

Green Chemistry

Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Qi, F. Liu, L. Zhang, L. Li, Y. Su, J. Yang, R. Hao, A. Wang and T. Zhang, *Green Chem.*, 2020, DOI: 10.1039/D0GC02280B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ARTICLE

Modulating trans-amination and hydrogenation towards the highly selective production of primary diamines from dialdehydes

Haifeng Qi,^{a,b} Fei Liu,^{*a} Leilei Zhang,^a Lin Li,^a Yang Su,^a Jingyi Yang,^{a,b} Rui Hao,^a Aiqin Wang^{*a,c} and Tao Zhang,^{a,c}Received 00th January 20xx,
Accepted 00th January 20xx

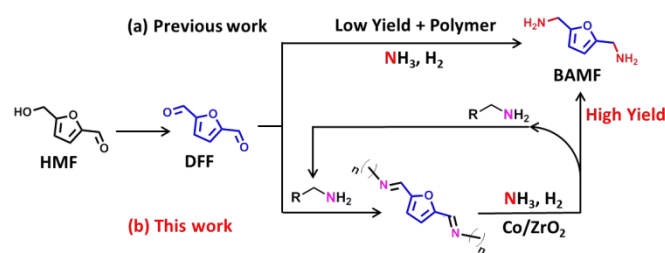
DOI: 10.1039/x0xx00000x

Bio-based primary diamines are important building blocks for sustainable bio-polymers, but their synthesis remains challenging due to the high susceptibility to polymerization. Herein, we develop a new strategy to suppress the polymerization by employing more nucleophilic alkylamine to arrest dialdehyde and Co/ZrO₂ catalyst to regulate the trans-amination and hydrogenation activity. With this strategy, 2,5-bis(aminomethyl)furan (BAMF), a promising monomer for production of new polyamides and polyureas, is successfully synthesized via reductive amination of biomass-derived 2,5-diformylfuran (DFF) under H₂ and NH₃ atmosphere with an unprecedentedly high selectivity up to 95%. This strategy is applicable to the reductive amination of other biomass-derived dialdehydes, thus paving a new way to the bio-based diamine monomers.

Introduction

Primary diamines are an important category of organonitrogen chemicals. Beyond acting as key intermediates for synthesis of pharmaceuticals and agrochemicals, they are more widely used as monomers for production of polyamides and polyureas.¹⁻⁶ For example, 1,6-hexanediamine (HDA) is the building block for production of PA-6,6, a commercial polyamide with annual production of several million tons.⁷ While the current production of diamines is mainly based on petroleum, there is great impetus to develop bio-based diamines due to the ever increased concerns on the depletion of petroleum as well as the associated CO₂ emissions.⁷⁻¹⁰ Among a variety of potential bio-based diamine monomers, 2,5-bis(aminomethyl)furan (BAMF) is one of the most promising diamines as it can offer versatile possibilities in constructing new bio-polymers with distinctive functions.¹¹⁻¹³ In principle, BAMF can be produced from renewable lignocellulose from the key platform molecule 5-hydroxymethylfurfural (HMF) via reductive amination under H₂ and NH₃ atmosphere (Scheme 1a).¹¹⁻¹⁵ Unfortunately, the selectivity to BAMF is far less satisfactory due to the high propensity of diamines to polymerization with dialdehydes. For example, Kim and coworkers investigated the direct reductive amination of 2,5-diformylfuran (DFF), a dialdehyde

obtained by oxidation of HMF, and got only 42.6% yield of BAMF along with the formation of a large amount of oligomers and polymers over Raney Ni catalyst.¹⁶ Zhou et al. reported a slightly higher yield of BAMF (60.7%) by directly using HMF as the substrate.¹⁷ Recently, Shi and coworkers achieved a greatly enhanced BAMF yield (85.9%) by means of a two-stage consecutive reaction process;¹⁸ nevertheless, the yield decreased dramatically to 63.7% during the third reuse and the mass balance was also less than 70%, indicating the occurrence of polymerization. Obviously, in spite of ready availability of dialdehydes from biomass, the reductive amination of dialdehydes remains a prohibitive challenge. Therefore, it is keenly desired to innovate catalytic strategy towards the highly selective production of primary diamines from dialdehydes.



Scheme 1. Different approaches to BAMF from HMF.

Based on the reaction mechanism of the reductive amination of aldehydes,¹⁹⁻²⁴ imines are formed first as the key intermediate to the target primary amines even without catalyst. However, this imination reaction is reversible, and the primary amines are more nucleophilic than ammonia and thereby tend to react with aldehydes to produce secondary and tertiary amines. What's worse, in the case of dialdehydes,

^a CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (China), Email: aqwang@dicp.ac.cn; fei.liu@dicp.ac.cn.

^b University of Chinese Academy of Sciences, Beijing 100049 (China).

^c State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (China).

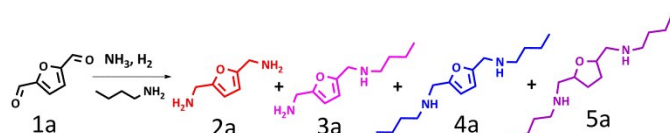
Electronic Supplementary Information (ESI) available: Experimental details, catalyst characterization and tests. See DOI: 10.1039/x0xx00000x

the primary di-imine intermediates are also prone to condense into oligomers before being hydrogenated into primary diamines.¹⁶ In order to suppress these side reactions, the concentration of primary di-imines must be kept very low and the unwanted high reactivity of the dialdehydes must be limited. In light of the higher nucleophilicity of alkylamine than ammonia and the reversibility of trans-amination,²⁵⁻²⁹ we envisage that by using alkylamine as a scavenger of dialdehyde and transition metal catalyst as a modulator to regulate the trans-amination and hydrogenation activity (Scheme 1b), side reactions between highly reactive dialdehyde and diamines would be suppressed to a great extent so that high yields of diamines might be achieved.

Results and discussion

Reductive amination under the presence of butylamine

Table 1. Reductive amination of DFF over supported metal catalysts^a



Entry	Catalysts	Yield (%) ^c			
		2a	3a	4a	5a
1	Co/ZrO ₂ -R623	91	3	n.d.	n.d.
2	Co/ZrO ₂ -R673	95	4	n.d.	n.d.
3	Co/Nb ₂ O ₅	85	n.d.	n.d.	n.d.
4	Co/SiO ₂	73	n.d.	n.d.	n.d.
5	Ni/ZrO ₂	75	5	n.d.	n.d.
6	Cu/ZrO ₂	n.d.	n.d.	n.d.	n.d.
7	Ru/ZrO ₂	56	12	n.d.	n.d.
8	Pd/ZrO ₂	n.d.	3	68	16
9	Pt/ZrO ₂	n.d.	12	65	n.d.
10	Ir/ZrO ₂	n.d.	7	61	n.d.
11	Rh/ZrO ₂	n.d.	5	25	63

^aReaction conditions: 30 mg catalyst, 0.25 mmol DFF, 0.75 mmol butylamine, 3 g methanol, 0.6 MPa NH₃, 2 MPa H₂, 373 K, 10 h, dodecane as internal standard; n.d.: not detected; ^bThe catalyst was pre-reduced at 673 K. ^cThe conversions of DFF were all >99%, and other products were oligomers and polymers.

We first investigated the reactivities of different alkylamines with DFF to evaluate their capabilities for scavenging dialdehydes. Short-chain aliphatic amines such as n-propylamine and n-butylamine are able to react rapidly with DFF immediately upon their mixing at RT, giving quantitative formation of secondary di-imines (Schiff base) and demonstrating their outstanding capability for scavenging dialdehydes (Fig. S1). In contrast, either the long-chain aliphatic amine (e.g., oleylamine) or secondary amine cannot fast scavenge dialdehyde. With the suitable scavenger in hand, we then evaluate various transition metal catalysts for the reductive amination of DFF to BAMF under the presence of excess amount of n-butylamine. To our delight, base metal catalysts including Co and Ni delivered promising activity and selectivity to BAMF (Table 1); in particular, Co/ZrO₂ afforded the highest BAMF yield (95%, entry 2) hitherto. It appears that

the support nature, e.g., redox or acid/base, does not significantly affect the catalytic performance (entry 1-4) provided that the Co species is completely reduced to metallic phase and highly dispersed on the support surface (see H₂-TPR, HRTEM and in-situ XRD, Fig 1 and Fig. S2-3). Different from Co and Ni, Cu was inactive at all for the reductive amination of DFF. In stark contrast to Co and Ni, all the noble metal catalysts except for Ru failed to give BAMF (entry 8-11); instead, they preferentially catalysed the hydrogenation of secondary di-imine, leading to the formation of N₁-butyl-2,5-bis(aminomethyl)furan (BBAF, 3a), N₁,N₂-dibutyl-2,5-bis(aminomethyl)furan (DBAF, 4a) or N₁,N₂-dibutyl-2,5-bis(aminomethyl)tetrahydrofuran (DBATHF, 5a) as the main products. These results suggest that the hydrogenating capability of noble metals is too strong to allow for the trans-amination between the secondary di-imine and NH₃. Distinctive from the other noble metals, Ru/ZrO₂ offered a moderate selectivity to BAMF (56%, and the optimization of solvent and butylamine amount see Fig. S4 and Fig. S5) under the presence of n-butylamine, in accordance with the superior activity of Ru for reductive amination reactions.^{19, 20, 23}

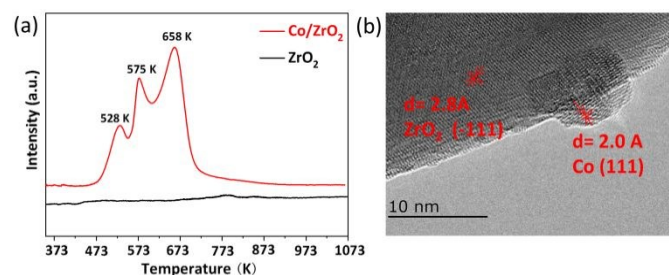


Figure 1. H₂-TPR profile (a) and HAADF-STEM image (b) of Co/ZrO₂ catalyst.

The success of this strategy is highly dependent on the employment of alkylamine as the DFF scavenger. Without alkylamine, one did not obtain any target product but only the formation of a large amount of oligomers and polymers (Fig. S6) irrespective of the catalyst nature. Moreover, short-chain aliphatic amines that are more rapidly reactive with DFF showed the more favourable effect in promoting the formation of BAMF (Fig. S7), confirming the key role of alkylamine as a scavenger in suppressing the polymerization reactions. More importantly, during the reaction the alkylamine was consumed only to a negligible extent (<5%), which allows for its good recycling.

Modulating trans-amination and hydrogenation

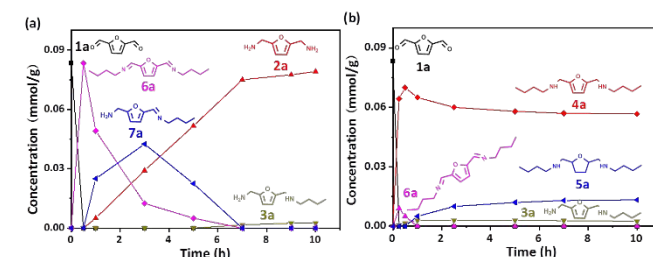


Figure 2. Reaction kinetic profiles for the reductive amination of DFF over (a) Co/ZrO₂ and (b) Pd/ZrO₂ catalysts. Reaction conditions: 30 mg catalyst, 0.25 mmol DFF, 0.75

mmol butylamine, 3 g methanol, 0.6 MPa NH₃, 2 MPa H₂, 373 K, dodecane as internal standard.

Besides the key role of alkylamine in arresting DFF, the capability of catalyst for modulating the trans-amination and hydrogenation is another key factor governing the reaction selectivity. Table 1 has clearly shown the dramatic difference in BAMF selectivity achieved on various metal catalysts, which should be due to their different capability for modulating the trans-amination and hydrogenation activity. In order to understand this process, we studied the reaction kinetics over Co/ZrO₂ and Pd/ZrO₂ catalysts (Fig. 2). In the case of Co/ZrO₂, the secondary di-imine **6a** was detected as the predominant intermediate at the beginning stage as a result of the fast reaction between n-butylamine and DFF, and it was then gradually consumed through trans-amination with NH₃ to form the primary imine and di-imine, which, upon being produced, must be immediately hydrogenated to the secondary intermediate **7a** and the final BAMF product (**2a**). During the whole process, only a negligible amount of **3a** was detected implying that the direct hydrogenation of secondary imine or di-imine was successfully suppressed. In stark contrast to Co/ZrO₂, Pd/ZrO₂ exhibits quite a different kinetic profile. Owing to the super-capability of Pd for hydrogenation, the secondary di-imine **6a**, upon being formed, was instantly hydrogenated to the secondary diamine (**4a**), which almost completely prevented the occurrence of trans-amination, and consequently the formation of primary diamine. Therefore, the high selectivity of Co/ZrO₂ can be attributed to its unique capability in modulating trans-amination and hydrogenation activity of the Schiff base. The control experiment (Fig. S8) revealed that, while DFF was quantitatively transformed into **6a** under the presence of n-butylamine and N₂, only approximately 10% yield of **6a** was obtained when NH₃ was added to the system, along with the formation of a large amount of dark brown oligomers and polymers (Fig. S9). This result suggests the occurrence of trans-amination reaction between **6a** and NH₃, which leads to the slow formation of primary di-imine (**8a**) and then causes the polymerization in case **8a** is not hydrogenated immediately. Furthermore, when we directly used Schiff base **6a** as the substrate to investigate the trans-amination behavior with or without catalyst (Fig. S10), we found that the Co/ZrO₂ catalyst could make the trans-amination reaction more sluggish, leading to a slower formation rate of the primary di-imine (**8a**), which is definitely favorable to the suppression of polymerization reactions associated with **8a**.

In order to understand the unique capability of Co/ZrO₂ for modulating the trans-amination and hydrogenation activity, we subsequently measured the adsorption capability for H₂ and NH₃. As shown in Fig. 3 and Table S1, both Co/ZrO₂ and Pd/ZrO₂ exhibit strong adsorption capacity for NH₃, which mainly reflects the strong interaction of support ZrO₂ with NH₃. In contrast, they show different adsorption strength towards H₂; Pd/ZrO₂ adsorbs H₂ more strongly with a higher adsorption heat and much more uptake than Co/ZrO₂. Moreover, after pre-adsorption of NH₃, Co/ZrO₂ did not show discernable H₂

uptake whereas Pd/ZrO₂ still maintained strong adsorption with H₂. These results imply that the relatively weak interaction of Co with H₂ leave room for the trans-amination between **6a** and NH₃, which agrees well with the calculation result reported on Ni.¹⁷ Kinetically, the primary imine is easier to be hydrogenated than the secondary imine. Even NH₃ deactivates the strong hydrogenation sites of the Co/ZrO₂ catalyst, the hydrogenation of primary imine can still proceed on weak hydrogenation sites. To further demonstrate the ability of Co/ZrO₂ to modulate the trans-amination and hydrogenation activity, we then used cyclopentanone as the substrate as its single functional group would allow for the detection of primary imine. When the secondary imine **1b** reacted with NH₃ over Co/ZrO₂, primary imine **2b** was formed as a result of trans-amination with a selectivity of 22% (the other 78% was oligmer, Fig. S11). Then, the mixture of **1b** and **2b** was submitted to hydrogenation over the Co/ZrO₂, and it was found that the hydrogenation of **1b** was completely suppressed while **2b** could be smoothly hydrogenated to the corresponding amine (Fig. S12). This result strongly suggests that, the competitive adsorption of the primary imine over the bulky secondary imine promote the preferential hydrogenation of the former, which in turn drive the trans-amination equilibrium to the primary imine side, and consequently lead to the high selectivity to the primary amine.

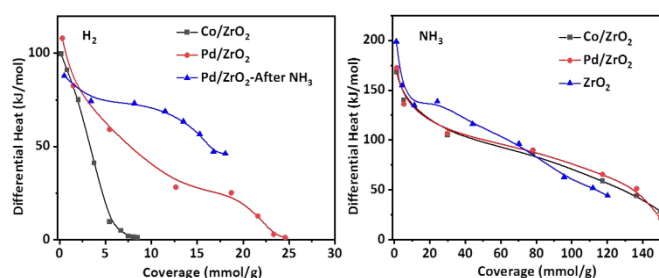
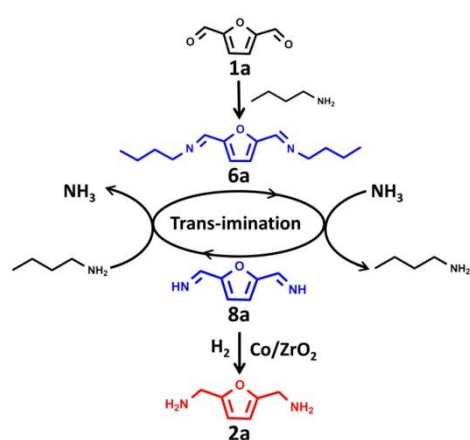


Figure 3. Differential adsorption heat of H₂ and NH₃ as a function of coverage on Co/ZrO₂, Pd/ZrO₂ and ZrO₂ samples.

Reaction mechanism

Based on these results, we propose the reaction mechanism illustrated in Scheme 2. In the first step, the excess amount of n-butylamine reacts quickly with DFF, forming secondary di-imine (**6a**), by which all the unwanted reactions associated with DFF such as condensation and polymerization can be completely prevented. Then, reversible trans-amination took place between **6a** and **8a** under the presence of NH₃, which results in the sluggish formation of primary di-imine (**8a**) due to the higher stability of **6a** than **8a**. Immediately upon its formation, **8a** can be instantly hydrogenated to the primary diamine BAMF. During the whole reaction process the highly reactive primary di-imine **8a** was not detected (Fig. 2), indicating it was consumed very rapidly by the subsequent hydrogenation. The nearly zero concentration of **8a** during the whole reaction process could also successfully avoid its condensation with the product **2a**. It should be emphasized that the higher nucleophilicity of butylamine than NH₃ not only

ensure the DFF react preferentially with butylamine instead of NH_3 , but also guarantee the subsequent trans-amination proceed slowly towards the primary mono- and di-imine. On the other hand, the employment of Co/ZrO_2 catalyst enable the trans-amination to proceed favorably over the hydrogenation of bulky secondary di-imine due to stronger adsorption of NH_3 than H_2 on the Co/ZrO_2 meanwhile allow for the subsequent hydrogenation of the primary di-imine. Moreover, the much lower concentration of 2a than NH_3 in the reaction system and the more bulky 2a than NH_3 hinder the reaction between 2a and 6a, making the reaction between 6a and NH_3 prevail. Evidently, the high selectivity to BAMF critically relies on the regulation of trans-amination and hydrogenation, which is accomplished by the employment of short-chain alkylamine and transition metal catalysts such as Co and Ni.



Scheme 2. Proposed mechanism for reductive amination of DFF over Co/ZrO_2 catalyst.

Potential for practical application

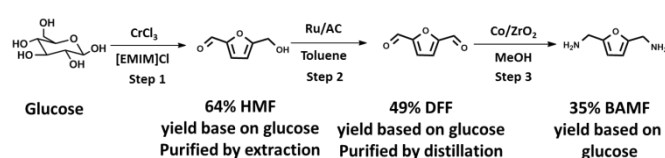


Figure 4. Product of BAMF based on glucose. Reaction conditions: Step 1: 500 mg glucose, 53 mg CrCl_3 , 5 g [EMIM]Cl (1-ethyl-3-methylimidazolium chloride) ionic liquid, 373 K, 3 h, after reaction, the product HMF was purified by extraction using glycol dimethyl ether and distillation; Step 2: 50 mg Ru/AC catalyst (Commercial), purified HMF from step 1, 5 g Toluene, 2 MPa O_2 , 383 K, 10 h, after reaction, the product DFF was purified by distillation; Step 3: 90 mg Co/ZrO_2 catalyst, a half of purified DFF from step 2, 2 mmol butylamine, 3 g methanol, 373 K, 10 h.

In addition to the unprecedentedly high selectivity to the primary diamines, this approach offers excellent reusability of the catalyst (Fig. S13a), and allows for the employment of relatively high concentration of dialdehyde substrate (up to 10%, Table S2), showing its great potential for practical application. The deactivation of 4th-run catalyst was attributed slight carbon coke, but recalcination and reduction can make Co/ZrO_2 get recovered (Fig. S13b). To further demonstrate this potential, we started from glucose and finally obtained 35% yield of BAMF based on glucose (Fig. 4). Moreover, the above

strategy is also applicable to the reductive amination of a broad scope of dialdehydes. As shown in Table 2, aromatic and cycloalkane dialdehydes substrates, which are potentially derived from lignocellulose,^{30, 31} could be successfully transformed into the corresponding primary diamines with excellent yields. More importantly, aliphatic dialdehydes such as 1,6-hexanedial could be successfully transformed into HDA in 63% yield, which provides an alternative pathway to HDA.

Table 2. Reductive amination of various dialdehydes over Co/ZrO_2 catalysts^a

Entry	Substrate	Yield (%)	
		Diamines	
1			93
2			97
3			93
4 ^b			81
5			90
6 ^c			63

^aReaction conditions: 30 mg Co/ZrO_2 catalyst, 0.25 mmol substrate, 0.75 mmol butylamine, 3 g methanol, 0.6 MPa NH_3 , 2 MPa H_2 , 373 K, 10h, dodecane as internal standard; ^b3 g toluene as solvent, 1 MPa NH_3 ; ^c4 MPa H_2 , 393 K.

Conclusions

In summary, we have developed a new approach to the highly selective synthesis of primary diamines from dialdehydes through modulating the trans-amination and hydrogenation activity, where the use of short-chain alkylamine to scavenge the highly reactive dialdehyde is the key to suppressing polymerization side reactions, and the suitable adsorption strength of Co towards NH_3 and H_2 is crucial to regulate the two competitive reactions. This strategy is expected to find wide applications in the synthesis of a broad scope of bio-based primary amines and diamines, thus help to construct sustainable polymer industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful for the support from the National Key R&D Program of China (2018YFB1501602), the National Natural Science Foundation of China (21690080, 21690084, 21673228, 21721004, and 21878289), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020100), and the Dalian National Laboratory for Clean Energy (DNL) Cooperation Fund, the CAS (DNL 180303).

Notes and references

View Article Online
DOI: 10.1039/D0GC02280B

- 1 Y. Wang, S. Furukawa, X. Fu and N. Yan, *ACS Catal.*, 2019, **10**, 311-335.
- 2 S. Imm, S. Bahn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas and M. Beller, *Angew. Chem. Int. Ed.*, 2011, **50**, 7599-7603.
- 3 J. L. Klinkenberg and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2011, **50**, 86-95.
- 4 W. Faveere, T. Mihaylov, M. Pelckmans, K. Moonen, F. Gillis-D'Hamers, R. Bosschaerts, K. Pierloot and B. F. Sels, *ACS Catal.*, 2019, **10**, 391-404.
- 5 M. Pelckmans, W. Vermandel, F. Van Waes, K. Moonen and B. F. Sels, *Angew. Chem. Int. Ed.*, 2017, **56**, 14540-14544.
- 6 Y. Zhang, X. Cui, F. Shi and Y. Deng, *Chem. rev.*, 2012, **112**, 2467-2505.
- 7 A. B. Dros, O. Larue, A. Reimond, F. De Campo and M. Pera-Titus, *Green Chem.*, 2015, **17**, 4760-4772.
- 8 V. Froidevaux, C. Negrell, S. Caillol, J. P. Pascault and B. Boutevin, *Chem. rev.*, 2016, **116**, 14181-14224.
- 9 M. Pelckmans, T. Renders, S. V. d. Vyver. and B. F. Sels, *Green Chem.*, 2017, **19**, 5303-5331
- 10 F. H. Isikgor and C. R. Becer, *Polym. Chem.*, 2015, **6**, 4497-4559.
- 11 D. Pingen, J. B. Schwaderer, J. Walter, J. Wen, G. Murray, D. Vogt and S. Mecking, *ChemCatChem*, 2018, **10**, 3027-3033.
- 12 X. Wang, W. Chen, Z. Li, X. Zeng, X. Tang, Y. Sun, T. Lei and L. Lin, *J. Energy Chem.*, 2018, **27**, 209-214.
- 13 Y. Xu, X. Jia, J. Ma, J. Gao, F. Xia, X. Li and J. Xu, *Green Chem.*, 2018, **20**, 2697-2701.
- 14 L. T. Mika, E. Csefalvay and A. Nemeth, *Chem. rev.*, 2018, **118**, 505-613.
- 15 H. Chang, A. H. Motagamwala, G. W. Huber and J. A. Dumesic, *Green Chem.*, 2019, **21**, 5532-5540.
- 16 N.-T. Le, A. Byun, Y. Han, K.-I. Lee and H. Kim, *Green and Sustainable Chemistry*, 2015, **05**, 115-127.
- 17 K. Zhou, H. Liu, H. Shu, S. Xiao, D. Guo, Y. Liu, Z. Wei and X. Li, *ChemCatChem*, 2019, **11**, 2649-2656.
- 18 H. Yuan, B. T. Kusema, Z. Yan, S. Streiff and F. Shi, *RSC Adv.*, 2019, **9**, 38877-38881.
- 19 G. Liang, A. Wang, L. Li, G. Xu, N. Yan and T. Zhang, *Angew. Chem. Int. Ed.*, 2017, **56**, 3050-3054.
- 20 T. Komanoya, T. Kinemura, Y. Kita, K. Kamata and M. Hara, *J. Am. Chem. Soc.*, 2017, **139**, 11493-11499.
- 21 T. Senthamarai, K. Murugesan, J. Schneidewind, N. V. Kalevaru, W. Baumann, H. Neumann, P. C. J. Kamer, M. Beller and R. V. Jagadeesh, *Nat. commun.*, 2018, **9**, 4123.
- 22 M. Chatterjee, T. Ishizaka and H. Kawanami, *Green Chem.*, 2016, **18**, 487-496.
- 23 D. Chandra, Y. Inoue, M. Sasase, M. Kitano, A. Bhaumik, K. Kamata, H. Hosono and M. Hara, *Chem. Sci.*, 2018, **9**, 5949-5956.
- 24 W. Guo, T. Tong, X. Liu, Y. Guo and Y. Wang, *ChemCatChem*, 2019, **11**, 4130-4138.
- 25 M. Ciaccia, R. Cacciapaglia, P. Mencarelli, L. Mandolini and S. Di Stefano, *Chem. Sci.*, 2013, **4**, 2253-2261.
- 26 L. M. Wang, J. Y. Yue, X. Cao and D. Wang, *Langmuir*, 2019, **35**, 6333-6339.
- 27 H. Fischer, F. X. DeCandis, S. D. Ogden. and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **102**, 1340-1347.
- 28 P. Kovaricek and J. M. Lehn, *J. Am. Chem. Soc.*, 2012, **134**, 9446-9455.
- 29 N. S. Gould, H. Landfield, B. Dinkelacker, C. Brady, X. Yang and B. Xu, *ChemCatChem*, 2020, **12**, 2106-2115.
- 30 C. Liu, H. Wang, A. M. Karim, J. Sun and Y. Wang, *Chem. Soc. Rev.*, 2014, **43**, 7594-7623.
- 31 D. Bai, Q. Chen, Y. Chai, T. Ren, C. Huang, I. D. V. Ingram, M. North, Q. Zheng and H. Xie, *RSC Adv.*, 2018, **8**, 34297-34303.