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Oxidative carboxylation of cycloheptene under solvent free conditions

Raiedhah Alsaiari

Chemistry department, college of science and art in sharurah, Najran University, Saudi Arabia

* Corresponding author's e-mail: kaade_77@hotmail.com

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Abstract: Efficient synthesis of cyclic carbonates is crucial due to their significant value in the chemical industry. A two-step procedure typically produces cyclic carbonates: first epoxidizing cycloheptene and then carboxylating it to form the cyclic carbonate. Combining these processes into a direct oxidative carboxylation reaction would be advantageous from an economic perspective, as it would eliminate the need for additional work-up procedures. Moreover, the effective capture and storage of CO₂, a significant contributor to global warming, would also be very advantageous. This study examines the process of oxidative carboxylation of cycloheptene. Supported ruthenium catalysts facilitate the epoxidation step, while a mixture of tetrabutylammonium bromide and zinc bromide enables the cycloaddition of carbon dioxide in the second step. The study evaluates the performance of the catalysts work in both phases and finds that the cyclic carbonate is produced with good selectivity using a one-pot, two-step method.

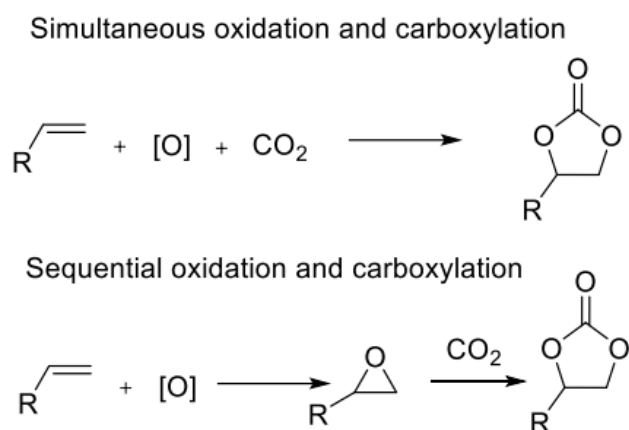
Introduction

The release of carbon dioxide, a significant component of greenhouse gas emissions, saw a substantial increase as a result of the burning of fossil fuels. This increase has directly and indirectly contributed to rising global temperatures and the emergence of environmental concerns (Li et al. 2023). Consequently, CO₂ has garnered significant attention in recent years, leading to extensive efforts in carbon capture, storage and utilization (Shao et al. 2022). CO₂ is a valuable C1 raw material for the synthesis of numerous high-value fine compounds, including methanol, formic acid, methane, olefins, amides, and cyclic carbonates. Its appeal lies in its abundance, low cost, non-toxic nature, and ready availability (Hou et al. 2023).

Extensive research over the past few decades has focused on the synthesis of cyclic carbonates via the cycloaddition of CO₂ to epoxides. This approach has resulted in the widespread use of cyclic carbonates in industries such as plastics, fuel additives, medical intermediates, and lithium batteries. These uses are largely attributed to the 100% atomic economy reaction (Pal et al. 2020, Bodzek 2022). Nevertheless, the use of epoxides as substrates in the CO₂ cycloaddition process faces challenges due to their high cost, toxicity, and instability under ambient conditions, which limits their practical implementation (Vely and Corma 2023). Currently, industrial synthesis of epoxides involves processes such as the chlorohydrin process, hydroperoxide process, and hydrogen peroxide combination

process. These methods produce epoxides from olefins but often result in significant costs and environmental concerns due to the formation of large quantities of by-products and wastewater. Since the production of epoxides necessitates the use of alkenes as an initial substrate, the direct oxidative carboxylation of olefins, as shown in Scheme 1, offers a more efficient and cost-effective strategy for synthesizing cyclic carbonates. This method eliminates the need for intermediate work-up operations, reducing both cost and environmental impact.

The conversion of olefins to cyclic carbonates via direct oxidative carboxylation involves two reactions: the epoxidation



Scheme 1: Approaches for oxidative carboxylation of olefins

of olefins and cycloaddition of CO₂ to the resulting epoxide. This method utilizes readily available olefin substrates and eliminates the need for epoxide separation, making it a more cost-effective and environmentally sustainable alternative to traditional approaches.

The oxidative carboxylation of olefins via direct methods has been recognized since 1962 (Verdol 1962). Nevertheless, the investigation of the epoxidation reaction and the cycloaddition of carbon dioxide (CO₂) to epoxides has mostly been conducted in isolation, with only a restricted body of literature addressing the integration of these processes (Han et al. 2015, Ramidi et al. 2015).

In most studies, the oxidants used were tert-butyl hydroperoxide (TBHP) (Maksimchuk et al. 2016, Evangelisti et al. 2017) or hydrogen peroxide (Sun et al. 2004). Molecular oxygen is the preferred oxidant due to its superior atom efficiency and environmentally friendly properties. However, it poses additional difficulties (Alsaari 2022, Alsaari 2022, Alsaari 2024). In the early twenty-first century, Aresta *et al.* documented the direct oxidative carboxylation of styrene, utilizing oxygen as the oxidizing agent. The catalysts employed were homogeneous rhodium complexes or various metal oxides, with dimethylformamide (DMF) serving as the solvent for the epoxidation of alkenes (Aresta and Dibenedetto 2002). Although dimethylformamide (DMF) was considered inert, it was subsequently demonstrated to act as an oxygen transfer agent, generating significant amounts of by-products, including N-formyl-N-methylformamide (Beier et al. 2012). This phenomenon diminishes the environmental benefits of utilizing oxygen as the oxidizing agent. Further advancements include the use of a homogeneous metalloporphyrin catalyst by Bai *et al.* to convert various olefins to cyclic carbonates. For styrene, the cyclic carbonate yield reached up to 89% (Bai and Jing 2010). Kumar et al. demonstrated the direct oxidative carboxylation of alkenes using a cobalt(II) acetylacetonate complex immobilized on magnetic chitosan, with isobutyraldehyde acting as a sacrificial reductant (Kumar et al. 2015). When carbon dioxide and oxygen were sequentially introduced as reaction gases, yields of up to 85% were achieved for propylene and butylene as starting materials.

The alignment of reaction conditions and catalyst suitability at each stage is crucial for the successful integration of the two phases. Previous studies have demonstrated that using tetrabutylammonium bromide (Bu₄NBr) as a catalyst in the cycloaddition reaction of carbon dioxide to epoxides leads to the deactivation of the MoO₂(acac)₂ catalyst used in the epoxidation step. This deactivation is thought to occur as a result of the breakdown of TBHP under the influence of bromide (Chen et al. 2011). To overcome this issue, the authors introduced tetrabutylammonium bromide (Bu₄NBr) only after the completion of the epoxidation step.

The objective of this investigation was to examine the feasibility of integrating two reaction steps: cycloheptene epoxidation and CO₂ cycloaddition to the formed epoxide. The study utilizes highly active supported ruthenium catalysts for the epoxidation of cycloheptene. Additionally, the catalytic system comprising Bu₄NBr and ZnBr₂ is examined for the cycloaddition of CO₂ to the generated epoxide, with the expectation that it will exhibit homogeneity under reaction conditions.

Experimental

The reagents utilized in this study were obtained from Sigma Aldrich and were utilized as supplied, including RuCl₃·xH₂O, cycloheptene, tert-butyl hydroperoxide (TBHP) (radical initiator), polyvinyl alcohol (PVA, Sigma-Aldrich, 80% hydrolyzed); sodium borohydride (NaBH₄, Sigma-Aldrich, 99.99%), TiO₂ and SiO₂. To provide a comparative analysis, three recognized techniques were used to synthesize the catalyst: sol-immobilization, wet impregnation and deposition precipitation. The quantity of catalyst metal deposited onto the support was expressed as a weight percentage.

Catalyst Preparation

Sol immobilization

A total of 2 g of ruthenium catalysts, with a 1% weight percentage, was synthesized using the sol-immobilization technique. An aqueous solution of RuCl₃·xH₂O was introduced into 450 mL of deionized water while being continuously stirred. The solution was then enriched with a newly prepared 1 wt% aqueous polyvinyl alcohol solution (Aldrich, >99%; PVA/Ru = 0.65 by weight). After 15 minutes of stirring, a newly prepared NaBH₄ solution (2.54 mL, 0.2 M, NaBH₄/Ru=5 by mol) was added, resulting in the formation of a dark-brown sol. The solution was stirred for a further 30 minutes, with the pH carefully lowered to 2 using a slow, dropwise addition of H₂SO₄. The colloidal mixture was then supplemented with 1.98 g of support (Aldrich) and stirred for 2 hours. Before use, the catalyst was filtered and extensively rinsed with around 2 liters of deionized water, and subsequent dried at 120 °C for 10 hours.

Wet-impregnation

To produce 0.5 g of supported metal catalyst using the wet-impregnation technique, the calculated quantity of RuCl₃·xH₂O was dissolved in an appropriate amount of distilled water. An exact quantity of support was introduced, and the mixture was evaporated while being continually agitated at 80 °C. Following a 16-hour drying process at 110 °C, the paste was pulverized into a fine powder and subjected to calcination at 300 °C for 3 hours, with a heating rate of 20 °C per minute.

Deposition precipitation

A catalyst composed of 1 wt% Ru/support was synthesized using the following methodology: 0.99 g of support material was mixed with 150 mL of distilled water and then agitated at 60 °C. A solution containing RuCl₃·xH₂O was then introduced, followed by the dropwise addition of a NaOH solution to maintain a stable pH of 9. After 1.5 hours of stirring, the solution was filtered, and the solid was rinsed with 1 L of distilled water. The catalyst underwent drying at 110 °C for 16 hours, followed by calcination in static air at 300 °C for 3 hours.

Reaction Procedures

The epoxidation processes were conducted using either a magnetically stirred, round-bottomed glass flask reactor with a 50 mL capacity, equipped with a reflux condenser, or a 50 mL Parr stainless steel autoclave with a Teflon inlet. The reactor was supplemented with cycloheptene, the catalyst,

and TBHP as a radical initiator. For autoclave reactions, the autoclave underwent three rounds of nitrogen purging prior to being pressurized to 10-15 bar with oxygen. The reaction mixture was continuously stirred at 80 °C for 24 hours. After cooling to room temperature, the solution was filtered, and the products were analyzed using gas chromatography. A Varian Star 3800 CX gas chromatograph equipped with a CP-wax 52 capillary column (25 m length, 0.35 mm ID, 0.2 micron film thickness) and a flame ionization detector (FID) was used for this purpose. Additionally, inductively coupled plasma mass spectrometry (ICP-MS) was performed using an Agilent 7900 ICP-MS in organic phase mode and a micromist nebulizer. Quantification was carried out by comparing the results to a calibration curve.

A 50 mL Parr stainless steel autoclave with a Teflon inlet was used to carry out the cycloaddition process. The autoclave was supplemented with epoxide, TBAB, and ZnBr₂. Prior to being charged with 15 bar CO₂, the reactor underwent three rounds of CO₂ purging. The reaction mixture was continuously stirred for a period of 5 to 16 hours with the temperature set at 80 °C. Once the solution had reached room temperature, it was filtered, and the reaction mixture was subjected to quantitative analysis using gas chromatography (as previously indicated). For qualitative analysis, the researchers used gas chromatography combined with mass spectrometry, specifically, the Walters GCT Premier GC coupled with an HP 6890N MS).

Cyclic carbonate was synthesized in a one-pot process using a 50 mL Parr stainless steel autoclave equipped with a Teflon inlet. The reactor was charged with ZnBr₂, Bu₄NBr, TBHP and cycloheptene. Prior to charging the autoclave with 10-20 bar CO₂ and 10 bar oxygen, the system underwent three oxygen purges. The reaction was conducted at 70-80 °C for a specified duration. Once the solution was cooled to ambient temperature, it was filtered, and the products were subsequently analyzed by gas chromatography according to the previously outlined procedure.

The epoxidation process was initially conducted in a one-pot, two-step methodology, either in an autoclave or a round-bottom flask, as previously described. After a 24-hour reaction, the reactor was depressurized and cooled to room temperature. Next, ZnBr₂ and Bu₄NBr catalysts were introduced into the reaction chamber. Following the reactor's closure, it was pressurized with 15 bar CO₂ and heated to 80 °C while being continuously stirred for three hours. Once the solution had been brought down to room temperature, it was filtered, and the products were subjected to gas chromatography analysis.

The following equation was used to calculate conversions based on corrected GC counts:

$$\text{Conversion factor (\%)} = \frac{\sum P_i}{(\sum P_i + \sum R_i)} \times 100 \quad (1)$$

Were:

P_i: the product selectivity I,

R_i: the reactant selectivity i

The calculation of selectivity was performed for each product as a percentage using equation (2).

$$\text{Selectivity (\%)} \text{ of product } i = \frac{P_i}{\sum P_i} \times 100 \quad (2)$$

Table 1: Surface area analysis for supported ruthenium catalysts

Catalyst	Surface area (m ² g ⁻¹)
TiO ₂	53
1%Ru/TiO ₂	46
Reused 1%Ru/TiO ₂	40

Results and Discussion

Characterization of supported ruthenium catalyst

BET

The presence of Ru within the support pores can be inferred by comparing the surface areas of the 1% Ru/TiO₂ catalyst with those of the undoped supports, as shown in Table 1. Similarly, the 1%Ru/TiO₂ catalyst exhibited a slight reduction in surface area, decreasing from 46 to 40 m² g⁻¹ after reuse. This decrease can likely be attributed to the adsorption of certain products and residual substrate on the catalyst surface. To minimize the margin of error, two independent measurements were conducted, resulting in a margin of error of 0.7 m² g⁻¹.

The characteristic XRD reflections of ruthenium were not observed, indicating that Ru was uniformly distributed across the TiO₂ support.

Oxidative Carboxylation of cycloheptene: One-pot approach

The study investigated the effectiveness of a 1% Ru/TiO₂ catalyst in the solvent-free epoxidation of cycloheptene. The reaction used TBHP as a radical initiator and air at atmospheric pressure as the main oxidant. One important factor influencing catalyst's activity is the preparation technique. Table 2 illustrates three different methods used to synthesize 1% Ru/TiO₂ catalyst. The catalysts prepared using the deposition-precipitation and wet-impregnation techniques exhibited similar activity levels. However, the sol-immobilization method produced catalysts with enhanced activity, likely due to a improved ruthenium dispersion and smaller nanoparticle dimensions. These findings

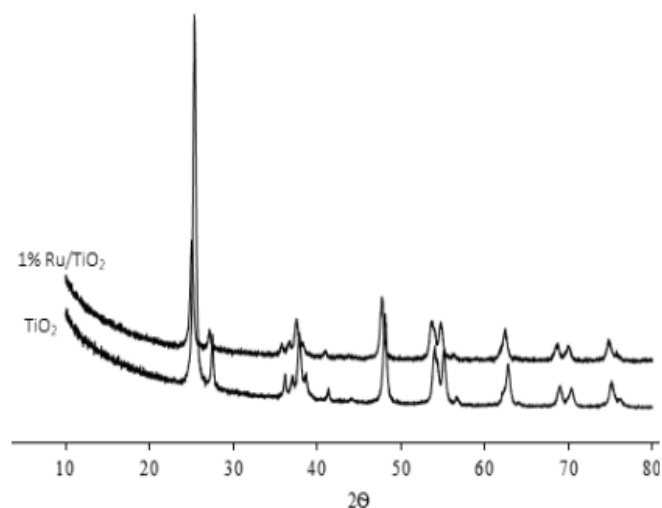


Fig 1: XRD patterns for TiO₂ and 1%Ru/TiO₂.

Table 2: Oxidation activity for cycloheptene with TBHP, TiO₂ and in the presence of 1%Ru/TiO₂ catalyst.

Catalyst	Reaction temperature (°C)	Conversion (%)	Selectivity (%)		
			Epoxide	Cy-one	Cy-ol
Blank	60	1.7	13	33	42
	70	5.6	14.2	31	44
TiO ₂	60	3.8	17	29	50
	70	6.4	18.8	44	30
1%Ru/TiO ₂ sol-immobilization	60	9.3	18	43	38
	70	12.6	23.4	45	29
1%Ru/TiO ₂ Wet-impregnation	70	10	19	47	27
1%Ru/TiO ₂ deposition precipitation	70	9.8	20.3	45	32
1%Ru/TiO ₂ [10 bar O ₂]	70	14.7	8	45	34

Reaction conditions: 1% Ru/TiO₂ (0.1 g), TBHP (0.01 mL), cycloheptene (5 mL), 900 rpm, 80°C, 24 h, atmospheric pressure.

suggest that sol-immobilization is the most effective method for synthesizing catalysts for cycloheptene epoxidation.

As shown in Table 2, both conversion and epoxide selectivity increased when compared to the blank reaction, which contained only the radical initiator. The enhanced selectivity and conversion rates can be attributed to the catalytic activity of the ruthenium-based catalysts. However, when the reaction was carried out under a pressure of 10 bar of oxygen, cycloheptene conversion increased at the expense of epoxide selectivity, highlighting a trade-off between these two factors.

Figure 2 displays the particle size distribution (PSD) and the transmission electron microscopy (TEM) analysis for the 1% Ru/TiO₂ catalyst synthesized using sol-immobilization method. The results indicate that the 1% Ru/TiO₂ sample predominantly consisted of nanoparticles, with the majority measuring less than 3-4 nm in size. Moreover, as shown in Fig. 2, the particle size distribution was relatively narrow, ranging from 1 to 7 nm. The enhanced effectiveness of this catalyst can be attributed to the improved Ru dispersion, which is directly linked to the small particles size.

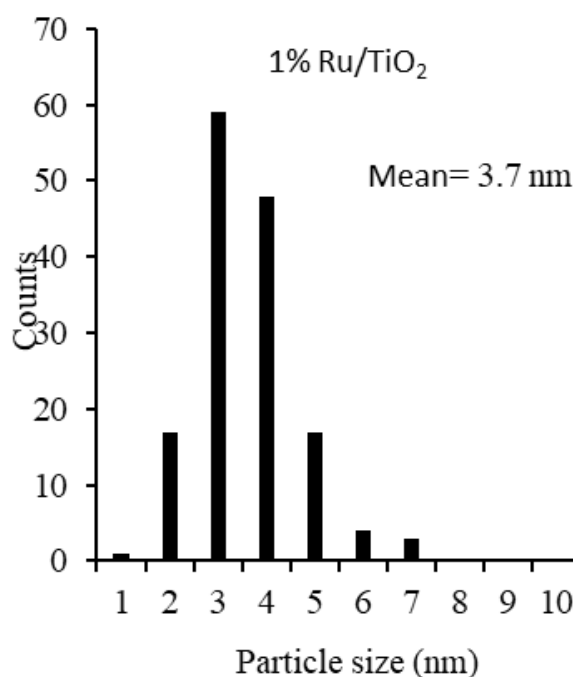
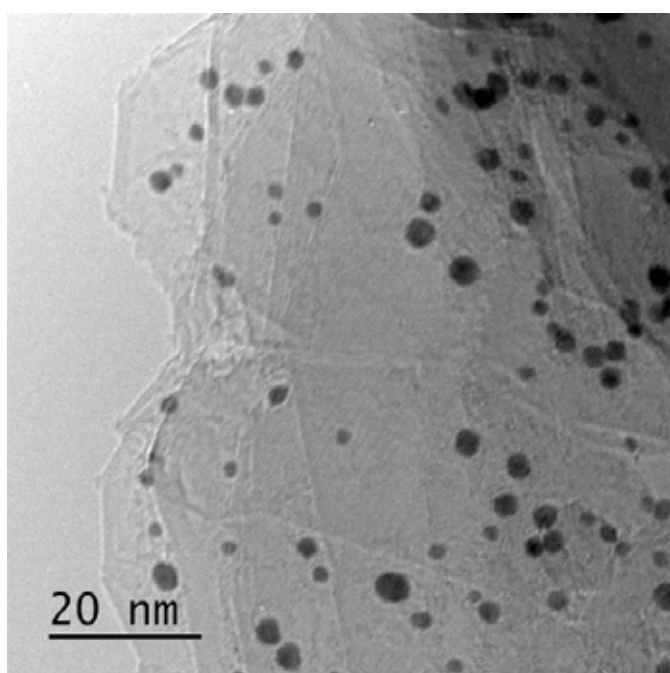


Fig 2: (a) Transmission electron microscopy (TEM) and (b) Particle size distribution (PSD) for 1% Ru/TiO₂ prepared by sol-immobilization method. Counts: number of occurrences of particles of indicated diameter within the sample assessed.

Table 3: Direct oxidative carboxylation of cycloheptene using 1% Ru/TiO₂- Bu₄NBr-ZnBr₂ catalyst

Catalyst	P _{O₂} (bar)	P _{CO₂} (bar)	Conversion (%)	Selectivity (%)	
				Epoxide	Cyclic carbonate
1% Au/TiO ₂ - Bu ₄ NBr-ZnBr ₂	10	10	18.5	2	3
	15	15	21.4	2.5	2.6
	15	10	20.2	3.1	3.2

Reaction conditions: 1% Ru/TiO₂ (0.1 g), Bu₄NBr (0.25 g), ZnBr₂ (0.1 g), cycloheptene (5 mL), 900 rpm, 80°C, 28h.

A comparable methodology could be employed to directly carboxylate cycloheptene, as evidenced by another study that previously reported remarkable outcomes in the direct oxidative carboxylation of styrene. In that study Napadensky and Sasson (1991) achieved styrene carbonate yields of up to 42% using a one-pot method with a Au/SiO₂-ZnBr₂/Bu₄NBr catalyst combination and TBHP as the main oxidant. Building on the effective catalytic properties of the heterogeneous 1% Ru/TiO₂ catalyst in converting cycloheptene into cyclic carbonate through aerobic epoxidation, a one-pot, single-step method was tested. This approach incorporated Bu₄NBr and ZnBr₂, which were expected to be uniformly distributed during the reaction. Oxygen served as the oxidizing agent, as outlined in Table 3. Based on the stoichiometric conversion of the epoxide, the selectivity towards cyclic carbonate was found to be unfavorable, falling below expectations, as shown in Table 3. In order to investigate potential deactivation issues, catalysts from both reaction stages were combined to analyze the individual steps contributing to the overall process.

Cycloaddition of CO₂ and epoxide in the presence of supported ruthenium catalysts

The used ruthenium catalysts were applied in the cycloaddition process, where carbon dioxide reacts with an epoxide, in order to evaluate their impact on the production of cyclic carbonate. Under the conditions tested, none of the catalysts used for epoxidation were effective in synthesizing cyclic carbonate,

Table 4: Effect of 1%Ru/TiO₂ catalyst on the cycloaddition of carbon dioxide to epoxide

Catalyst	Reaction time	Conversion (%)	Cyclic carbonate selectivity (%)
Blank	5	1	0
1% Ru/TiO ₂	5	1.5	0
1% Ru/TiO ₂ (0.35g)	5	1.5	0
Bu ₄ NBr-ZnBr ₂	5	54	57
	8	75	68
	16	80	69
1% Ru/TiO ₂ - Bu ₄ NBr-ZnBr ₂	16	80	67

Reaction conditions: 1% Ru/TiO₂ (0.1 g), Bu₄NBr (0.25 g), ZnBr₂ (0.1 g), epoxide (5 mL), 900 rpm, 80°C, 20 bar CO₂.

as shown in Table 4. Notably, a larger quantity of catalyst (0.35 g) was used compared to the amount (0.1 g) used in the previously reported epoxidation process. The carboxylation catalytic system, comprising Bu₄NBr and ZnBr₂ achieved a cyclic carbonate selectivity of 69% with an 80% conversion, as shown in Table 3. Importantly, the inclusion of the supported ruthenium catalyst did not adversely affect this exceptional outcome. These results indicate that the presence of the supported ruthenium catalyst has no effect on the activity of the Bu₄NBr and ZnBr₂ catalytic system. This observation is a positive indication of the potential optimization of the process.

Epoxidation of cycloheptene in presence of Bu₄NBr and ZnBr₂

Given that the presence of the supported ruthenium catalyst did not affect the synthesis of cyclic carbonates in the cycloaddition of carbon dioxide, further investigation focused on the epoxidation phase, specifically examining the impact of Bu₄NBr and ZnBr₂ in the reaction mixture. Typically, cyclic carbonates are synthesized from epoxides in an autoclave under a specific CO₂ pressure. Therefore, the aforementioned one-pot reaction was executed under elevated pressure conditions. Using 10-15 bar of oxygen for the epoxidation of cycloheptene resulted in a higher conversion but a lower epoxide selectivity (8.6%) compared to the selectivity of 23.4% observed in the epoxidation process at ambient pressure. When Bu₄NBr and ZnBr₂ were introduced into the epoxidation process, the epoxide selectivity significantly decreased, even with an increased reaction time. Furthermore, the addition of Bu₄NBr and ZnBr₂ to a radical initiator (TBHP)-only blank epoxidation reaction led to a reduction in conversion efficiency, with no discernible selectivity towards the epoxide. As shown in Table 5, the supported ruthenium catalysts became inactive when the salts were introduced. Based on these findings, it is evident that the epoxidation reaction becomes less selective with catalysts facilitating the cycloaddition reaction. This suggests that Bu₄NBr and ZnBr₂ are likely detrimental to the 1%Ru/TiO₂ catalyst. Therefore, it is clear that the current catalytic system may not be suitable for producing carbonates from alkenes in a single-pot reaction.

To better understand the origin of the catalyst deactivation and whether it can be mitigated, the nature of Ru catalyst deactivation was studied. The deactivation phenomenon process, characterized by rapid agglomeration and immobilization or deposition of the catalyst on the inner walls of the flask, was observed visually during the reaction in the round-bottom flask. Quaternary ammonium salts are known

Table 5: Effect of Bu₄NBr-ZnBr₂ on cycloheptene epoxidation using supported ruthenium catalysts under atmospheric pressure of air.

Catalyst	Co-catalyst	Conversion (%)	Epoxide selectivity (%)
Blank	-	5.6	14.2
Blank	Bu ₄ NBr-ZnBr ₂	1.3	0
1% Ru/TiO ₂	-	12.6	23.4
	(10 bar O ₂)	14.7	8
	(15 bar O ₂)	16.7	8.6
1% Ru/TiO ₂	Bu ₄ NBr-ZnBr ₂	6.4	9.5
1% Ru/TiO ₂ (28 h)	Bu ₄ NBr-ZnBr ₂	6.8	8.3
1% Ru/TiO ₂	ZnBr ₂	5.8	7.6

Reaction conditions: 1% Ru/TiO₂ (0.1 g), Bu₄NBr (0.25 g), ZnBr₂ (0.1 g), cycloheptene (5 mL, TBHP (0.01mL), 900 rpm, 80°C, 24 h, atmospheric pressure.

to break down hydroperoxides, which may contribute to the observed deactivation. Additionally, ZnBr₂ likely facilitates excessive oxidation of the epoxide, resulting in ring-opening and the formation of other byproducts. When supported ruthenium catalysts are combined with second-step catalysts, a decrease in epoxide selectivity is observed (as seen in Table 5) which likely due to these interactions. One potential reason for this phenomenon could be the micellar formations in the presence of quaternary ammonium salts. The polar salts adhere to the polar solid catalyst in the non-polar cycloheptene environment, while the hydrophobic butyl groups of quaternary ammonium salts create a micelle-like structure by surrounding the catalyst and penetrating the cycloheptene solution. Furthermore, the addition of zinc bromide alone may result in the formation of ZnO or the immobilization of ZnBr₂ on the surface of the catalyst. Both of these effects could explain the observed increase in selectivity towards cracking products, as presented in Table 5.

Direct Oxidative Carboxylation of cycloheptene: one-pot, two-step approach

One of the ongoing challenges in this system is preventing the deactivation of solid catalysts during the epoxidation reaction when using Bu₄NBr and ZnBr₂. To avoid catalyst deactivation from the sequential addition of Bu₄NBr and ZnBr₂, a one-pot, two-step method has been explored for the direct oxidative carboxylation of alkene. The cyclic carbonate selectivity was low when the epoxidation process was carried out under high oxygen pressure, even when Bu₄NBr and ZnBr₂ were not added during the first 24 hours, as shown in Table 2. Conversely, when the epoxidation process is initially performed at atmospheric pressure, as illustrated in Table 5, the epoxide selectivity reached 23.4%. To optimize the process, the reaction was completed by first performing the epoxidation step in a glass reactor under atmospheric pressure. The reaction mixture was then transferred to the autoclave for the cycloaddition step, where Bu₄NBr and ZnBr₂ were added, followed by purging with the required CO₂ pressure. The results of this procedure are summarized in Table 6. It is evident that the highest cyclic carbonate selectivity observed was 19% directly from cycloheptene, indicating that over 80% of the produced epoxide was successfully converted into cyclic carbonate. Based on these results, a two-step strategy currently appears to be the most optimal method for the oxidative carboxylation of cycloheptene.

Conclusion

The present study investigated the use of active supported ruthenium catalysts for the epoxidation of cycloheptene. When Bu₄NBr and ZnBr₂ were used in conjunction with the supported ruthenium catalyst in a single-step process for the oxidative carboxylation of cycloheptene, a decrease in cyclic carbonate selectivity was observed, primarily due to catalyst deactivation. Although the ruthenium catalyst did not interfere with the cycloaddition process, the presence of Bu₄NBr and ZnBr₂ caused a significant reduction in epoxide selectivity. An in-depth deactivation analysis revealed the formation of an organic polymer-like coating on the catalyst's surface in the presence of Bu₄NBr. To mitigate deactivation issues, a one-pot, two-step method for the oxidative carboxylation of cycloheptene is recommended. Performing the epoxidation

Table 6: One-pot two-step approach for the direct synthesis of cyclic carbonate starting from cycloheptene using 1% Ru/TiO₂-Bu₄NBr-ZnBr₂.

Entry	P _{O₂} (bar)	P _{CO₂} (bar)	Conversion of cycloheptene (%)	Selectivity (%)	
				Epoxide	Cyclic carbonate
1	10	20	14.7	1.5 (8)	5.7
	15	20	16.8	2 (8.6)	5.4
2	- ^b	20	12.9	2.4 (23.4)	19
3c	- ^b	20	12	3 (21.5)	17.3

Reaction conditions: 1% Ru/TiO₂ (0.1 g), Bu₄NBr (0.25 g), ZnBr₂ (0.1 g), cycloheptene (5 mL, TBHP (0.01mL), 900 rpm, 80°C, 24 h epoxidation+ 8 h cycloaddition of CO₂ with the formed 1,2-epoxydecane. Catalyst for the cycloaddition was added after the epoxidation step.

^a Epoxide selectivity after epoxidation step in brackets. ^b Atmospheric pressure of air. Reaction solution was transferred into an autoclave after the epoxidation. ^c 1% Au/SiO₂ (0.1 g).

step at atmospheric pressure can significantly improve the selectivity for cyclic carbonate.

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