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Benzotriazolium Ionic Liquid Immobilized on Periodic Mesoporous Organosilica as an Effective Reusable Catalyst for Chemical Fixation of CO_2 into Cyclic Carbonates

Jing Rui Li, Yu Lin Hu*

College of Materials and Chemical Engineering, Key laboratory of inorganic nonmetallic crystalline and energy conversion materials, China Three Gorges University, Yichang 443002, China

* Corresponding author's e-mail address: huyulin1982@163.com

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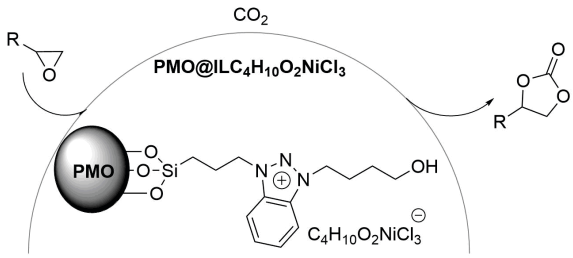
Abstract: A type of dichloro(dimethoxyethane)nickel anionic benzotriazolium ionic liquid-functionalized periodic mesoporous organosilicas were synthesized and tested as effective and practical heterogeneous catalysts in the cycloaddition of CO_2 with epoxides. The catalyst PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) showed brilliant catalytic activity for the synthesis of cyclic carbonates with high yields and selectivities under solvent- and cocatalyst-free conditions. We also found that the catalytic activity could be significantly influenced by the hydroxyl groups sites of periodic mesoporous organosilica and the active sites (hydroxyl groups/ dichloro(dimethoxyethane)nickel anion) of the benzotriazolium-cation ionic liquid, probably due to an intensification of intramolecular synergistic effect. The catalytic process displayed ease of recovery, excellent stability and recyclability for at least five runs without significant loss of its catalytic activity.

Keywords: immobilized ionic liquid, periodic mesoporous organosilica, recyclable catalyst, carbon dioxide, cyclic carbonates.

INTRODUCTION

CHEMICAL transformation of carbon dioxide into valuable intermediates has attracted broad attention, as CO_2 is an economical and nontoxic C1 building block in organic synthesis.[1–3] One of the most attractive protocols is the cycloaddition of CO_2 and epoxides to afford cyclic carbonates, which can be widely used in fine chemicals and organic reactions.[4–6] Generally, the transformation from epoxides and carbon dioxide into cyclic carbonates can proceed with alkali metal salts,[7,8] quaternary ammonium and phosphonium salts catalysts.[9,10] However, most of these systems often need solvents or homogeneous additives, high pressures and temperatures. Recently, considerable effort has been devoted to the development of efficient catalytic systems for the synthesis of cyclic carbonates such as nano-PDA/KI,[11] ZnI_2/NEt_3,[12] $(Cp_2TiCl_2)/KI$,[13] $ZnCl_2/Al_2O_3$-TBAI,[14] Zn-SBA-15/KI,[15] metal complexes,[16–19] organocatalysts,[20–22] MOFs,[23–25] MgO/TBAB/Bu_4NBr,[26] Bp-Zn@MA,[27] H-MFeSN,[28] and others.[29–31] In spite of their potential utility, however, most of them still have problems such as harsh reaction conditions, use of expensive reagents, cumbersome product isolation and catalyst reusability procedures. Thus, the development of new catalytic systems for the cycloaddition that are more sustainable, more efficient and more environmentally friendly is still a challenging goal.

Ionic liquids (ILs) have attracted much attention because of the excellent properties and have meaningful applications in many fields, such as catalysis, chemical conversion, etc.[32–34] Studies involving the utilization of ionic liquids as catalysts for the transformation of CO_2 into cyclic carbonates have also been reported.[35–37] Although, these functionalized ILs catalysts are quite effective but their practical applications are restricted by some defects in the separation and recyclability. Hence, the development of



Scheme 1. Catalytic synthesis cyclic carbonates from CO_2 and epoxides with PMO@IL$C_4H_{10}O_2NiCl_3$.

easy recovery and recyclable ionic liquid-based heterogeneous catalysts are always in demand. Immobilization of Ionic liquids onto porous solid supports to explore heterogeneous supported ILs has gained comprehensive attention.[38–41] Among these soild supports, periodic mesoporous organosilicas (PMOs) have attracted increasing attention because of their combined advantages of large specific surface areas, tunable pore sizes, uniform distribution of functional groups, chemical and thermal stabilities, as well as highly ordered mesostructure properties.[42–50] As part of our ongoing interest in the development of efficient and environmentally friendly catalytic systems, herein, we intend to perform immobilization of benzotriazolium ionic liquid onto periodic mesoporous organosilica to design multifunctional immobilized ionic liquids. The obtained PMO@IL$C_4H_{10}O_2NiCl_3$ with different ionic liquid concentration have been employed as heterogeneous and recyclable catalysts in the cycloaddition of CO_2 with epoxides under cocatalyst- and solvent-free conditions (Scheme 1). Additionally, the recyclability and reusability of the catalyst was also investigated.

RESULTS AND DISCUSSION

The catalytic activities of PMO@IL$C_4H_{10}O_2NiCl_3$(x) were tested in the model reaction of CO_2 cycloaddition with propylene oxide to produce propylene carbonate. As shown in Table 1, the efficiency of PMO@IL$C_4H_{10}O_2NiCl_3$ with different ionic liquid concentration was screened. The immobilized ILs catalysts include PMO@IL$C_4H_{10}O_2NiCl_3$(0.4), PMO@IL$C_4H_{10}O_2NiCl_3$(0.6), PMO@IL$C_4H_{10}O_2NiCl_3$(0.8), PMO@IL$C_4H_{10}O_2NiCl_3$(1.0), and PMO@IL$C_4H_{10}O_2NiCl_3$(1.2) could significantly enhance the catalytic activity of cycloaddition (Table 1, entries 1–5), and PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) showed the highest catalytic activity with 95.1 % yield and 99.7 % selectivity (Table 1, entry 4). It was found that the reaction did not accomplished in the absence of catalyst, even the reaction time was prolonged to 24 h (Table 1, entry 9). For comparison, it was also observed that the cycloaddition could not be carried out successfully if there was only bulk ionic liquid of IL$C_4H_{10}O_2NiCl_3$ or ILCl and PMO support catalysts (Table 1, entries 6–8). Therefore, PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) is thought to the suitable catalyst for the reaction. Then, the effect of catalyst dosage on the cycloaddition was examined. The yield of propylene carbonate increased with the catalyst amount of the catalyst was increased from 5 mg to 20 mg (Table 1, entries 4, 10-12), while a further increase in the catalyst amount did not gave more product (Table 1, entries 13 and 14). Therefore, the best result was obtained with 20 mg catalyst.

The effect of the reaction temperature on the cycloaddition was studied over the catalyst PMO@IL$C_4H_{10}O_2NiCl_3$(1.0), and the results are revealed in Figure 1. As shown in the figure, the yield and selectivity of propylene carbonate were significantly increased with the increase of reaction temperature. While, the temperature was further increased from 110°C to 130°C, the yield and selectivity of propylene carbonate showed a slight decrease. The reason may be that the overly high temperatures can increase the occurrence of side reactions of isomerization and ring opening of propylene oxide, which was determined by GC analysis. These results indicated that the suitable temperature was 110 °C. The

Table 1. Catalyst screening for CO_2 cycloaddition to propylene oxide.[a]

Entry	Catalyst	Catalyst / mg	Time / h	Yield / %[b]	Selectivity / %[b]
1	PMO@IL$C_4H_{10}O_2NiCl_3$(0.4)	20	5	57.0	99.0
2	PMO@IL$C_4H_{10}O_2NiCl_3$(0.6)	20	5	82.4	99.4
3	PMO@IL$C_4H_{10}O_2NiCl_3$(0.8)	20	3.5	93.5	99.3
4	PMO@IL$C_4H_{10}O_2NiCl_3$(1.0)	20	3.5	95.1	99.7
5	PMO@IL$C_4H_{10}O_2NiCl_3$(1.2)	20	3.5	95.3	99.4
6	IL$C_4H_{10}O_2NiCl_3$	20[c]	12	89.5	94.5
7	ILCl	20[c]	12	46.7	91.3
8	PMO	20[c]	12	24	93.1
9	–	–	24	0	0
10	PMO@IL$C_4H_{10}O_2NiCl_3$(1.0)	5	6	43.7	99.4
11	PMO@IL$C_4H_{10}O_2NiCl_3$(1.0)	10	4	83.2	99.3
12	PMO@IL$C_4H_{10}O_2NiCl_3$(1.0)	15	3.5	92.1	99.4
13	PMO@IL$C_4H_{10}O_2NiCl_3$(1.0)	25	3.5	95.0	99.3
14	PMO@IL$C_4H_{10}O_2NiCl_3$(1.0)	30	3.5	94.7	99.1

[a] Reaction conditions: propylene oxide (10 mmol), CO_2 (1.0 MPa), catalyst, 110 °C.
[b] Determined by using GC;
[c] Reaction temperature is 150 °C.

effects of initial pressure on the cycloaddition was also studied (Figure 2). As shown in the figure, the yield and selectivity of propylene carbonate were strengthened gradually with the CO_2 pressure was increased from 0.2 MPa to 1.0 MPa. However, the yield and selectivity of propylene carbonate showed a visible decrease when CO_2 pressure was above 1.0 MPa. The reason may be that too high CO_2 pressure retard the interaction of propylene oxide, CO_2 and PMO@IL$C_4H_{10}O_2NiCl_3$(1.0), which reduced the concentration of propylene oxide and lead to low yields and selectivities.[13–16] It can be observed that the proper pressure was 1.0 MPa.

The stability and reusability are important properties for the designed catalyst PMO@IL$C_4H_{10}O_2NiCl_3$(1.0), which was evaluated in the cycloaddition of propylene oxide with

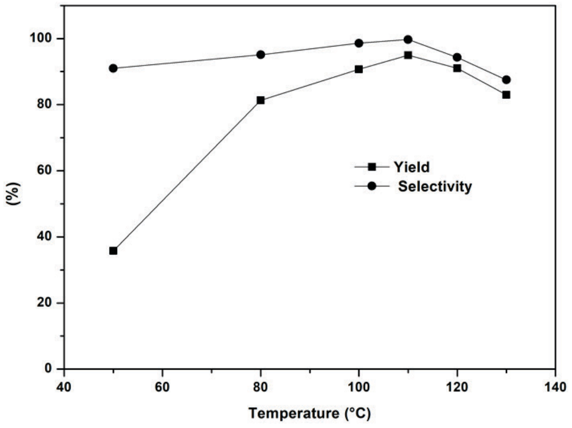


Figure 1. The effect of the reaction temperature on the cycloaddition. Reaction conditions: propylene oxide (10 mmol), PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) (20 mg), CO_2 pressure (1.0 MPa), 3.5 h.

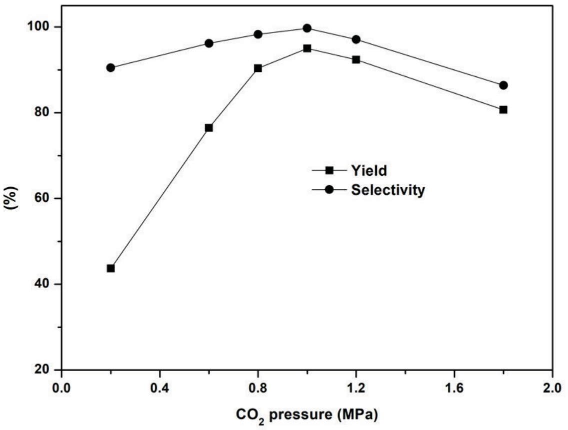


Figure 2. The effect of the CO_2 pressure on the cycloaddition. Reaction conditions: propylene oxide (10 mmol), PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) (20 mg), 110 °C, 3.5 h.

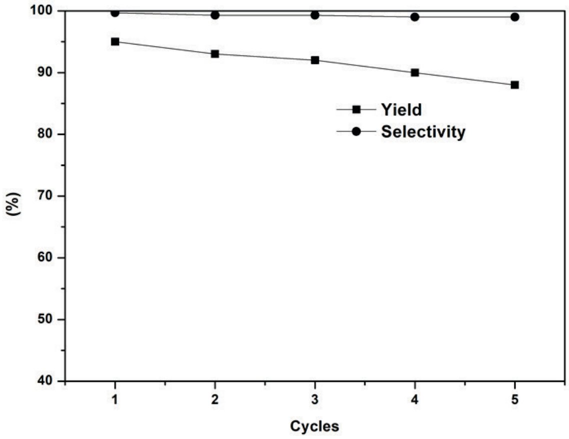


Figure 3. Reusability test of catalyst for synthesis of propylene carbonate.

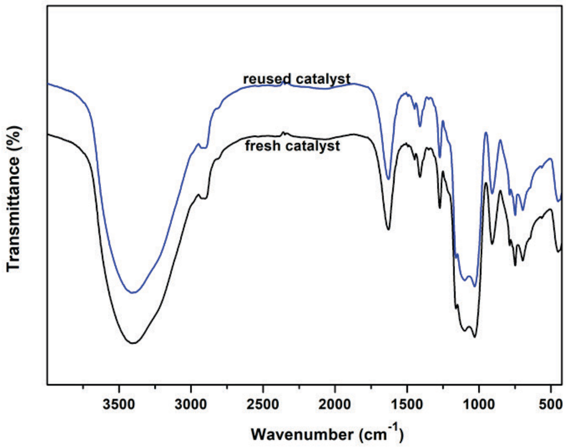


Figure 4. FT-IR spectra of fresh and reusable catalyst.

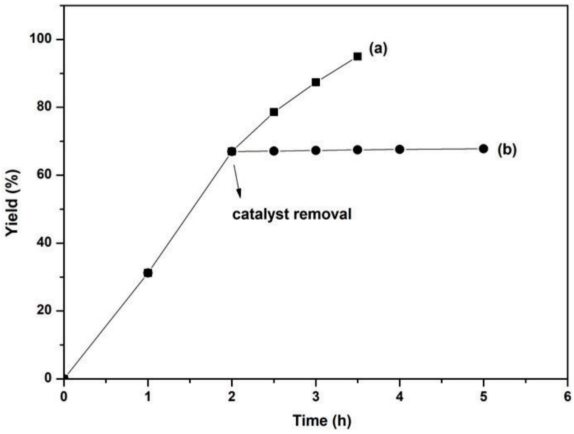
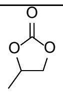
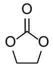
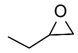
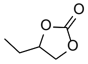
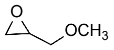
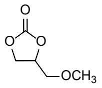
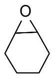
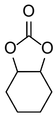
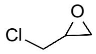
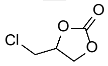
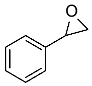
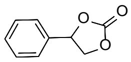


Figure 5. Hot filtration test and leaching effect of PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) for synthesis of propylene carbonate. Reaction conditions: propylene oxide (10 mmol), CO_2 (1.0 MPa) at 110 °C with catalyst (a) and catalyst removal (b) after 2 h.

CO_2 under optimized conditions (Figure 3). The catalyst could be easily recovered by simple filtration, and then reused directly in the following runs. The results demonstrated that the catalyst can be recycled for five consecutive runs without significant loss in catalytic activity. In addition, FT-IR spectra for the recovered catalyst after five runs was similar to that of fresh catalyst, indicating that its characteristic framework did not change significantly during the reaction (Figure 4). Furthermore, a hot filtration test confirmed that the reaction follows a heterogeneous pathway and no obvious active species leaching was present in the catalytic process (Figure 5). These results clearly illustrating the excellent stability and recyclability of the designed catalyst.

The versatility of the catalyst PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) for the cycloaddition of CO_2 with different substituted epoxide substrates were studied under the optimal reaction conditions, and corresponding results were detailed in Table 2. The CO_2 cycloaddition with different terminal epoxides containing electron withdrawing and electron donating groups exhibited good to excellent yields. All the terminal cyclic carbonates were obtained with good to high yields (84.0 %~97.6 %) and excellent selectivity (> 99 %) within the reaction time of less than 5 h. However, the reaction of cyclohexene oxide requires a longer time of 5 h to obtain a good yield (Table 2, entry 5), which may be ascribed to the steric hindrance obstructed the nucleophilic attack of anion.

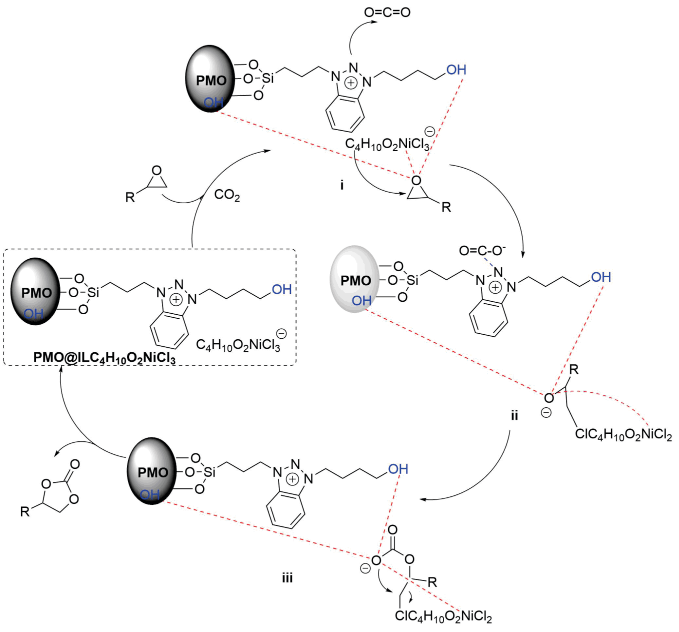
Table 2. Formation of cyclic carbonates from diverse epoxides and CO_2.[a]

Entry	Epoxide	Product	Time / h	Yield / %[b]	Selectivity / %[b]
1			3.5	95.1	99.7
2			3.5	94.3	99.3
3			3.5	92.8	99.5
4			3.5	97.6	99.4
5			5.0	84.0	99.2
6			3.5	90.0	99.1
7			4.0	89.5	99.3

[a] Reaction conditions: propylene oxide (10 mmol), CO_2 (1.0 MPa), PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) (20 mg), 110 °C.

[b] Determined by using GC.

On the basis of the above results and those previously reported works,[12–15,18–21] a possible mechanism is proposed in Scheme 2. First, epoxide could be activated through the coordination of active nickel anion and hydroxyl sites of PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) and the oxygen of epoxide, resulting in the polarization of C–O bond, so as to form the intermediate **i**, together with the adsorption and activation of CO_2 by the benzotriazolium cation to form carbonate species. Meanwhile, the nucleophilic attack of



Scheme 2. Proposed possible reaction mechanism for the synthesis of cyclic carbonates.

anion on the less sterically hindered carbon atom of epoxide generates the intermediate **ii**. Then, there is nucleophilic attack of the oxygen anion (**ii**) on the C atom of the activated CO_2, forming the acyclic carbonate anion **iii**. Finally, cyclic carbonate is formed by subsequent intramolecular cyclic step, and the catalyst is regenerated to promote the next catalytic cycle.

CONCLUSION

In conclusion, this work demonstrates the synthesis of a type of multifunctional periodic mesoporous organosilica-grafted benzotriazolium ionic liquids PMO@IL$C_4H_{10}O_2NiCl_3$ possessing dichloro(dimethoxyethane)nickel anion and hydroxyl functionalized groups. The presence of an intramolecular synergistic effect of hydroxyl groups and dichloro(dimethoxyethane)nickel anion of ionic liquid makes them suitable as effective heterogeneous catalysts in the cycloaddition of CO_2 to epoxides. The catalytic results demonstrated that PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) showed higher activity than other ionic liquid concentration immobilized ILs catalysts. Moreover, PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) with excellent stability is a reusable catalyst that can be recycled for five consecutive times without significant loss of activity. These discoveries suggests that PMO@IL$C_4H_{10}O_2NiCl_3$(1.0) can act as a potentially active novel heterogeneous catalyst for the cycloaddition.

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Supplementary Information. The information of materials, supported ILs catalysts preparation, experimental process for cycloaddition, characterization of immobilized ILs are summarized in the supporting information. Supporting information to the paper is attached to the electronic version of the article at: https://doi.org/10.5562/cca3668.

REFERENCES

[1] M. Irfan, Y. Bai, L. Zhou, M. Kazmi, S. Yuan, S. M. Mbadinga, S. Z. Yang, J. F. Liu, W. Sand, J. D. Gu, B. Z. Mu, *Bioresource Technol.* **2019**, *288*, 121401. https://doi.org/10.1016/j.biortech.2019.121401

[2] K. Didehban, E. Vessally, M. Salary, L. Edjlali, M. Babazadeh, *J. CO_2 Util.* **2018**, *23*, 42–50. https://doi.org/10.1016/j.jcou.2017.10.025

[3] H. Salehizadeh, N. Yan, R. Farnood, *Chem. Eng. J.* **2020**, *390*, 124584. https://doi.org/10.1016/j.cej.2020.124584

[4] T. K. Pal, D. De, P. K. Bharadwaj, *Coordin. Chem. Rev.* **2020**, *408*, 213173. https://doi.org/10.1016/j.ccr.2019.213173

[5] R. R. Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal.* **2018**, *8*, 419–450. https://doi.org/10.1021/acscatal.7b03580

[6] J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663–674. https://doi.org/10.1021/ie020678i

[7] J. W. Huang, M. Shi, *J. Org. Chem.* **2003**, *68*, 6705–6709. https://doi.org/10.1021/jo0348221

[8] J. Song, Z. Zhang, B. Han, S. Hu, W. Li, Y. Xie, *Green Chem.* **2008**, *10*, 1337–1341. https://doi.org/10.1039/b815105a

[9] J. Q. Wang, K. Dong, W. G. Cheng, J. Sun, S. J. Zhang, *Catal. Sci. Technol.* **2012**, *2*, 1480–1484. https://doi.org/10.1039/c2cy20103h

[10] Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai, *Org. Lett.* **2010**, *12*, 5728–5731. https://doi.org/10.1021/ol102539x

[11] Z. Yang, J. Sun, X. Liu, Q. Su, Y. Liu, Q. Li, S. Zhang, *Tetrahedron Lett.* **2014**, *55*, 3239–3243. https://doi.org/10.1016/j.tetlet.2014.04.033

[12] J. Ma, L. Lu, Q. Mei, Q. Zhu, J. Hu, B. Han, *ChemCatChem* **2017**, *9*, 4090. https://doi.org/10.1002/cctc.201700771

[13] D. Bai, G. Nian, G. Wang, Z. Wang, *Appl. Organometal. Chem.* **2013**, *27*, 184. https://doi.org/10.1002/aoc.2967

[14] G. N. Bondarenko, E. G. Dvurechenskaya, O. G. Ganina, F. Alonso, I. P. Beletskaya, *Appl. Catal. B: Environ*. **2019**, *254*, 380–390. https://doi.org/10.1016/j.apcatb.2019.04.024

[15] M. Liu, K. Gao, L. Liang, J. Sun, L. Sheng, M. Arai, *Catal. Sci. Technol.* **2016**, *6*, 6406–6416. https://doi.org/10.1039/C6CY00725B

[16] A. J. Kamphuis, F. Milocco, L. Koiter, P. P. Pescarmona, E. Otten, *ChemSusChem* **2019**, *12*, 3635. https://doi.org/10.1002/cssc.201900740

[17] X. Jiang, F. Gou, F. Chen, H. Jing, *Green Chem*. **2016**, *18*, 3567–3576. https://doi.org/10.1039/C6GC00370B

[18] M. Mandal, *J. Organomet. Chem*. **2020**, *907*, 121067. https://doi.org/10.1016/j.jorganchem.2019.121067

[19] J. Yi, S. Sun, Z. Li, X. Gao, X. Sun, N. Wang, J. Li, *Appl. Organometal. Chem.* **2020**, *34*, e5382. https://doi.org/10.1002/aoc.5382

[20] R. K. Tak, P. Patel, S. Subramanian, R. I. Kureshy, N. H. Khan, *ACS Sustainable Chem. Eng.* **2018**, *6*, 11200–11205. https://doi.org/10.1021/acssuschemeng.8b02566

[21] E. M. Mayaa, E. Rangel-Rangela, U. Díazc, M. Iglesias, *J. CO_2 Util*. **2018**, *25*, 170–179. https://doi.org/10.1016/j.jcou.2018.04.001

[22] K. Takaishi, T. Okuyama, S. Kadosaki, M. Uchiyama, T. Ema, *Org. Lett.* **2019**, *21*, 1397–1401. https://doi.org/10.1021/acs.orglett.9b00117

[23] V. Sharma, D. De, R. Saha, R. Das, P. K. Chattaraj, P. K. Bharadwaj, *Chem. Commun.* **2017**, *53*, 13371–13374. https://doi.org/10.1039/C7CC08315G

[24] F. Norouzi, H. R. Khavasi, *ACS Omega* **2019**, *4*, 19037–19045. https://doi.org/10.1021/acsomega.9b02035

[25] K. Nath, C. K. Karan, K. Biradha, *Cryst. Growth Des.* **2019**, *19*, 6672–6681. https://doi.org/10.1021/acs.cgd.9b01046

[26] A. H. Chowdhury, P. Bhanja, N. Salam, A. Bhaumik, S. M. Islam, *Mol. Catal*. **2018**, *450*, 46–54. https://doi.org/10.1016/j.mcat.2018.03.003

[27] J. Chen, H. Li, M. Zhong, Q. Yang, *Green Chem*. **2016**, *18*, 6493–6500. https://doi.org/10.1039/C6GC02367C

[28] K. Cho, S. M. Lee, H. J. Kim, Y. J. Ko, E. J. Kang, S. U. Son, *Chem. Eur. J*. **2020**, *26*, 788. https://doi.org/10.1002/chem.201904344

[29] M. Ding, H. L. Jiang, *ACS Catal.* **2018**, *8*, 3194–3201. https://doi.org/10.1021/acscatal.7b03404

[30] M. J. Kelly, A. Barthel, C. Maheu, O. Sodpiban, F. B. Dega, S. V. C. Vummaleti, E. Abou-Hamad, J. D. A. Pelletier, L. Cavallo, V. D'Elia, J. M. Basset, *J. CO_2 Util.* **2017**, *20*, 243–252. https://doi.org/10.1016/j.jcou.2017.05.020

[31] M. Faisal, Z. U. Rehman, Q. ul Aein, A. Saeed, *Mater. Chem. Phys*. **2019**, *231*, 272–280. https://doi.org/10.1016/j.matchemphys.2019.04.042

[32] M. Bakherad, M. Javanmardi, R. Doosti1, R.Tayebee, *Croat. Chem. Acta* **2017**, *90*, 53–58. https://doi.org/10.5562/cca3013

[33] S. J. Zhang, X. M. Lu, *Ionic liquids: from fundamental research to industrial applications*, Science Press, Beijing, **2006**.

[34] J. Zhou, H. Sui, Z. Jia, Z. Yang, L. He, X. Li, *RSC Adv.* **2018**, *8*, 3283–328642. https://doi.org/10.1039/C8RA06384B

[35] J. Qiu, Y. Zhao, Z. Li, H. Wang, M. Fan, J. Wang, *ChemSusChem* **2017**, *10*, 1120. https://doi.org/10.1002/cssc.201601129

[36] Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C. T. Curtis, F. M. Kerton, *Catal. Sci. Technol.* **2014**, *4*, 1513–1528. https://doi.org/10.1039/C3CY00998J

[37] R. B.Mujmule, M. P. R. Rao, P. V. Rathod, V. G. Deonikar, A. A. Chaugule, H. Kim, *J. CO_2 Util.* **2019**, *33,* 284–291. https://doi.org/10.1016/j.jcou.2019.06.013

[38] L. C. Tomé, I.l M. Marrucho, *Chem. Soc. Rev.* **2016**, *45*, 2785–2824. https://doi.org/10.1039/C5CS00510H

[39] R. Fehrmann, A. Riisager, M. Haumann, *Supported ionic liquids: Fundamentals and applications*, Wiley-VCH Verlag GmbH & Co. KGaA, **2014**. https://doi.org/10.1002/9783527654789

[40] N. Yao, C. Chen, D. J. Li, Y. L. Hu, *J. Environ. Chem. Eng.* **2020**, *8*, 103953. https://doi.org/10.1016/j.jece.2020.103953

[41] G. O. Yahaya, F. Hamad, A. Bahamdan, V. V. R.Tammana, E. Z. Hamad, *Fuel Process. Technol.* **2013**, *113*, 123–129. https://doi.org/10.1016/j.fuproc.2013.03.028

[42] P. V. D. Voort, D. Esquivel, E. D. Canck, F. Goethals, I. V. Driessche, F. J. Romero-Salguero, *Chem. Soc. Rev.* **2013**, *42*, 3913–3955. https://doi.org/10.1039/C2CS35222B

[43] M. Waki, S. Inagaki, *Micropor. Mesopor. Mater.* **2019**, *284*, 10–15. https://doi.org/10.1016/j.micromeso.2019.04.007

[44] D. Levy, M. Zayat, *The Sol-Gel Handbook*, Wiley-VCH Verlag GmbH & Co. KGaA, **2015**. https://doi.org/10.1002/9783527670819

[45] F. Lin, M. Mertens, P. Cool, S. V. Doorslaer, J. *Phys. Chem. C* **2013**, *117*, 22723–22731. https://doi.org/10.1021/jp4061076

[46] Q. Yang, J. Liu, L. Zhang, C. Li, *J. Mater. Chem.* **2020**, *8,* 103953.

[47] A. M. Kaczmarek, S. Abednatanzi, D. Esquivel, C. Krishnaraj, H. S. Jena, G. Wang, K. Leus, R. V. Deun, F. J. Romero-Salguero, P. V. D. Voort, *Micropor. Mesopor. Mater.* **2020**, *291*, 109687. https://doi.org/10.1016/j.micromeso.2019.109687

[48] B. Karimi, H. M. Mirzaei, A. Mobaraki, H. Vali, *Catal. Sci. Technol.* **2015**, *5*, 3624–3631. https://doi.org/10.1039/C5CY00267B

[49] E. Gu, W. Zhong, X, Liu, *RSC Adv.* **2016**, *6*, 98406–98412. https://doi.org/10.1039/C6RA20566F

[50] L. Carneiro, A. R. Silva, M. A. O. Lourenço, A. Mayoral, I. Diaz, P. Ferreira, *Eur. J. Inorg. Chem.* **2016**, 413. https://doi.org/10.1002/ejic.201501196