

Mechanochemically Prepared Supported Ionic Liquids for Efficient Glycerol Valorization to Glycerol Carbonate

Patcharaporn Inrirai, Juan Jose Villora-Picó, Ciara Cassidy, Daniel Goma Jiménez, Nancy Artioli, and Haresh Manyar*



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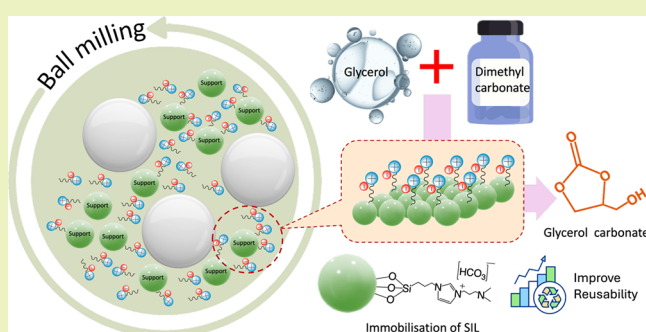
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ABSTRACT: The valorization of glycerol, a major byproduct of the biodiesel industry, into high value chemicals offers a sustainable pathway to support circular economy objectives within biorefineries. Among various transformation routes, the transesterification of glycerol with dimethyl carbonate (DMC) to produce glycerol carbonate (GC) is particularly attractive due to its green chemistry credentials and industrial relevance. In this study, supported ionic liquids (SILs) based on imidazolium cations with intrinsic basicity were synthesized and immobilized onto solid supports to develop efficient and reusable catalysts for this process. A solvent-free mechanochemical approach using ball milling was employed to immobilize the ionic liquids on CeO_2 , SiO_2 , Al_2O_3 , MCM-41, and SBA-15 supports. The resulting catalysts were extensively characterized using XRD, FTIR, N_2 physisorption, CO_2 -TPD, solid state NMR and SEM techniques. Among the tested catalysts, the $\text{N}(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ exhibited the highest activity, achieving 97% glycerol conversion and 94% GC yield at 90 °C in 60 min with a glycerol to DMC molar ratio of 1:3. Moreover, the SiO_2 supported ionic liquid catalyst demonstrated greater stability and reusability over multiple cycles compared to its CeO_2 based counterpart. These results highlight the potential of immobilized SILs as robust and sustainable catalysts for the efficient valorization of glycerol to glycerol carbonate.

KEYWORDS: glycerol carbonate, CO_2 valorization, supported ionic Liquids (SILs), transesterification



1. INTRODUCTION

The urgent need to transition away from fossil fuels as the primary energy source has led to an increased pursuit of alternative and sustainable energy solutions.¹ Biofuels have emerged as a very attractive choice owing to their renewable source, low toxicity, and biodegradable nature.^{2–4} Nonetheless, the production of biofuels presents significant challenges. Notably, for every 100 kg of biodiesel produced, approximately 10 kg of crude glycerol are generated as a byproduct.⁵ Traditionally, glycerol has found applications in the cosmetic, pharmaceutical, and food industries.^{3,6–8} Yet, the rapid expansion of the biodiesel market has led to a sharp increase in global glycerol production, far exceeding demand.⁹ This imbalance has caused a steep decline in glycerol's market value and has created logistical and environmental challenges for producers, especially as crude glycerol cannot be freely discarded due to its potentially harmful environmental impact.¹⁰ Consequently, there is an urgent need to develop sustainable and economically viable strategies for glycerol valorization.

Among the various valorization pathways, converting glycerol into glycerol carbonate (GC) is particularly promising due to GC's potential use as a biofuel additive and other valuable applications.^{11,12} GC can be synthesized by several routes, including transesterification of glycerol with dimethyl carbonate or via

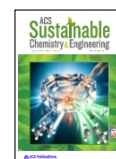
reactions involving carbonylating agents such as phosgene, urea, carbon dioxide and carbon monoxide. However, the use of highly toxic reagents like phosgene and carbon monoxide is discouraged.¹³ Although urea and CO_2 represent greener alternatives, they often result in low yields, the former due to the need to continuously remove ammonia to shift the equilibrium,¹⁴ and the latter due to the inherent thermodynamic stability of the CO_2 molecule.¹⁵ In contrast, transesterification with DMC offers multiple advantages, including methanol as the only byproduct, which is easily separated to facilitate easy downstream purification of GC.¹⁶ The process operates under mild conditions, delivers high product yields, and uses DMC, a commercially available, non-toxic reagent that can be synthesized from renewable feedstocks such as methanol, urea, and carbon dioxide.¹⁷ This makes transesterification with DMC a highly promising and economically viable

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route for GC production aligned with circular economy and green chemistry principles.¹⁸

A wide range of catalysts have been explored for the transesterification of glycerol with dimethyl carbonate, with basic catalysts generally providing the highest activity.¹⁷ Catalyst basicity correlates strongly with performance since a higher density of strong basic sites tends to increase the reaction rate.¹⁸ Common catalysts include alkali metal bases, such as KOH, K_2CO_3 , CH_3OK , alongside imidazolium-derived base catalysts.^{19,20} While efficient, many such catalysts require post-reaction neutralization, producing large quantities of inorganic salt waste.²¹ The amines like triethylamine avoid the neutralization issues, but introduce complexity in catalyst recovery and product purification due to distillation requirements.²² To overcome these challenges, heterogeneous catalysts have gained attraction for their ease of separation. Examples include metal oxides,^{23–26} hydrotalcite-like compounds,²⁷ and zeolites.²⁸ Despite good catalytic performance, these systems often suffer from deactivation over repeated cycles or lead to product contamination.^{23,25}

Ionic liquids (ILs) have attracted significant interest as catalysts in organic synthesis because of their unique physicochemical properties, including high thermal stability, negligible volatility, and tunable polarity.^{29–31} The ability to tailor their cation and anion combinations allows development of ILs with acidic or basic character. Basic ionic liquids have proven effective in achieving high conversion and selectivity in catalytic processes.³² In 2009, Naik et al.³³ reported the use of [BMIM-2- CO_2] for synthesis of glycerol carbonate, demonstrating the viability of IL-based catalysis in this transformation.³³ Since then, other basic ionic liquids such as [Bmim]OH, [Bmim]Im, [Amim]OH, and [Amim]Im have been shown to reach glycerol conversions above 98% and selectivity up to 100% toward glycerol carbonate.³² More recently, Wang et al.³⁴ synthesized guanidine-based ionic liquids with various combinations of cations and anions; among them, [TMG][TFE] exhibited outstanding performance due to its strong basicity, achieving 92% conversion, over 95% selectivity. Despite these advantages, ILs face barriers to large scale industrial use, mainly due to high manufacturing costs³⁵ and difficulties in recovery and reuse. As with other homogeneous systems, the separation of ionic liquids (ILs) typically requires energy intensive operations that yield low recovery efficiencies, often below 50%.²¹ This combination of cost and limited recyclability constrains their practical implementation.

To address these challenges, supported ionic liquids (SILs) were considered as an effective strategy to overcome the recyclability limitations of free ionic liquids. SILs involve immobilizing ionic liquids onto solid supports, enabling easier catalyst recovery and reuse. This approach preserves the catalytic advantages of ILs while enabling easy separation and reuse,^{36–38} combining the benefits of homogeneous and heterogeneous catalysis.³⁹ Porous materials such as silica,^{40–42} alumina,⁴³ ceria,⁴⁴ manganese oxide,^{45,46} and zeolites⁴⁷ are commonly employed supports offering high surface areas and tunable surface chemistry to promote IL stability. Supported ILs reduce leaching, improve thermal stability, and enhance recyclability. However, traditional immobilization techniques such as covalent anchoring,⁴⁸ physical impregnation,⁴⁹ and intercalation⁵⁰ often involve multistep procedures and harsh synthesis conditions, limiting scalability for industrial applications. For instance, conventional wet grafting/impregnation routes for immobilizing imidazolium-based ILs on silica require multi-

step reflux protocols (24–96 h) followed by lengthy purification, such as Soxhlet extraction and multi-solvent washing, rendering these methods highly energy- and time-intensive.^{51–55} In this context, Liu et al.⁵⁶ developed a heterogeneous catalyst by encapsulating the basic ionic liquid [APmim]OH within ZIF-8, a metal organic framework (MOF), which was subsequently immobilized on CaMgAl-layered double hydroxides. Similarly, Gao et al.⁵⁷ anchored [BMIm]OH onto a calcium oxide-functionalized NaY zeolite, achieving glycerol conversions of 98.2% and yields up to 97.5% in the synthesis of glycerol carbonate, along with excellent reusability.⁵⁷ While these examples confirm the catalytic potential of supported ionic liquids, they still rely on relatively elaborate preparation protocols involving multiple solvents and processing steps, raising broader concerns over the sustainability and scalability of such routes.^{58,59} Recently, more sustainable approaches like solvent-free mechanochemical synthesis via ball milling have been developed to immobilize ILs efficiently, enabling synthesis under ambient conditions with strong IL-support interactions and efficient surface modification without the need for organic solvents or thermal treatment.⁶⁰

In this work, we prepared a series of heterogeneous catalysts by supporting functionalized imidazolium based ILs on various inorganic solids (Figure 1). The study focuses on comparing the catalytic performance of three structurally distinct ILs sharing a common imidazolium core but differing at the N3 position with diethylamino, dimethylamino, and butyl substituents. Initially, these ILs were supported on SiO_2 and CeO_2 , with further exploration of additional supports using the most promising IL. Immobilization was achieved by mechanochemical ball milling, a solvent-free and scalable method consistent with sustainable approach to chemistry. The catalysts were evaluated for glycerol transesterification with DMC, with recyclability and catalytic stability assessed over multiple reaction cycles.

2. EXPERIMENTAL SECTION

2.1. Materials

Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%), sodium hydroxide (NaOH, >98%), sodium carbonate (Na_2CO_3 , >99.5%), ethanol (C_2H_5OH , >99.8%), crystalline silicon dioxide (SiO_2 , 99%), SBA-15, MCM-41, imidazole ($C_3H_4N_2$, 99%), acetonitrile (C_2H_3N , >99.9%), hexane (C_6H_{14} , >97%), 1-Bromobutane (C_4H_9Br , 99%), potassium bicarbonate ($KHCO_3$, >99.5%), Glycerol carbonate ($C_4H_6O_4$, >90.0%), and glycidol ($C_3H_6O_2$, 96%) were purchased from

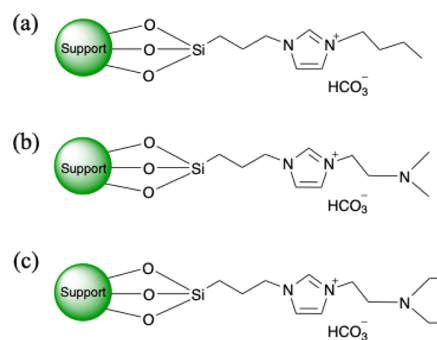


Figure 1. Supported ionic liquid catalysts (SILC). (a) Supported-[Im][HCO_3], (b) Supported- $N(CH_3)_2$ -[Im][HCO_3], and (c) Supported- $N(Et)_2$ -[Im][HCO_3].

Sigma-Aldrich. Glycerol ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, >99%), *p*-Xylene (C_8H_{10} , >99%) and aluminium oxide (Al_2O_3 , 99.9%) were purchased from Alfa Aesar. Dimethyl carbonate (>99%), Methanol (CH_3OH , 99.8%), (3-chloropropyl)-trimethoxysilane ($\text{C}_6\text{H}_{15}\text{ClO}_3\text{Si}$, >98%) and *N,N*-diethyl-2-amino-1-bromoethane hydrobromide ($\text{C}_6\text{H}_{15}\text{Br}_2\text{N}$, >98%) were purchased from Thermo Scientific. 2-Bromo-*N,N*-dimethylethanamine hydrobromide ($\text{C}_4\text{H}_{11}\text{Br}_2\text{N}$, >97%) was acquired from Synthonix. Crude glycerol was acquired from Oleon. All chemicals were used directly without further treatment unless otherwise specified.

2.2. Synthesis of CeO_2 Support

Cerium oxide (CeO_2) was synthesized using a precipitation method. Briefly, 0.138 mol of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was dissolved in 100 mL of deionized water to form the precursor solution. A basic solution containing 0.4 mol of NaOH and 0.1 mol of Na_2CO_3 in 250 mL of deionized water was prepared separately and slowly added to the cerium nitrate solution under continuous stirring until the pH reached 11. The resulting suspension was stirred overnight to ensure complete precipitation. The precipitate was then collected via vacuum filtration, washed thoroughly with deionized water until neutral pH was achieved, and dried in an oven at 105 °C overnight. The dried solid was subsequently calcined at 500 °C for 6 h. Finally, the calcined material was ground using a mortar and pestle and sieved through a 230 mesh sieve to obtain uniform particles with an average size of approximately 63 μm , approximately 20 g of CeO_2 was obtained.

2.3. Synthesis of $\text{N}(\text{Et})_2\text{-[Im][HCO}_3\text{]}$ Ionic Liquid

To synthesize the $\text{N}(\text{Et})_2\text{-[Im][HCO}_3\text{]}$ ionic liquid, (3-chloropropyl)-trimethoxysilane (5 mmol), imidazole (5 mmol), and acetonitrile (20 mL) were added into a 100 mL round-bottom flask. The reaction mixture was stirred at 80 °C for 24 h under a N_2 atmosphere to synthesize the imidazolium-functionalized silane intermediate. Subsequently, the resulting intermediate (5 mmol) and *N,N*-diethyl-2-amino-1-bromoethane hydrobromide (5 mmol) were dissolved in acetonitrile (20 mL) and refluxed at 80 °C for a further 24 h under N_2 atmosphere. After the reaction mixture was cooled to room temperature, NaOH (0.25 g) was added, and the system was stirred for another 4 h. The resulting solution was filtered, and the solvent was removed by vacuum filtration. The solid product was washed with hexane (3×10 mL), and the resulting solid was dried in oven at 60 °C for 24 h to yield approximately 0.8–0.9 g of $\text{N}(\text{Et})_2\text{-[Im][Br]}$, the synthesized step is displayed as Scheme 1.

The bicarbonate-functionalized IL, $\text{N}(\text{Et})_2\text{-[Im][HCO}_3\text{]}$, was prepared following a reported procedure with slight modification⁶⁰ as shown in Scheme 2. In brief, $\text{N}(\text{Et})_2\text{-[Im][Br]}$ (5 mmol) and potassium bicarbonate (5.25 mmol, 1.05 equiv.) were dried at 60 °C overnight. 30 mL of methanol was added, and the mixture was stirred at room temperature for 24 h. The resulting KBr precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure to obtain approximately 0.9–1.0 g of pure IL, $\text{N}(\text{Et})_2\text{-[Im][HCO}_3\text{]}$. Other bifunctional ILs were synthesized using similar procedures, differing only in the brominated alkanes used. Table 1 shows the list of ILs were synthesized in this study.

2.4. Immobilization of IL on Various Supports

The immobilization of bifunctional IL on various supports was performed using a mechanochemical ball milling method. Typically, an IL, $\text{N}(\text{Et})_2\text{-[Im][HCO}_3\text{]}$ (30 wt % relative to the total catalyst) and support metal oxide (CeO_2 , SiO_2 , Al_2O_3 , MCM-41, SBA-15, 70 wt %) were well mixed and transferred into a 125 mL agate grinding jar containing three agate balls (20 mm in diameter). The solid mixture was milled at 450 rpm for 1 h using a Retsch PM100 planetary ball mill. After milling, the resulting solid was washed with ethanol and dried overnight in an oven at 80 °C, approximately 85–90% of catalyst was recovered after the immobilization process. The resulting supported Ionic liquid structures are displayed in Figure 1.

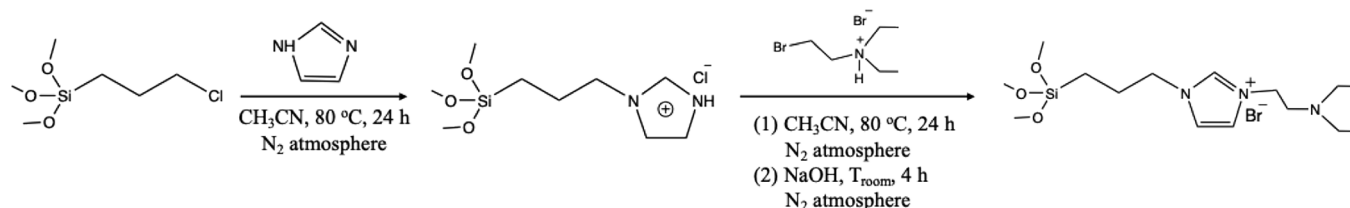
2.5. Catalyst Characterization

The prepared catalysts were characterized using various techniques, including N_2 physisorption, elemental analysis, powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), CO_2 temperature-programmed desorption ($\text{CO}_2\text{-TPD}$), scanning electron microscopy (SEM), and solid state NMR. Textural properties were investigated via nitrogen adsorption-desorption isotherms using a surface area and porosity analyzer. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, while pore volume and pore size distribution were determined using the Barrett-Joyner-Halenda (BJH) model. XRD patterns were recorded on a PANalytical diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm) in reflection mode. Data were collected over a 2θ range of 5–80° with a step size of 0.02° to examine the crystallographic phases of the samples. FTIR spectra were acquired using an Agilent Cary 630 FTIR spectrometer equipped with an ATR sampling module over the range of 4000–450 cm^{-1} to identify surface functional groups. Thermal stability was analyzed by TGA on a TA Instruments Q5000 analyzer under an air flow, using a heating rate of 10 °C min^{-1} from ambient temperature to 900 °C. The basicity of the catalysts was determined by $\text{CO}_2\text{-TPD}$, performed using a Micromeritics AutoChem II 2920 instrument. The surface morphology of the samples was examined by SEM using an FEI Quanta FEG Environmental SEM. C and N compositions of ILs and SILs were characterized by elemental analysis (CHNS) using a Perkin Elmer 2400 series 2 elemental analyzer. The magic angle spinning (MAS) ^{29}Si NMR spectra were recorded on a 400 MHz AVANCE III Bruker spectrometer (9.4 Tesla) equipped with a 4 mm double-resonance MAS probe.

2.6. Reaction Procedure and Analysis Method

Catalytic activity was evaluated in a 100 mL glass batch reactor equipped with magnetic stirring and a reflux condenser. The reactor was maintained in an isothermal oil bath at a desired temperature and mechanically agitated. In a typical reaction, glycerol, dimethyl carbonate, and catalyst were loaded into the glass reactor and stirred at 800 rpm for 1 h.^{61,62} Reaction products were analyzed using a Clarus 500 gas chromatograph (PerkinElmer) equipped with a Zebron ZB-Wax capillary column. *p*-Xylene was used as the internal standard. For reusability studies, the catalyst was recovered from the reaction mixture by centrifugation, washed thoroughly with ethanol,

Scheme 1. Synthesis of $\text{N}(\text{Et})_2\text{-[Im][Br]}$ Ionic Liquid



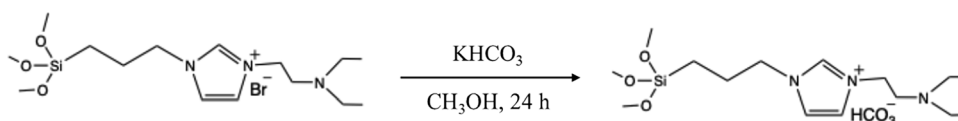
Scheme 2. Synthesis of N(Et)₂-[Im][HCO₃] Ionic Liquid

Table 1. Ionic Liquids Used in This Study

No.	Structure	IUPAC name	Abbreviation	Element content (%) ^a	
				C	N
1		1-(3-(trimethoxysilyl)propyl)-3-butylimidazolium hydrogen carbonate	[Im][HCO ₃]	21.6	3.5
2		1-(3-(trimethoxysilyl)propyl)-3-N,N-Dimethylethylamine imidazolium hydrogen carbonate	N(CH ₃) ₂ -[Im][HCO ₃]	24.3	11.6
3		1-(3-(trimethoxysilyl)propyl)-3-N,N-Diethylethylamineimidazolium hydrogen carbonate	N(Et) ₂ -[Im][HCO ₃]	34.2	11.6

^aCHNS Elemental analysis.

and dried overnight at 80 °C. The dried catalyst was reused directly in subsequent reaction cycles without further treatment. The experiments were performed in duplicate, and the results were used to calculate error bars.

The conversion of glycerol, and yield of glycerol carbonate was calculated as follows:

$$\text{Gly conversion (\%)} = \left(\frac{N_{\text{Gly},0} - N_{\text{Gly},t}}{N_{\text{Gly},0}} \right) \times 100 \quad (1)$$

$$\text{GC yield (\%)} = \left(\frac{N_{\text{GC},t}}{N_{\text{Gly},0}} \right) \times 100 \quad (2)$$

where $N_{\text{Gly},0}$ and $N_{\text{Gly},t}$ is the mole of glycerol at initial time and t time, respectively, and $N_{\text{GC},t}$ is the mole of glycerol carbonate at t time. The quantity of each substrate was calculated using the relative response factor (RF) values provided Table S1.

¹H NMR of the commercial glycerol, glycerol carbonate, glycidol, and the reaction mixture were analysed using Brukers Ultrashield plus 400 MHz NMR with DMSO- d_6 as a solvent.

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization

X-ray diffraction patterns of CeO₂-SIL catalyst and SiO₂-SIL catalyst with two different cationic groups, N(CH₃)₂-[Im][HCO₃] and N(Et)₂-[Im][HCO₃] are shown in Figure 2. These are compared with the corresponding pristine support. As shown in Figure 2(a), the pristine CeO₂ exhibits sharp diffraction peaks at 2θ values of 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, and 76.7°, which correspond to the (111), (200), (220), (311), (222), (400), and (331) planes of a cubic fluorite structure (JCPDS No. 34-0394),^{63,64} confirming its high crystallinity. Upon immobilization of [Im][HCO₃], N(CH₃)₂-[Im][HCO₃], and N(Et)₂-[Im][HCO₃] on CeO₂, the characteristic CeO₂ peaks remain clearly visible, with only minor reductions in peak intensity and slight broadening. This indicates that the structural integrity of

the CeO₂ support is retained following IL immobilization, and the IL phase is either amorphous or present in a highly dispersed form on the surface. In addition, low-intensity diffraction peaks at 2θ values of 23.4°, 27.1°, and 38.6° were observed, which are attributed to residual KBr remaining from the IL synthesis. The XRD patterns of the SiO₂ supported materials are presented in Figure 2(b). Pristine SiO₂ sample exhibited multiple diffraction peaks, with the most intense reflection observed at $2\theta = 26.6^\circ$, corresponding to the (101) plane. Additional weaker peaks appeared at 2θ values of 20.9°, 36.6°, 39.5°, 40.3°, 42.5°, 45.8°, 50.2°, 54.9°, and 60.0°, which can be assigned to the (100), (110), (102), (111), (200), (201), (112), (202), and (211) planes, respectively.⁶⁵ These reflections suggest that the SiO₂ employed here possesses a degree of structural ordering, potentially due to semi-crystalline domains.⁶⁶ After the immobilization of imidazolium-based ionic liquids, [Im][HCO₃], N(CH₃)₂-[Im][HCO₃], and N(Et)₂-[Im][HCO₃] onto the SiO₂ surface, the diffraction peaks corresponding to the native SiO₂ substrate exhibit reduced intensity and minor broadening. The reduction in crystallinity indicated successful immobilization of the ionic liquids, which probably form a thin amorphous or nanocrystalline layer on the SiO₂ surface. In all cases, the IL-immobilized SiO₂ materials continue to display the prominent peak at 26.6°, although with reduced intensity, indicating stability of the original support structure. The appearance of minor new peaks in some modified samples suggests the existence of short-range ordered domains associated with the IL, particularly in materials containing larger cationic substituents like N(Et)₂.

Figure 3 shows the FTIR spectra of the three synthesized ionic liquids. The bands in the 3100–2800 cm⁻¹ region are attributed to C–H stretching vibrations. All three ILs exhibit characteristic peaks in the 1600–1400 cm⁻¹ range, which can be assigned to the C=N and C=C stretching vibrations of the imidazolium ring,⁵⁵ as well as the C=O and C–O stretching modes associated with the hydrogen carbonate (HCO₃⁻) anion.^{23,63} Moreover, the bands observed in the 1000–1100 cm⁻¹ region and the peak centered at approximately 800 cm⁻¹ correspond to Si–O–Si/

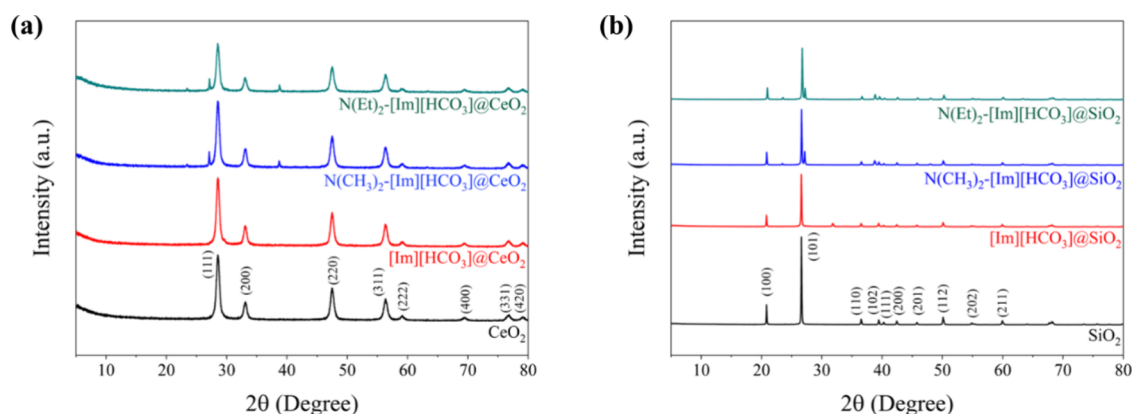


Figure 2. X-ray diffraction patterns of (a) CeO₂-SIL catalyst and (b) SiO₂-SIL catalyst.

Si–O–C and Si–C vibrations, respectively,⁶⁷ confirming successful modification at the N1 position of the imidazolium ring with trimethoxysilane groups. The methyl and ethyl C–H stretching bands for N(CH₃)₂-[Im][HCO₃] and N(Et)₂-[Im][HCO₃] ionic liquids are also observed as peak centered around 2900 cm^{−1}.

The CHNS results (Table 1) confirm successful synthesis of all three ionic liquids, with experimental N content in close agreement with theoretical values, validating the intended imidazolium and amine structures. The slightly lower experimental C content compared to theoretical values can be attributed to partial hydrolysis or condensation of the trimethoxysilyl groups, a common and expected behavior for silane precursors, without altering the core IL framework. Overall, these results support the successful formation and structural integrity of the synthesized ILs.

The FTIR spectra of CeO₂ and CeO₂-supported ionic liquids are shown in Figure 4(a). Pristine CeO₂ displayed a broad absorption band centered at approximately 450 cm^{−1}, which is characteristic of the Ce–O–Ce stretching vibrations the fluorite-type lattice of ceria.⁶⁴ This vibrational feature remained present in all SIL-catalysts, indicating that the underlying crystalline structure of CeO₂ support is preserved following IL immobilization. Upon the immobilization of imidazolium-based ILs, [Im][HCO₃], N(CH₃)₂-[Im][HCO₃], and N(Et)₂-[Im][HCO₃], additional bands appeared in the mid-infrared region, confirming the successful anchoring of the IL species. A distinct and intense band observed near 875 cm^{−1} is

attributed to the out-of-plane bending vibration of the carbonate group (CO₃^{2−}) originating from the HCO₃[−] anion.^{23,63} Similarly, the peak at 1397 cm^{−1} corresponds to the asymmetric stretching of the C–O bond in the carbonate group, further affirming the presence of the bicarbonate counterion within the immobilized ILs. Notable absorption bands in the 1571–1600 cm^{−1} region are attributed to C=O stretching of the bicarbonate anion and C=N stretching of the imidazolium ring respectively,⁶⁸ which further supports the successful immobilization of the SIL. These features are especially prominent in the spectra of SILs containing N(CH₃)₂ and N(Et)₂ substituents, likely due to enhanced electronic interactions contributed by the alkyl functionalities. In addition, the region near 1450 cm^{−1} exhibits absorptions attributed to C–H bending vibrations.^{23,63} A weak, broad band in the 1600–1700 cm^{−1} region is assigned to the C=C stretching vibration of the imidazolium ring.

The FTIR spectra of SiO₂ and SiO₂-supported ILs materials are shown in Figure 4(b). Pristine SiO₂ exhibited distinct vibrational features characteristic of crystalline quartz. A broad and intense band centered near 1100 cm^{−1} is attributed to the asymmetric stretching vibrations of Si–O–Si linkages, while additional peaks at 798 cm^{−1} and 460 cm^{−1} are assigned to symmetric Si–O–Si stretching and O–Si–O bending vibrations, respectively.^{65,66,69} Following immobilization of the imidazolium-based ILs, [Im][HCO₃], N(CH₃)₂-[Im][HCO₃], and N(Et)₂-[Im][HCO₃], additional spectra are observed, confirming the presence of ILs. A notable band at approximately 875 cm^{−1} is consistently observed in all SIL samples, corresponding to the out-of-plane bending vibration of the carbonate group (CO₃^{2−}) originating from the HCO₃[−] anion. The absorption band at 700–900 cm^{−1} was attributed to C–H bending vibrations of the outer imidazole ring,⁵⁷ that is overlap with Si–O–Si stretching. A small broadening in the spectrum around 1500–1600 cm^{−1} are observed upon IL immobilization, can be attributed to C=N stretching vibrations of the imidazolium⁶⁸ and C=O stretching of the bicarbonate anion.

The successful immobilization IL on the SiO₂ support was confirmed by ²⁹Si MAS NMR spectroscopy, as shown in Figure S4. a strong peak at −66.91 ppm assigned to the T³ species of the organosilane (fully condensed, three Si–O–Si bonds to the support surface), alongside a peak at −99.34 ppm and −105.35 ppm corresponding to the Q³ signal of the SiO₂. The presence of the T³ resonance demonstrates that the organosilane, confirming the formation of covalent Si–O–Si

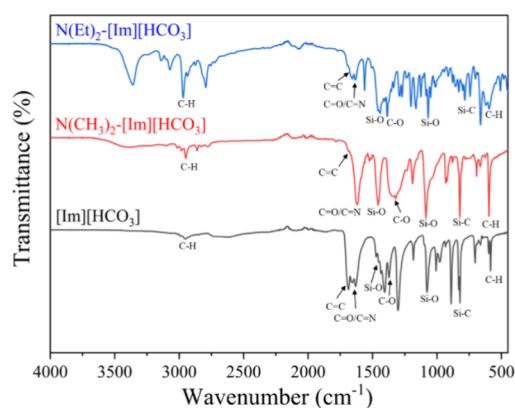


Figure 3. FTIR spectra of different ionic liquids.

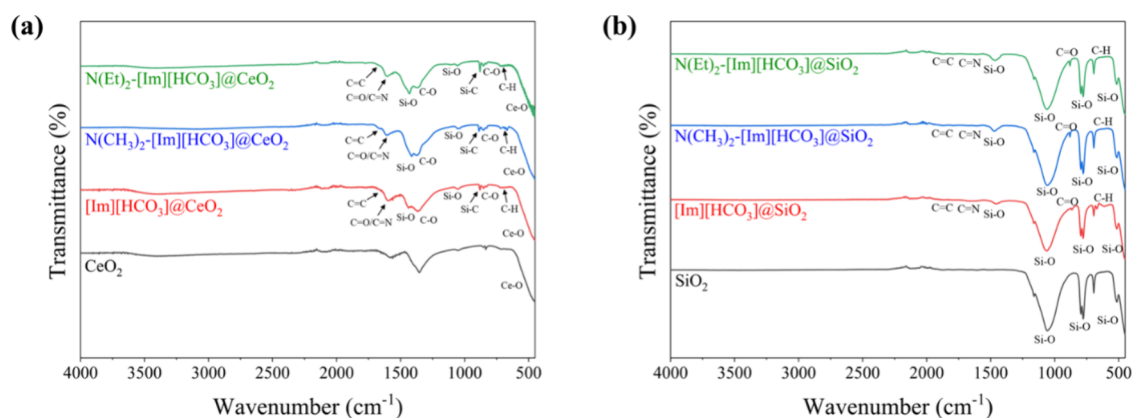


Figure 4. FTIR spectra of (a) CeO₂-SIL catalyst and (b) SiO₂-SIL catalyst.

linkages between the ionic liquid and the silica surface.^{60,70} The elemental analysis, as summarized in Table 3, revealed the presence of C and N, which were not observed in the parent CeO₂ and SiO₂, which are characteristic elements of the imidazolium-based ionic liquid. These results clearly demonstrate the immobilization of the ionic liquid onto both supports.

The temperature-programmed desorption of CO₂ (CO₂-TPD) profiles are depicted in Figure 5(a,b), showing the basicity of CeO₂-SIL catalyst and SiO₂-SIL catalyst, respectively, across a temperature range of 50 °C to 800 °C. In Figure 5(a), the pristine CeO₂ sample exhibited a small desorption peak below 200 °C, indicating the presence of weak basic sites, along with a broad, less intense desorption extending into the moderate (200–570 °C) and strong (>570 °C) basicity.⁷¹ Upon immobilization of various ILs onto CeO₂, significant changes are observed. The [Im][HCO₃]@CeO₂ catalyst showed a strong desorption peak shifting toward the strong basic site region, suggesting an enhancement of stronger basic sites due to the IL. For N(CH₃)₂-[Im][HCO₃]@CeO₂ and N(Et)₂-[Im][HCO₃]@CeO₂, desorption peaks also appear within the moderate basicity range, indicating that these substituents increase the density of moderate basic sites. In Figure 5(b), the pristine SiO₂ support showed no measurable CO₂ desorption signal, confirming the absence of basic sites. However, once ILs are supported on SiO₂, new desorption peaks appeared. The [Im][HCO₃]@SiO₂ catalyst displayed a moderate desorption peak shifting towards the strong basic site region, suggesting a broader basicity profile introduced by the

IL. While the substituted N(CH₃)₂-[Im][HCO₃]@SiO₂ and N(Et)₂-[Im][HCO₃]@SiO₂ primarily enhance the moderate basic sites, as shown by distinct desorption peaks within the 200–570 °C range.

The basicity of the SIL catalysts is reported using two different metrics, total basicity (mmol g⁻¹ catalyst), reflecting the overall density of basic sites in the composite as quantified by CO₂-TPD, and intrinsic basicity (mmol g⁻¹ IL), which normalizes this value to the mass of immobilized IL (determined by TGA, Table 2). The latter reflects the intrinsic contribution of the ionic liquid, independent of support mass and IL loading.

In terms of total basicity, both supports showed a marked increase after IL immobilization. The total basicity of pristine CeO₂ increased from 0.3594 mmol g⁻¹ to 0.7074 mmol g⁻¹ after the immobilization of [Im][HCO₃]. Likewise, N(CH₃)₂-[Im][HCO₃]@CeO₂ and N(Et)₂-[Im][HCO₃]@CeO₂ exhibited total basicity of 0.6772 and 0.5345 mmol g⁻¹, respectively. Similarly, the essentially non-basic SiO₂ (0.0358 mmol g⁻¹) rose to 0.7743 mmol g⁻¹ for [Im][HCO₃]@SiO₂, the highest among all samples, with the N(CH₃)₂-[Im][HCO₃]@SiO₂ and N(Et)₂-[Im][HCO₃]@SiO₂, giving 0.4289 and 0.5103 mmol g⁻¹, respectively.

The lower basicity of the amine derived SILs compared to the [Im][HCO₃] material can be attributed to the distinct chemical identity and local environment of their basic sites. In the [Im][HCO₃] system, the bicarbonate anion (HCO₃⁻) is a free and delocalized species that provides strong Brønsted basicity and high proton accepting ability. In contrast, under the

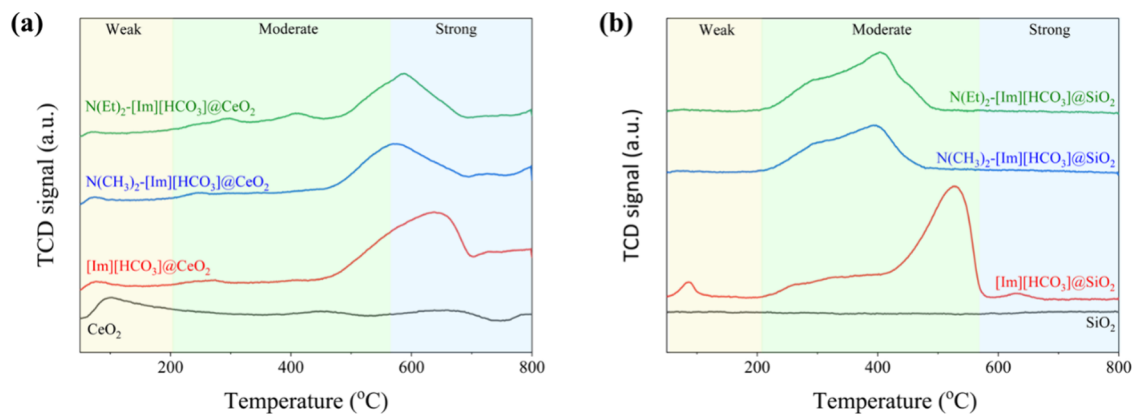


Figure 5. CO₂-TPD profiles of prepared catalysts (a) CeO₂-SIL catalyst and (b) SiO₂-SIL catalyst.

Table 2. Ionic Liquid Loading (wt %), Normalized Basicity, and Glycerol Conversion

entry	catalysts	IL loading ^a (wt %)	total basicity ^b (mmol g ⁻¹ catalyst)	normalized basicity ^c (mmol g ⁻¹ IL)	glycerol conversion ^d (%)
1	CeO ₂	-	0.3594	-	61.9
2	[Im][HCO ₃]@CeO ₂	14.8	0.7074	2.72	96.6
3	N(CH ₃) ₂ -[Im][HCO ₃]@CeO ₂	15.4	0.6772	2.42	97.7
4	N(Et) ₂ -[Im][HCO ₃]@CeO ₂	16.6	0.5345	1.43	81.9
5	SiO ₂	-	0.0358	-	0.4
6	[Im][HCO ₃]@SiO ₂	15.1	0.7743	4.92	96.8
7	N(CH ₃) ₂ -[Im][HCO ₃]@SiO ₂	15.9	0.4289	2.51	97.9
8	N(Et) ₂ -[Im][HCO ₃]@SiO ₂	13.4	0.5103	3.58	95.5

^awt % of IL loading was determined based on TGA results. ^bTotal basicity was evaluated using CO₂ TPD analysis. ^cIntrinsic basicity of SILs normalized to wt % of IL. ^dGlycerol conversion determined by GC using internal standard.

anhydrous conditions of CO₂-TPD, tertiary amines interact with CO₂ via a different pathway. Rather than forming a strongly bound CO₂ adduct, tertiary amines predominantly promote bicarbonate formation, which typically requires water. Therefore, in the absence of H₂O (dry conditions), CO₂ adsorption on tertiary amines is expected to be weak, and any uptake is likely governed by electrostatic interactions and van der Waals forces.^{72,73}

When normalized to IL mass, however, this trend shifts [Im][HCO₃]@SiO₂ and [Im][HCO₃]@CeO₂ show intrinsic basicity of 4.92 and 2.71 mmol g⁻¹ IL, while N(CH₃)₂-[Im][HCO₃]@SiO₂ and N(Et)₂-[Im][HCO₃]@SiO₂ give 2.51 and 3.58 mmol g⁻¹ IL, respectively. These results indicate that the SiO₂ supported ILs despite lower basicity of pristine

silica support, can possess higher intrinsic IL basicity attributed to SILs component.

To assess the thermal stability of the synthesized ionic liquids and support ionic liquids, thermogravimetric analysis was performed (Figure 6). In case of the unimmobilized ILs, an initial mass loss is observed below 100 °C, which is attributed to the removal of physisorbed water or residual moisture present.⁷⁴ The main thermal degradation of the ILs occurs in two distinct stages: the first between approximately 100–250 °C, and the second beginning around 600 °C,⁷⁵ with thermal stability strongly influenced by the cation structure.^{76,77} The IL based on [Im][HCO₃] begins to decompose at approximately 150 °C, whereas N(CH₃)₂-[Im][HCO₃] displays lower thermal stability. As previously reported, the presence of amino groups

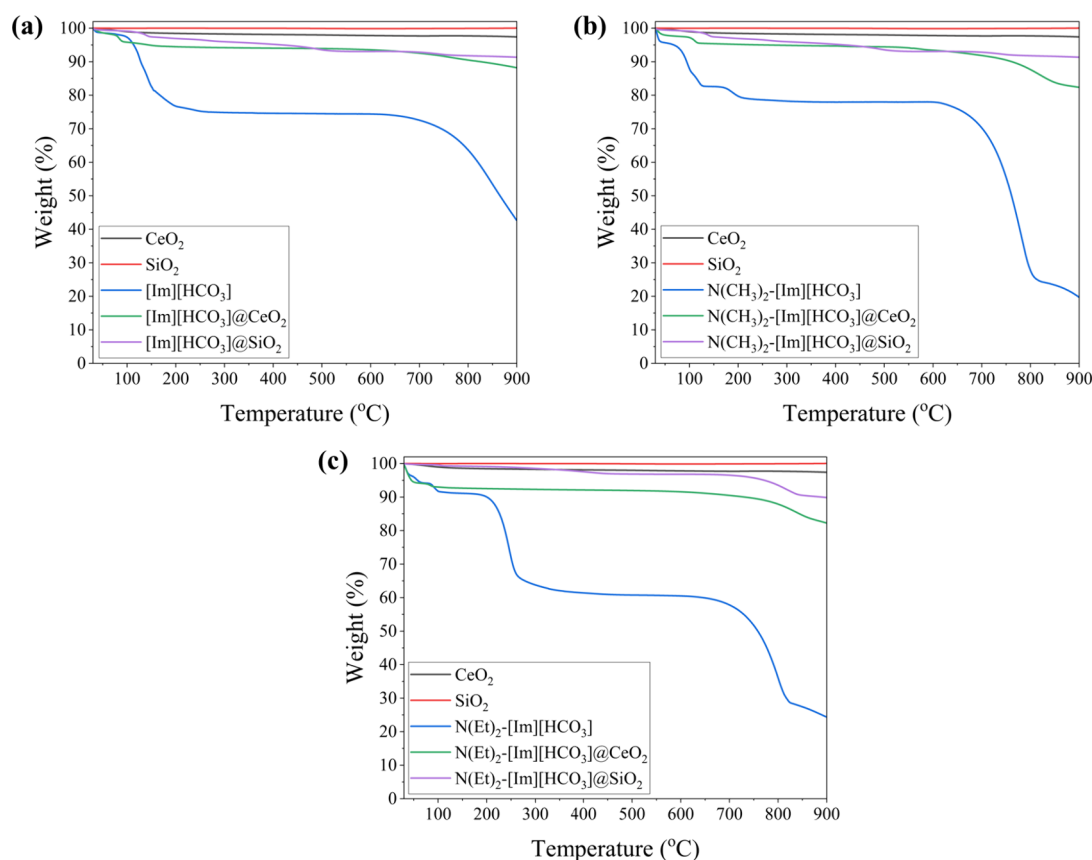


Figure 6. Thermogravimetric analysis (TGA) curves of (a) Supported-[Im][HCO₃], (b) Supported-N(CH₃)₂-[Im][HCO₃], and (c) Supported-N(Et)₂-[Im][HCO₃].

in the cationic side chain can reduce the thermal resistance of the IL due to their higher chemical reactivity and the ease of C–N bond cleavage.⁷⁶ In contrast, the $N(\text{Et})_2\text{[Im][HCO}_3\text{]}$ derivative exhibits improved thermal stability, which may be attributed to the increased steric hindrance conferred by the ethyl substituents. These bulkier side groups can enhance van der Waals interactions and spatial shielding, thereby stabilizing the cation during thermal degradation processes and partially protecting the bicarbonate anion from early decomposition.⁷⁸ At higher temperatures, the second degradation stage corresponds to the complete decomposition of organic moiety. In this phase, the presence of the SiO_2 support contributes to the stabilization of the system by offering a thermally robust surface to which the IL is anchored.⁷⁹

Regarding the immobilized ILs on CeO_2 and SiO_2 , a significantly higher mass loss is observed compared to the corresponding unmodified supports, confirming successful incorporation of the ILs. This weight loss occurs mainly between 200 °C and 500 °C, a range characteristic of the thermal degradation of imidazolium-based ILs, thereby indicating the presence of a substantial amount of anchored IL in the composite. The profile, intensity, and shift of the thermal degradation peaks compared to the free IL suggest that the immobilization was effective and that meaningful interactions exist between the IL and the support surface.⁶⁰

Table 3 summarizes the textural properties of all catalysts synthesized in this study, including BET surface area, pore volume, and average pore diameter. Pure CeO_2 exhibited a relatively high BET surface area of $26.23 \text{ m}^2 \text{ g}^{-1}$, in contrast to SiO_2 , which showed a significantly lower value of $5.40 \text{ m}^2 \text{ g}^{-1}$. However, displayed a larger average pore diameter (13.50 nm) than SiO_2 (7.98 nm).

Upon immobilization of the $[\text{Im}][\text{HCO}_3]$ ionic liquid on CeO_2 , the BET surface area decreased to $18.68 \text{ m}^2 \text{ g}^{-1}$, while the average pore diameter increased to 17.09 nm. Further modification with ILs, such as $N(\text{CH}_3)_2\text{[Im][HCO}_3\text{]}$ and $N(\text{Et})_2\text{[Im][HCO}_3\text{]}$, altered the surface area and porosity. $N(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@CeO}_2$ had a BET surface area of $24.64 \text{ m}^2 \text{ g}^{-1}$ and a slightly decreased pore volume ($0.06 \text{ cm}^3 \text{ g}^{-1}$), whereas $N(\text{Et})_2\text{[Im][HCO}_3\text{]@CeO}_2$ exhibited a lower surface area ($18.81 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.05 \text{ cm}^3 \text{ g}^{-1}$) yet maintained a relatively large pore diameter (12.23 nm).

In contrast, for the immobilization of SiO_2 with ILs, the BET surface area of $[\text{Im}][\text{HCO}_3]\text{@SiO}_2$ remained nearly unchanged at $5.15 \text{ m}^2 \text{ g}^{-1}$ compared to pristine SiO_2 . Interestingly, the

immobilization of $N(\text{CH}_3)_2\text{[Im][HCO}_3\text{]}$ and $N(\text{Et})_2\text{[Im][HCO}_3\text{]}$ onto SiO_2 led to notable increases in surface area to 7.03 and $7.61 \text{ m}^2 \text{ g}^{-1}$, respectively. Corresponding pore volumes were observed to be similar to pristine SiO_2 . However, the average pore diameters increased to 9.20 nm and 8.34 nm, respectively.

Across all samples, the measured average pore diameters ranged from 7.98 to 17.09 nm, which are substantially larger than the molecular sizes of the reactants, glycerol (0.65 nm) and dimethyl carbonate (0.55 nm), and the product, glycerol carbonate (0.52 nm). These findings suggest that the pore systems of the catalysts are sufficiently open to accommodate the reactant and product molecules, thereby facilitating effective catalytic performance.

The porous structure of both the initial supports and the prepared catalysts was evaluated by N_2 adsorption-desorption isotherms (Figure 7 and Table 3). CeO_2 exhibited a type IV isotherm, characteristic of mesoporous materials, as evidenced by the presence of a hysteresis loop. This material also shows a higher specific surface area ($26.23 \text{ m}^2 \text{ g}^{-1}$) and greater pore volume ($0.08 \text{ cm}^3 \text{ g}^{-1}$) compared to SiO_2 , which displays a type II isotherm typically associated with non-porous or macroporous solids. The immobilization of ILs on the surface of both materials does not lead to significant alterations in their porosity (Figure S2). However, a slight decrease in surface area is observed in the catalysts based on CeO_2 , suggesting that the ILs may partially block micropores or occupy part of the internal porous structure.

The morphologies of the synthesized catalyst were investigated using SEM analysis (Figure 8). Pristine CeO_2 (Figure 8(a)), prepared by precipitation, exhibited densely packed, irregularly shaped particles with relatively large sizes. In contrast, pristine SiO_2 (Figure 8(e)) showed more porous and open structure, as well as smaller, loosely aggregated particles. Noticeable morphological changes are observed as a result of the immobilization of ionic liquids. The immobilization of $[\text{Im}][\text{HCO}_3]$ and its amine-functionalized derivatives results in partial surface amorphization, as evidenced by the increased fragmentation and reduced compactness of $\text{CeO}_2\text{-SIL}$ catalysts (Figure 8(b–d)). Similarly, the $\text{SiO}_2\text{-SIL}$ catalysts (Figure 8(f–h)) exhibited increased aggregation and the appearance of surface texture. The $N(\text{Et})_2\text{[Im][HCO}_3\text{]@SiO}_2$ (Figure 8(h)) displays rod-like features, which suggest heterogeneous deposition. Following IL immobilization, the observed morphological changes suggest increased surface disorder, which may enhance catalytic accessibility.

Table 3. BET Surface Area, Pore Volume, Average Pore Diameter, Total Basicity of Prepared Catalysts, and Elemental Analysis

catalyst	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	pore volume ($\text{cm}^3 \text{ g}^{-1}$)	average pore diameter (nm)	element content (%) ^a	
				C	N
CeO_2	26.23	0.08	13.50	-	-
$[\text{Im}][\text{HCO}_3]\text{@CeO}_2$	18.68	0.06	17.09	1.86	1.05
$N(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@CeO}_2$	24.64	0.06	12.53	2.17	0.30
$N(\text{Et})_2\text{[Im][HCO}_3\text{]@CeO}_2$	18.81	0.05	12.23	2.45	0.84
SiO_2	5.40	0.01	7.98	-	-
$[\text{Im}][\text{HCO}_3]\text{@SiO}_2$	5.15	0.01	6.81	1.89	0.50
$N(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$	7.03	0.01	9.20	1.58	0.79
$N(\text{Et})_2\text{[Im][HCO}_3\text{]@SiO}_2$	7.61	0.01	8.34	3.92	1.35

^aCHNS Elemental analysis

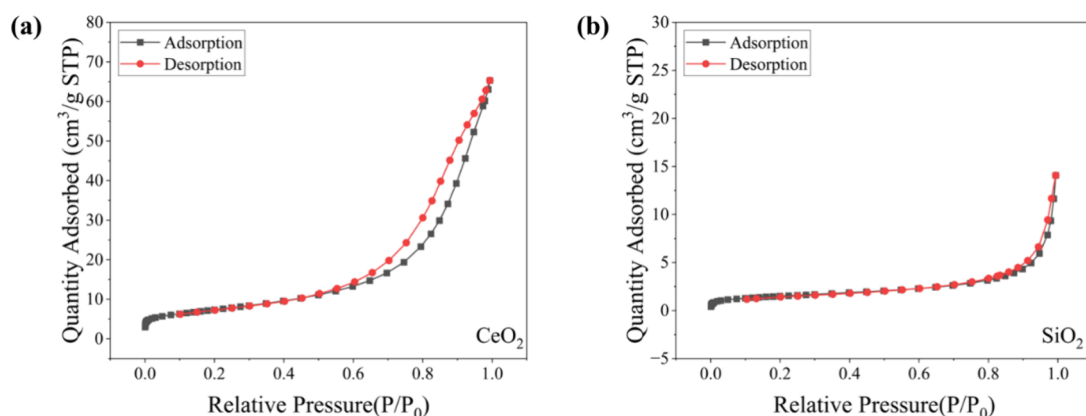


Figure 7. N_2 adsorption-desorption isotherms of (a) CeO_2 and (b) SiO_2 support.

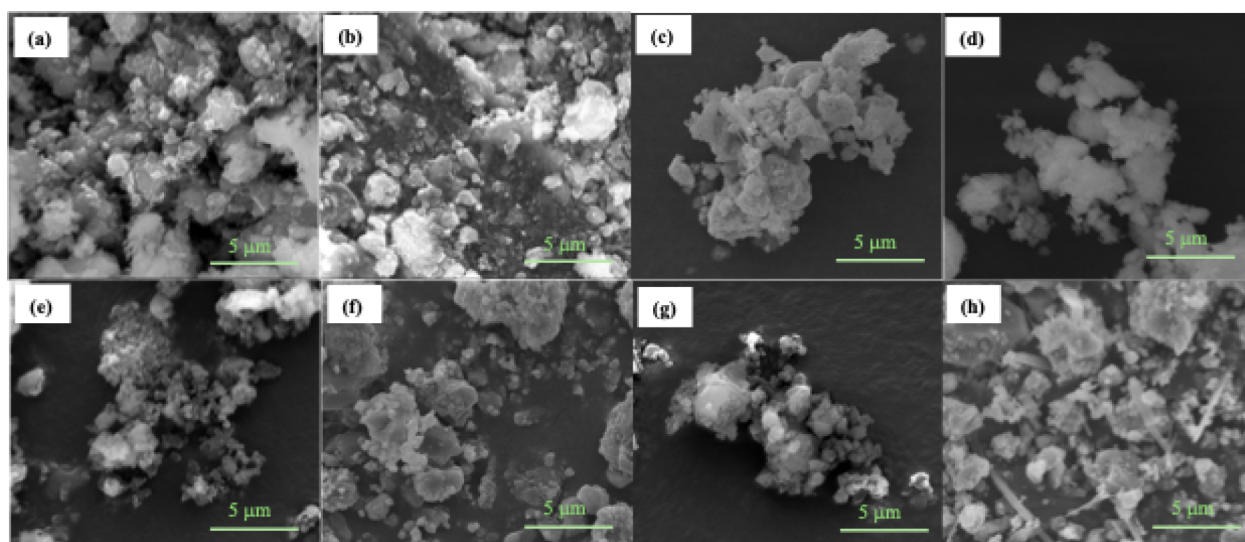


Figure 8. SEM images of (a) CeO_2 , (b) $[Im][HCO_3]@CeO_2$, (c) $N(CH_3)_2-[Im][HCO_3]@CeO_2$, (d) $N(Et)_2-[Im][HCO_3]@CeO_2$, (e) SiO_2 , (f) $[Im][HCO_3]@SiO_2$, (g) $N(CH_3)_2-[Im][HCO_3]@SiO_2$, and (h) $N(Et)_2-[Im][HCO_3]@SiO_2$.

3.2. Activity of Imidazolium-Based Ionic Liquids

Prior to evaluating the catalytic activity of the synthesized ILs and SILs, two control experiments were performed. In the first experiment, no catalyst was used under identical reaction conditions, and less than 0.5% glycerol conversion was observed after 1 h. In the second control experiment, to assess the influence of residual bromide on the catalyst surface, the reaction mixture was doped with 0.0075 g of KBr, which corresponded to 5 wt % residual KBr on the catalyst surface. Under these conditions, less than 0.5% glycerol conversion was observed, indicating that residual bromide has no measurable influence on glycerol transesterification. The catalytic activity of the synthesized imidazolium-based ionic liquids is shown in Figure 9. All tested ILs exhibited high catalytic activity, achieving glycerol conversions exceeding 80% within 1 h. Among them, $[Im][HCO_3]$ afforded the highest glycerol conversion (90%), whereas $N(Et)_2-[Im][HCO_3]$ delivered the highest GC selectivity (99%) while maintaining a comparably high conversion of 84% and 83% of GC yield. This superior selectivity is particularly advantageous for minimizing by-product formation and

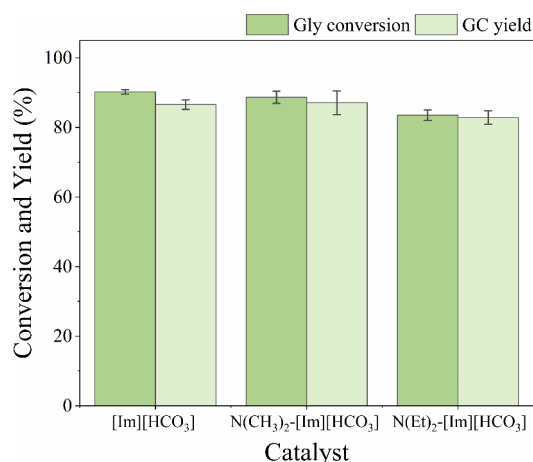


Figure 9. Glycerol conversion and glycerol carbonate yield of different imidazolium-based ionic liquids. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 3 wt % catalyst loading, 90 °C, and 1 h.

enhancing overall process efficiency, as it reduces the burden of downstream purification and maximizes glycerol valorization. Furthermore, all synthesized ILs remained completely miscible with the reaction mixture after reaction, confirming their homogeneous catalytic behavior. Given its outstanding GC selectivity and operational practicality, $N(\text{Et})_2\text{-[Im][HCO}_3\text{]}$ was selected for further investigation in the subsequent support-screening studies.

To evaluate the catalytic performance of the imidazolium-based ionic liquids including $[\text{Im}][\text{HCO}_3]$, $N(\text{CH}_3)_2\text{-[Im][HCO}_3]$, and $N(\text{Et})_2\text{-[Im][HCO}_3]$, the reaction mixtures were also analyzed by ^1H NMR spectroscopy (400 MHz, DMSO-d_6).⁸⁰ As shown in Figures S10–S12 the spectra from all three IL-catalyzed reactions display proton resonances that closely match those of commercial glycerol carbonate (Sigma-Aldrich), shown in Figure S6. The strong spectral agreement confirmed the successful formation of GC in each case.

3.3. Effect of Different Solid Supports on Supported Ionic Liquid (SIL) Activity

The influence of different supports on catalytic performance was investigated by immobilizing $N(\text{Et})_2\text{-[Im][HCO}_3]$ on five different solid supports via a solvent-free ball milling method. The results from catalytic activity testing as shown in Figure 10. The $\text{SiO}_2\text{-SIL}$ catalyst, $N(\text{Et})_2\text{-[Im][HCO}_3]\text{@SiO}_2$ exhibited the highest activity, achieving 95% glycerol conversion and 93% of GC yield. This was closely followed by the $\text{CeO}_2\text{-SIL}$ catalyst, $N(\text{Et})_2\text{-[Im][HCO}_3]\text{@CeO}_2$ achieved 85% conversion and GC yields ($\sim 80\%$). In contrast, IL immobilized on Al_2O_3 , MCM-41, and SBA-15 showed moderate activity, with approximately 75% glycerol conversion and slightly decreased selectivity compared to the SiO_2 and CeO_2 . Al_2O_3 typically exhibits acidic rather than basic surface sites, which seem to be less favorable for promoting the transesterification of glycerol with DMC. Although, MCM-41 and SBA-15 are mesoporous silica materials with high surface area, however the high wt % of IL immobilized on MCM-41 and SBA-15, may possibly lead to inaccessible pores causing diffusion limitation, which could be causing reduction in the catalytic efficiency.^{65,66} This is supported by N_2 adsorption-desorption analysis (Figure S2)

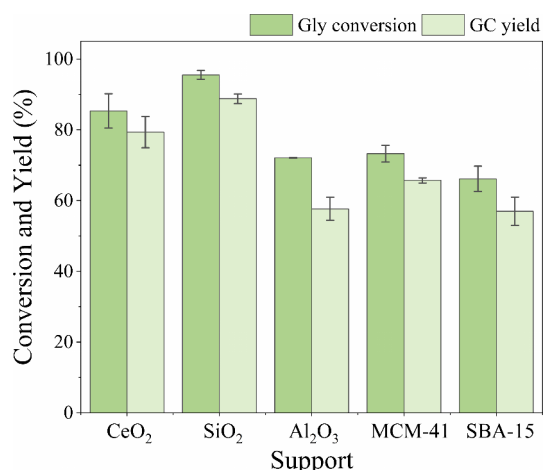


Figure 10. Glycerol conversion and glycerol carbonate yield of $N(\text{Et})_2\text{-[Im][HCO}_3]$ on different types of support. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 0.5 g SIL catalyst, 90 °C, and 1 h.

and BET results (Table S2), which showed a marked reduction in adsorbed N_2 quantity, surface area, and pore volume after IL immobilization on MCM-41 and SBA-15, along with a shift of the capillary condensation step to higher relative pressure for MCM-41, consistent with substantial narrowing or partial blockage of the mesopores by the immobilized IL. These results suggest that the nature of the support significantly affects both conversion and selectivity, likely due to differences in surface area, surface acidity or basicity, and interaction with the IL immobilized phase. Based on their superior catalytic performance, SiO_2 and CeO_2 were selected as the most promising supports for further investigation using a range of structurally varied ionic liquids.

3.4. Effect of Ball Milling Speed

The effect of milling speed during the immobilization step was investigated by preparing $N(\text{CH}_3)_2\text{-[Im][HCO}_3]\text{@SiO}_2$ at three different ball milling speeds (150, 300, and 450 rpm), as shown in Figure 11. The catalyst prepared at 150 rpm gave a glycerol conversion of 64%. Increasing the milling speed led to a progressive improvement in catalytic activity, with the sample prepared at 450 rpm achieving 97% glycerol conversion. In contrast, selectivity was not significantly affected by milling speed, and all catalysts exhibited nearly 100% glycerol carbonate selectivity. TGA analysis (Figure S3) showed that the catalysts prepared at 150 and 300 rpm exhibited lower weight loss than that prepared at 450 rpm, indicating lower IL loading at these lower milling speeds. This suggests that the enhanced catalytic activity observed at 450 rpm is attributed primarily to the higher IL loading achieved, likely due to the increased impact and shear forces promoting more effective immobilization of the IL onto the support, while improved dispersion and accessibility of active sites may also contribute to the improved catalytic performance.

3.5. Activity of $\text{CeO}_2\text{-}$ and $\text{SiO}_2\text{-}$ Supported Ionic Liquid Catalysts (SILC)

As shown in Figure 12(a, b), the immobilization of ionic liquids onto CeO_2 and SiO_2 supports significantly enhances their catalytic performance in the conversion of glycerol to glycerol

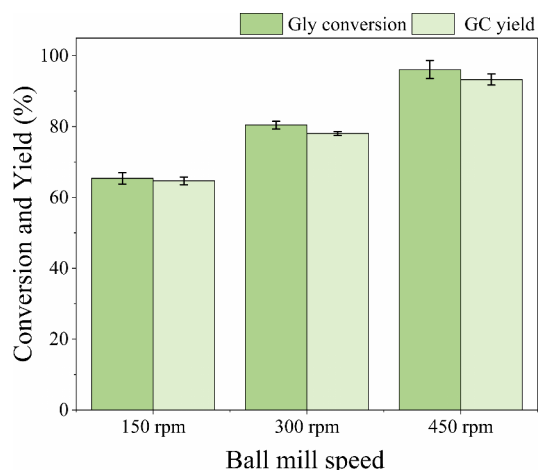


Figure 11. Glycerol conversion and glycerol carbonate yield of $N(\text{CH}_3)_2\text{-[Im][HCO}_3]\text{@SiO}_2$ with different ball milling speed. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 0.5 g of $N(\text{CH}_3)_2\text{-[Im][HCO}_3]\text{@SiO}_2$, 90 °C, and 1 h.

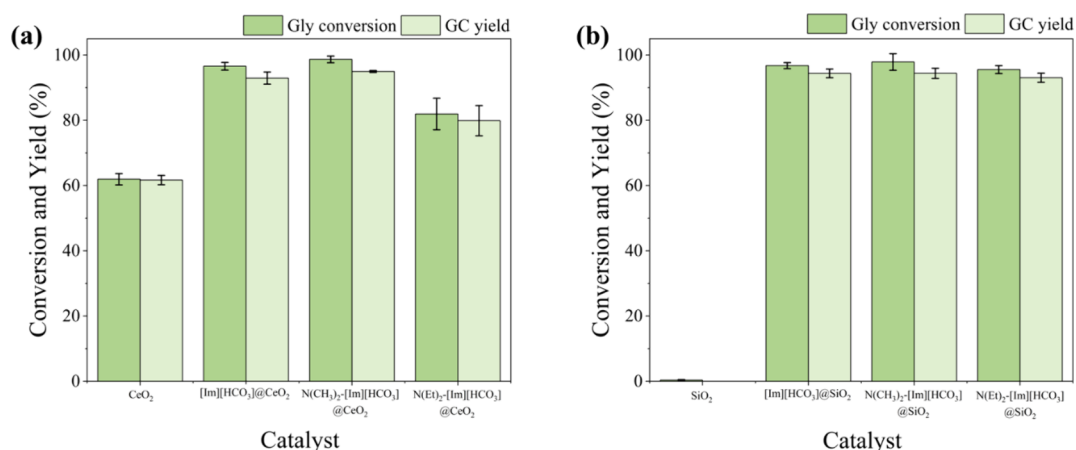


Figure 12. Glycerol conversion and glycerol yield selectivity of (a) CeO₂-SIL catalyst, and (b) SiO₂-SIL catalyst. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt % catalyst loading, 90 °C, and 1 h.

carbonate. Pristine SiO₂ exhibited negligible glycerol conversion due to its extremely low surface basicity (0.0358 mmol g⁻¹, Table 2). Upon SIL, however, all SiO₂-SIL catalysts achieved over 95% conversion, highlighting the critical role of surface basicity in activating glycerol and dimethyl carbonate. In comparison, pristine CeO₂ showed moderate catalytic activity, achieving approximately 62% glycerol conversion. This can be attributed to its inherent surface basicity (0.3594 mmol g⁻¹) and redox capability, particularly the Ce⁴⁺/Ce³⁺ transition and associated oxygen vacancies, which facilitate DMC activation. Immobilization of ILs with CeO₂ further improved its performance, with all CeO₂-SIL catalysts reaching glycerol conversions near or above 95%.

Among the SILs, those containing the dimethylamino-functionalized IL (N(CH₃)₂-[Im][HCO₃]) supported on both CeO₂ and SiO₂, exhibited the highest activity and GC selectivity, although [Im][HCO₃]@CeO₂ and [Im][HCO₃]@SiO₂ possessed the highest total basicity values respectively (0.7074 and 0.9193 mmol g⁻¹), and they showed good catalytic activity similar to N(CH₃)₂-substituted ILs. The enhanced performance of N(CH₃)₂-substituted ILs may arise from the increased electron-donating ability of the amino group, which likely improves reactant activation through stronger interactions with glycerol and DMC. Therefore, catalytic activity appears to result from a combined effect of surface basicity, the nature of the IL functional group, and the physicochemical properties of the support.

In the ¹H NMR spectra of the samples were analyzed as shown in Figures S8 and S9, a multiplet at δ 5.27–4.78 ppm (H₁, OH) corresponds to the methylene proton adjacent to the hydroxyl group, while multiplets at δ 4.62–4.38 ppm (H₁, CH) and δ 4.35–4.10 ppm (H₁, CH₂) are attributed to the methylene protons adjacent to the carbonate ring and the terminal hydroxyl group, respectively. A broad multiplet in the range of δ 3.75–3.17 ppm (H₂, CH–CH₂) corresponds to the second methylene group. The integration of these peaks closely matches the expected proton ratio of glycerol carbonate (1:2:2:1),^{80,81} confirming the successful formation of the target product.

Further insight into the selectivity of the catalytic system was obtained by comparing the ¹H NMR spectrum of the reaction mixture catalyzed by N(CH₃)₂-[Im][HCO₃]@SiO₂ with those

of commercial standards of glycerol, glycerol carbonate, and glycidol (Figure S14). The spectrum of the reaction mixture shows an excellent match with the reference spectrum of glycerol carbonate, confirming it as the dominant product. The characteristic resonances corresponding to glycerol carbonate (peaks i–k) are visible and well resolved in the reaction mixture. In contrast, signals corresponding to unreacted glycerol (peaks b and c) are largely absent, indicating efficient glycerol conversion under the reaction conditions. More importantly, no significant signals are observed at the chemical shifts assigned to glycidol (peaks d–g), which is a known side product typically formed via intramolecular dehydration of glycerol. The absence of these signals strongly suggests that the formation of glycidol is either negligible or completely suppressed in this system. These results highlight the high activity and selectivity of the N(CH₃)₂-[Im][HCO₃]@SiO₂ catalyst toward glycerol carbonate formation, with minimal side reactions. This selectivity is particularly advantageous in avoiding undesired byproducts, supporting the utility of this catalytic system for clean and efficient glycerol valorization.

3.6. Catalyst Reusability

The reusability of SIL catalysts, N(CH₃)₂-[Im][HCO₃]@CeO₂ and N(CH₃)₂-[Im][HCO₃]@SiO₂, was assessed over multiple recycles to evaluate their stability and long-term performance. Both fresh catalysts initially exhibited excellent activity, achieving approximately 95% glycerol conversion and nearly 100% selectivity toward glycerol carbonate, as shown in Figure 13(a,b). Notable differences in catalytic stability were observed following subsequent recycles, indicating the nature of the interactions between the IL and the support material. Besides enhanced stability, the immobilization of ionic liquids on solid surfaces facilitates the recovery and separation of the catalyst by simple filtration, providing a practical benefit over traditional homogeneous ionic liquid systems.

For N(CH₃)₂-[Im][HCO₃]@CeO₂, a sharp decline in glycerol conversion was observed during the first recycle, dropping to around 40% glycerol conversion, and further decreased to approximately 20% after the second recycle. These values were notably lower than the conversion obtained using pure CeO₂, which exhibited about 65% conversion under the same conditions. This loss of catalyst activity could be attributed to the

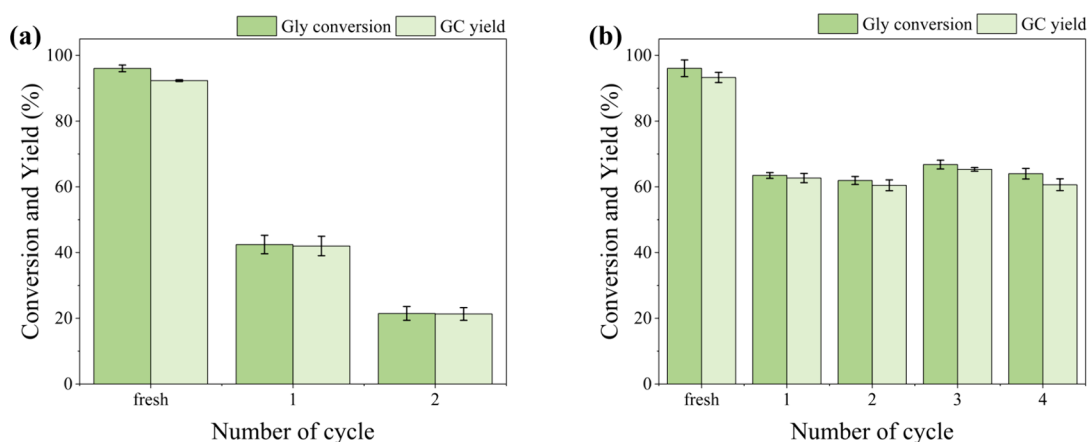


Figure 13. Effect of Supported- $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]}$ reusability on glycerol conversion and glycerol carbonate yield (a) $\text{CeO}_2\text{-SiL}$ catalyst, and (b) $\text{SiO}_2\text{-SiL}$ catalyst. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt % catalyst loading, 90 °C, and 1 h.

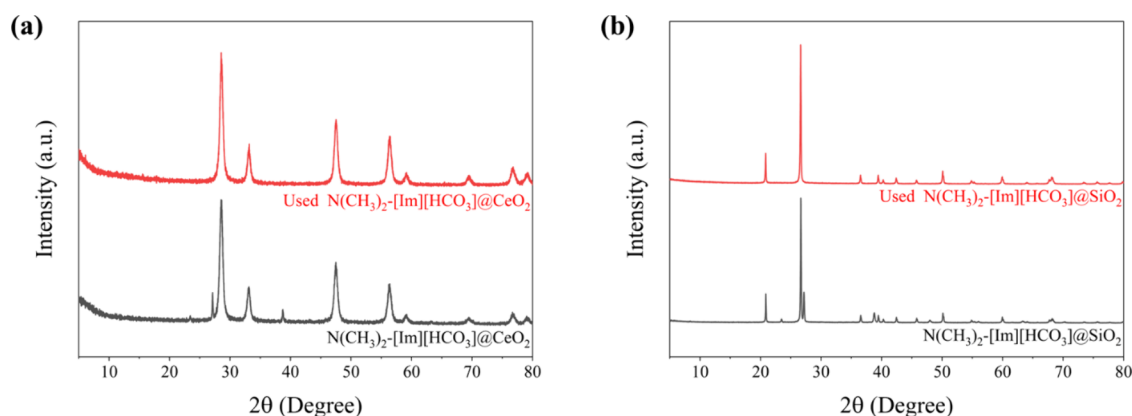


Figure 14. X-ray diffraction patterns of catalyst before and after reaction (a) $\text{CeO}_2\text{-SiL}$ catalyst, and (b) $\text{SiO}_2\text{-SiL}$ catalyst.

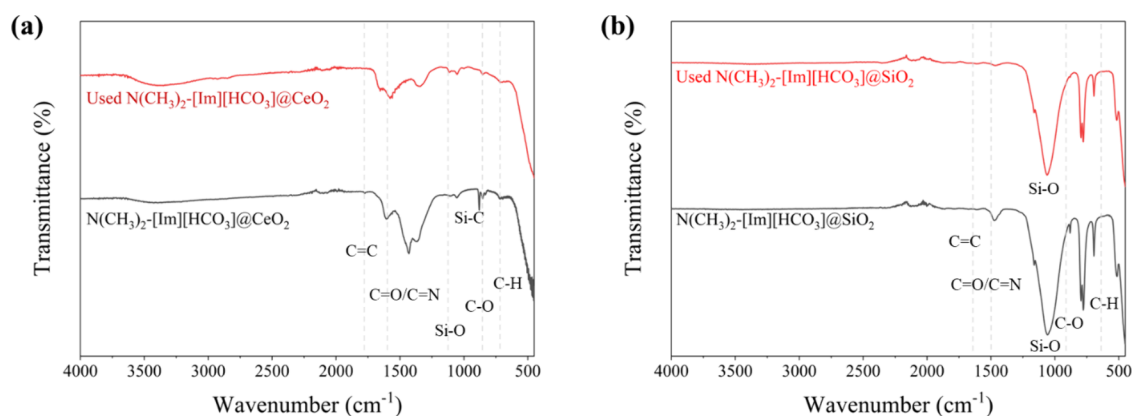


Figure 15. FTIR spectra of catalyst before and after reaction (a) $\text{CeO}_2\text{-SiL}$ catalyst, and (b) $\text{SiO}_2\text{-SiL}$ catalyst.

leaching of the IL from the CeO_2 surface during the reaction. The immobilization of ILs on oxide surfaces is strongly influenced by the presence of surface hydroxyl ($-\text{OH}$) groups, which can form covalent bonds with the IL. However, in this case, CeO_2 was calcined above 400 °C during preparation, significantly reducing the number of available $-\text{OH}$ groups.

Consequently, a portion of the IL may have been only physically adsorbed rather than covalently immobilized, rendering it more susceptible to leaching during catalysis. In addition, the formation of weak $\text{Ce}-\text{O}-\text{Si}$ linkages may show insufficient stability to anchor the IL on the support, further contributing to IL active sites loss and partial deactivation of the CeO_2

support. Beyond IL leaching, the reduced activity of the recycled catalyst may also result from adsorption of reaction intermediates or products on the CeO_2 surface, which can block active sites and limit their accessibility. Together, IL leaching and this surface fouling likely account for the lower activity of the recycled CeO_2 -SIL catalyst relative to both its fresh form and the bare CeO_2 support.

In contrast, $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$ demonstrated much better reusability. Although the glycerol conversion decreased to about 60% after the first reuse, the catalytic activity remained relatively stable over the subsequent three cycles, consistently maintaining conversion above 60% with nearly unchanged GC yield, as shown in Figure 13(b). This enhanced durability is attributed to the strong Si–O–Si covalent bonding between the IL and the silica surface, which provides more robust immobilization. Although some loosely bound IL or physical absorbed IL may have lost after the first use, leading to initial decrease in activity during first recycle, a significant fraction remained stably anchored on the support, as evidenced by sustained catalytic activity over subsequent recycles. The activity of the reused SiO_2 -SIL catalyst was still substantially higher than that of pure SiO_2 , which showed negligible conversion, indicating the retention of IL after multiple recycling.

XRD patterns of $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@CeO}_2$ fresh and used catalyst, (Figure 14(a)) revealed that the crystalline structure of the CeO_2 support was largely preserved, with only minor peak broadening observed in the used catalyst. This suggests that although the support remained structurally intact, the active SIL phase may have been lost. In contrast, the XRD pattern of the SiO_2 -SIL catalyst (Figure 14(b)) showed the persistence of characteristic crystalline reflections associated with the SIL even after use, reinforcing that a significant portion of the SIL remained immobilized on the silica surface. The diffraction peaks corresponding to residual KBr in the fresh catalysts disappeared after the first reaction cycle for both the CeO_2 -SIL catalyst and SiO_2 -SIL catalyst.

FTIR spectra provided further insight into the chemical stability of the SILs. The fresh CeO_2 -SIL catalyst exhibited distinct bands around 1650 cm^{-1} corresponding to the C=O stretching of the anion and bands near $1570\text{--}1600\text{ cm}^{-1}$ related to C=N in the imidazolium ring. Additional peaks near 1450 cm^{-1} were assigned to $\text{N}(\text{CH}_3)_2$ bending vibrations, while bands around $1100\text{--}1050\text{ cm}^{-1}$ were attributed to Si–O–Si stretching⁶⁹ (Figure 15(a)). All spectra exhibit a broad absorption band around 450 cm^{-1} , attributed to Ce–O and Ce–O–Ce stretching vibrations.⁶⁴ The peak, approximately 887 cm^{-1} , corresponds to the out-of-plane C–O stretching vibrations of the carbonate group (CO_3^{2-}). In the used catalyst, a noticeable decrease in the intensity of these bands was observed. FTIR analysis of $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$ revealed characteristic bands corresponding to the IL in the fresh catalyst. The absorption band at 771 cm^{-1} was attributed to C–H bending vibrations of the outer imidazole ring.⁵⁷ A broad band centered near 1100 cm^{-1} was assigned to the stretching vibrations of Si–O–Si linkages, while distinct bands corresponding to $\text{N}(\text{CH}_3)_2$ functional groups confirmed the presence of the IL (Figure 15(b)). A weak, broad band in the $1500\text{--}1600\text{ cm}^{-1}$ region, assigned to C=N stretching of the imidazolium ring, together with the band at approximately 875 cm^{-1} corresponding to C–O stretching, was still observed for the used catalyst, indicating that a fraction of the IL remained on the surface, although partial loss had occurred. Consistent with this

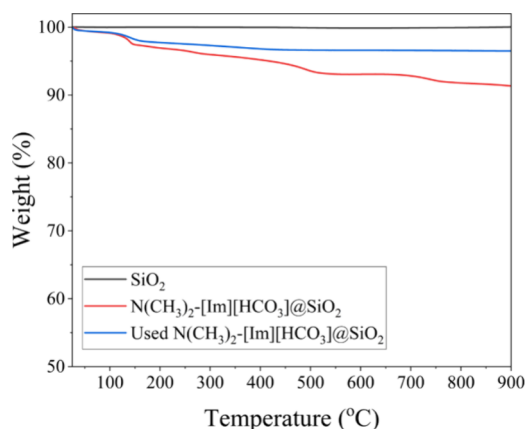


Figure 16. Thermogravimetric analysis (TGA) curves of SiO_2 , $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$, and used $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$.

observation, the TGA profile of the used $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$ catalyst (Figure 16) shows a lower overall mass loss compared with the fresh material. Importantly, the decomposition pattern remains distinct from that of the unmodified SiO_2 support, confirming that IL species are retained on the silica surface after the first cycle. From the TGA data, the used catalyst was estimated to have lost approximately 10 wt % of the immobilized IL during the first run.

These findings suggest SiO_2 is relatively better support in terms of the stability and reusability of SIL catalysts. The loss of surface hydroxyl groups during high temperature treatment, along with weak support and IL interactions, can lead to partial IL leaching and catalyst deactivation, as seen in the CeO_2 -SIL catalyst. In contrast, the SiO_2 -SIL catalyst, benefiting from strong covalent bonding and more compatible surface chemistry, maintained its structure and activity over multiple cycles.

Due to the partial loss of IL from the SiO_2 surface after the first reaction cycle, the catalytic activity of the used $\text{N}(\text{CH}_3)_2\text{[Im][HCO}_3\text{]@SiO}_2$ decreased, resulting in 60% glycerol conversion. The residual activity is attributed to the IL active sites that remained immobilized on the SiO_2 surface. To restore performance to a level comparable to the fresh catalyst, a regeneration strategy was examined. The used catalyst was re-ball-milled with additional IL, and the regenerated material exhibited improved activity. As shown in Figure 17, glycerol conversion increased to 83%, which is noticeably higher than that obtained using the used catalyst directly.

This recovery in activity is consistent with the FTIR results (Figure 18). After re-ball milling with IL, the regenerated catalyst showed higher band intensities in the $1500\text{--}1600\text{ cm}^{-1}$ region and at approximately 875 cm^{-1} compared with the used catalyst. These bands correspond to the C=N stretching vibration of the imidazolium ring and the C–O stretching vibration, respectively. The enhanced intensity of these characteristic signals confirms that re-ball milling effectively replenishes the IL content and increases the number of accessible IL active sites on the catalyst surface.

3.7. Turnover Frequency (TOF)

The yield and turnover frequency (TOF) of the supports and the SIL catalysts are summarized in Table 4. To assess the

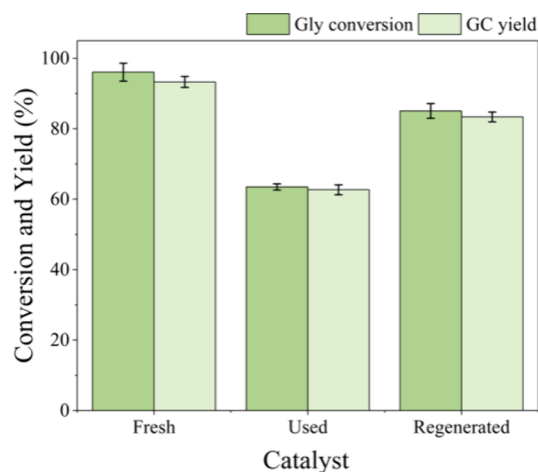


Figure 17. Glycerol conversion and glycerol yield selectivity of fresh, used, and regenerated $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ catalysts. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt % catalyst loading, 90 °C, and 1 h.

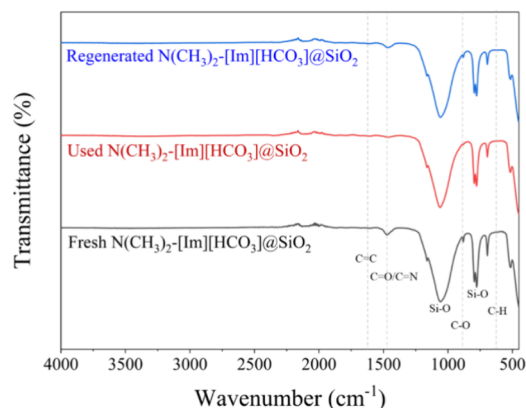


Figure 18. FTIR spectra of fresh $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ catalyst, used $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ catalyst, and regenerated $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ catalyst.

Table 4. Catalytic Performance of Various Catalysts Showing Yield and TOF

entry	catalysts	yield ^a (%)	TOF ^b (h ⁻¹)
1	CeO ₂	61.7	183.6
2	[Im][HCO ₃]@CeO ₂	92.9	147.0
3	$N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@CeO}_2$	93.9	156.5
4	$N(\text{Et})_2\text{-[Im][HCO}_3\text{]@CeO}_2$	79.9	164.6
5	SiO ₂	0.0	11.2
6	[Im][HCO ₃]@SiO ₂	94.4	134.3
7	$N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$	94.4	247.7
8	$N(\text{Et})_2\text{-[Im][HCO}_3\text{]@SiO}_2$	93.0	203.8

^aYield determined by GC using internal standard. ^bTOF = TON / reaction time (h) at 1 h reaction time.

influence of catalyst basicity on performance, the relationship between the normalized basicity (expressed as mmol g⁻¹ IL) and TOF was examined (Tables 3 and 4). The catalysts based on [Im][HCO₃] and $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]}$, immobilized on

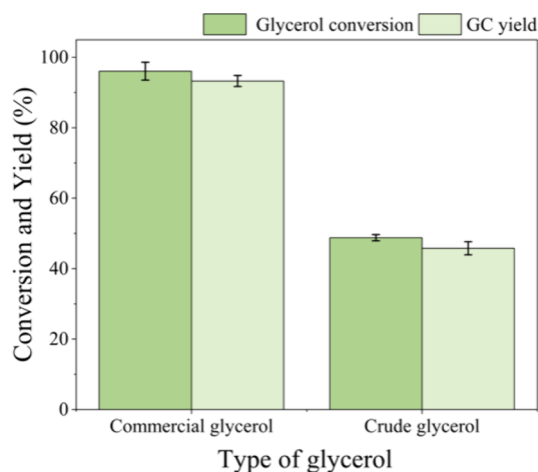


Figure 19. Glycerol conversion and glycerol yield selectivity of $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ using commercial and crude glycerol. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt % catalyst loading, 90 °C, and 1 h.

both CeO₂ and SiO₂, exhibited relatively high normalized basicity values (approximately 2.4–5.9 mmol g⁻¹ IL) and delivered high TOF values (~147–247 h⁻¹) with yields above 92%. In addition, $N(\text{Et})_2\text{-[Im][HCO}_3\text{]@SiO}_2$ showed comparable catalytic performance to Entries 2, 3, 5, and 6. In contrast, $N(\text{Et})_2\text{-[Im][HCO}_3\text{]@CeO}_2$ displayed moderate total basicity (0.53 mmol g⁻¹ catalyst) but a lower normalized basicity (1.42 mmol g⁻¹ IL), which was accompanied by reduced glycerol conversion (81.9%) and yield (79.9%). This suggests that the quality and accessibility of the IL-derived basic sites, as reflected by normalized basicity, are more critical to catalytic performance than the total basicity per gram of catalyst alone.

Notably, $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ achieved the highest TOF (247.7 h⁻¹) despite having only moderate total basicity (0.4289 mmol g⁻¹ catalyst), highlighting the importance of normalized basicity as a descriptor of catalytic efficiency. By comparison, the bare SiO₂ support, with very low total and normalized basicity (0.036 mmol g⁻¹), showed the poorest activity (TOF = 11.2 h⁻¹). Overall, the TOF values correlate more strongly with normalized basicity than with total basicity, indicating that catalysts possessing higher intrinsic IL basicity provide more reactive and accessible sites, thereby improving substrate activation and enhancing catalytic performance.

3.8. Practical Applicability

The catalytic performance of $N(\text{CH}_3)_2\text{-[Im][HCO}_3\text{]@SiO}_2$ was evaluated using both commercial glycerol and crude glycerol to assess its practical applicability (Figure 19). Commercial glycerol is highly purified and contains minimal impurities, whereas crude glycerol obtained from biodiesel production typically contains water, residual methanol, inorganic salts, and fatty acid methyl ester (FAME) residues. These impurities can absorb on the catalyst surface and partially block active sites, thereby reducing catalytic activity. In this study, the SIL catalyst was tested for the transesterification of glycerol with DMC using both feedstocks under identical reaction conditions. A significant decrease in activity was observed when

Scheme 3. A Plausible Mechanism of Transesterification between Glycerol and DMC Over SIL Catalyst

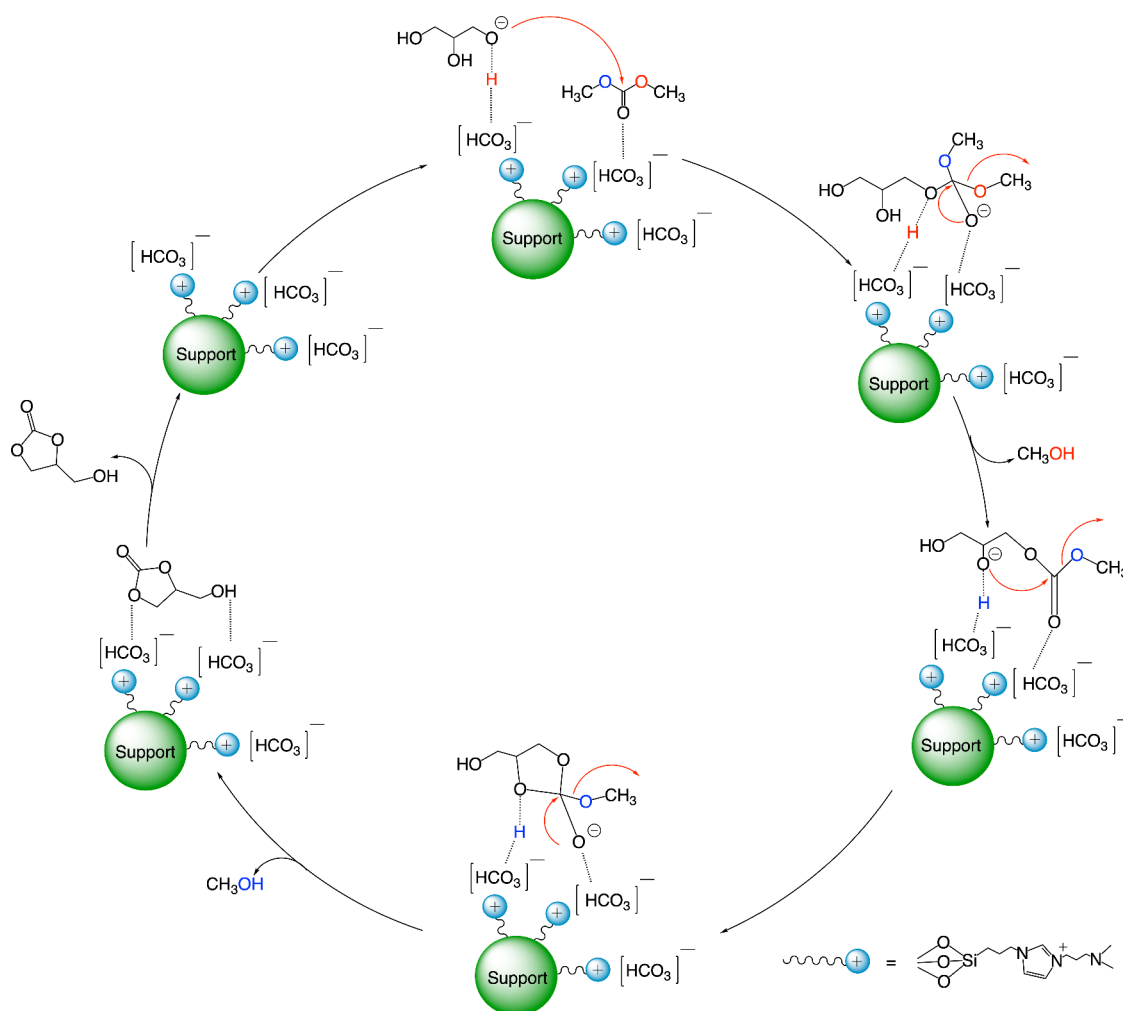


Table 5. Comparison of Prepared Catalyst with Other Reported Catalyst for Synthesis of Glycerol Carbonate

catalyst	DMC to gly ratio	condition	GC yield (%)	IL loading (%)	TOF (h ⁻¹)	ref
[APmim]OH/ZIF-8/LDH	3	75 °C, 80 min	96.5	3 wt %	n/a	56
[TMG][TfE]	2	80 °C, 30 min	87.7	0.1 mol %	1754.0	34
[Bmim]Im	2.5	70 °C, 90 min	98.4	10 mol %	6.6	32
Poly(VIMC ₈)[IM]	2.5	70 °C, 90 min	85.5	10 mol %	n/a	82
[Mor _{1,4}][N(CN) ₂]	3	120 °C, 13 h	100	15 mol %	0.4	21
N(CH ₃) ₂ -[Im][HCO ₃] <i>@</i> SiO ₂	3	90 °C, 60 min	94.4	3 mol % ^a	247.7	in this work

^aIL loading (%) in the reaction was calculated based on the amount of wt % of IL was immobilized on solid support according to TGA results.

crude glycerol was used, with glycerol conversion decreasing from 94% for commercial glycerol to 48% for crude glycerol. This reduction indicates that water and associated impurities in crude glycerol adversely affect catalytic efficiency. Nevertheless, the selectivity toward glycerol carbonate remained nearly 100% for both feedstocks. Overall, these results demonstrate the potential of the developed catalyst system for crude glycerol valorization, while highlighting the need for further optimization and or simple pre-treatment strategies to

improve catalyst tolerance toward impurities present in real bio-diesel derived glycerol streams.

3.9. Reaction Mechanism

A plausible reaction pathway for the transesterification of glycerol with dimethyl carbonate is illustrated in Scheme 3, utilizing a supported-N(CH₃)₂-[Im][HCO₃]. This system acts as a bifunctional base catalyst, where the hydrogen carbonate anion serves as a mild Brønsted base. At the same time, the N(CH₃)₂-

functionalised cation enhances the local electron density, promoting catalytic basicity and reactant activation. Glycerol initially interacts with the hydrogen carbonate anion, which absorbs a proton from one of its hydroxyl groups. The presence of the electron-donating $N(CH_3)_2$ group on the imidazolium cation enhances the local basicity and facilitates this deprotonation process, generating a reactive glyceroxide species. The generated glyceroxide anion then undergoes a nucleophilic attack on the electrophilic carbonyl carbon of DMC, yielding a methyl glyceryl carbonate intermediate. This step is critical for the formation of the carbonate linkage, and methanol is a by-product. A second -OH group on the same glycerol molecule subsequently attacks the carbonate moiety, resulting in intramolecular cyclisation to form the five-membered glycerol carbonate ring. During the catalytic cycle, the bicarbonate anion may intermittently transform into carbonic acid, which rapidly decomposes into carbon dioxide and water under reaction conditions. The immobilization of the SIL provides effective catalyst recycling and minimizes leaching, while the support serves as a suitable surface area that enhances dispersion and substrate accessibility.

3.10. Catalytic Activity Comparison

Table 5 compares the performance of various catalytic systems reported for glycerol carbonate synthesis via transesterification of glycerol with dimethyl carbonate. IL based catalysts, such as [APmim]OH/ZIF-8/LDH (GC yield 96.5% at 75 °C, 80 min, 3 wt %) and [Bmim]Im (98.4% at 70 °C, 90 min, 10 mol %), demonstrate high efficiency under relatively mild conditions. However, these systems often involve either homogeneous ionic liquids or complex composite supports, which can limit catalyst recovery, recyclability, and scalability.^{32,56} In addition, [Bmim]Im exhibited a relatively low TOF (6.6 h^{-1}) despite the high IL loading (10 mol %). The poly(VIMC8)[IM] catalyst also shows good activity (85.5%), but it relies on a polymeric IL matrix with high IL loading (10 mol %), which may introduce mass transfer limitations.⁸²

In contrast, the $N(CH_3)_2$ -[Im][HCO₃]₃@SiO₂ catalyst developed in this work exhibits high performance, achieving a GC yield of 94.4% at 90 °C within 60 min using only 3 mol % IL loading. Notably, a high TOF of 247.7 h^{-1} was obtained for $N(CH_3)_2$ -[Im][HCO₃]₃@SiO₂, confirming the high catalytic efficiency of this supported ionic liquid system for glycerol transesterification with DMC. This performance is attributed to the bifunctional nature of the IL, combining Brønsted basicity from the [HCO₃]⁻ anion with enhanced reactant activation from the tertiary amine functionality, together with the advantages of a solid support that facilitates catalyst separation and reuse.

Overall, the supported ionic liquid catalysts presented in this study offer an effective balance of high yield, short reaction time, and mild operating conditions, together with easy separation and reusability. These features make them promising and scalable alternatives to homogeneous IL systems for sustainable glycerol carbonate production.

4. CONCLUSIONS

Supported ionic liquids (SILs) have gained considerable attention as catalysts due to their potential in enabling resource-efficient chemical transformations. Their tunable properties, achieved through structural modifications of the organic cation

can enhance product purity, improve selectivity, and minimize the formation of undesired by-products. In this study, imidazolium-based ILs incorporating hydrogen carbonate anions demonstrated excellent catalytic activity in the transesterification of glycerol with dimethyl carbonate, achieving glycerol conversions above 80% and selectivity toward glycerol carbonate exceeding 95%.

To overcome challenges related to catalyst recovery and reuse, ILs were successfully immobilized onto solid supports via mechanochemical ball milling. This solvent-free approach improved both catalyst stability and reusability. Among the support materials investigated, CeO₂ and SiO₂ delivered superior catalytic performance compared to Al₂O₃, MCM-41, and SBA-15. In particular, the $N(CH_3)_2$ -[Im][HCO₃]₃@SiO₂ catalyst achieved approximately 97% glycerol conversion and 94% GC yield, with glycidol detected only in trace amounts.

Furthermore, the SiO₂-SIL catalyst exhibited excellent reusability, maintaining glycerol conversion above 60% over at least three consecutive cycles. In contrast, the bare SiO₂ support showed negligible catalytic activity. These results underscore the effectiveness of immobilizing ILs on suitable supports to enhance catalytic activity, stability, and recyclability in sustainable glycerol valorization.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. <https://pubs.acs.org/doi/10.1021/acssuschemeng.6c04868>.

GC calibration curve and Relative Response Factor (RF) of each substrate. Full spectral characterization (¹H-NMR) of glycerol carbonate, reaction mixture using three structures of IL as catalyst, and reaction mixture using SIL as catalyst (DOCX)

■ AUTHOR INFORMATION

Corresponding Author

Harsh Manyar – School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom;

ORCID.org/0000-0002-7990-4410;

Email: h.manyar@qub.ac.uk

Authors

Patcharaporn Inrirai – School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom; Faculty of Food and Agricultural Technology, Pibulsongkram Rajabhat University, 156 MuS, Phlai Chumphon, Mueang, Phitsanulok 65000, Thailand

Juan Jose Villora-Picó – School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom

Ciara Cassidy – School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom

Daniel Goma Jiménez – School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building,

Stranmillis Road, Belfast BT9 5AG, United Kingdom;
Department of Chemical Engineering, University of the Basque
Country (UPV/EHU), P.O. Box 644, Bilbao E48080, Spain;
ID orcid.org/0000-0002-9950-0122

Nancy Artioli – Department of Civil, Environmental,
Architectural Engineering and Mathematics, University of
Brescia, Via Branze, 43, Brescia 25123, Italy; ID orcid.org/0000-0002-3747-474X

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acssuschemeng.6c04868>

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Notes

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ABBREVIATIONS

DMC dimethyl carbonate
GC glycerol carbonate
GLY glycerol
IL ionic liquid
SIL supported ionic liquid

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