1	$\text{Sm}_2\text{O}_3$	11.7	88.9	10.4	195
2	$\text{Eu}_2\text{O}_3$	18.5	97.4	18.0	308
3	$\text{CeO}_2$	24.1	95.7	23.1	402
4	$\text{Nd}_2\text{O}_3$	29.7	92.6	27.5	495
5	$\text{Y}_2\text{O}_3$	38.7	96.9	37.5	645
6	$\text{Pr}_2\text{O}_3$	55.6	96.8	53.8	927
7	$\text{La}_2\text{O}_3$ -600	68.9	98.1	67.6	1149
8 <sup>a</sup>	$\text{La}_2\text{O}_3$ -600	60.5	4.4	2.6	–
9 <sup>b</sup>	$\text{La}_2\text{O}_3$ -600	45.2	98.6	89.1	1506
10 <sup>c</sup>	$\text{La}_2\text{O}_3$ -600	30.9	97.9	90.8	1545

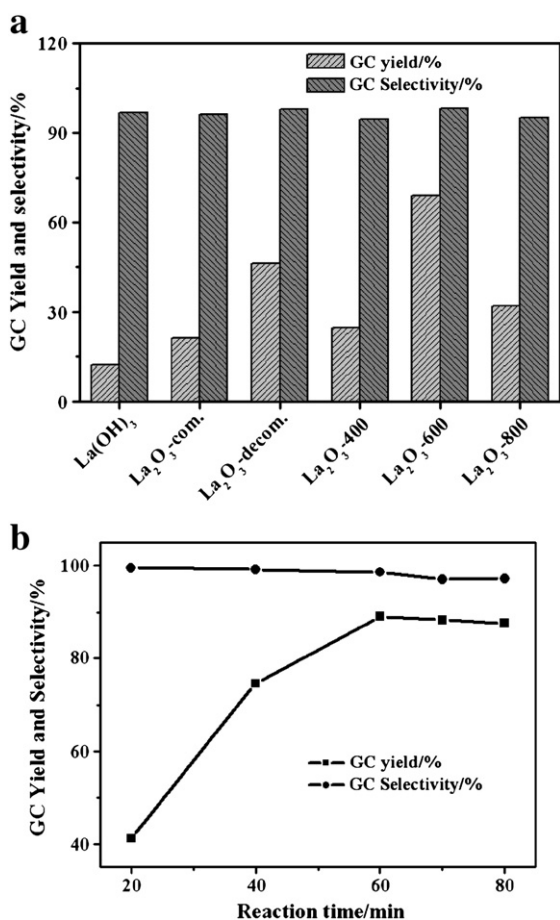
Reaction conditions: 6 g urea, 9.2 g glycerol, 0.06 g catalyst,  $140^\circ\text{C}$ , 3 kPa, 1 h.

TOF: calculated based on the mole of glycerol converted per gram catalyst per hour.

<sup>a</sup> atmospheric pressure, nitrogen as passing gas,  $140^\circ\text{C}$ , 4 h.

<sup>b</sup> 200 mmol glycerol, glycerol/urea = 2.

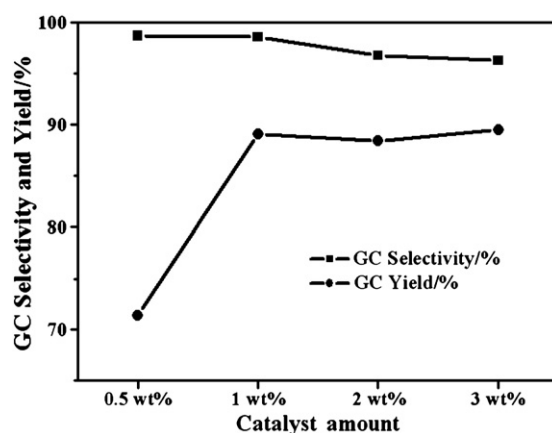
<sup>c</sup> 300 mmol glycerol, glycerol/urea = 3.



**Fig. 4.** a. Catalytic performance for GC synthesis over various catalysts. Reaction conditions: 6 g urea, 9.2 g glycerol, 0.06 g catalyst, 140 °C, 3 KPa, 1 h. **Fig. 4 b.** Influence of reaction time on the yield of GC over La<sub>2</sub>O<sub>3</sub>-600. Reaction conditions: 6 g urea, 18.4 g glycerol, 0.06 g catalyst, 140 °C, 3 KPa.

La<sub>2</sub>O<sub>3</sub>-600 with moderate surface area exhibited higher catalytic activity, i.e. 89.1% of GC yield with 98.6% selectivity, suggesting that the catalytic activity cannot be simply correlated to the surface area of the catalysts. The possible reason for the varied catalytic activity may derive from the various surface acid-base properties, as measured by CO<sub>2</sub>-TPD. The catalytic activity can be roughly correlated to the order of the basicity in strong region (except for the La-com), suggesting that the strong basicity plays an important role for its superior activity. The possible reason for the low activity of La<sub>2</sub>O<sub>3</sub>-com is the too strong basicity, thus resulting strong interaction with the reactants and block the active sites [5]. In combination of the XRD result, it can be found that the La<sub>2</sub>O<sub>3</sub>-600 and La<sub>2</sub>O<sub>3</sub>-decom with higher proportion of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phase compared to other lanthanum oxides tested exhibited higher catalytic activity. However, among the La<sub>2</sub>O<sub>3</sub>-600 and La<sub>2</sub>O<sub>3</sub>-decom, the La<sub>2</sub>O<sub>3</sub>-600 with lower proportion of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phase demonstrated relatively higher catalytic activity. Accordingly, it was suggested that the catalyst with appropriate amount of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phase can result in better enhancement of catalytic activity, and the La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> crystalline phase was considered to play an important role in catalytic behavior via influencing the content of the strong basic sites on catalyst surface, as measured by CO<sub>2</sub>-TPD. Taking into account all the features aforementioned, it can be deduced that the basic sites with appropriately strong strength, other than weak, medium or too strong strength, probably were more effective for the title reaction. Considering the origins of the basicity in strong region, the reaction probably conducted on the Lewis basic sites.

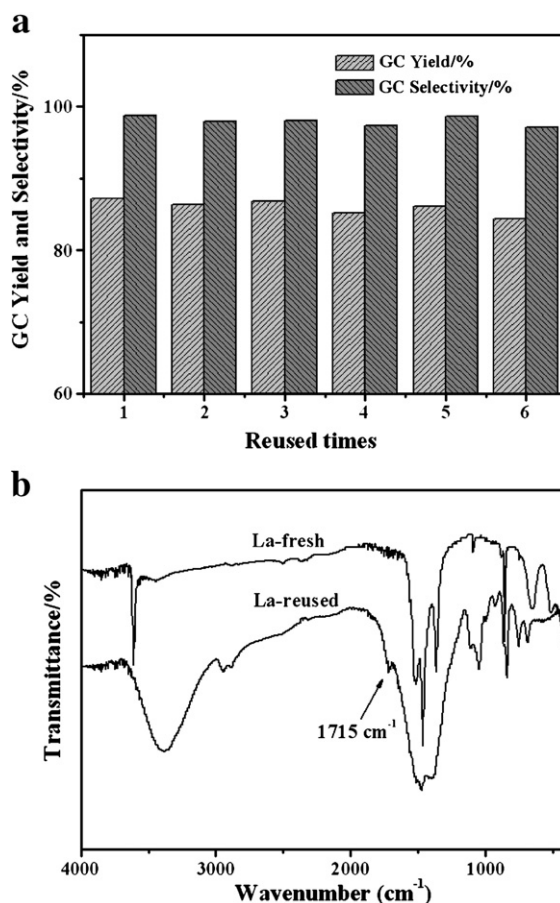
A typical reaction profile for the influence of reaction time on GC synthesis over La<sub>2</sub>O<sub>3</sub>-600 catalyst is presented in Fig. 4b. The results indicate that the reaction processed rapidly within initial 40 min, and



**Fig. 5.** The influence of catalyst amount on the synthesis of GC from glycerol and urea. Reaction conditions: 6 g urea, 18.4 g glycerol, 1 h, 140 °C, 3 KPa.

reached the highest yield of GC when the reaction time reaches 1 h. GC yield slightly decreased to 87.6% with 97.2% selectivity when the reaction time prolonged to 80 min.

The influence of catalyst amount on the synthesis of GC was investigated in the range from 0.5 to 3 wt.% at 1 h reaction time, respectively, and the results are shown in Fig. 5. 71.4% of GC yield with 98.7% selectivity was obtained at catalyst amount of 0.5 wt.%, whereas 88.4 to 89.5% of GC yield was obtained when the catalyst amount increased to 2 or 3 wt.%, and the corresponding GC selectivity decreased



**Fig. 6.** (a) Effects of recycling times on GC synthesis. **Fig. 6 (b)** FT-IR spectra of fresh and reused La<sub>2</sub>O<sub>3</sub>-600 (6th) catalysts.

simultaneously from 98.6 to 96.3%. The formation of reaction intermediate of 2, 3-dihydroxypropyl carbamate was observed as another byproduct and responsible for the decreased selectivity. It can be seen that the GC yield has witnessed obvious increase when the catalyst amount increased from 0.5 to 1 wt.% with similar selectivity, however, further increasing the catalyst amount to above 1 wt.%, i.e. 2 or 3 wt.%, cannot improve the GC yield and selectivity remarkably.

### 3.2.2. Catalyst recycling

The stability of catalyst was investigated, as shown in Fig. 6(a). GC yield of 84.3% with 97.1% selectivity can be obtained even after six consecutive runs. The remained catalytic performance indicated that the catalytic activity of the catalyst can be essentially preserved during the recycling tests investigated. As confirmed by XRD characterization aforementioned, the structure of the catalyst was essentially maintained during the recycling tests, and it was considered to contribute for the good recycling behavior.

Fig. 6(b) shows the FT-IR spectra of the catalyst fresh and reused for six runs. In comparison with the fresh one, the new band at  $1715\text{ cm}^{-1}$  is assigned to carbonyl stretching of the 2, 3-dihydroxypropyl carbamate that resides on the catalyst surface, which was considered as the reaction intermediate [4–7].

## 4. Conclusions

Lanthanum oxide catalyst prepared by precipitation method and activated at  $600\text{ }^{\circ}\text{C}$  was found to exhibit good catalytic performance in the synthesis of GC from inexpensive urea and glycerol. The higher TOF of  $1506\text{ mmol/g}\cdot\text{h}$  was achieved as compared to the previous reports.

The basic sites with strong strength were considered to play an important role for the superior catalytic activity. Accordingly, the catalyst containing appropriate amount of  $\text{La}_2\text{O}_2\text{CO}_3$  phase exhibited higher catalytic activity. The catalyst can be reused without significant loss in catalytic activity during the recycling tests. The facile synthesis, high catalytic performance, easy separation and good recyclability make this catalyst a candidate for application in industrial manufacture of GC.

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