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CO₂ transformation under mild conditions using tripolyphosphate-grafted KCC-1-NH₂

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Abstract

Fibrous nanosilica (KCC-1) as a catalyst support was investigated in terms of stability, recycling, and reusability. For the first time, CO_2 transformation was performed via the synthesis and application of KCC-1 together with sodium tripolyphosphate (STPP) and 3-aminopropyltriethoxysilane (APTES) as its functionalized derivative. Fo this goal, KCC-1/STPP NPs were applied to act as a nanocatalyst with excellent catalytic activities under green reaction conditions.

Keywords

Carbon dioxide, Nanoparticles (NPs), Green chemistry, TPP, KCC-1 Introduction

Green chemistry has recently attracted attention for coping with the difficulty of the transformation of CO_2 as a greenhouse gas. This problem can be solved by the application of CO_2 as a cheap, renewable, and safe C1 building block for synthesizing dimethyl carbonate (DMC) [1-2], formic acid (FA) [3], carbamic esters (urethanes) [4], cyclic carbonates (CCs)

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[5], methanol [6], and polycarbonates (PCs) [7] as useful organic compounds. CO_2 can be also used for carboxylative cyclization of propargylic amines to synthesize 2-oxazolidinones that significantly act as chemical intermediates [8] and chiral auxiliaries [9] and play an important role in antibacterial drugs [10]. CO_2 may be fixed by the mentioned process, which provides a very clean atom-economic reaction.

Periodic MesoporousOrganosilicas (PMOs) have been identified as a new class of functionalized ordered nanoporoussilicas. They aresynthesized by simultaneously hydrolyzing and condensing organic-bridged alkoxysilane precursors. These materials have been recently studied for their high surface areas, tuneable pore sizes and volumes, robust stabilities, and excellent lipophilicities. Compared to ordered mesoporoussilicas carrying terminal functional groups, PMOs have their functional groups embedded homogeneously inside their walls instead of pore fibers, thus providing an improved mechanical and hydrothermal stability. Numerous PMOs have recently been employed in association with their varied bridging ligands of organic functional groups as supporters and catalysts in several chemical processes. In a typical chemical process, their metal contents can be readily recovered and reused [11-22]. Preparation of metal-containing PMOs is usually performed by either impregnating metal complexes into PMO samples with proper ligands or hydrolyzing and co-condensing tetraethyl orthosilicate (TEOS) bridged with metal complexes in the presence of cationic surfactant as a template.

KCC-1 serves as an excellent nominated support for designing efficient nanocatalysts that satisfy the desired conditions, KCC-1 high surface area is its unique feature resulted from its fibrous morphology rather than mesoporous channels found in SBA-15 and MCM-41 [23-28]. Functionalization has been previously reported to be done through modification of KCC-1 fibers following its synthesis. During the modification process, KCC-1-NH₂ is involved in a reaction with APTES and then as a ligand or pseudo-chelator for controlling metal leaching [29-34]. In this study, the effectiveness of KCC-1 fibrous morphology in a variety of applications was compared with that of the conventional ordered mesoporous silica. Mild reaction conditions were considered for this green catalyst [35-39]. We developed a new stable and sustainable catalyst support via KCC-1/STPP bond [40]. We believe that this unique silica-supported catalyst is very useful as providing significantly enhanced accessibility to active sites. As a nano-labyrinth, KCC-1/STPP holds STPP, which is used for chemoselectively synthesizing CCs (Scheme 1).

Results and discussion

The structure of the KCC-1/ATPP proposed interaction of tripolyphosphate with aminopropyltriethoxysilane within the fibers of KCC-1 is shown in scheme 2. We were intrigued by the possibility of applying nanotechnology for designing a novel, active, and recyclable recoverable nano-catalyst.

Having proven the correct and complete synthesis of the catalyst, its performance and stability were tested by the syntheses of compounds 1-4. To optimize the reaction conditions and obtain the best catalytic activity, the reaction of CO₂ and 1-butyl-2-phenylaziridine for the synthesis of 5-aryl-2oxazolidinones (Compound 1), the reaction of CO2 and 2-methy-4-phenylbut-3-yn-2-ol for the synthesis of α -alkylidene CCs (Compound 2), the reaction of CO₂ and propylene oxide for the preparation of CCs (Compound 3), and the reaction of CO2 and 2-aminobenzonitrile for the synthesis of quinazoline-2,4(1H,3H)-dione (Compound 4) were employed as the desired models to be conducted under different reaction parameters, such as catalyst amount, temperature, time, and solvent. Initially, the reactions were carried out in several solvents to study the catalyst efficiency. In this research, conventional heating was applied for the synthesis of Compound 1 in the presence 0.7 mg of the catalyst at a CO₂ pressure of 0.5 bar at room temperature for 30 min under solvent-free conditions. The conditions for the synthesis of Compound 2 in the presence 0.7 mg of the catalyst included heating at 80°C at a CO₂ pressure of 1 bar for 120 min under solvent-free conditions. The synthesis of Compound 3 in the presence of 0.7 ng of the catalyst was conducted by heating it at 100oC at a CO2 pressure of 1 bar for 60 min under solvent-free conditions. Finally, the more efficient conditions of heating at 70°C in the presence of 0.7 mg of the catalyst at a CO₂ pressure of 1.5 bar for 50 min under solvent-free conditions were found for the synthesis of Compound 4 (Table 1).

For further investigating the catalyst efficiency, different control experiments were performed, the information of which are displayed in Table 2. Initially, the standard reaction with KCC-1 revealed the formation of none of the desired product after 1 h of the reaction time (Table 2, Entry 1). Also, no reaction was observed when KCC-1–NH₂ was utilized as the catalyst (Table 2, Entry 2). APTES could not provide a satisfactory catalytic activity under mild reactions. Based on these disappointing results, we continued the studies to ameliorate the product yield by adding tripolyphosphate (TPP). Notably, there were many differences in the reaction yields when the reaction was carried out with KCC-1/STPP NPs and TPP nano-catalyst. These results demonstrated that –NH₂ and TPP did not have any catalytic roles individually (Table 2, Entries 2 and 3). These observations showed that the reaction cycle was simultaneously catalyzed by –NH₂ and TPP species supports on KCC-1/STPP nanostructure (Table 2, Entry 4). Thus, KCC-1/STPP was applied in the subsequent studies because of its high reactivity and selectivity and easy separation. Also, the nano-catalyst activity and selectivity could be manipulated by tailoring its chemical and physical properties, such as size, shape, composition, and morphology. To assess the exact impact of KCC-1 presence in the catalyst, KCC-

1/STPP NPs were compared with SiO₂/ATPP NPs. To this end, we examined SiO₂/STPP and KCC-1/ATPP NPs, which had similar compositions, but different structures. When SiO₂/STPP was used as the catalyst, the desired product showed a fair-to-average yield, while KCC-1/STPP NPs provided a good yield (Table 2, Entries 4 and 5).

study the prospective and general applicability of the developed protocol, the carboxylative cyclization reactions of CO_2 with a variety of aziridines were examined under optimized reaction conditions (Table 3). TPP-functionalized KCC-1-NH2 NPs had a very high basic catalytic activity and excellent regioselectivity towards the cycloaddition of CO2 with aziridines. In each case, 5-aryl-2-oxazolidinones were obtained with excellent isolated yields in the presence of KCC-1/STPP (Scheme 3).

Propargyl alcohols associated with a variety of alkyl and aryl substituents at the propargylic position were effective substrates to give the corresponding carbonates of 2a–2d with good-to-excellent yields even under the mentioned CO2 conditions (Scheme 4, Table 4).

Since KCC-1/STPP was the most active one-component catalyst, it was tested for the conversions of other terminal epoxides into the corresponding CCs (3a–1) (Scheme 5), the results of which are exhibited in Table 5. In each case, CCs were obtained with good-to-excellent isolated yields after 100 min using 0.7 mg of the catalyst at a constant CO_2 pressure at 100°C under solvent-free conditions.

KCC-1/STPP was also tested for the conversions of the other six 2-aminobenzonitriles into quinazoline-2,4(1H,3H)-diones (4a-f) (Scheme 6), the results of which are represented in Table 6. In each case, quinazoline-2,4(1H,3H)-diones were obtained with good-to-excellent isolated yields in the presence of KCC-1/STPP NPs.

We compared the catalytic performance of our catalyst with those reported for the syntheses of 5-aryl-2-oxazolidinone α -alkylidene CC, quinazoline-2,4(1H,3H)-dione, and CCs in the literature. Tables 7-10 clearly demonstrate that a lower temperature and CO₂ pressure, minimum catalyst amount, and shorter reaction time are required for CO₂ transformation using KCC-1/STPP NPs. (see also Figure S 1, Supplemental Materials).

It is important to note that the heterogeneous property of KCC-1/STPP facilitates its efficient recovery from the reaction mixture during the work-up procedure. The activity of the recycled catalyst was also examined under the optimized conditions. After the completion of the reaction, the catalyst was separated by filtration, washed with methanol, and dried at the pump. The recovered catalyst was reused for 10 consecutive cycles without any significant loss of the catalytic activity (Figure S1). Inductively Coupled Plasma (ICP) analysis showed that the amount of STPP leaching into the

reaction mixture was very low (0.3 ppm). These observations indicated that the catalyst was stable and could tolerate the present reaction conditions.

Experimental

Materials and Methods

The chemical materials were purchased from Fluka and Merck in high purities. Their melting points determined in open capillaries by using an Electrothermal 9100 apparatus were uncorrected. FT-IR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. Their morphologies were analyzed using High-Resolution Transmission Electron Microscopy (HRTEM) on a JEOL transmission electron microscope operating at 200 kV. The phosphorous content of the catalyst was determined by an OPTIMA 7300DV ICP analyzer. The X-ray powder diffraction data were obtained by using Bruker D8 Advance with Cu karadition. The Thermo-Gravimetric Analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10°C min–1 under nitrogen. NMR spectra were recorded in CDCl3 on a BrukerAvance DRX-400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The purity determinations of the products and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

General Procedure for the Preparation of KCC-1 NPs

Tetraethylorthosilicate (TEOS) (2.5 g) was dissolved in a solution of cyclohexane (30 mL) and 1pentanol (1.5 mL). A stirred solution of cetylpyridinium bromide (CPB 1 g) and urea (0.6 g) in water (30 mL) was then added. The resulting mixture was continually stirred at room temperature for 45 min and then placed in a teflon-sealed hydrothermal reactor to be heated at 120°C for 5 h. The formed silica was isolated by centrifugation, washed with deionized water and acetone, and dried in a drying oven. This material was then calcined in air at 550°C for 5 h. [41]

General Procedure for the Preparation of KCC-1-NH₂ NPs

KCC-1 NPs (2 mmol) and THF (20 mL) were mixed together in a beaker and then, NaH (20 mmol) was dispersed in the mixture via ultrasonication. APTES (22 mmol) was added drop-wise at room temperature and stirred at 60°C for further 16 h. The resultant products were collected and washed with ethanol and deionized water in sequence and then dried under vacuum at 60°C for 2 h for further use [41].

General Procedure for the Preparation of KCC-1/ATPP NPs

TPP (5 mmol) was dispersed in dry CH_2Cl_2 (20 mL), to which KCC-1-NH₂ (0.1 g) nanoparticles were then added. Afterwards, the mixture was heated up to 60°C under nitrogen atmosphere for 12 h. The

resulting solid was separated by filtration and washed 3 times with CH_2Cl_2 , ethanol, and water. After drying it under vacuum at room temperature, KCC-1/STPP was obtained as a white powder [41].

General procedures for preparation of 5-aryl-2-oxazolidinones (Compound 1)

1-butyl-2-phenylaziridine (1 mmol) and KCC-1/STPP NPs (0.7 mg) were mixed together. The autoclave was closed, purged twice with CO2 gas, pressurized to 0.5 MPa of CO_2 , and heated at room temperature for 30 min. Then, the reactor was cooled to ambient temperature and the resulting mixture was transferred to a 50 mL round-bottom flask. During completion, the reaction progress was monitored by TLC. After completion, EtOH was added to the reaction mixture and the catalyst was separated by filtration. Then, the solvent was removed from the solution under reduced pressure and the resulting product was purified by recrystallization using n-hexane/ethyl acetate.

General procedures for preparation of a-alkylidene cyclic carbonates(Compound 2)

KCC-1/STPP NPs (0.7 mg) and 2-methy-4-phenylbut-3-yn-2-ol (1 mmol) were charged into the reactor vessel without using any co-solvent. The reactor vessel was placed under 1 MPa of CO₂ and then heated to 80°C for 120 min. Next, the reactor was cooled to ambient temperature and the resulting mixture was transferred to a 50-mL round-bottom flask. During completion, the reaction progress was monitored by TLC. Upon completion, EtOH was added to the reaction mixture and the catalyst was separated by filtration. Then, the solvent was removed from the solution under reduced pressure and the resulting product was purified by recrystallization using n-hexane/ethyl acetate.

General procedures for preparation of cyclic carbonate (Compound 3)

KCC-1/STPP NPs (0.7 mg) and epoxide (1 mmol) were charged into the reactor vessel without using any co-solvent. The reactor vessel was placed under 1 MPa of CO_2 and heated to 100°C for 60 min. Then, the reactor was cooled to ambient temperature and the resulting mixture was transferred to a 50 mL round-bottom flask. During completion, the reaction progress was monitored by TLC. After being completed, EtOH was added to the reaction mixture and the catalyst was separated by filtration. Next, the solvent was removed from the solution under reduced pressure and the resulting product was purified by recrystallization using n-hexane/ethyl acetate.

General procedures for preparation of quinazoline-2,4(1H,3H)-dione (Compound 4)

2-aminobenzonitrile (1 mmol) and KCC-1/STPP NPs (0.7 mg) were mixed together. The autoclave was closed, purged twice with CO_2 gas, pressurized to 1.5 MPa of CO_2 , and heated at 70oC for 50 min. Then, the reactor was cooled to ambient temperature and the resulting mixture was transferred to a 50 mL round-bottom flask. During completion, the reaction progress was monitored by TLC. Following its completion, EtOH was added to the reaction mixture and the catalyst was separated by filtration. Afterwards, the solvent was removed from the solution under reduced pressure and the resulting product was purified by recrystallization using n-hexane/ethyl acetate. The products are known and their sample characterization data is presented in the Supplemental Materials.

Conclusions

In summary, we reported a novel design of a catalyst support via KCC-1-NH₂ bond of TPP (KCC-1/STPP), which exhibited an excellent catalytic activity with the syntheses of 5-aryl-2-oxazolidinones, α -alkylidene CCs, CC, and quinazoline-2,4(1H,3H)-dione. This synthetic method provided a green method for effectively preparing a low-cost ionic liquid-based catalyst as a promising approach to the development of other useful materials. The significant features of this newly developed procedure were easy separation of the catalyst from the reaction mixture based on heterogeneous properties, as well as its reusability, operational simplicity, and high yields.

References

- 1 He, J. M.; Sun, Y.; Han, B. Angew. Chem. Int. Ed., 2013, 52, 9620-9633.
- 2 Honda, M.; Tamura, M.; Nakagawa Y.; Tomishige, K. Catal. Sci. Technol., 2014, 4, 2830-2845.
- 3 Tanaka, R.; Yamashita, M.; Nozaki, K. J. Am. Chem. Soc., 2009, 131, 14168-14169.
- 4 Yoshida, M.; Hara, N.; Okuyama, S. Chem. Commun., 2000, 36, 151-152.
- 5 Vara, B. A.; Struble, T. J.; Wang, W.; Dobish, M. C.; Johnston, J. N. J. Am. Chem. Soc., 2015, 137, 7302-7305.
- Wesselbaum, S.; vomStein, T.; Klankermayer, J.; Leitner, W. Angew. Chem., Int. Ed., 2012, 51, 7499-7502.
- 7 Darensbourg, D. J.; Moncada, A. I.; Choi, W.; Reibenspies, J. H. J. Am. Chem. Soc.,
 2008, 130, 6523-6533.
- § Aurelio, L.; Brownlee, R. T. C.; Hughes, A. B. Chem. Rev., 2004, 104, 5823-5846.
- ⁹ Chung, C. W. Y.; Toy, P. H. *Tetrahedron: Asymmetry*, **2004**, *15*, 387-399.
- 10 Mukhtar, T. A.; Wright, G. D. Chem. Rev., 2005, 105, 529-542.
- 11 Wan, H.; Wu, Z.; Chen, W.; Guan, G.;Cai, Y.; Chen, C.; Li, Z.; Liu, X. J. Mol. Catal.
 A: Chem., 2015, 398, 127-132.
- 12 Litschauer, M.; Neouze, M.A. J. Mater. Chem., 2008, 18, 640-646.

- 13 Sadeghzadeh, S.M. Catal. Sci. Technol., 2016, 6, 1435–1441.
- 14 Zhang, Y.; Zhang, Y.; Pei, Q.;Feng, T.; Mao, H.; Zhang, W.; Wu, S.; Liu, D.; Wang, H.; Song, X.M. Appl. Surf. Sci., 2015, 346, 194-200.
- 15 Li, P.H.; Li, B.L.; Hu, H.C.; Zhao, X.N.; Zhang, Z.H. Catal. Commun. 2014, 46, 118-122.
- 16 Sobhani, S.; Honarmand, M. Appl. Catal., A, 2013, 467, 456-462.
- 17 Hamadi, H.;Kooti, M.;Afshari, M.;Ghiasifar, Z.; Adibpour, N. J. Mol. Catal. A: Chem. 2013, 373, 25-29.
- 18 Liu, Y.;Tian, A.; Wang, X.; Qi, J.; Wang, F.; Ma, Y.; Ito, Y.; Wei, Y. J. Chromotogr. A, 2015, 1400, 40-46.
- Liu, W.; Wang, D.; Duan, Y.; Zhang, Y.; Bian, F. Tetrahedron Lett., 2015, 56, 1784-1789.
- 20 Sadeghzadeh, S.M. Catal. Commun., 2015, 72, 91-96.
- 21 Sadeghzadeh, S. M. Microporous Mesoporous Mater., 2016, 234, 310-316.
- 22 Wang, P.; Kong, A.G.; Wang, W.J.; Zhu, H.Y.; Shan, Y.K. Catal. Lett., 2010, 135, 159-164.
- 23 Sadeghzadeh, S. M. RSC Adv., 2015, 5, 58947-68952.
- 24 Sadeghzadeh, S.M.; Zhiani, R.; Emrani, S.; Abasian, M. J. Organomet. Chem., 2018, 855, 1-6.
- 25 Polshettiwar, V.; Cha, D.; Zhang, X. X.; Basset, J. M. Angew. Chem., Int. Ed., 2010, 49, 9652-9656.
- 26 Lilly Thankamony, A.S., Lion, C.; Pourpoint, F.; Singh, B.; Perez Linde, A.J.; Carnevale, D.; Bodenhausen, G.; Vezin, H.; Lafon, O.; Polshettiwar, V. Angew. Chem. Int. Ed. 2015, 54, 2190-2193.
- 27 Bouhrara, M.; Ranga, C.; Fihri, A.; Shaikh, R. R.; Sarawade, P.; Emwas, A. H.; Hedhili, M. N.; Polshettiwar, V. ACS Sustainable Chem. Eng., 2013, 1, 1192-1199.
- 28 Dhiman, M.; Chalke, B.; Polshettiwar, V. ACS Sustainable Chem. Eng., 2015, 3, 3224-3230.
- 29 Fihri, A.; Bouhrara, M.; Cha, D.; Almana, N.; Polshettiwar, V. ChemSusChem 2012, 5, 85-89.
- 30 Fihri, A.; Bouhrara, M.; Patil, U.; Cha, D.; Saih, Y.; Polshettiwar, V. ACS Catal., 2012, 2, 1425-1431.
- 31 Sadeghzadeh, S.M.; Zhiani, R.; Emrani, S.RSC Adv., 2017, 7,24885-24894.

- 32 Le, X.; Dong, Z.; Liu, Y.; Jin, Z. Huy, T. D.;Leb, M.; Ma, J. J. Mater. Chem. A, 2014, 2, 19696-19706.
- 33 Le, X.; Dong, Z.; Li, X.; Zhang, W.; Le, M.; Ma, J.Catal. Commun., 2015, 59, 21-25.
- 34 Sadeghzadeh, S.M.; Zhiani, R.; Emrani, S. RSC Adv., 2017, 7, 32139-32145.
- 35 Singh, R.; Bapat, R.; Qin, L.; Feng, H.; Polshettiwar, V. ACS Catal., 2016, 6, 2770-2784.
- 36 Sun, Z.; Li, H.; Guo, D.; Sun, J.; Cui, G.; Liu, Y.; Tian, Y.; Yan, S. J. Mater. Chem. C, 2015, 3, 4713-4722.
- 37 Yu, K.; Zhang, X.; Tong, H.; Yan, X.; Liu, S. Mater. Lett. 2013, 106, 151-154.
- 38 Dong, Z.; Le, X.; Dong, C.; Zhang, W.; Li, X.; Ma, J. Appl. Catal, B, 2015, 162, 372-380.
- 39 Dong, Z.; Le, X.; Li, X.; Zhang, W.; Dong, C.; Ma, J. Appl. Catal., B, 2014, 158-159, 129-135.
- 40 Le, X.; Dong, Z.; Zhang, W.; Li, X.; Ma, J. J. Mol. Catal. A: Chem., 2014, 395, 58-65.
- 41 Sadeghzadeh, S.M.; Zhiani, R.; Khoobi, M.; Emrani, S. Microporous Mesoporous Mater., 2018, 257, 147-153.
- 42 Nale, D.B.; Rana, S.; Parida, K.; Bhanage, B.M. Appl. Catal., A, 2014, 469, 340-349.
- 43 Watile, R.A.; Bhanage, B.M. Indian J. Chem., 2012, 51, 1354-1360.
- 44 Du, Y.; Wu, Y.; Liu, A.H.; He, L.N. J. Org. Chem., 2008, 73, 4709-4712.
- 45 Wu, Y.; He, L.N.; Du, Y.; Wang, J.Q.; Miao, C.X.; Li, W. Tetrahedron, 2009, 65, 6204-6210.
- 46 Yang, Z.Z.: He, L.N.; Peng, S.Y.; Liu, A.H. Green Chem., 2010, 12, 1850-1854.
- 47 Song, Q.W., Yu, B.; Li, X.D.; Ma, R.;Diao, Z.F.; Li, R.G.; Li, W.; He, L.N. Green Chem., 2014, 16, 1633-1638.
- 48 Wang, M.Y.; Song, Q.W.; Ma, R.; Xie, J.N.; He, L.N. Green Chem., 2016, 18, 282-287.
- 49 Sun, J.; Ren, J.; Zhang, S.; Cheng, W. Tetrahedron Lett,, 2009, 50, 423-426.
- 50 Lan, D.-H.; Chen, L.; Au, C.-T.; Yin, S.-F. Carbon 2015, 93, 22-31.
- 51 Xiao, L.; Su, D.; Yue, C.; Wu, W. J. CO₂Utiliz. 2014, 6, 1-6.

- 52 Mirabaud, A.; Mulatier, J.C.; Martinez, A.; Dutasta, J.P.; Dufaud, V. ACS Catal., 2015, 5, 6748-6752.
- 53 Mizuno, T.; Iwai, T.; Ishino, Y. Tetrahedron Lett., 2004, 45, 7073-7075.
- 54 Patil, Y. P.; Tambade, P. J.; Jagtap, S. R.; Bhanage, B. M. Green Chem. Lett. Rev. 2008, 1, 127-132.
- 55 Patil, Y. P.; Tambade, P. J.; Deshmukh, K. M.; Bhanage, B. M. Catal. Today, 2009, 148, 355-360.
- 56 Patil, Y. P.; Tambade, P. J.; Parghi, K. D.; Jayaram, R. V.; Bhanage, B. M. Catal. Lett., 2009, 133, 201-208.
- 57 Gao, J.; He, L. N.; Miao, C. X.; Chanfreau, S. Tetrahedron, 2010, 66, 4963-4067.
- 58 Jiarong, L.; Xian, C.; Daxin, S.; Shuling, M.; Qing, L.; Qi, Z.; Jianhong, T. Org. Lett., 2009, 11, 1193-1196.

Table 1Optimization of the reaction conditions for the syntheses of Compound 1, 2, 3, and 4 in terms of temperature, CO₂ pressure, catalyst amount, time, and product yield

-	Entry	CO_2	Temp.	Time	Amount	\bigtriangledown	Yield (%) ^a		
		pressure	(°C)	(min)	catalyst	Compound	Compound	Compound	Compound
		(MPa)		\bigcirc	(6)	1	2	3	4
-	1	2	120	140	0.3	61	23	42	50
	2	2	120	140	0.5	82	55	50	68
	3	Ź	120	140	0.7	95	94	97	93
	4	2	120	140	0.9	95	94	97	93
\mathcal{C}	5	2	100	140	0.7	95	94	97	93
	6	2	80	140	0.7	95	94	73	93
	7	2	60	140	0.7	95	54	56	82
	8	2	40	140	0.7	95	22	25	58
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9	1.5	100	140	0.7	95	94	97	93
10	1	100	140	0.7	95	94	97	79
11	0.5	100	140	0.7	95	32	49	28
12	1.5	100	120	0.7	95	94	97	93
13	1.5	100	100	0.7	95	79	97	93
14	1.5	100	80	0.7	95	62	97	93

^a Isolated yields.

 Table 2The impacts of different catalysts for the syntheses of Compounds 1-4a

Entry	Catalyst	Yield (%) ^b				
		Compound 1	Compound 2	Compound 3	Compound 4	
1	KCC-1	-		- <	-	
2	KCC-1-NH ₂	-		-	-	
3	TPP	-	<u> 10-</u> n	-	-	
4	KCC-1/ATPP	95	94	97	93	
5	SiO ₂ /ATPP	65	52	39	48	

^aReaction conditions: aziridune, propargyl alcohol, epoxide, or 2-aminobenzonitrile (1 mmol), catalyst (3mg), CO₂, 2 MPa at 100 °C in 180 min.

^bIsolated yield.

Table3The syntheses of 5-aryl-2-oxazolidinone derivatives catalyzed by KCC-1/ATPP NPsa

Entry	R ₁	Compound	Yield (%) ^b
1	Н	1a	95
2	CH_3	1b	93
3	CH_2CH_3	1c	96

4	CH ₂ CH ₂ CH ₃	1d	92
5	CH ₂ CH ₂ CH ₂ CH ₃	1e	97

^aReaction condition: aziridine derivatives (1 mmol), KCC-1/ATPP NPs (0.7 mg), CO₂ 0.5 MPa at room temperature in 30 min.

^bYield refers to isolated product.

Table 4:	The syntheses	of α-alkylidene	CC derivatives	catalyzed by	KCC-1/ATPP NPsa
	2	2		2 2	

Entry	R ₁	R_2	Compound	Yield (%) ^b
				$\left(\right)$
1	Н	CH ₃	2a	94
2	Η	CH ₂ CH ₃	2b	90
3	Н	Ph	2c	92
4	Ph	CH_3	2d	89
			\sim	

^aReaction condition: propargyl alcohol derivatives (1 mmol), KCC-1/ATPP NPs (0.7 mg), CO₂ 1 Mpa at 80 °C in 120 min.

^bYield refers to isolated product.

Table 5The syntheses of CC derivatives catalyzed by KCC-1/STPP NPsa

	\bigwedge			
	Entry	R	Compound	Yield (%) ^b
	1	Me	3a	97
	2	Ph	3b	90
\mathcal{C}	3	$4-ClC_6H_4$	3с	92
	4	$4-BrC_6H_4$	3d	89
	5	HOCH ₂	3e	83
V	6	ClCH ₂	3f	94

7	PhOCH ₂	3g	88
8	Bu ⁿ	3h	91
9	Oct ⁿ	3i	93
10	$4-MeC_6H_4$	3j	91
11	4-MeSC ₆ H ₄	3k	86
12	Et	31	94

^aReaction condition: epoxide derivatives (1 mmol), KCC-1/ATPP NPs(0.7 mg), CO₂ i MPa at 100 °C in 100 min.

^bYield refers to isolated product.

Table 6The syntheses of quinazoline-2,4(1H,3H)-dione derivatives catalyzed by KCC-1/STPP NPs

Entry	R	Compound	Yield (%)
			\searrow
1	Н	4a	93
2	D.		05
2	Br	42	95
3	Б		00
3		40	90
4	CI	4d	94
			<i>.</i>
5	Me	4e	89
6	NO_2	4f	91
\sim			

^aReaction condition: 2-aminobenzonitrile (1 mmol), KCC-1/ATPP NPs(0.7 mg), CO₂ 1.5 MPa at 50 °C in 70 min.

^bYield refers to isolated product.

Table7A comparison of the catalytic efficiency of KCC-1/STPP NPs with various catalysts for the synthesis of 5-aryl-2-oxazolidinone

-	Entry	Catalyst	MPa (CO ₂)	Solvent	Temperature (C ⁰)	Amount Catalyst	Time	Yield (%)
-	1	Amine@MCM-41	5	-	40	25 wt%	8 h	92 ^[42]
	2	CSHB	5	-	70	20 wt%	7 h	61 ^[43]
	3	PEG ₆₀₀₀	8	-	100	0.8 mol (%)	5 min	_[44]
	4	$\mathrm{Bu}_4\mathrm{NBr}$	8	-	100	0.8 mol (%)	5 min	6[44]
	5	Bu ₄ NBr/PEG ₆₀₀₀	8	-	100	0.8 mol (%)	5 min	38[44]
	6	PEG ₆₀₀₀ (NBu ₃ Br) ₂	8	-	100	0.8 mol (%)	5 min	71 ^[44]
	7	I_2	8	CH_2Cl_2	40	20 mol (%)	4 h	30 ^[45]
	8	LiBr	8	CH_2Cl_2	40	20 mol (%)	4 h	31 ^[45]
	9	AlCl ₃	8	CH_2Cl_2	40	20 moi (%)	4 h	22 ^[45]
	10	$ZnCl_2$	8	CH_2Cl_2	40	20 mol (%)	4 h	1 ^[45]
	11	Morpholine	8	-	40	20 mol (%)	4 h	3 ^[45]
	12	ZrOCl ₂ .8H ₂ O	8	-	40	20 mol (%)	4 h	41 ^[45]
	13	DMAP	8	$\overline{)}$	40	20 mol (%)	4 h	1 ^[45]
	14	DBN	8	<u> </u>	40	20 mol (%)	4 h	$0.4^{[45]}$
	15	DBU	8	-	40	20 mol (%)	4 h	_[45]
	16	DABCO	8	CH_2Cl_2	40	20 mol (%)	4 h	_[45]
	17	НМТА	8	CH_2Cl_2	40	20 mol (%)	4 h	_[45]
	18	{C4DABCO]Br	6	-	90	1 mol (%)	3 h	85 ^[46]
(C	19	[C₄DABCO]OH	6	-	90	1 mol (%)	3 h	56 ^[46]
	20	[C ₄ DABCO]Cl	6	-	90	1 mol (%)	3 h	43 ^[46]
5	21	[C ₈ DABCO]Br	6	-	90	1 mol (%)	3 h	75 ^[46]
	22	[C ₈ DABCO]BF ₄	6	-	90	1 mol (%)	3 h	26 ^[46]

23	[C ₈ DABCO]PF ₆	6	-	90	1 mol (%)	3 h	19 ^[46]
24	[C ₈ DABCO]NTf ₂	6	-	90	1 mol (%)	3 h	11 ^[46]
25	[C ₁₂ DABCO]Br	6	-	90	1 mol (%)	3 h	70 ^[46]
26	[C ₄ MIm]Br	6	-	90	1 mol (%)	3 h	76 ^[46]
27	[C ₄ MIm]BF ₄	6	-	90	1 mol (%)	3 h	14 ^[46]
28	KCC-1/ATPP	0.5	-	r.t.	0.4 mol (%)	30 min	95

^aReaction conditions: aziridine (1 mmol), and CO₂ in different solvents and in different amounts of catalyst, temperature, and time.

Table8A comparison of the catalytic efficiency of KCC-1/STPP NPs with various catalysts for the synthesis of α -alkylidene CC

-	-	C 1	105	~ 1			m:	× 71 1 1
	Entry	Catalyst	MPa	Solvent	Temperature	Amount	Time	Yield
			(CO ₂)		(C ₀)	Catalyst		(%)
-	1	DBU	0.5	<u> </u>	50	2 mol (%)	6 h	_[47]
	2	Ph ₃ P	0.5	<u>\</u>	50	2 mol (%)	6 h	_[47]
	3	CuCl	0.5	-	50	2 mol (%)	6 h	_[47]
	4	AgNO ₃ /Ph ₃ P	0.5	-	50	2 mol (%)	6 h	_[47]
	5	AgOAc/Ph ₃ P	0.5	-	50	2 mol (%)	6 h	<1[47]
	6	Ag_2WO_4/Ph_3P	0.5	-	50	2 mol (%)	6 h	45 ^[47]
	7	AgI/Ph ₃ P	0.5	-	40	2 mol (%)	6 h	_[47]
6	8	Ag ₂ WO ₄ /DBU	0.5	-	40	2 mol (%)	6 h	2 ^[47]
	9	Ag ₂ WO ₄ /2,2-Bipyridine	0.5	-	40	2 mol (%)	6 h	_[47]
\geq	10	Ag ₂ WO ₄ /TMEDA	0.5	-	40	2 mol (%)	6 h	_[47]
	11	$({}^{n}C_{7}H_{15})_{4}NBr$	0.5	-	60	2.5 mol (%)	20 h	_[48]
	12	$K_8[\alpha\text{-}SiW_{11}O_{39}]$	0.5	-	60	2.5 mol (%)	20 h	_[48]

13	$K_6[SiW_{11}O_{39}Cu]$	0.5	-	60	2.5 mol (%)	20 h	43 ^[48]
14	CuCl ₂	0.5	-	60	2.5 mol (%)	20 h	67 ^[48]
15	$CuCl_2 + (^nC_7H_{15})_4NBr$	0.5	-	60	2.5 mol (%)	20 h	68 ^[48]
16	$[({}^{n}C_{7}H_{15})_{4}N]_{6}[\alpha$ -SiW ₁₁ O ₃₉ Co]	0.5	-	60	2.5 mol (%)	20 h	66 ^[48]
17	$[({}^{n}C_{7}H_{15})_{4}N]_{6}[\alpha-SiW_{11}O_{39}Fe]$	0.5	-	60	2.5 mol (%)	20 h	18[45]
18	$[({}^{n}C_{7}H_{15})_{4}N]_{6}[\alpha-SiW_{11}O_{39}Ni]$	0.5	-	60	2.5 mol (%)	20 h	16 ^[48]
19	$[({}^{n}C_{7}H_{15})_{4}N]_{6}[\alpha-SiW_{11}O_{39}Zn]$	0.5	-	60	2.5 mol (%)	20 h	45[48]
20	$[(^{n}C_{7}H_{15})_{4}N]_{6}[\alpha\text{-SiW}_{11}O_{39}Mn]$	0.5	-	60	2.5 mol (%)	20 h	43 ^[48]
21	KCC-1/ATPP	1	-	80	04 mol (%)	2 h	94
					\sim		

^aReaction conditions: propargyl alcohol (1 mmol), and CO_2 in different solvents and in different amounts of catalyst, temperature, and time.

Table9A Comparison of the catalytic efficiency of KCC-1/STPP NPs with various catalysts for the synthesis of CC

	Entry	Catalyst	MPa	Solvent	Temperature	Amount	Time	Yield	
			(00)))	(C^{O})	Catalyst	(h)	(%)	
			(342)						
	1	NaBr	2	H ₂ O	125	1 mmol	1	30 ^[49]	
	2	KBr	2	H ₂ O	125	1 mmol	1	52 ^[49]	
	3	KI	2	H_2O	125	1 mmol	1	68 ^[49]	
(4	B∕u₄NBr	2	H ₂ O	125	1 mmol	1	86 ^[49]	
	5	Bu ₄ NCl	2	H_2O	125	1 mmol	1	46 ^[49]	
(\bigcirc)	6	Bu ₄ NI	2	H_2O	125	1 mmol	1	88 ^[49]	
\rightarrow	7	[bmim]Br	2	H_2O	125	1 mmol	1	87 ^[49]	
	8	[bmim]Cl	2	H_2O	125	1 mmol	1	42 ^[49]	
	9	[bmim]I	2	H ₂ O	125	1 mmol	1	90 ^[49]	

10	GO-DMEDA-I	2	_	120	0.65 mol(%)	3	89 ^[50]	
10		2		120	0.05 mor (70)	5	0)	
11	Mim	1.5	-	120	1 mol (%)	2	_[51]	
12	HBimBr	1.5	-	120	1 mol (%)	2	$77.7^{[51]}$	
							FO 2 ^[51]	\land
13	HMimBr	1.5	-	120	0.5 mol (%)	2	59.8 ^[31]	
14	HFimBr	15	_	120	$1 \mod (\%)$	2	85 8 ^[51]	$\langle \rangle \rangle$
14	membr	1.5		120	1 mor (70)	2	05.0	\bigcirc
15	HMimCl	1.5	-	120	1 mol (%)	2	47.4 ^[51]	
							$\langle \rangle \rangle$	\sum
16	HPyBr	1.5	-	120	1 mol (%)	2	31.6 ^[51]	
17		1.5		120	1 1 (0/)	$\left(\begin{array}{c} \end{array} \right)$	24.0511	
17	HTeaBr	1.5	-	120	1 mol (%)	(2	34.9	
18	$Ft N^+Cl^-$	1	_	100	1 mol (%)	74	63 ^[52]	
10		1		100		$\mathcal{D}\mathcal{T}$	05	
19	$n-Bu_4N^+Cl^-$	1	-	100	1 mol (%)	24	61 ^[52]	
					$\langle \rangle \rangle$			
20	$n-Bu_3MeN^+Cl^-$	1	-	100	1 moi (%)	24	58 ^[52]	
					\sim			
21	KCC-1/ATPP	1	-	100	0.4 mol (%)	1.7	97	
				\wedge $\setminus \setminus / \land$				

^aReaction conditions: epoxide (1 mmol), CO₂ in different solvents associated with different catalyst amounts, temperatures, and times

 $// \land$

Table10A comparison of the catalytic efficiency of KCC-1/STPP NPs with various catalysts for the synthesis of quinazoline-2,4(1H,3H)-dione

			$\langle \langle \rangle / \rangle $	\sim				
-	Entry	Catalyst	MPa(CO ₂)	Solvent	Temperature	Amount	Time	Yield
					(C^{O})	Catalyst	(h)	(%)
-	1		2		120		10	[55]
	1		3	-	120	-	18	
	2	Cs ₂ CO ₃	3	-	120	5 mol (%)	18	10 ^[55]
	3	t-BuOK	3	-	120	5 mol (%)	18	[55]
(4	KF	3	-	120	5 mol (%)	18	5 ^[55]
	5	Et ₃ N	3	-	120	5 mol (%)	18	28 ^[55]
ľ,	6	[Bmim]BF ₄	3	-	120	5 mol (%)	18	[55]
	7	[Bmim]HSO ₄	3	-	120	-	18	[55]

8	[Bmim]OH	3	-	120	10 mol (%)	18	91 ^[55]
9	TMG	10	-	120	5 mol (%)	4	89 ^[57]
10	MgO/ZrO ₂	3.7	DMF	130	10 mol (%)	12	92 ^[57]
11	CuCl ₂	5	DMF	200	1 equiv	5	20 ^[56]
12	HgCl ₂	5	DMF	200	1 equiv	5	15[58]
13	FeCl ₃	5	DMF	200	1 equiv	5	_[58]
14	AlCl ₃	5	DMF	200	1 equiv	5	[58]
15	SnCl ₂	5	DMF	200	1 equiv	5	[58]
16	${\rm TiCl}_4$	5	DMF	200	1 equiv	5	2 ^[58]
17	$ZnCl_2$	5	DMF	200	5 equiv	5	90 ^[58]
18	K ₂ CO ₃	1.3	DMF	100	0.2 5 equiv	4	35 ^[54]
19	Na ₂ CO ₃	1.3	DMF	100	0.25 equiv	4	0 ^[54]
20	KF	1.3	DMF	106	0.25 equiv	4	40 ^[54]
21	КОН	1.3	DMF	100	0.25 equiv	4	55 ^[54]
22	Cs ₂ CO ₃	1.3	DMF	100	0.25 equiv	4	94 ^[54]
23	DBU	19	<u> </u>	80	0.1equiv	4	91 ^[53]
24	KCC-1/ATPP	1.5	-	50	0.4 mol (%)	1.2	93

^aReaction conditions: 2-aminobenzonitrile (1 mmol), and CO_2 in different solvents and in different amounts of catalyst, temperature, and time.



Scheme 1: CO₂ transformation in the presence of KCC-1/STPP NPs



Scheme 4Carboxylative cyclization of propargyl alcohols with CO2



Scheme5The synthesis of CCs in the presence of KCC-1/STPP NPs



Scheme6The syntheses of quinazoline-2,4(1H,3H)-diones in the presence of KCC-1/STPP NPs