碱性分子筛作用下甘油与碳酸二甲酯反应制碳酸甘油酯

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摘要: 报道了温和条件下甘油和碳酸二甲酯在一系列碱性催化剂作用下合成碳酸甘油酯的活性规律和构效关系。结果表明, 在所选择的催化剂中, NaY 分子筛对目标反应具有较高的活性和最高的目的产物选择性; 另外, 甘油和碳酸二甲酯的反应对催化剂的孔道结构具有特殊的要求, 3A, 4A 和 NaZSM-5 等孔径较小 (< 0.6 nm) 的分子筛没有催化活性, 而孔径较大的 NaY 和 Na β 则表现出较高的催化活性。

关键词: 碳酸甘油酯; 甘油; 碳酸二甲酯; 分子筛; NaY; 酯交换

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Transesterification of Glycerol with Dimethyl Carbonate to Glycerol Carbonate over Na-Based Zeolites

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Abstract: Glycerol carbonate (GC) was synthesized via transesterification of glycerol with dimethyl carbonate under mild conditions over a series of base zeolites. It was found that the NaY zeolite exhibited a higher selectivity for GC (100%) than heterogeneous bases (such as CaO and SrO) or homogeneous catalysts (such as NaOH and K_2CO_3). Further experiments over different base zeolites disclosed that this transesterification reaction depended strongly on catalyst structure. Base zeolites with small pore diameter such as 3A, 4A, and NaZSM-5 were inactive, while NaY and Na β with larger pore diameter exhibited excellent GC yields under mild conditions.

Key words: glycerol carbonate; glycerol; dimethyl carbonate; zeolite; NaY; transesterification

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With fossil fuels being consumed rapidly and increasing concerns around greenhouse gas emissions, there is much interest in using renewable feedstocks with low carbon dioxide emission as an alternative energy source to petroleum-based materials [1,2]. The sustainable production of biodiesel from biomass has not only received much attention from many academic researchers but has also caused many governments to increase their production for economic and environmental reasons [3]. However, the grow-

ing production of biodiesel through the transesterification of triglycerides with methanol has generated a large surplus of glycerol as major byproduct (ca. 10 wt% of manufactured biodiesel). Many biodiesel production factories view crude glycerol as a waste product and dispose of surplus glycerol by incineration.

The catalytic conversion of this biodiesel-derived glycerol into valuable products is a topic of great interest and has received much attention over recent years [4,5]. Glyc-

erol is an excellent building block which can be converted into various derivatives, for instance, it can be used as a feedstock for the production of propanediols [6], hydroxyacetone [7,8], glycerin ethers [9,10], and glyceride [11]. Recently, the catalytic synthesis of glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, CAS 931-40-8, abbreviated as GC) from biodiesel-based glycerol has attracted much attention.

GC is a rather new compound with promising high potential in the chemical industry because of its unique properties (such as biodegradability, low toxicity, high boiling point, low flammability, and moisturizing ability). GC can be used as a component in gas separation membranes, polyurethane foams, coatings, paints, and detergents, and can also be used as a green solvent in the cosmetics industry [12,13]. At the same time, GC is an intermediate in the synthesis of a series of chemicals, such as glycidol which is a precursor for the production of a number of polymers. More recently, it was reported that GC and its derivatives can be used as electrolytes in lithium ion batteries instead of ethylene and propylene carbonates [14].

Several syntheses routes of GC from glycerol have been proposed, such as the phosgenation between glycerol and phosgene (reaction (1), Scheme 1) [15], the direct carbonylation of glycerol with carbon dioxide (reaction (2)) [16–18], the glycerolysis of urea (reaction (3)) [19–22], and the oxidative carbonylation of glycerol with a gaseous mixture of carbon monoxide and oxygen over metallic catalysts (reaction (4)) [23,24]. However, some of these methods are problematic. For example, the starting materials are toxic and corrosive (reaction (1)), the direct reaction between glycerol and carbon dioxide must be performed at high

pressure, catalyzed by Sn-base complexes and the GC yield is relatively low. The glycerolysis of urea is carried out under vacuum to shift the equilibrium to GC production by continuously removing ammonia (reaction (3)). CO is inflammable and the process is dangerous in the oxidative carbonylation of glycerol with a gaseous mixture of carbon monoxide and oxygen over metallic catalysts (reaction (4)).

Among these proposed routes for GC production from glycerol, one convenient method that should be emphasized is the transesterification between glycerol and organic carbonates (such as dimethyl carbonate, diethyl carbonate, and ethylene carbonate (reactions (5) and (6), Scheme 1) [25–30]. This transesterification reaction could be performed under mild conditions (323–343 K) with various catalysts such as the homogeneous catalyst K_2CO_3 [31], the enzymatic catalyst Novozym 435 (a *Candida antarctica* lipase) [32], and the ionic liquid catalyst imidazolium-2-carboxylates [33]. However, problems associated with these catalysts, such as liquid pollution and separation issues, have hindered their application at large scale. From the viewpoint of green and sustainable chemistry, it is of great importance to find a suitable heterogeneous catalyst to replace the homogeneous ones.

Over the past five years, several heterogeneous catalytic systems have been reported for use in the transesterification reaction between glycerol and dimethyl carbonate (DMC) to GC. Ochoa-Gomez et al. [34] found that CaO is highly active for this reaction, but the CaO catalyst is deactivated quickly because of the leaching of Ca ions. Simanjuntak et al. [35] disclosed that CaO would dissolve in the glycerol and DMC reaction mixture, and homogenous $Ca(C_3H_7O_3)(OCO_2CH_3)$ that is formed in situ would in-

Scheme 1. Synthesis of glycerol carbonate (GC) via different routes.

crease the formation of GC. Recently, it has been reported that Mg/Al hydrotalcites also exhibited good activity for the transesterification reaction between glycerol and DMC, but this reaction should be performed in *N,N*-dimethylformamide (DMF) solvent [36,37].

In this work, the transesterification reaction between glycerol and DMC was performed over a series of base zeolites and compared with solid bases (such as MgO, CaO, SrO, and hydrotalcite) and homogeneous bases (such as NaOH and K₂CO₃). The catalytic activity of these base zeolites associated with their structure are discussed.

1 Experimental

1.1 Catalyst preparation

Commercial MgO, CaO, and SrO (AR grade, Sinopharm Chemical Reagent Co., Ltd, China) were calcined at 1173 K for 8 h before used. Commercial K₂CO₃, NaOH, DMC, and glycerol (AR grade, Aldrich, Shanghai Branch, China) were used without further treatment. Mg-Al hydrotalcites (HT, Mg/Al = 3) were synthesized by a conventional coprecipitation method as described in previous work [38,39]. The obtained solid was dried at 383 K in an oven overnight. NaA zeolites were purchased from Sinopharm Chemical Reagent Co., Ltd, China. NaZSM-5 (Si/Al ratio of 25.0), Na β (Si/Al ratio of 24.6), and NaY (Si/Al ratio of 2.4) zeolite powders were purchased from Nankai University Catalyst Co. The solid zeolite catalysts were dried at 383 K overnight and calcined at 773 K for 4 h before use.

1.2 Catalytic reactions

A controlled amount of DMC, methanol, and glycerol were mixed in a 100 ml round bottom three-neck jacketed glass reactor fitted with magnetic stirrer, reflux condenser, sampling device, and thermometer. The mixture was heated with stirring (1200 r/min) to the desired temperature and the catalyst was subsequently added to start the reaction. After reaction, the solid catalyst was removed by centrifugation and the liquid mixture was analyzed using an FID gas chromatograph (Shimadzu, 14 B) equipped with 30 m capillary column (DB-WAX 52 CB, USA). All products detected in the mixture were verified by a GC-MS system (Agilent 6890) and quantified using an internal calibration method.

2 Results and discussion

2.1 Catalyst screening

A series of homogeneous and heterogeneous bases were tested in the transesterification reaction between glycerol

Table 1 Synthesis of GC from glycerol and DMC over different base catalysts

Catalyst	Base strength H_0 [38–42]	Glycerol conversion (%)	Glycidol selectivity (%)	GC selectivity (%)
— ^a	—	0	—	—
NaOH ^b	13–15	77	77	23
K ₂ CO ₃	15.0	62	49	51
MgO	15.0	21	0	100
CaO	26.5	53	25	75
SrO	26.5	61	28	72
HT	13.7–16.5	30	0	100
NaY	9.3	54	0	100

Reaction conditions: glycerol 54.3 mmol, DMC 162.9 mmol, CH₃OH 10 ml, catalyst 0.5 g, 343 K, 2 h. ^aCatalyst-free. ^bCatalyst 0.2 g.

and DMC at 343 K for 2 h with results summarized in Table 1. It was confirmed that the transesterification reaction cannot proceed without catalysts. Similar results reported by Takagaki et al. [37] also indicated that this reaction must be catalyzed by a base. The conversion of glycerol over NaOH and K₂CO₃ reached 77% and 62%, respectively. However, the selectivity for GC in these homogeneous base-catalyzed mixtures was relatively low and a large amount of glycidol (derived from GC decomposition) was formed. These results are similar to those published previously [34]. On the solid base surface, the detected conversion of glycerol decreased in the order of SrO, CaO, NaY, HT, and MgO. However, glycidol formed in CaO and SrO catalyzed solutions, which might be attributed to the strong basicity of CaO and SrO, and/or the partial solubility of CaO [35] and SrO in the reaction mixture [42,43]. Among these solid bases, the excellent performance of NaY should be emphasized as only GC formed even at higher glycerol conversion.

Figure 1(a) shows the transesterification kinetics for the reaction between glycerol and DMC over NaY at 343 K in methanol. The conversion of glycerol increased rapidly over the first 4 h and then changed slightly over the following 4 h at 343 K. The selectivity for GC remained higher than 99%. Figure 1(b) shows the transesterification kinetics of the reaction between glycerol and DMC over SrO at 343 K in methanol. It was found that the selectivity for GC decreased gradually with increasing conversion of glycerol. These results indicate that the transesterification reaction between glycerol and DMC performed in base catalyzed solution, and the detected conversion of glycerol increased with the basic catalyst strength. Strong bases (such as homogeneous NaOH, K₂CO₃, and heterogeneous CaO, SrO) catalyzed the formation of byproducts because GC decomposed easily in these homogeneous base solutions [19,26]. Those heterogeneous bases with suitable base strength (such as NaY and HT) exhibited obvious advantages for excellent selectivity

Fig. 1. Transesterification kinetics for reaction of DMC and glycerol over NaY (a) and SrO (b). Reaction conditions: glycerol 54.3 mmol, DMC 162.9 mmol, CH₃OH 10 ml, catalyst 0.5 g, 343 K.

for GC and ease in separation with NaY exhibiting the best performance for this reaction.

On the basis of the results summarized in Table 1, it can be inferred that the catalytic transesterification of glycerol with DMC would proceed according to the following steps [19,26]. Glycerol is first activated in the base solution to a glycerol anion [43,44], which reacts with DMC to a hydroxyl alkyl carbonate. This hydroxyl alkyl carbonate transforms quickly to GC after the removal of another alcohol. Finally, a byproduct (glycidol) is formed via the decomposition of GC over stronger base sites. The reaction mechanism is summarized in Scheme 2.

2.2 Transesterification reaction over various zeolites

Table 2 summarizes the activity of different base zeolites for the transesterification reaction between glycerol and DMC. Surprisingly, 3A, 4A, and NaZSM-5 zeolites were inactive for this reaction. In contrast, Na β and NaY were

Scheme 2. Synthesis of GC from glycerol and DMC over base catalysts.

able to convert 37% and 80% of the glycerol, respectively, at 343 K and 4 h. At first, these results were postulated to the activity of these catalysts being proportioned to the number of basic sites in the catalysts, but this hypothesis cannot explain the obvious difference between NaZSM-5 and Na β because they have a similar number of basic sites (0.63–0.64 mmol/g). Apart from the basic sites in catalysts, the pore structure of these zeolites would play a critical role in this reaction. Those zeolites with small pore diameter (such as 3A, 4A, and NaZSM-5 that contain 8- or 10-numbered ring-structured pore channels) exhibited poor activity. Na β and NaY contain a 12-numbered ring-structured pore channel and were more active for this reaction. The lower activity of Na β than NaY could be attributed to the fact that the amount of basic sites in Na β (0.64 mmol/g) is lower than that of NaY (4.2 mmol/g).

The molecular geometrical parameters of DMC, glycerol, and GC were calculated using ChemOffice[®] and are summarized in Table 3. On the basis of these parameters and the pore structure of the zeolites tested, the poor activity of 3A, 4A, and NaZSM-5 are reasonable because GC cannot form in the poor channels of these catalysts. Glycerol (0.47–0.52 nm in diameter) [45] can move through the pore channels of NaZSM-5, but GC (0.33 nm in diameter and 0.65 nm in length) is larger than that of the NaZSM-5 channel space. NaZSM-5 can therefore not provide an available space for this reaction and GC diffusion is restricted. On the other hand, NaY with bigger pore channel (0.74 nm $\times$ 0.74 nm)

Table 2 Synthesis of GC from glycerol and DMC over various zeolite catalysts

Catalyst	Molecular formula	Basic site (mmol/g)	Ring	Pore channel (nm)	Glycerol conversion (%)	GC selectivity (%)
3A	Na ₈ K ₄ [Al ₁₂ Si ₁₂ O ₄₈] ₈	1.02	8	0.31 $\times$ 0.35	0	0
4A	Na ₁₂ [Al ₁₂ Si ₁₂ O ₄₈] ₈	1.02	8	0.41 $\times$ 0.41	0	0
NaZSM-5	Na _{3.7} [Al _{3.7} Si _{92.3} O ₁₉₂]	0.63	10	0.51 $\times$ 0.55, 0.53 $\times$ 0.56	0	0
Na β	Na _{2.5} [Al _{2.5} Si _{61.5} O ₁₂₈]	0.64	12	0.66 $\times$ 0.67, 0.56 $\times$ 0.56	37	100
NaY	Na _{1.88} [Al ₂ Si _{14.8} O _{13.5}]	4.20	12	0.74 $\times$ 0.74	80	100

Reaction conditions: glycerol 54.3 mmol, DMC 162.9 mmol, CH₃OH 10 ml, catalyst 0.5 g, 343 K, 4 h.

Table 3 Geometrical parameters of molecules in transesterification reaction

Substance	Geometrical parameter (nm)	
	Diameter	Length
DMC	0.37	0.45
Glycerol	0.47	0.52
GC	0.33	0.65

allows for the entrance and diffusion of both reactants (glycerol and DMC), and desired product (GC). The excellent performance of NaY could be attributed to its larger pore diameter and higher number of basic active sites.

2.3 Transesterification of glycerol and DMC in different solvents

The results from the transesterification of glycerol and DMC over NaY in different solvents are summarized in Table 4. The conversion of glycerol was the lowest (25%) when the reaction was performed without solvent at 343 K for 4 h, and the solvent polarity played a crucial role in glycerol conversion and GC selectivity. Dimethyl sulfoxide (DMSO) can improve glycerol conversion slightly to 45%. The conversion of glycerol further increased to 75% in ethanol solution, but byproducts formed easily, and the selectivity for GC decreased to 80%. The detected conversion of glycerol in DMF is similar to that in methanol, however, the selectivity for glycidol increased to 2%. Methanol is the optimal solvent for this reaction as it shows the highest conversion of glycerol, the highest GC selectivity, lowest price, and ease of GC separation.

Table 4 Transesterification of glycerol with DMC over NaY in various solvents

Solvent	Glycerol conversion (%)	Glycidol selectivity (%)	GC selectivity (%)	Others (%)
DMSO	45	2	96	2
DMF	80	2	98	0
Ethanol	75	5	80	15
Methanol	80	1	99	0
—*	25	0	100	0

Reaction conditions: glycerol 54.3 mmol, DMC 162.9 mmol, solvent 10 ml, catalyst 0.5 g, 343 K, 4 h.

*Solvent free.

2.4 Recycling of NaY

Figure 2 shows the activity of the recycled NaY catalyst for the transesterification of glycerol and DMC in methanol solvent. The catalyst was washed with methanol (5 ml $\times$ 5) and calcined at 773 K (1 h) after each recycle. The mass

Fig. 2. Recycling of NaY in transesterification between glycerol and DMC. Reaction conditions: glycerol/NaY=10/1 (mass ratio), DMC 162.9 mmol, CH₃OH 10 ml, 343 K, 4 h.

ratio between glycerol and NaY was controlled at 10 in each cycle. It was found that the conversion of glycerol decreased slightly from 79% to 78% in the first three cycles, and then remained stable. The selectivity for GC is higher than 99% throughout these cycles.

The XRD patterns of the fresh and 5-recycled NaY (Fig. 3) show that the crystalline structure of NaY zeolite remained stable, which is consistent with its activity (Fig. 2). These results indicate that NaY zeolite is an efficient catalyst for the transesterification of glycerol and DMC to GC, which is active, selective, and can be recycled.

Fig. 3. XRD patterns of fresh (1) and 5-recycled (2) NaY catalyst.

3 Conclusions

The transesterification reaction between glycerol and DMC is unfavored thermodynamically and must be catalyzed by a base. NaOH and K₂CO₃ exhibit higher glycerol conversions, but result in the formation of large amounts of byproduct. NaY zeolite exhibited excellent performance for

this reaction among the tested solid bases as only GC formed even at higher glycerol conversion, and NaY zeolite could be recycled. The excellent performance of NaY can be attributed to its larger pore diameter and higher number of base sites.

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