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A green and highly efficient synthesis of 5-hydroxymethylfurfural from monosaccharides using a novel binary ionic liquid mixture

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ABSTRACT

We reported the development of 5-hydroxymethylfurfural (HMF) synthesis from monosaccharides using a binary ionic liquid as a reaction medium. Brønsted–Lewis acidic ionic liquid (BLAIL) was synthesized from DABCO, 1,4butane sultone, and AlCl₃ under mild conditions. The BLAIL was found to be a suitable catalyst for the synthesis of HMF from monosaccharides in [Emim]Cl as a solvent. Under the optimized conditions, the yields of the HMF from glucose and fructose were 30.5 % and 96.5 %, respectively. The influence of time, temperature, catalytic loading, and substrate on the reaction was systematically investigated. The binary ionic liquid mixture could be reused three times without a noticeable drop in the activity. The isolation of HMF was easily performed through a liquid-liquid extraction method, which could be applied to the industrial process.

1. Introduction

The use of renewable feedstock for biofuel and chemical production has attracted much attention for future applications due to the diminishing fossil fuel and the growing global warming [1-4]. Biomass is vital renewable energy and can be used as raw materials to synthesize biofuels and value-added chemicals [5-7]. Recently, 5-hydroxymethylfurfural (HMF), recognized as a building block for synthesizing chemicals and fuels, can be obtained from carbohydrates [2,8,9]. Carbohydrates, including cellulose, glucose, and fructose, have been employed as starting materials to produce HMF [10-12]. Traditionally, polar organic solvents, including dimethyl sulfoxide, N,N-dimethylacetamide, and N, N-dimethylformamide were employed as the solvents for the synthesis of HMF from the carbohydrates using an acidic catalyst [13-17]. These reactions can proceed in these solvents under medium to high-temperature conditions [18,19]. However, the process suffered from the high boiling point of these solvents, making the separation of HMF difficult [20]. The extraction of HMF using nonpolar solvents gets a problem because DMSO can be miscible with various solvents easily [21]. In recent years, the process in a two- or three-phase system was also employed for HMF synthesis, but HMF was obtained in low to moderate yields in some reported literature [22-24].

Recently, ionic liquids have attracted much attention due to significant advantages including solvents for separation processes [25-32] and media for chemical and biochemical reactions [33,34]. For biomass conversion, ionic liquids (ILs) have been introduced as green, active, and tunable reaction media in organic synthesis to substitute expensive catalysts and hazardous volatile organic solvents [35-37]. ILs demonstrate the remarkable ability of solubilizing carbohydrates [38-40]. ILs have also been employed extensively as a useful solvent in the dehydration of hexoses into HMF [41-43]. Li and coworkers reported the use of acidic ion-exchange resin in [Bmim]Cl ionic liquid for dehydration of fructose [44]. Chinnappan et al. developed a new method for synthesis HMF from fructose using metal complexes in pyridinium dibromide ionic liquid with satisfactory yields [45]. Recently, ILs possessing dual roles as solvents/catalysts in the synthesis of HMF have also been reported by Liu et al. [46] and Zhang et al. [43]. There have been some issues, including the high temperature, low yield, or long reaction time using ionic liquids [22,46,47]. Besides, studies on the ILs-promoted synthesis of HMF at room temperature have not been reported. Thus, various types of ILs have been prepared and tested for their catalytic activity at room temperature.

Production of HMF from fructose with high yields under mild conditions is a challenging topic of great importance. Here, we synthesized a

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Scheme 1. Synthesis of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y].

new BLAIL from DABCO and employed it as a catalyst for the dehydration of monosaccharides into HMF. Brønsted-Lewis acidic ionic liquids have been attracted much attention due to the simultaneous possessing characteristic properties of ILs with strong Brønsted and Lewis acidity [48]. Thus, these ILs can prompt the conversion of monosaccharides into HMF under mild conditions.

2. Experimental

2.1. Synthesis of ILs

1,4-bis(4-sulfobutyl)-DABCO-1,4-diium tetrachloroaluminate ([DABCO(C₄H₈SO₃H)₂][Al_xCl_y]) was prepared by a modified procedure as in a previous literature [48]. [DABCO(C₄H₈SO₃H)₂][Al_xCl_y] was prepared through a one-pot synthesis (Scheme 1). A mixture of DABCO (1 mmol), 1,4-butane sultone (2 mmol), and toluene (10 mL) was heated for 12 h under reflux to provide the zwitterion. HCl (3 M, 3 mL) was then added to the resulting zwitterion, followed by stirring at room temperature in 2 h. Next, AlCl₃ (2 mmol) in toluene was added, and the reaction mixture was stirred for 24 h under reflux. After synthesis of [DABCO (C₄H₈SO₃H)₂][AlCl₄]₂, the residual toluene was removed by rotary evaporator at 50 °C. The crude [DABCO(C₄H₈SO₃H)₂][Al_xCl_v] was washed with acetone (3 \times 15 mL) to eliminate non-ionic residues. [DABCO(C₄H₈SO₃H)₂][Al_xCl_v] was then dried under vacuum for 10 h to obtain the pure product. The structure of $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$ was then authenticated by FT-IR. Raman, TGA, ¹H & ¹³C-NMR, and HRMS.

2.2. The typical procedure for the preparation of HMF

In a typical experiment, carbohydrate (1 mmol) was placed in a 10 mL round-bottomed vessel, and a mixture of [Emim]Cl (6 mmol) - $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$ (0.1 mmol) was added. The vessel was fitted with a Teflon cap, and the reaction mixture was heated for a period of time at a selected temperature. The progress of the reaction was checked by TLC and monitored by HPLC to determine the amount of HMF remaining in the reaction mixture. Upon the completion of the reaction, the pure HMF was obtained from the reaction mixture by solvent liquid-liquid extraction with diethyl ether/ethyl acetate. All experiments were carried out in triplicates were less than 2.5 %. The HMF was characterized by FT-IR, HRMS, and NMR.

FT-IR (KBr, cm⁻¹): 3421, 2920, 2851, 1716, 1457, 1022.

 $^{1}\mathrm{H}$ NMR (500 MHz, CDCl₃) δ 9.58 (s, 1 H), 7.21 (d, J =3.2 Hz, 1 H), 6.51 (d, J =3.2 Hz, 1 H), 4.71 (s, 2 H).

HRMS (ESI) *m/z* calcd for [M]⁺ C₆H₇O₃ 127.0395, found 127.0379.

2.3. Recycling of catalytic system

The experiments to test the reusability of $[DABCO(C_4H_8SO_3H)_2]$ $[Al_xCl_y]/[Emim]Cl$ were carried out as follows. After completion of the reaction, the HMF was extracted using the mixture of ethyl acetate/ diethyl ether = 9/1 (5 \times 10 mL). The catalytic system was dried under vacuum for 10 h and was reused for the consecutive runs.

3. Results and discussion

[DABCO(C₄H₈SO₃H)₂][Al_xCl_y] was synthesized following the procedure described in Scheme 1. First, commercially available DABCO reacted with 1,4-butane sultone to afford the zwitterion (A). Next, the zwitterion (A) was treated with HCl to form chloride ionic liquid (B) as a white liquid. Afterward, the chloride ionic liquid (B) was further treated with AlCl₃ in toluene to obtain $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$. The characterization of [DABCO(C4H8SO3H)2][AlxCly] was confirmed by FT-IR, and the peaks at 1160 and 1210 cm^{-1} can be assigned to S=O stretching vibration. Additional peaks at 3452 cm⁻¹ and 2964 cm⁻¹ were attributed to O-H and aliphatic CH- vibration, which confirmed the successful preparation of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y] (Supporting Information, SI, Fig. S1) [48]. The formation of [DABCO (C₄H₈SO₃H)₂][Al_xCl_y] was demonstrated by ¹H and ¹³C NMR with the presence of chemical shifts in the upfield region (SI, Fig. S2). HRMS (ESI) was recorded in positive-ion mode showing the presence of main [DABCO(C₄H₈SO₃H)₂] cation (*m*/*z* 385.1421) (SI, Fig. S3). HRMS (ESI) was recorded in negative-ion mode showing the presence of main AlCl₄-, Al₂Cl₅-, and Al₂Cl₇- (*m/z* 168.8519, 228.0743, 302.8713) (SI, Fig. S4). Furthermore, as can be seen in the Raman spectrum of [DABCO $(C_4H_8SO_3H)_2][Al_xCl_v]$, the signals appeared at 245 cm⁻¹ and 500 cm⁻¹ can be assigned to Al-Cl stretching modes of the Al_xCl_y anion (SI, Fig. S5) [49].

The TGA curve of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y] showed a weight loss at 100 °C due to the presence of moisture. Next, a sharp decrease in weight loss observed at about 218 °C – 350 °C was mainly assigned to the decomposition of [DABCO(C₄H₈SO₃H)₂]. The next weight loss at 351 °C – 500 °C was attributed to chloroaluminate counteranions (SI, Fig. S6).

The acidity of Brønsted–Lewis acidic ionic liquids was determined by FT-IR spectroscopy. Pyridine is used to consider Lewis and Brønsted acidities because Brønsted and Lewis acids can be reacted with pyridine to provide the [Pyridine-H]⁺ cation and the Pyridine–Lewis acid complex [48,50]. As seen in the FTIR spectrum, the cation of [PyridineH]⁺



Fig. 1. Effect of temperature and time.



Fig. 2. Effect of the catalytic amount.

showed an absorption peak at 1547 cm⁻¹ in the FT-IR spectra, and the absorption peak of the complex of Pyridine–Lewis is close to 1441 cm (SI, Fig. S7), which indicated that $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$ possessed both Brønsted and Lewis acidity types. Besides, acetonitrile is a weak base and it is used to demonstrate the presence of a Lewis acid. The CN group can react with Lewis acid to produce a CN–Lewis complex, which shows absorption peaks at 2200–2400 cm⁻¹ in the FT-IR spectra, and when the intensity of Lewis acid is increasing, these absorption peaks can move to higher wavenumbers (SI, Fig. S8).

3.1. The effect of temperature and time on the conversion of glucose into HMF

The as-synthesized $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$ was used as a homogeneous catalyst for the conversion of glucose into HMF. Reaction time and temperature were initially investigated systematically to obtain the optimal conditions in the procedure (Fig. 1). The reaction was carried out with [Emim]Cl (6 mmol), glucose (1 mmol) in the presence of 30 mol% of $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$ catalyst at various temperatures for different times. It was observed that the reaction harshly proceeded at 60 °C to give less than 1% HMF yield. The yield could be improved at higher temperatures. The good yield of HMF was obtained at 110 °C for 2 h. However, the HMF is not stable in acidic conditions at high temperatures for a long reaction time. Thus, the increase of



Fig. 3. Effect of deep eutectic solvents on HMF yield under the present method.

temperature and time was not conducive to synthesize HMF under the present condition due to the occurrence of the side reaction [21,51–53].

3.2. The effect of catalytic amount on the conversion of glucose into HMF

After screening conditions, we found that the reaction temperature was good at 110 °C, and the best yield was obtained for 1 h with 30.5 % of HMF (Fig. 2). It was observed that the desired product was decreased with prolonged reaction time. We then decided to consider the effect of the catalytic amount. The reaction was carried out at 110 °C in the presence of 10 mol%, 20 mol%, 30 mol%, 40 mol%, and 50 mol% [DABCO(C₄H₈SO₃H)₂][Al_xCl_v] catalyst, respectively. It should be noted that HMF was not obtained in the absence of the [DABCO(C₄H₈SO₃H)₂] [Al_xCl_y] catalyst. The use of 10 mol% catalyst afforded 12.8 % yield for 1 h. An increasing catalyst concentration at 20 mol% afforded 15.2 % HMF for 2 h. As mentioned earlier, the use of 30 mol% [DABCO $(C_4H_8SO_3H)_2$ [Al_xCl_y] catalyst provided the best yield of HMF with 30.5 % for 1 h. Increasing the catalyst concentration from 40 mol% to 50 mol % led to a drop in the reaction yield. The possible explanation for this phenomenon can arise from the facts that: (1) highly viscous [DABCO $(C_4H_8SO_3H)_2$ [Al_xCl_y] in high concentrations can prevent the diffusion of reactants, and (2) the increasing pH of the reaction media can unwantedly result in the generation of side products. [ref.].

3.3. Effect of deep eutectic solvents on HMF yield

The catalytic activity of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y] on the conversion of glucose was also compared with deep eutectic solvents (a new type of ionic liquids) (Fig. 3). Deep eutectic solvents were prepared as the procedure described in previous literature [54]. It was found that the reaction using deep eutectic solvents ([choline chloride][FeCl₃]₂ and [choline chloride][SnCl₂]₂) proceeded with cumbersome, affording less than 1% yield. CrCl₃ was reported as a suitable catalyst for glucose conversion into HMF [55]. The deep eutectic solvent between choline chloride and CrCl3 was found to be the best candidate in the reaction condition. However, the HMF yields dropped quickly under prolonged reaction time when compared with [DABCO(C₄H₈SO₃H)₂][Al_xCl_y] catalyst. Our result may not be comparable to the previous work wherein tin phosphate catalyst [56] (58.3 % yield) at 120 °C for 180 min or CrCl₃/HCl catalyst [55] (35 % yield) at 150 °C for 180 min to convert glucose into HMF. Nonetheless, our method is still acceptable from the environmental viewpoint due to the absence of metal salts and/or organic solvents.



Fig. 4. Optimization of the reaction condition using $[DABCO(C_4H_8SO_3H)_2]$ $[Al_xCl_y]$ catalyst on HMF synthesis from fructose.



Fig. 5. Effect of temperature on HMF synthesis from fructose in the presence of 5 mol% $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$.

3.4. The optimization of reaction condition on the synthesis of HMF from fructose at room temperature (RT)

We then explore the substrate scope in our method, and fructose was chosen for investigation. HMF from fructose was obtained in 46 % yield in the presence of 1 mol% of $[DABCO(C_4H_8SO_3H)_2][Al_xCl_y]$ at room temperature. When 5 mol% of catalyst was used, the HMF yield could be improved significantly, with 65 % for 24 h. An increase of catalytic amount to 10 mol% did not provide a better yield (Fig. 4).

3.5. The optimization of reaction temperature for HMF synthesis from fructose

The HMF yield can be dramatically enhanced by increasing the reaction temperature. In the present method, the temperature could exhibit a significant effect on the reaction rate (Fig. 5). The reaction proceeded slowly at room temperature to furnish 65 % of HMF yield for 24 h. However, the HMF yield could be improved to 99 % at 80 °C for 8 h in the presence of 5 mol% of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y]. Increasing the reaction temperature to 120 °C resulted in decreasing HMF yield due to the side reaction [21].

3.6. Reusability of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y]/[Emim]Cl

Recoverability and reusability of the catalyst are highly preferable in terms of green chemistry. To emphasize the significant point of the catalytic system, the recycling experiments of [DABCO(C₄H₈SO₃H)₂] [Al_xCl_y]/Emim]Cl system were investigated in the synthesis of HMF at 110 °C for 1 h using 1 mmol of glucose dissolved in 6 mmol of [Emim]Cl and 30 mol% of [DABCO(C₄H₈SO₃H)₂][Al_xCl_y]. After completion, the reaction mixture was extracted with ethyl acetate/diethyl ether (5 \times 10 mL). Organic solvents were decanted, and the residue catalyst was dried under vacuum for 10 h. Then, a new run was performed by adding the fresh glucose (1 mmol) to the remaining [DABCO(C₄H₈SO₃H)₂] [Al_xCl_y]/[Emim]Cl and heated under optimized conditions. Experimental results indicated that the [DABCO(C₄H₈SO₃H)₂][Al_xCl_y]/ [Emim]Cl catalytic system could be recycled three times with a little loss in catalytic performance (Fig. 6). The recovered [DABCO(C₄H₈SO₃H)₂] [Al_xCl_v]/[Emim]Cl catalytic system was confirmed by FTIR without significant change in functionality as compared with the fresh [DABCO (C₄H₈SO₃H)₂][Al_xCl_y]/[Emim]Cl (SI, Fig. S9).

4. Conclusions



We developed a new catalytic system for the conversion of monosaccharides to HMF. The new DABCO-based dicationic ionic liquid

Fig. 6. Extraction phase and recycling of the catalytic system [DABCO(C₄H₈SO₃H)₂][Al_xCl_v]/[Emim]Cl.

[DABCO(C₄H₈SO₃H)₂][Al_xCl_y] was easily synthesized from DABCO *via* a three-step, one-pot procedure and characterized by FT-IR, ¹H & ¹³C NMR, TGA, Raman, and HRMS (ESI). HMF yields were obtained in high yields from fructose in the presence of the [DABCO(C₄H₈SO₃H)₂] [Al_xCl_y]/[Emim]Cl under a mild condition. The results showed that [DABCO(C₄H₈SO₃H)₂][Al_xCl_y]/[Emim]Cl efficiently facilitated HMF formation from fructose (96.5 %, 80 °C, 1.5 h) glucose (30.5 %, 110 °C, 1 h). The HMF could be separated from the reaction mixture by liquid-liquid extraction, and the catalyst system [DABCO(C₄H₈SO₃H)₂][Al_xCl_y]/[Emim]Cl could be recovered and reused three times for glucose conversion with a little loss in catalytic activity. The high yield under mild conditions and the easy separation of HMF could be of significant advantages for industrial applications.

CRediT authorship contribution statement

Ha Bich Phan: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing. Quyen Bich Thi Nguyen: Methodology, Investigation, Data curation. Cam Manh Luong: Methodology, Investigation, Data curation. Kim Nguyen Tran: Methodology, Investigation, Data curation. Phuong Hoang Tran: Conceptualization, Methodology, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111428.

References

- R.J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Chem. Rev. 113 (2013) 1499.
- [2] L.T. Mika, E. Csefalvay, A. Nemeth, Chem. Rev. 118 (2018) 505.
- [3] K. Dong, J. Zhang, W. Luo, L. Su, Z. Huang, Chem. Eng. J. 334 (2018) 1055.
- [4] O.O. James, S. Maity, L.A. Usman, K.O. Ajanaku, O.O. Ajani, T.O. Siyanbola,
- S. Sahu, R. Chaubey, Energy Environ. Sci. 3 (2010) 1833.[5] J. Tuteja, H. Choudhary, S. Nishimura, K. Ebitani, ChemSusChem 7 (2014) 96.
- [6] G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu, X. Hou, Green Chem. 18 (2016) 2302.
- [7] M. Hong, S. Wu, J. Li, J. Wang, L. Wei, K. Li, Catal. Commun. 136 (2020), 105909.
- [8] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, Chem. Rev. 118 (2018) 11023.
- [9] P. Pal, S. Saravanamurugan, ChemSusChem 12 (2019) 145.

- [10] P. Zhou, Z. Zhang, Catal. Sci. Technol. 6 (2016) 3694.
- [11] J.A. Melero, J. Iglesias, A. Garcia, Energy Environ. Sci. 5 (2012) 7393.
- [12] M. Zuo, Z. Li, Y. Jiang, X. Tang, X. Zeng, Y. Sun, L. Lin, RSC Adv. 6 (2016) 27004.
 [13] L.-K. Ren, L.-F. Zhu, T. Qi, J.-Q. Tang, H.-Q. Yang, C.-W. Hu, ACS Catal. 7 (2017) 2199
- 2199.
 - [14] S. Ravi, Y. Choi, J.K. Choe, Appl. Catal B: Environ. 271 (2020), 118942.
 [15] Y. Wang, Z. Hu, G. Fan, J. Yan, G. Song, J. Li, Waste Biomass Valori. 10 (2018) 2263.
 - [16] Z. Wei, J. Lou, Z. Li, Y. Liu, Catal. Sci. Technol. 6 (2016) 6217.
 - [17] K. Beckerle, J. Okuda, J. Mol. Catal. A Chem. 356 (2012) 158.
 - [18] H. Yang, F. Zhou, H. Chen, J. Li, H. Ma, K. Chen, X. Lu, P. Ouyang, J. Fu, Ind. Eng. Chem. Res. 59 (2020) 4905.
 - [19] S. de Paiva Silva Pereira, J. Oliveira Santana Varejão, Â. de Fátima, S.A. Fernandes, Ind. Crops Prod. 138 (2019), 111492.
 - [20] X. Zheng, X. Gu, Y. Ren, Z. Zhi, X. Lu, Biofuels Bioprod. Bioref. 10 (2016) 917.
 [21] M.R. Whitaker, A. Parulkar, P. Ranadive, R. Joshi, N.A. Brunelli, ChemSusChem 12 (2019) 2211.
 - [22] C. Tian, X. Zhu, S.H. Chai, Z. Wu, A. Binder, S. Brown, L. Li, H. Luo, Y. Guo, S. Dai, ChemSusChem 7 (2014) 1703.
 - [23] J. Zhou, Z. Xia, T. Huang, P. Yan, W. Xu, Z. Xu, J. Wang, Z.C. Zhang, Green Chem. 17 (2015) 4206.
 - [24] Y. Muranaka, K. Matsubara, T. Maki, S. Asano, H. Nakagawa, K. Mae, ACS Omega 5 (2020) 9384.
 - [25] N. Papaiconomou, J.-M. Lee, J. Salminen, M. von Stosch, J.M. Prausnitz, Ind. Eng. Chem. Res. 47 (2008) 5080.
 - [26] J.-M. Lee, J.M. Prausnitz, Chem. Phys. Lett. 492 (2010) 55.
 - [27] J.-M. Lee, Chem. Eng. J. 172 (2011) 1066.
 - [28] J.-M. Lee, Fluid Phase Equilib. 319 (2012) 30.
 - [29] P. Weerachanchai, Z. Chen, S.S.J. Leong, M.W. Chang, J.-M. Lee, Chem. Eng. J. 213 (2012) 356.
 - [30] P. Weerachanchai, K.H. Lim, J.-M. Lee, Bioresour. Technol. 156 (2014) 404.
 [31] P. Weerachanchai, Y. Wong, K.H. Lim, T.T.Y. Tan, J.-M. Lee, ChemPhysChem 15
 - (2014) 3580.
 - [32] Y. Wong, Z.J. Chen, T.T.Y. Tan, J.-M. Lee, Ind. Eng. Chem. Res. 54 (2015) 12150.
 - [33] J.-M. Lee, S. Ruckes, J.M. Prausnitz, J. Phys. Chem. B 112 (2008) 1473.
 - [34] D.D. Patel, J.-M. Lee, Chem. Rec. 12 (2012) 329.
 - [35] T. Stahlberg, W. Fu, J.M. Woodley, A. Riisager, ChemSusChem 4 (2011) 451.
 - [36] A.S. Amarasekara, Chem. Rev. 116 (2016) 6133.
 [37] M.A. Martins, C.P. Frizzo, A.Z. Tier, D.N. Moreira, N. Zanatta, H.G. Bonacorso, Chem. Rev. 114 (2014) PR1.
 - [38] H. Niedermeyer, J.P. Hallett, I.J. Villar-Garcia, P.A. Hunt, T. Welton, Chem. Soc. Rev. 41 (2012) 7780.
 - [39] P.V. Rathod, R.B. Mujmule, W.-J. Chung, A.R. Jadhav, H. Kim, Catal. Lett. 149 (2019) 672.
 - [40] S. El Sayed, A. Bordet, C. Weidenthaler, W. Hetaba, K.L. Luska, W. Leitner, ACS Catal. 10 (2020) 2124.
 - [41] S. Marullo, C. Rizzo, A. Meli, F. D'Anna, ACS Sus. Chem. Eng. 7 (2019) 5818.
 - [42] Y. Xiao, X. Huang, RSC Adv. 8 (2018) 18784.
 - [43] J. Zhang, X. Yu, F. Zou, Y. Zhong, N. Du, X. Huang, ACS Sus. Chem. Eng. 3 (2015) 3338.
 - [44] Y. Li, H. Liu, C. Song, X. Gu, H. Li, W. Zhu, S. Yin, C. Han, Bioresour. Technol. 133 (2013) 347.
- [45] A. Chinnappan, A.H. Jadhav, H. Kim, W.-J. Chung, Chem. Eng. J. 237 (2014) 95.
 [46] W. Liu, J. Holladay, Catal. Today 200 (2013) 106.
- [47] F. D'Anna, S. Marullo, P. Vitale, C. Rizzo, P. Lo Meo, R. Noto, Appl. Catal. A: Gen. 482 (2014) 287
- [48] K. Parvanak Boroujeni, P. Ghasemi, Catal. Commun. 37 (2013) 50.
- [49] H.-J. Himmel, Eur. J. Inorg. Chem. 2005 (2005) 1886.
- [50] Y. Jiang, H. Zang, S. Han, B. Yan, S. Yu, B. Cheng, RSC Adv. 6 (2016), 103774.
- [51] B. Girisuta, L.P.B.M. Janssen, H.J. Heeres, Green Chem. 8 (2006) 701.
- [52] S.H. Mushrif, S. Caratzoulas, D.G. Vlachos, Phys. Chem. Chem. Phys. 14 (2012) 2637.
- [53] L. Yang, G. Tsilomelekis, S. Caratzoulas, D.G. Vlachos, ChemSusChem 8 (2015) 1334.
- [54] H. Qin, X. Hu, J. Wang, H. Cheng, L. Chen, Z. Qi, Green Energy Environ. 5 (2020) 8.
 [55] T. Dallas Swift, H. Nguyen, A. Anderko, V. Nikolakis, D.G. Vlachos, Green Chem.
- 17 (2015) 4725.
 [56] Q. Hou, M. Zhen, L. Liu, Y. Chen, F. Huang, S. Zhang, W. Li, M. Ju, Appl. Catal. B: Environ. 224 (2018) 183.