

Article

Transformation of CO₂ with Glycerol to Glycerol Carbonate over ETS-10 Zeolite-Based Catalyst

Zhangxi Gao ¹, Mei Xiang ², Mingyang He ¹, Weiyou Zhou ¹, Jiayao Chen ², Jiamin Lu ², Zeying Wu ^{1,2,*} and Yaqiong Su ^{3,*} 

¹ Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

² Research Center of Secondary Resources and Environment, School of Chemical Engineering and Materials, Changzhou Institute of Technology, Changzhou 213032, China

³ Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, State Key Laboratory of Electrical Insulation and Power Equipment, School of Chemistry, Xi'an Jiaotong University, Xi'an 710049, China

* Correspondence: wuzy@czu.cn (Z.W.); yqsu1989@xjtu.edu.cn (Y.S.)

Abstract: Catalytic conversion of CO₂ with the surplus glycerol (GL) produced from biodiesel manufacturing has attracted much academic and industrial attention, which proves the urgent requirement for developing high-performance catalysts to afford significant environmental benefits. Herein, titanasilicate ETS-10 zeolite-based catalysts with active metal species introduced by impregnation were employed for coupling CO₂ with GL to efficiently synthesize glycerol carbonate (GC). The catalytic GL conversion at 170 °C miraculously reached 35.0% and a 12.7% yield of GC was obtained on Co/ETS-10 with CH₃CN as a dehydrating agent. For comparison, Zn/ETS-10, Cu/ETS-10, Ni/ETS-10, Zr/ETS-10, Ce/ETS-10, and Fe/ETS-10 were also prepared, which showed inferior coordination between GL conversion and GC selectivity. Comprehensive analysis revealed that the presence of moderate basic sites for CO₂ adsorption-activation played a crucial role in regulating catalytic activity. Moreover, the appropriate interaction between cobalt species and ETS-10 zeolite was also of great significance for improving the glycerol activation capacity. A plausible mechanism was proposed for the synthesis of GC from GL and CO₂ in the presence of CH₃CN solvent over Co/ETS-10 catalyst. Moreover, the recyclability of Co/ETS-10 was also measured and it proved to be recycled at least eight times with less than 3% decline in GL conversion and GC yield after a simple regeneration process through calcination at 450 °C for 5 h in air.

Keywords: CO₂; glycerol; glycerol carbonate; ETS-10 zeolite; cobalt-based catalyst



Citation: Gao, Z.; Xiang, M.; He, M.; Zhou, W.; Chen, J.; Lu, J.; Wu, Z.; Su, Y. Transformation of CO₂ with Glycerol to Glycerol Carbonate over ETS-10 Zeolite-Based Catalyst.

Molecules **2023**, *28*, 2272. <https://doi.org/10.3390/molecules28052272>

Academic Editor: Igor Djerdj

Received: 31 January 2023

Revised: 19 February 2023

Accepted: 21 February 2023

Published: 28 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The concentration of carbon dioxide in the atmosphere has increased significantly by about 40% since the beginning of the industrial revolution [1–3]. Consequently, the capture, storage, and transformation of CO₂ have increasingly become the focus of worldwide attention [4–6]. Meanwhile, the correlative exhaustion of fossil resources also stimulated a thriving development of biodiesel fuel, which led, in turn, to a glycerol (GL) surplus all over the world [7]. As a result, the over-produced glycerol has been the major by-product during biomass utilization and has contributed to more than 67% of the global GL manufacturing and processing industry, thereby giving rise to a decreased market competitiveness and increased disposal difficulties [8,9]. Hence, consumption of glycerol through a green and economical process seems to be attractive and urgently needed. Among a series of attempts that have been being undertaken for bio-glycerol valorization, the pathway of coupling CO₂ to synthesize glycerol carbonate (GC) proves to be attractive, which succeeds in realizing a value-added conversion of the two cheap and waste raw materials with high atom efficiency (87%) [10–12]. However, due to the thermodynamics limitation, this sustainable

development strategy severely suffered from the apparent contradiction between glycerol conversion and GC yield [13].

A large number of homogeneous (Cs_2CO_3 [14], $^n\text{Bu}_2\text{SnO}$ [15], and KI [16]) and heterogeneous catalysts ($\text{La}_2\text{O}_2\text{CO}_3\text{-ZnO}$ [17], $\text{CeO}_2\text{-ZrO}_2$ [18], zeolite Y [19], and ZIF-8 [20]), have been reported and designed to improve the carboxylation of GL with CO_2 . Whereas by feat of harsh reaction conditions (high temperature and pressure) and indispensable dehydrating agents (mainly 2-cyanopyridine or acetonitrile), both GL conversion and GC yield are still far from satisfactory under the current catalytic reaction system. This can be owing to, on the one hand, the poor recyclability and separation difficulties of homogeneous catalysts, and on the other hand, the inadequate acid-base sites and specific surface area of heterogeneous catalysts. While for the latter, with competitive GC yields and notable advantages in easing product separation and purification, it has been proved to be worth more in-depth research. The future efforts can be directed towards enhancing the surface adsorption and activation of CO_2 and glycerol of heterogeneous catalysts by enlarging the active specific surface area, creating high density of Lewis acid and basic sites.

Zeolites characterized by a high specific surface area and adjustable acid/basic sites have been considered as potential candidates for catalyzing glycerol direct carbonylation with CO_2 [21–23]. Especially, titanosilicate zeolite ETS-10, that enjoys unique a framework and chemical compositions deserves the attention [24,25]. As one of the few zeolites that are with intrinsic Lewis basic sites, ETS-10 has proved to be promising in CO_2 adsorption and activation, during which the coordinately unsaturated TiO_6 building unit played the decisive role [26,27]. Furthermore, it has also displayed extraordinary performance for glycerol transesterification as a heterogeneous base catalyst, which was turned out to depend mainly on the interaction between Lewis basic sites (TiO_6^{2-}) and glycerol hydroxyl groups [28]. Added to these advantages is the porous structure that comprises chains of corner-sharing TiO_6 octahedra surrounded by SiO_4 tetrahedra, leading to an effective pore size of about 0.8 nm [29,30]. Thus, considering the actual molecular dimension of CO_2 and glycerol is 0.12 nm and 0.62 nm [31], respectively, there will be easy access for them to catalytic active sites if ETS-10 is employed as catalyst.

Hence, in this work, a series of ETS-10 based catalysts were prepared and used for catalytic transformation of CO_2 and GL, among which Co/ETS-10 exhibited the highest catalytic activity (GL conversion: 35.0%; GC yield: 12.7%). Notably, herein, the obtained result is even obviously superior to those that have been reported previously. This is largely due to the multiple active centers constructed by the strong interaction between the cobalt species and the unique ETS-10 framework, which indeed fulfills the requirement for simultaneous activation of CO_2 and glycerol. Therefore, CO_2 molecules can be adsorbed and activated by the Lewis basic sites on the ETS-10 zeolite surface, which were then inserted into the cobalt glycerate generated by the Co species with Lewis acidity to form the crucial intermediate species for the following intramolecular rearrangement process, and finally produce the target product GC.

2. Results and Discussion

2.1. Catalyst Characterization

The XRD patterns of various ETS-10 based catalysts are shown in Figure 1a, which exhibit well-resolved peaks related to the ETS structure between 5° and 45° . While comparing those metal introduced ETS-10 zeolite catalysts with the pristine one, the decreased crystallinity suggested that the incorporation of metal species did indeed threaten the integrity of the zeolite framework to varying degrees, which can be further confirmed by the N_2 adsorption-desorption analysis data (Table 1). The BET-specific surface area reduced to $283.4 \text{ m}^2/\text{g}$ (Zn/ETS-10) from $324.4 \text{ m}^2/\text{g}$ (ETS-10) gave a good interpretation of the negative influence on the ETS-10 structure integrity due to the metal species and their different interactions with zeolite support. It is worth noting that even though the actual metal contents detected by ICP analysis were around 4%, there seems no metal particles can be observed in the XRD patterns, indicating the high dispersion of the metal species.

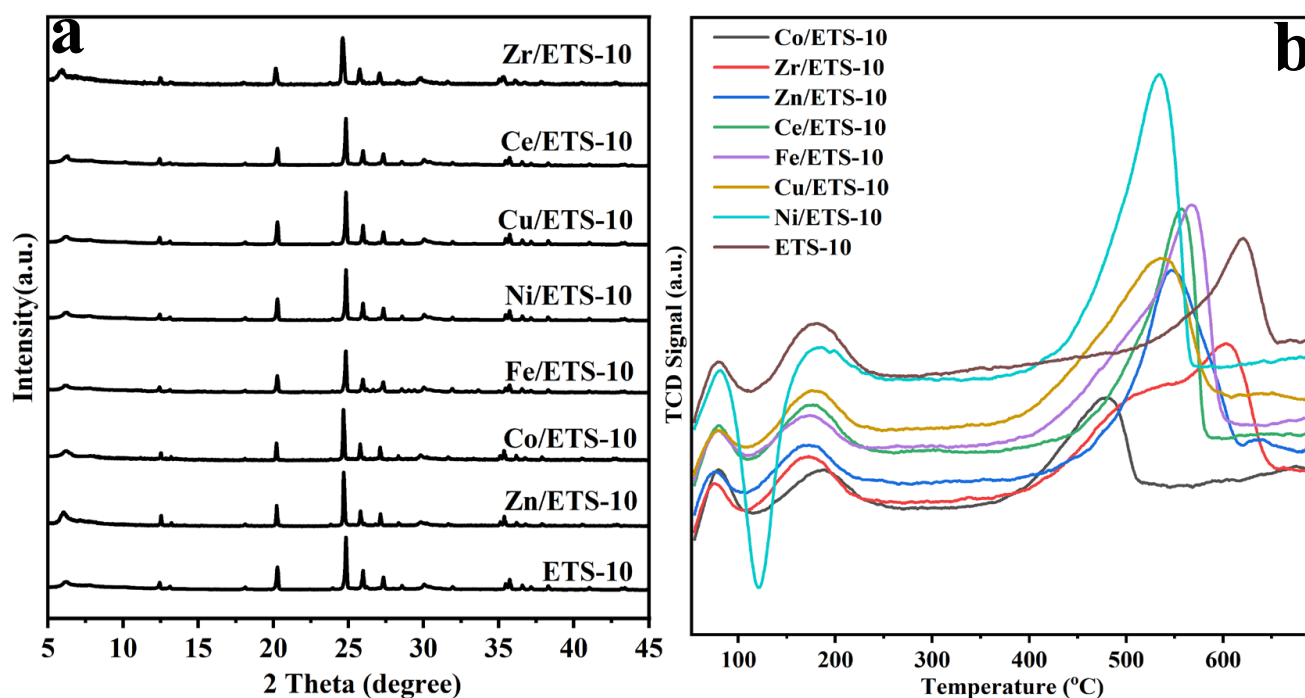


Figure 1. (a) XRD patterns and (b) CO₂-TPD profiles of different ETS-10 zeolite-based catalysts.

Table 1. Physicochemical properties of different ETS-10 zeolite-based samples.

Samples	C ^a	S _{BET} ^b	Metal Contents ^c	CO ₂ Adsorption			
				Temperature of Peak ^d		Desorbed CO ₂ Amounts ^e	
ETS-10	98.7	324.4	-	78.2	178.3	620.0	0.37
Co/ETS-10	93.6	302.3	4.3	79.1	179.7	476.3	0.44
Zr/ETS-10	93.7	299.4	4.1	75.0	166.9	514.4	0.61
Zn/ETS-10	90.2	283.4	4.4	74.9	166.4	551.1	0.50
Ce/ETS-10	94.3	309.7	4.2	78.7	168.4	557.0	0.68
Fe/ETS-10	93.2	307.9	4.1	78.4	166.4	565.9	0.74
Cu/ETS-10	95.1	310.6	4.4	78.2	172.0	532.8	0.74
Ni/ETS-10	92.3	309.4	4.3	88.0	170.7	533.8	1.41

^a Crystallinity calculated by the Scherrer equation (%). ^b BET surface area (m²/g). ^c The actual metal contents detected by ICP (wt%). ^d Temperature of the peak by CO₂-TPD (°C). ^e Total basic sites amount (mmol·CO₂/g).

Figure 1b reveals the basic properties of different ETS-10 zeolite-based samples determined by CO₂-TPD. Obviously, there were alkaline sites of different strength distributed on the catalyst, most of which were characterized by medium-strong alkalinity with the CO₂ desorption temperature above 400 °C. This can be related to the unidentate carbonates formed on O²⁻ ions that are located in the structural unit of the Ti-O-Ti chain [32]. Despite the relatively weak peak intensities, two broad peaks centered at about 80 °C and 180 °C were presented for all eight samples, which resulted from the interactions between CO₂ and the weak basic surface hydroxyl groups on ETS-10 zeolite [26]. In addition, the quantitative analysis of CO₂-TPD test was also performed to help visualize the overall CO₂ adsorption capacity of different catalyst samples (Table 1). Firstly, according to the comparison between ETS-10 and those metal-based samples, the most visible changes were the distribution of the desorption temperature in the high region. For ETS-10, the most salient desorption peak was at 620 °C, while all the others showed an evident lower temperature distribution (<600 °C). Nevertheless, the increase of the total desorption quantity of CO₂ was visible to the naked eye for the metal introduced samples. Ni/ETS-10 was no doubt the most prominent one with the highest amount of desorbed CO₂ (1.41 mmol/g), indicating a promising CO₂ adsorption capacity. Fe/ETS-10, Ce/ETS-10, and Cu/ETS-10

showed similar basic characteristics with the desorption temperature distribution and the total CO₂ desorption quantity being parallel. Zn/ETS-10 and Co/ETS-10 were the two extraordinary samples with the quantitative result being not comparable. For Zn/ETS-10, it benefited from the strong interaction between zinc species and ETS-10 zeolite, which was mainly featured in the dominance of strong alkaline sites. However, meanwhile, the interaction was in fact a two-edged sword, which has proved to be adverse to keeping the catalyst structure integrity. As a consequence, the seriously decreased crystallinity (90.2%) brought disadvantages to the physico-chemical properties of the corresponding catalyst. When it came to Co/ETS-10, it unexpectedly exhibited the lowest CO₂ desorption amount of 0.44 mmol/g among a series of metal-introduced ETS-10 zeolite catalyst samples with the desorption temperature shifting even below 500 °C. Apparently, the intriguing anomaly could not be simply attributed to the decreased catalyst crystallinity, which should be closely related to the metal species themselves and their distinct interaction with the zeolite support. In fact, although the CO₂ adsorption capacity of Co/ETS-10 was inferior to other catalyst samples, the total amount of desorbed CO₂ was almost 15 times more than that of Co₃O₄ reported previously (about 0.03 mmol/g) [33,34], further illustrating that the integration of the cobalt species and ETS-10 zeolite did generate a peculiar interaction. Given the relative specificity of Co/ETS-10, further investigations were carried out for taking a closer look at the interaction between metal Co species and ETS-10 zeolite.

Figure 2 shows the SEM images of as-synthesized ETS-10 and Co/ETS-10 samples. On the whole, both samples displayed structured crystals with a typical bipyramidal truncated shape, and the layer stacked ETS-10 crystals were all with uniform size (4–6.5 µm) and minor surface defects. This indicates that the incorporation of the Co species into ETS-10 does not cause any observable structure destructions to the zeolite support, which also demonstrates their moderate interaction and is in line with the XRD and N₂ adsorption-desorption results.

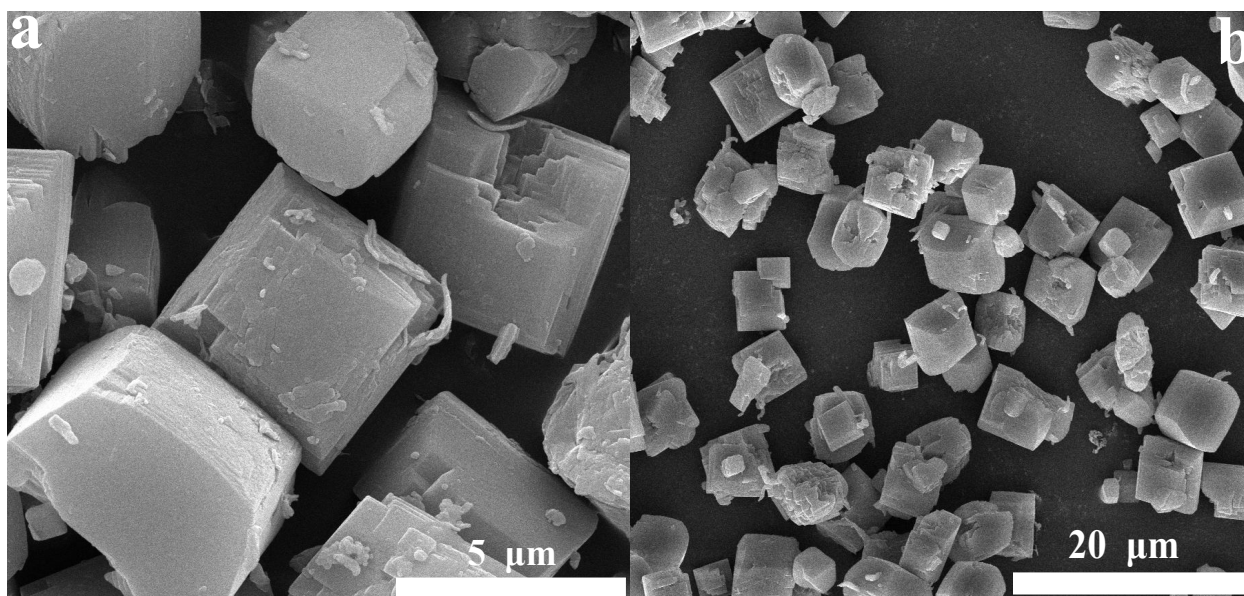


Figure 2. SEM images of (a) ETS-10 zeolite and (b) Co/ETS-10 catalyst sample.

The surface composition and chemical bonding states of the metal active sites on Co/ETS-10 were then determined by XPS. As can be seen from Figure 3, there are six characteristic peaks from the Co 2p XPS spectrum. The peaks at 779.6 eV and 794.2 eV are affiliated to Co 2p_{3/2} and Co 2p_{1/2} for Co³⁺ species. Another two characteristic peaks appearing at 781.4 and 796.1 eV are attributed to Co 2p_{3/2} and Co 2p_{1/2} for Co²⁺ species, which are accompanied by two shake-up satellite peaks located at 786.0 eV and 802.9 eV. Interestingly, when compared with the XPS spectra of Co₃O₄ reported previously [35,36],

the peak positions for Co^{3+} species in Co/ETS-10 are shifted toward lower binding energies, suggesting a possible existence of electron transfer between the Co species and the ETS-10 zeolite support. Furthermore, according to the semi-quantitative analysis, the surface concentrations of Co^{2+} for Co/ETS-10 is 73%, higher than that for Co_3O_4 reported (69%), indicating the lower average oxidation valence state of the cobalt species presented in Co/ETS-10 [37,38]. This may be related to the coordination interaction between Co species and TiO_6 building units with two negative charges in ETS-10 zeolite.

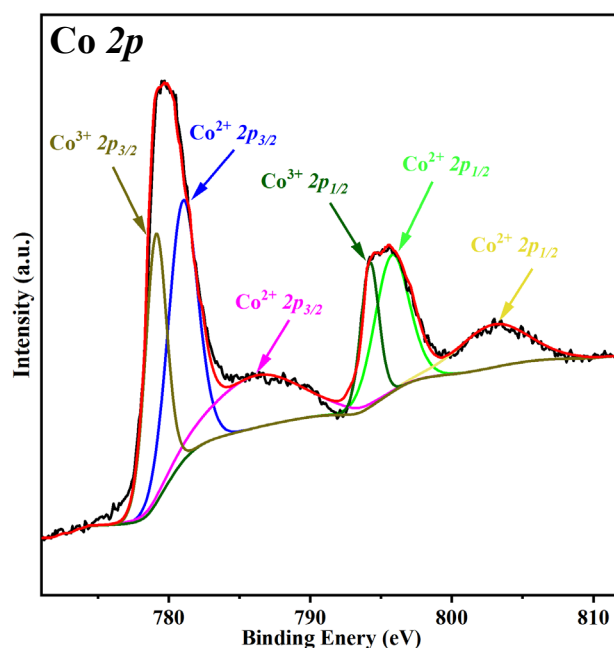


Figure 3. XPS spectra of Co 2p for Co/ETS-10 catalyst sample.

2.2. Catalytic Activity

A series of metal-based ETS-10 zeolite catalysts were firstly used for the transformation of glycerol and CO_2 to GC (Figure 4a). A blank control experiment was also carried out with virtually no GC formed, demonstrating the necessity of introducing a catalyst for promoting CO_2 and glycerol activation-conversion. Moreover, it also substantiated the importance for employing the appropriate solvent. Herein, acetonitrile, one of the most often used solvents, proved to play a fundamental role in activating glycerol, leading to nearly 17% glycerol being converted. This can be owing to the acetamide generated from the hydrolysis of acetonitrile, that can induce the coupling reaction to remove the by-product H_2O , which thus benefited by breaking the strict thermodynamic limitation and facilitated the reaction equilibrium shifting to right [39,40]. When compared to the experimental run with pure ETS-10 adopted, a marked improvement of both GL conversion (24.5%) and GC selectivity (9.8%) was obtained, which can be attributed to the enhanced CO_2 adsorption-activation capacity that resulted from the unique framework of ETS-10 zeolite. Indeed, it has been reported in our previous work, that the peculiar structure unit of the $-\text{Ti}-\text{O}-\text{Ti}-$ chain that is characterized by the extraordinary and strong donor capability, did meet the demands of CO_2 activation, therefore, greatly promoted the correspondingly catalytic performance for CO_2 transformation [27,41]. For all supported catalysts, most of them showed higher GL conversion and GC yield than the metal-free catalyst samples, except Ni/ETS-10, which may be due to its excessive basicity. Obviously, Co/ETS-10 and Zn/ETS-10 each occupied the highest GL conversion and GC selectivity, respectively. As a matter of fact, zinc-based catalysts have been widely reported and recognized as the most potential candidate for synthesizing GC from glycerol and CO_2 [17,20,42]. While in this work, it seems that Zn/ETS-10 is slightly inferior to Co/ETS-10 with 0.5% less of the total GC yield. Considering the impressive GC selectivity, the disadvantages of Zn/ETS-10 in GL

conversion may be related to the lower degree of glycerol and CO₂ activation. This can be associated directly with the crystallinity deterioration of ETS-10 zeolite resulting from Zn introduction, which gave rise to the strong electronic interaction between zinc species and O atoms in the zeolite skeleton. Thus, a distortion of the Ti-O-Ti chain took place, which then resulted in the structure damage of ETS-10 zeolite and brought negative influence on the relevant catalytic performance. In other words, further investigations in developing more moderate and effective ways to introduce zinc species are need in the future. For Cu/ETS-10, Ce/ETS-10, and Fe-ETS-10 catalysts, they were all highly enthusiastic about converting glycerol, but their capacity in boosting GC selectivity was too common to be on par with Co/ETS-10 and other catalysts that have been reported [39,40,43]. Another notable sample was Zr/ETS-10, of which the introduced Zr species seems to play little or no role in the GC formation. This result can be interpreted as the composite demands for a certain amount of basic sites, the binding energy of the metal species and their interaction with catalyst supports. Though the incorporation of Zr⁴⁺ into ETS-10 zeolite endowed the catalyst with more medium and strong basic sites, the fairly low binding energy seriously pulled down the activation of glycerol [18,44–46].

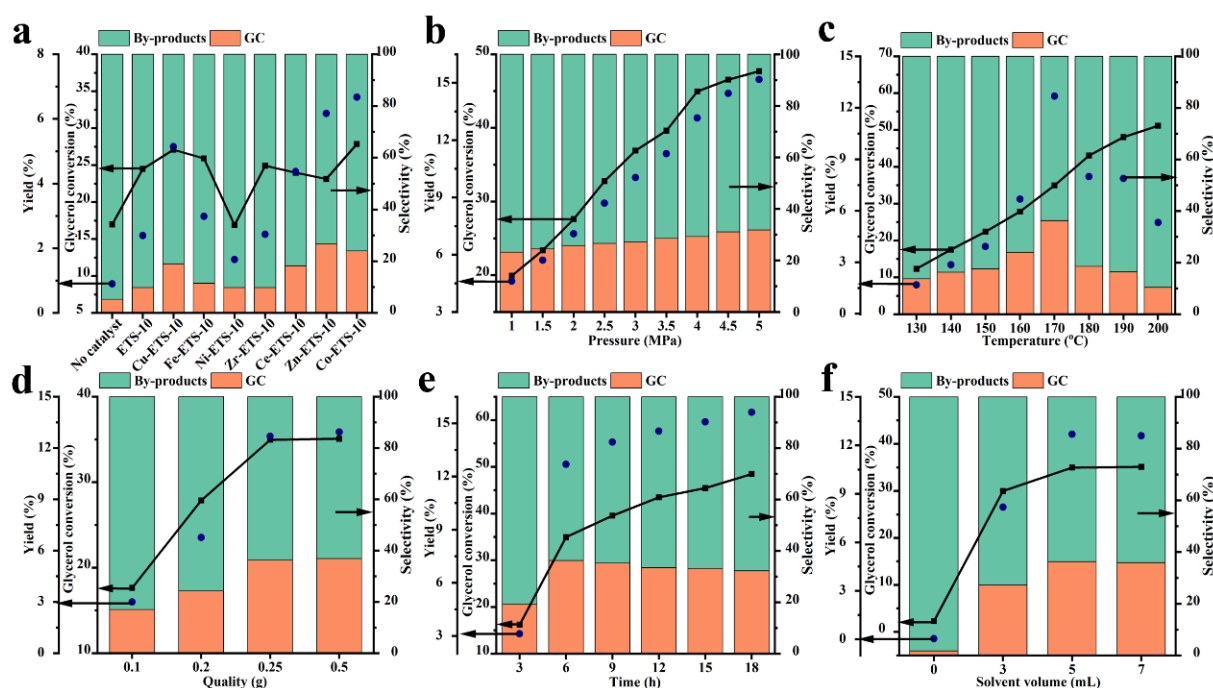


Figure 4. (a) the activity of the different catalysts for converting CO₂ and glycerol into GC, and the catalytic performance of Co/ETS-10 for GC formation as a function of (b) pressure, (c) temperature, (d) catalyst quality, (e) reaction time, and (f) solvent volume (reaction conditions: 170 °C, 4 MPa, 0.25 g catalyst, 6 h, and 5 g CH₃CN).

The effect of pressures on the carbonylation of glycerol with CO₂ was then investigated. As can be shown in Figure 4b, both the glycerol conversion and GC yield monotonically increased with the initial reaction pressure. This can be attributed to, on the one hand, as the main reaction feedstock, the presence of more CO₂ can bring it into sufficient contact with other reactant molecules and catalytic centers, which thus is favorable for the reaction to proceed in the desired direction. On the other hand, higher pressure provided an easier dissolution of CO₂ molecules in the acetonitrile solution, leading to convenient access for CO₂ adsorption-activation. Consequently, with the pressure increased from 1.0 MPa to 5.0 MPa, the conversion of glycerol dramatically increased from 20.4% to 29.4%. For the GC yield, the growth was also obvious before the reaction pressure was increased to 4.0 MPa, after which it slowed down with only 0.8% more GC yield was obtained. Therefore, taking

the actual requirements of industrial application, a relatively low operating pressure is safer and cost-effectiveness.

Figure 4c shows the effect of the reaction temperature on the carbonylation of glycerol with CO₂. As a typical exothermic reaction, the glycerol conversion deservedly benefited from the elevated temperature, which can be put down to the facilitated activation of low-energy molecules and lowered reaction energy barrier with temperature increased. Nevertheless, the selectivity of GC decreased significantly if the reaction temperature increased higher than 170 °C. This is because, on the one hand, the glycerol dehydration reaction can be intensified at a high temperature to produce glycidyl glycerol. On the other hand, the produced acetamide from acetonitrile hydrolysis will be further hydrolyzed to acetic acid, which then reacts with glycerol and leads to the formation of by-products glyceryl monoacetate and glyceryl diacetate. Moreover, according to the previous literature reports, the formed GC could be easily decomposed or converted in the presence of amine groups. Consequently, an excessive increase of reaction temperature will go against the GC selectivity, and it seems to be optimal to set the reaction temperature at 170 °C in this work.

It is widely known that the amount of catalyst definitely works for improving the catalytic performance by adjusting the active sites. Typically, the more catalysts added, the more the active sites are accessible to reactants. As shown in Figure 4d, increasing the catalyst dosage from 0.1 g to 0.25 g, a growth leap in glycerol conversion and GC selectivity took shape, after which the rising tendency came to a standstill. This can be demonstrated as being available for more and more indispensable active sites that remarkably enhanced the activation of CO₂ and glycerol and facilitated their subsequent combination to efficiently produce GC. In spite of being beneficial to promoting catalytic reactivity, there seems no need to blindly increase the catalyst's quantity to more than 0.25 g, where the catalytic active sites in the reaction system are perfectly adequate.

As presented in Figure 4e, even though there was obvious growth that occurred on the glycerol conversion with the reaction time prolonged, the rise in GC selectivity unexpectedly derailed, which was maximized at 6 h and then began declining gradually accompanied by an increased formation of glycerol monoacetate. This may be related to the side reaction of the active hydroxyl group on GC and acetic acid from CH₃CN hydrolysis. Additionally, it is possible that with the presence of more and more GC in the reaction system, self-polymerization took place to produce oligomers under the given reaction conditions, which accordingly brought down the GC yield.

Thanks to the crucial role that CH₃CN played in positively affecting the reaction process, the influence of the CH₃CN dosage was then explored for optimization. Firstly, it can be seen from Figure 4f that with no acetonitrile used as dehydrating agent, the glycerol was less likely to be converted into GC. As the amount of acetonitrile was increased from 3 mL to 5 mL, either the conversion of glycerol or the selectivity of GC increased significantly, after which the reactivity enhancement appeared to not come into play by keeping on increasing the usage of CH₃CN. Admittedly, the transformation of CO₂ and glycerol to GC can be improved by the enhanced hydrolysis efficiency from excess CH₃CN, however, acetic acid would be produced at the same time and reacted with glycerol, leading to the generation of undesired by-products and the decline of GC selectivity. Therefore, a moderate amount of 5 mL CH₃CN is exactly good for GC synthesis.

Further studies on the catalyst prepared by various active metal species mentioned above for the carbonylation reaction of glycerol with CO₂ were then reimplemented under the optimized reaction conditions of 170 °C, 4 MPa, 5 mL CH₃CN, 6 h, and 0.25 g catalyst (Table 2). Clearly, all catalysts enjoyed a significant improvement of glycerol conversion and GC yield, among which Co/ETS-10 was still comprehensively superior. To further obtain a better insight into the distinguished catalytic performance of Co/ETS-10, a comparison with Co₃O₄ was conducted, which has been reported with dominantly advantageous binding energy that greatly benefited glycerol activation [47]. As a consequence, Co₃O₄ showed a comparable glycerol conversion with Co/ETS-10. While the evident weakness in yielding GC of Co₃O₄ reconfirmed the significance of ETS-10 zeolite, which has proved to

be indispensable for adsorption and activation of both glycerol and CO₂. What is more, as can be seen from Table 3, the catalytic performance of Co/ETS-10 not only preceded those catalysts mentioned above, but also was preeminent among various catalysts reported previously [17,48–50].

Table 2. Carbonylation of glycerol with CO₂ over different metal-based ETS-10 zeolite catalysts under the optimized reaction conditions (170 °C, 4 MPa, 6 h, 0.25 g catalyst and 5 mL CH₃CN).

Catalyst	C _{GL} (%)	S _{GC} (%)	Y _{GC} (%)
ETS-10	33.6	13.9	4.7
Cu-ETS-10	35.6	23.9	8.5
Fe-ETS-10	33.4	25.9	8.7
Ni-ETS-10	29.6	14.1	4.3
Zr-ETS-10	33.6	14.1	4.7
Ce-ETS-10	32.7	29.9	9.8
Zn-ETS-10	32.7	35.6	11.7
Co-ETS-10	35.0	36.3	12.7

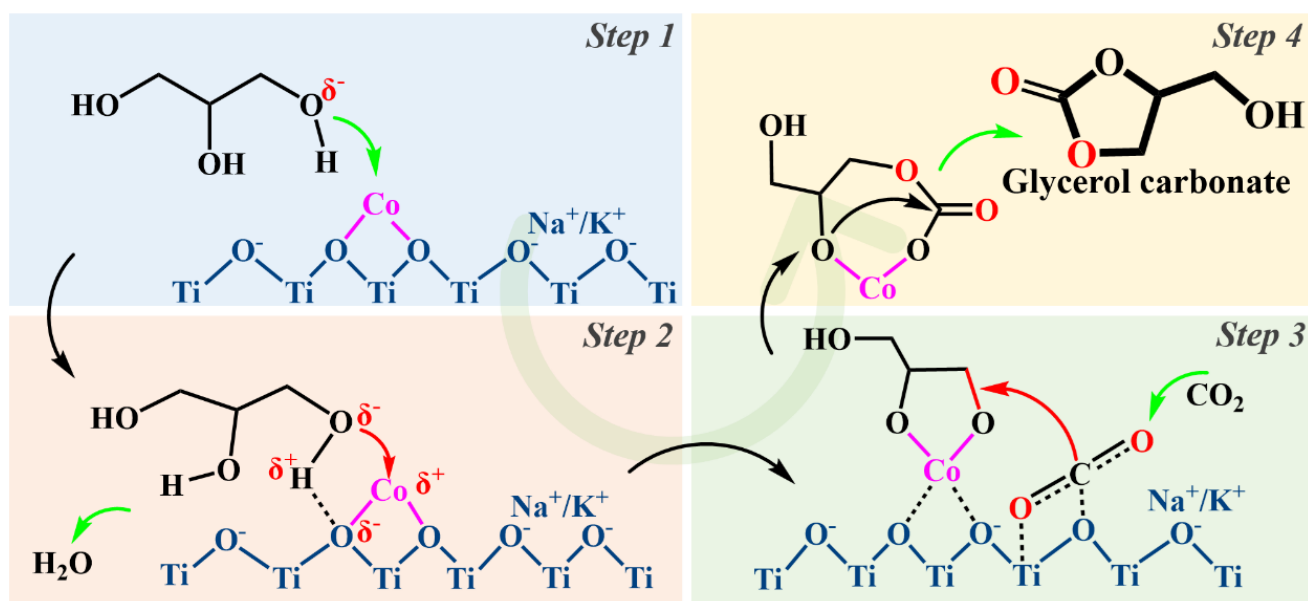
Table 3. Catalytic conversion of CO₂ and glycerol into GC over different heterogeneous catalysts reported previously.

Catalyst	Reaction Conditions	C _{GL} (%)	S _{GC} (%)	Y _{GC} (%)	Ref
Co ₃ O ₄	Dehydrating agent: 5 mL CH ₃ CN, 4.6 g glycerol, 0.1 g catalyst, 4.5 MPa of CO ₂ , 12 h, 170 °C	20.6	37.9	7.8	[48]
Cu/La ₂ O ₃ Cu/Mg-Al-Zr Cu/MgO	Dehydrating agent: 10 mL CH ₃ CN, 4.6 g glycerol, 0.08 g catalyst, 7.0 MPa of CO ₂ , 3 h, 150 °C	8.9	29.3	2.6	[49]
		11.5	20.9	2.4	
		8.6	26.1	2.2	
Co(OAc) ₂ Zn(OAc) ₂ Mn(OAc) ₂	Dehydrating agent: 65 mL CH ₃ CN, 36.8 g glycerol, 0.921 g catalyst, 2.0 MPa of CO ₂ , 2 h, 160 °C	29.0	12.4	3.6	[50]
		38.9	6.9	2.7	
		31.4	11.1	3.5	
Co(NO ₃) ₂ ZnO	Dehydrating agent: 5 mL CH ₃ CN, 4.6 g glycerol, 0.1 g catalyst, 5.5 MPa of CO ₂ , 12 h, 160 °C	71.4	10.1	7.2	[17]
		24.8	18.1	4.5	

On account of the discussion above and referring to those previous reports [20,40,51,52], a feasible mechanism was proposed for the coupling process of GC synthesis. As is shown in Scheme 1, the oxygen atom on the hydroxyl group of glycerol attacked the Co species to produce cobalt glycerate and water molecules as main intermediates. At the same time, the activated CO₂ adsorbed on the basic sites (TiO₆^{2−}) of ETS-10 zeolite was inserted into the cobalt glycerate to form another important intermediate of the seven-membered ring, which then underwent intramolecular rearrangement for the target product GC coming into being. This process proceeded smoothly mainly thanks to the multiple catalytically active centers constructed by the suitable interaction between the cobalt species and the ETS-10 framework, which indeed fulfilled the requirement for simultaneous activation of CO₂ and glycerol with high efficiency.

2.3. Catalyst Stability

Catalyst stability is important for practical industrial applications. Hence, the stability of the Co/ETS-10 catalyst after eight cycles under the desired reaction conditions was evaluated. As revealed in Figure 5, Co/ETS-10 proved itself to be reasonably stable with less than 3% decline in glycerol conversion and glycerol carbonate yield. Notably, the glycerol conversion and glycerol carbonate yield can even be sustained at a consistent level during the first five test runs.



Scheme 1. The possible catalytic mechanism for GC formation from CO₂ and glycerol on Co/ETS-10 catalyst.

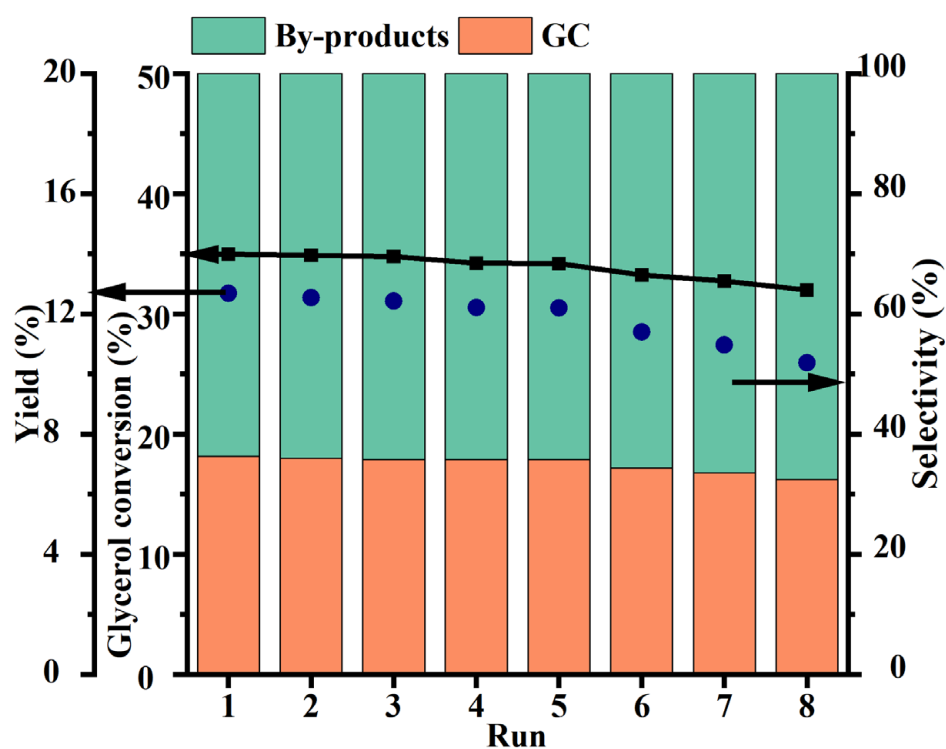


Figure 5. Stability of the Co/ETS-10 catalyst (reaction conditions: 170 °C, 4 MPa, 0.25 g catalyst, 6 h, and 5 mL CH₃CN).

3. Experimental Methods

3.1. Materials

Cerium nitrate hexahydrate (AR, 99%) and zirconium nitrate pentahydrate (AR, 99%) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Iron nitrate non-hydrate (AR, ≥98.5%), cobalt nitrate hexahydrate (AR, ≥99%), nickel nitrate hexahydrate (AR, 98%), cupric nitrate trihydrate (AR, 99%), zinc nitrate hexahydrate (AR, 99%), glycerol (ACS, ≥99.5%), and tetraethylene glycol (AR, 99%) were supplied by Aladdin Chemistry

Co., Ltd. (Shanghai, China). Acetonitrile (AR, 99%) and ethanol (AR, 99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Other reagents were of analytical grade and all of the reagents were used as received without further purification.

3.2. Preparation of ETS-10 Zeolite-Based Catalysts

ETS-10 was prepared by a hydrothermal approach reported previously with a molar composition of $1.0 \text{ TiO}_2/7.1 \text{ SiO}_2/4.4 \text{ Na}_2\text{O}/1.9 \text{ K}_2\text{O}/164 \text{ H}_2\text{O}$ [27]. Typically, the synthesis was started from the dropwise addition of 5.9 g TiCl_3 solution (15–20 wt% in 30 wt% HCl) to the alkaline solution consisting of 9.3 mL waterglass solution ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio: 3.2, density: 1.2 g/cm^3) and 10 mL aqueous NaOH (3.5 mol/L). Subsequently, 5.2 mL KF aqueous solution (5.8 mol/L) was introduced to obtain the final slurry gel, which was then transferred into the Teflon-lined autoclave and crystallized at 230°C for 72 h. The products were recovered by filtration, washed with deionized water, dried at 100°C and calcined in air at 450°C for 5 h. The obtained ETS-10 zeolite samples were used to prepare series of metal-based catalysts by an incipient impregnation method with a 5 wt% metal loading. Taking Co/ETS-10 as an example, 1.0 g ETS-10 was mixed uniformly with 0.5 mL $\text{Co}(\text{NO}_3)_2$ aqueous solution (1.7 mol/L), after which the resulted solid product was air dried overnight. A further drying at 120°C for 12 h was then carried out before being calcined at 450°C for 5 h to afford the final Co/ETS-10 catalyst sample. By the same way, other catalysts were also prepared with nitrate precursors, including $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

3.3. Catalyst Characterization

Phase identification of all samples was performed by powder X-ray diffraction (XRD) measurements using a Rigaku powder X-ray diffractometer (D/Max 2500, Rigaku, Tokyo, Japan). The diffraction peaks were scanned from 5° to 45° . The actual metal contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES-PerkinElmer Optima 3300DV). The specific surface area of the catalysts was measured at -196°C using an adsorption apparatus (Micromeritics ASAP 2460, Micromeritics, Norcross, GA, USA) and was estimated from the adsorption data using the Brunauer–Emmett–Teller (BET) equation. The morphology was observed by field-emission scanning electron microscopy (Hitachi S-4800, Hitachi, Tokyo, Japan).

The catalyst's basicity was evaluated using the temperature-programmed desorption of CO_2 on a Micromeritics ASP 2920 instrument (Micromeritics, Norcross, GA, USA), by which the corresponding CO_2 adsorption capacity was also calculated. A 200 mg sample was placed in a quartz tube and then the temperature was raised from room temperature to 450°C for 2 h, after which it cooled to 100°C to allow CO_2 gas to be passed through for 30 min. Following this was the physical removal of CO_2 by flowing helium for 2 h at 100°C with the overall flow rate of the gas being fixed at $10 \text{ m}^3/\text{min}$. Subsequently, the spectra were recorded at a heating rate of $10^\circ\text{C}/\text{min}$ from 100°C to 650°C . The oxidation states of the metal atoms were determined by X-ray photoelectron spectroscopy (XPS), which was performed on a VG ESCA Lab 250 photoelectron spectrometer (Thermo Fisher Scientific Company, Waltham, MA, USA) using an Al $K\alpha$ X-ray resource ($h\nu = 1486.6 \text{ eV}$).

3.4. Catalytic Activity Test

A typical implementation with acetonitrile being used as a dehydrating agent is as follows. Initially, 4.6 g glycerol, 5 mL acetonitrile, and 0.25 g catalyst were mixed in a high-pressure stainless-steel reactor (200 mL). Then, 1 mL tetraethylene glycol was added into the reaction mixture as an internal standard substance. Then, the reactor was sealed and purged with CO_2 3 times before being pressurized to 4 MPa. Finally, the autoclave was heated to the reaction temperature and maintained for a certain reaction time with stirring (600 r/min). Following the reaction, the reactor was firstly cooled to room temperature and depressurized. The liquid fraction separated by centrifugation was quantitatively and qualitatively analyzed by gas chromatograph (GC) and GC-mass instruments equipped

with FID detectors. The remaining solid catalyst was washed with ethanol, dried, and calcinated for recycling.

For product's analysis, the GC oven temperature was set at 120 °C and increased by a ramping rate of 25 °C/min until it reached 230 °C. The FID and injection temperatures were set at 300 °C. The reactant conversion (C_{GL}), product yield (Y_{GC}), and selectivity (S_{GC}) were calculated using the following formulas:

$$\text{Conversion (\%)} = \frac{\text{initial mole of glycerol} - \text{mole of glycerol unconverted}}{\text{initial mole of glycerol}} \times 100\%$$

$$\text{Yield (\%)} = \frac{\text{mole of glycerol carbonate}}{\text{theoretical mole of glycerol carbonate}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{mole of glycerol carbonate produced}}{\text{initial mole of glycerol} - \text{mole of glycerol unconverted}} \times 100\%$$

4. Conclusions

A series of ETS-10 zeolite-based catalysts were used to investigate the coupling process of CO₂ and glycerol to produce glycerol carbonate. For comparison, different metal species were employed and studied, among which Co/ETS-10 catalyst presented obvious advantages in both glycerol conversion and glycerol carbonate selectivity. Despite the excellent GC selectivity of Zn/ETS-10, the destructive effect of Zn on the structure of ETS-10 is not negligible, leading to the impaired competitiveness. This deserves further investigation in the future. For Cu/ETS-10, Ce/ETS-10, and Fe/ETS-10 catalysts, the obtained GC yield was mediocre. The excessive basicity of Ni/ETS-10 and the low binding energy of Zr⁴⁺ in Zr/ETS-10 were responsible for their own poor catalytic performance. Comprehensive analysis revealed that the presence of moderate Lewis basic sites on ETS-10 zeolite and their synergistic effect with the introduced Co species were vital for the activation of CO₂ and glycerol to form the desired GC. As a result, Co/ETS-10 with fair structural integrity, appropriate Lewis basic, and acid strength was proved to be the highest reactive among the studied catalysts for GC formation, giving a 35.0% glycerol conversion and 12.7% GC under a mild condition of 170 °C, 4.0 MPa initial pressure, 5 mL CH₃CN, and 6 h. The last but not least, the catalytic performance of Co/ETS-10 can be well maintained at 170 °C after eight cycles with only less than 3% decline in glycerol conversion and GC yield, indicating its excellent stability and reusability.

Author Contributions: Conceptualization, M.X. and Z.W.; Validation, Z.G.; Investigation, Z.G., M.H., W.Z., J.C. and J.L.; Resources, M.X. and Z.W.; Writing—original draft, Z.G., M.X. and Z.W.; Writing—review & editing, Z.G., M.X. and Z.W.; Visualization, Z.G.; Supervision, Z.W. and Y.S.; Funding acquisition, Z.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (No. 22208032), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (No. 20KJB530006, 20KJB150044), Science and Technology Foundation of Changzhou (No. CJ20200042), Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology (No. BM2012110), Y. Su acknowledges the “Young Talent Support Plan” of Xi’an Jiaotong University.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Bezi, H.; Mance, D.; Bala, D. Panel Evidence from EU Countries on CO₂ Emission Indicators during the Fourth Industrial Revolution. *Sustainability* **2022**, *14*, 12554. [\[CrossRef\]](#)
2. Shahbaz, M.; Balsalobre, D.; Shahzad, S.J.H. The Influencing Factors of CO₂ Emissions and the Role of Biomass Energy Consumption: Statistical Experience from G-7 Countries. *Environ. Model. Assess.* **2019**, *24*, 143–161. [\[CrossRef\]](#)
3. Zhang, C. Absorption principle and techno-economic analysis of CO₂ absorption technologies: A review. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *657*, 12045. [\[CrossRef\]](#)
4. Chai, S.; Ngu, L.H.; Bing, S.H. Review of carbon capture absorbents for CO₂ utilization. *Greenh. Gases Sci. Technol.* **2022**, *12*, 394–427. [\[CrossRef\]](#)
5. Biswal, T.; Shadangi, K.P.; Sarangi, P.K.; Srivastava, R.K. Conversion of carbon dioxide to methanol: A comprehensive review. *Chemosphere* **2022**, *298*, 134299. [\[CrossRef\]](#)
6. Sun, S.; Sun, H.; Williams, P.T.; Wu, C. Recent advances in integrated CO₂ capture and utilization: A review. *R. Soc. Chem.* **2021**, *5*, 4546–4559.
7. Wang, Y. Sustainable value-added C₃ chemicals from glycerol transformations: A mini review for heterogeneous catalytic processes. *Chin. J. Chem. Eng.* **2019**, *27*, 1536–1542. [\[CrossRef\]](#)
8. Khademi, M.H.; Lotfi-Varnoosfaderani, M. Use of biomass-derived glycerol as an alternative to fossil fuels for aniline production: Energy saving and environmental aspects. *Fuel* **2022**, *310*, 122359. [\[CrossRef\]](#)
9. Nomanbhay, S.; Mei, Y.O.; Chew, K.W.; Show, P.L.; Chen, W.H. Organic Carbonate Production Utilizing Crude Glycerol Derived as By-Product of Biodiesel Production: A Review. *Energies* **2020**, *13*, 1483. [\[CrossRef\]](#)
10. Zhou, C.H.; Beltrami, J.N.; Fan, Y.X.; Lu, G.Q. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37*, 527–549. [\[CrossRef\]](#)
11. Sonnat, M.O.; Amigoni, S.; Taffin de Givenchy, E.P.; Darmanin, T.; Choulet, O.; Guittard, F. Glycerol carbonate as a versatile building block for tomorrow: Synthesis, reactivity, properties and applications. *Green Chem.* **2013**, *15*, 283–306. [\[CrossRef\]](#)
12. Aresta, M.; Dibenedetto, A.; Nocito, F.; Pastore, C. A study on the carboxylation of glycerol to glycerol carbonate with carbon dioxide: The role of the catalyst, solvent and reaction conditions. *J. Mol. Catal. A Chem.* **2006**, *257*, 149–153. [\[CrossRef\]](#)
13. Li, J.; Wang, T. Chemical equilibrium of glycerol carbonate synthesis from glycerol. *J. Chem. Thermodyn.* **2011**, *43*, 731–736. [\[CrossRef\]](#)
14. Huang, S.; Ma, J.; Li, J.; Ning, Z.; Wei, W.; Sun, Y. Efficient propylene carbonate synthesis from propylene glycol and carbon dioxide via organic bases. *Catal. Commun.* **2008**, *9*, 276–280. [\[CrossRef\]](#)
15. George, J.; Patel, Y.; Pillai, S.M.; Munshi, P. Methanol assisted selective formation of 1,2-glycerol carbonate from glycerol and carbon dioxide using n-Bu₂SnO as a catalyst. *J. Mol. Catal. A Chem.* **2009**, *304*, 1–7. [\[CrossRef\]](#)
16. Hu, J.; Li, J.; Gu, Y.; Guan, Z.; Mo, W.; Ni, Y.; Li, T.; Li, G. Oxidative carbonylation of glycerol to glycerol carbonate catalyzed by PdCl₂(phen)/KI. *Appl. Catal. A Gen.* **2010**, *386*, 188–193. [\[CrossRef\]](#)
17. Li, H.; Gao, D.; Gao, P.; Wang, F.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y. The synthesis of glycerol carbonate from glycerol and CO₂ over La₂O₂CO₃–ZnO catalysts. *Catal. Sci. Technol.* **2013**, *3*, 2801–2809. [\[CrossRef\]](#)
18. Liu, J.; Li, Y.; Liu, H.; He, D. Transformation of CO₂ and glycerol to glycerol carbonate over CeO₂–ZrO₂ solid solution—Effect of Zr doping. *Biomass Bioenergy* **2018**, *118*, 74–83. [\[CrossRef\]](#)
19. Ozorio, L.P.; Pianzoli, R.; da Cruz Machado, L.; Miranda, J.L.; Turci, C.C.; Guerra, A.C.; Mota, C.J. Metal-impregnated zeolite Y as efficient catalyst for the direct carbonation of glycerol with CO₂. *Appl. Catal. A Gen.* **2015**, *504*, 187–191. [\[CrossRef\]](#)
20. Hu, C.; Chang, C.W.; Yoshida, M.; Wang, K.H. Lanthanum nanocluster/ZIF-8 for boosting catalytic CO₂/glycerol conversion using MgCO₃ as a dehydrating agent. *J. Mater. Chem. A* **2021**, *9*, 7048–7058. [\[CrossRef\]](#)
21. Pan, S.; Zheng, L.; Nie, R.; Xia, S.; Chen, P.; Hou, Z. Transesterification of Glycerol with Dimethyl Carbonate to Glycerol Carbonate over Na-based Zeolites. *Chin. J. Catal.* **2012**, *33*, 1772–1777. [\[CrossRef\]](#)
22. Marakatti, V.S.; Halgeri, A.B. Metal ion-exchanged zeolites as highly active solid acid catalysts for the green synthesis of glycerol carbonate from glycerol. *RSC Adv.* **2015**, *5*, 14286–14293. [\[CrossRef\]](#)
23. Algoufi, Y.T.; Hameed, B.H. Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over K-zeolite derived from coal fly ash. *Fuel Process. Technol.* **2014**, *126*, 5–11. [\[CrossRef\]](#)
24. Xiang, M.; Zhang, F.; Tong, L.; Wang, H.; Deng, Y. Development of the hierarchical ETS-10 zeolite catalyst for improving the aqueous-phase biomass hydrodeoxygenation activity. *J. Mater. Sci.* **2020**, *55*, 10505–10521. [\[CrossRef\]](#)
25. Avila, A.M.; Perez, L.E.; Rajendran, A. Conceptual design of adsorptive recovery of ethane from residue gas stream using Na-ETS-10. *Sep. Purif. Technol.* **2020**, *251*, 117302. [\[CrossRef\]](#)
26. Park, S.W.; Yun, Y.H.; Kim, S.D.; Yang, S.T.; Ahn, W.S.; Kim, G. CO₂ retention ability on alkali cation exchanged titanium silicate, ETS-10. *J. Porous Mater.* **2010**, *17*, 589–595. [\[CrossRef\]](#)
27. Xiang, M.; Gao, Z.; Ji, X.; Li, D.; Deng, Y.; Ding, Y.; Yu, C.; Zhang, W.; Zhang, Z.; Wu, Z. Boosting CO₂ hydrogenation to methane over Ni-based ETS-10 zeolite catalyst. *Front. Chem.* **2022**, *10*, 1041843. [\[CrossRef\]](#)
28. Xiang, M.; Wu, D. Transition metal-promoted hierarchical ETS-10 solid base for glycerol transesterification. *RSC Adv.* **2018**, *8*, 33473–33486. [\[CrossRef\]](#)
29. Shough, A.M.; Doren, D.J.; Ogunnaike, B. Transition Metal Substitution in ETS10: DFT Calculations and a Simple Model for Electronic Structure Prediction. *Chem. Mater.* **2009**, *21*, 1232–1241. [\[CrossRef\]](#)

30. Wang, X.; Jacobson, A.J. Crystal structure of the microporous titanasilicate ETS-10 refined from single crystal X-ray diffraction data. *Chem. Commun.* **1999**, *11*, 973–974. [\[CrossRef\]](#)
31. Polychronopoulou, K.; Dabbawala, A.A.; Sajjad, M.; Singh, N.; Anjum, D.H.; Baker, M.A.; Charisiou, N.D.; Goula, M.A. Hydrogen production via steam reforming of glycerol over Ce-La-Cu-O ternary oxide catalyst: An experimental and DFT study. *Appl. Surf. Sci.* **2022**, *586*, 152798. [\[CrossRef\]](#)
32. GalioLu, S.; Zahmak Ran, M.; Kalay, Y.E.; Zkar, S.; Akata, B. Effect of silver encapsulation on the local structure of titanasilicate ETS-10. *Microporous Mesoporous Mater.* **2012**, *159*, 1–8. [\[CrossRef\]](#)
33. Li, G.; Yu, X.; Yin, F. Production of hydrogen by ammonia decomposition over supported Co₃O₄ catalysts. *Catal. Today* **2022**, *402*, 45–51. [\[CrossRef\]](#)
34. Shimura, K.; Miyazawa, T.; Hanaoka, T. Fischer–tropsch synthesis over alumina supported cobalt catalyst: Effect of promoter addition. *Appl. Catal. A Gen.* **2015**, *494*, 1–11. [\[CrossRef\]](#)
35. Qin, H.; Wang, H.; Xia, Q.; Zheng, C.; Zhang, X.; Wu, Y.; Peng, L.; Yang, F.; Zhao, S. Efficient CO catalytic oxidation by the combination of cobalt and excellent carrier Ta₂O₅. *Fuel* **2023**, *333*, 126179. [\[CrossRef\]](#)
36. Barreca, D.; Massignán, C.; Daolio, S.; Fabrizio, M.; Piccirillo, C.; Armelao, L.; Tondello, E. Composition and Microstructure of Cobalt Oxide Thin Films Obtained from a Novel Cobalt(II) Precursor by Chemical Vapor Deposition. *Chem. Mater.* **2001**, *13*, 588–593. [\[CrossRef\]](#)
37. Castner, D.G.; Watson, P.R.; Chan, I.Y. X-ray absorption spectroscopy, x-ray photoelectron spectroscopy, and analytical electron microscopy studies of cobalt catalysts. *J. Phys. Chem.* **1989**, *93*, 3188–3194. [\[CrossRef\]](#)
38. Matsubara, H.; Yamamoto, K.; Tsuji, E.; Okumura, K.; Nakamura, K.; Suganuma, S.; Katada, N. Position and Lewis acidic property of active cobalt species on MFI zeolite for catalytic methylation of benzene with methane. *Microporous Mesoporous Mater.* **2021**, *310*, 110649. [\[CrossRef\]](#)
39. Fao, G.D.; Catherine, H.N.; Huang, C.-H.; Lee, Y.L.; Jiang, J.C.; Hu, C. Unraveling the effects of P and S doping over g-C₃N₄ in strengthening Lewis basicity for CO₂/glycerol conversion: A theoretical and experimental study. *Carbon* **2023**, *201*, 129–140. [\[CrossRef\]](#)
40. Hu, C.; Yoshida, M.; Chen, H.-C.; Tsunekawa, S.; Lin, Y.-F.; Huang, J.-H. Production of glycerol carbonate from carboxylation of glycerol with CO₂ using ZIF-67 as a catalyst. *Chem. Eng. Sci.* **2021**, *235*, 116451. [\[CrossRef\]](#)
41. Januário, E.; Nogueira, A.; Pastore, H. ETS-10 Modified with Cu_xO nanoparticles and their application for the conversion of CO₂ and water into Oxygenates. *J. Braz. Chem. Soc.* **2018**, *29*, 1527–1537. [\[CrossRef\]](#)
42. Li, H.; Xin, C.; Jiao, X.; Zhao, N.; Xiao, F.; Li, L.; Wei, W.; Sun, Y. Direct carbonylation of glycerol with CO₂ to glycerol carbonate over Zn/Al/La/X (X=F, Cl, Br) catalysts: The influence of the interlayer anion. *J. Mol. Catal. A Chem.* **2015**, *402*, 71–78. [\[CrossRef\]](#)
43. Liu, J.; Li, Y.; Zhang, J.; He, D. Glycerol carbonylation with CO₂ to glycerol carbonate over CeO₂ catalyst and the influence of CeO₂ preparation methods and reaction parameters. *Appl. Catal. A Gen.* **2016**, *513*, 9–18. [\[CrossRef\]](#)
44. Leungcharoenwattana, T.; Jitkarnka, S. Bio-based chemical production from glycerol conversion with ethanol co-feeding over Zr-promoted MgAl-layered double oxide catalysts: Impact of zirconium location. *J. Clean. Prod.* **2020**, *273*, 123201. [\[CrossRef\]](#)
45. Tiwari, A.; Agarwal, S.; Shrivastava, K.; Ichikawa, T.; Jain, A.; Singh, R. XPS Investigation on Improving Hydrogen Sorption Kinetics of the KSiH₃ System by Using Zr-Based Catalysts. *Materials* **2022**, *15*, 7454. [\[CrossRef\]](#)
46. Lu, Y.; Xie, X.; Fang, W. Insight into the Property Modification of Zr incorporated Alumina Binary Mixed Oxides by XRD, TEM, XPS, TPD and IR. *ChemistrySelect* **2020**, *5*, 7928–7933. [\[CrossRef\]](#)
47. Lu, Y.; Fan, D.; Chen, Z.; Xiao, W.; Yang, X. Anchoring Co₃O₄ nanoparticles on MXene for efficient electrocatalytic oxygen evolution. *Sci. Bull.* **2019**, *65*, 460–466. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Rubio-Marcos, F.; Calvino-Casilda, V.; Bañares, M.; Fernandez, J. Novel hierarchical Co₃O₄/ZnO mixtures by dry nanodispersion and their catalytic application in the carbonylation of glycerol. *J. Catal.* **2010**, *275*, 288–293. [\[CrossRef\]](#)
49. Zhang, J.; He, D. Surface properties of Cu/La₂O₃ and its catalytic performance in the synthesis of glycerol carbonate and monoacetin from glycerol and carbon dioxide. *J. Colloid Interface Sci.* **2014**, *419*, 31–38. [\[CrossRef\]](#)
50. Huang, X.; Guo, Y.; Zou, Y.; Jiang, J. Electrochemical oxidation of glycerol to hydroxypyruvic acid on cobalt (oxy) hydroxide by high-valent cobalt redox centers. *Appl. Catal. B Environ.* **2022**, *309*, 121247. [\[CrossRef\]](#)
51. Li, H.; Jiao, X.; Li, L.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y.; Zhang, B. Synthesis of glycerol carbonate by direct carbonylation of glycerol with CO₂ over solid catalysts derived from Zn/Al/La and Zn/Al/La/M (M= Li, Mg and Zr) hydrotalcites. *Catal. Sci. Technol.* **2015**, *5*, 989–1005. [\[CrossRef\]](#)
52. Su, X.; Lin, W.; Cheng, H.; Zhang, C.; Wang, Y.; Yu, X.; Wu, Z.; Zhao, F. Metal-free catalytic conversion of CO₂ and glycerol to glycerol carbonate. *Green Chem.* **2017**, *19*, 1775–1781. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.