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Mechanistic insights to drive catalytic hydrogenation of formamide intermediates to methanol via deaminative hydrogenation

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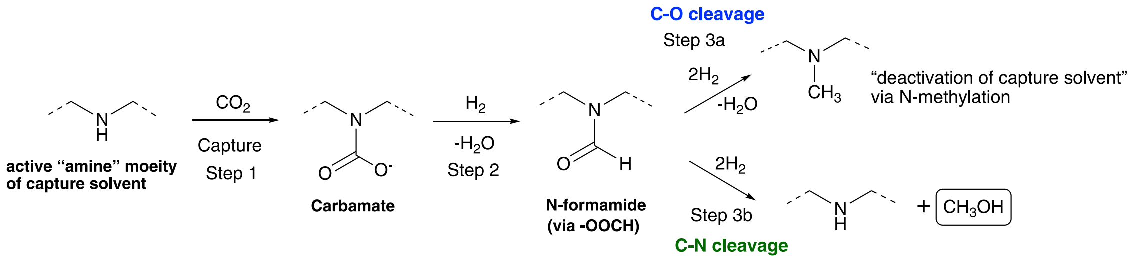
Amine-promoted hydrogenation of CO_2 to methanol typically proceeds via a formamide intermediate when amines are used as additives or if the hydrogenation is performed in carbon capture solvents. The catalysts used for the hydrogenation of the formamide intermediate dictate the selectivity of the products formed: 1) Deoxygenative hydrogenation (C−O bond cleavage) resulting in N-methylation of amine and deactivation of the solvent, 2) Deaminative hydrogenation (C−N bond cleavage) resulting in formation of methanol and regeneration of the solvent. To date, catalytic reductions of CO_2 with amine promoters suffer from poor selectively for methanol which we attribute to the limiting formamide intermediate, though to date, the conditions that favor C−N cleavage have yet to be fully understood. To better understand the reactivity of the formamide intermediates, a range of heterogenous catalysts were used to study the hydrogenation of formamide. Well-known gas phase CO_2 hydrogenation catalysts catalyze the hydrogenation of formamide to N-methyl product via C−O bond cleavage. However, the selectivity can be readily shifted to selective C−N bond cleavage by addition of an additive with sufficient basicity for both homogenous and heterogeneous catalytic systems. The base additive shifts the selectivity by deprotonating a hemiaminal intermediate formed *in situ* during the formamide hydrogenation. This prevents dehydration process leading to N-methylated product, which is a key capture solvent deactivation pathway that hinders amine use in carbon capture, utilization, and storage (CCUS). The findings from this study provide a roadmap on how to improve the selectivity of known heterogenous catalysts, enabling catalytic reduction of captured CO_2 to methanol.

KEYWORDS

methanol synthesis, hydrogenation, C-N cleavage, N-methylation, catalysis

1 Introduction

Anthropogenic CO_2 emissions are considered as a main driver of global warming and climate change. To mitigate the rise in CO_2 concentrations in the atmosphere, recycling of CO_2 to fuels and materials may help provide economic incentives to jump-start the transition to a CO_2-neutral, then ultimately a CO_2-negative economy (Al-Mamoori



SCHEME 1
Hydrogenation of CO_2 to methanol in the presence of a capture solvent.

et al., 2017; Bui et al., 2018; Gabrielli et al., 2020; Wei et al., 2022). We have recently posited that an *integrated* CO_2 capture and conversion to materials (IC^3M) approach, where the capture and conversion are performed in the same medium, such that the process can minimize or partially offset the energy intensive CO_2 desorption, compression, and transportation stages (Heldebrant et al., 2022). In an IC^3M approach, the captured CO_2 can be directly converted to value-added chemicals which are then transported from the CO_2 capture site instead of pipelines to move compressed supercritical CO_2. Recent studies have focused on examining the viability of different media, catalysts, and experimental conditions for varied IC^3M approaches (Heldebrant et al., 2022; Siegel et al., 2023).

CO_2 capture solvents are most commonly studied than solids due to low capture costs, fast kinetics, enhanced heat and mass transfer, and ease of handling in a continuous flow process (Heldebrant and Kothandaraman, 2020; Heldebrant et al., 2022). Aqueous organic amines (such as 30wt% aqueous monoethanol amine) are the first-generation solvents that are commonly used for CO_2 capture, with recent second-generation aqueous amines such as CANSOLV, piperazine and KS-1 have shown significant improvement in efficiency (Heldebrant and Kothandaraman, 2020). Recently, third generation solvents have been designed for water-lean conditions, lessening their energy demand. Irrespective of whether water-based or water-lean solvents are used, primary and/or secondary amines are the active moieties, reacting with CO_2 to form carbamate and/or bicarbonate species. The catalytic reduction of carbamate and/or bicarbonate species to products, such as formates, methanol and cyclic carbonates, has been demonstrated (Li et al., 2013; McNamara and Hicks, 2014; Rezayee et al., 2015; Kothandaraman et al., 2016a; Kothandaraman et al., 2016b; Lao et al., 2016; Kar et al., 2018; Kar et al., 2019; Kothandaraman et al., 2019; Kothandaraman and Heldebrant, 2020b; Sen et al., 2020; Kothandaraman et al., 2021; Wei et al., 2021; Kothandaraman et al., 2022a; Heldebrant et al., 2022). Among these products, methanol is attractive as a fuel and feedstock for production of various value-added chemicals, representing a large market for CO_2 reuse.

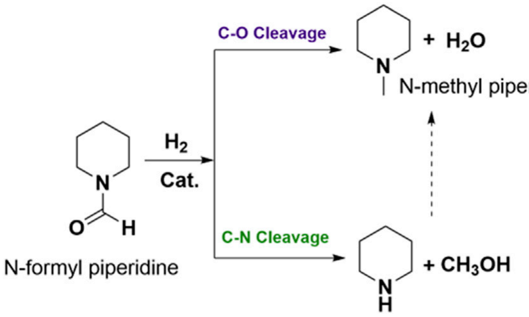
Unlike the traditional gas phase CO_2 reduction to methanol (Porosoff et al., 2016; Huš et al., 2017; Pavlišič et al., 2020; Prasnikar et al., 2021; Kanuri et al., 2022), in the low-temperature amine-promoted catalytic reductions, ammonium carbamate/bicarbonate are reduced to methanol via a formamide intermediate (Scheme 1) (Rezayee et al., 2015; Kothandaraman et al., 2016a; Everett and Wass, 2017; Kar et al., 2018; Kothandaraman et al., 2022b). The hydrogenation of the formamide intermediate has been typically identified as a rate determining step (Kothandaraman and Heldebrant, 2020a; Rayder et al., 2020). One of the main challenges with integrated capture and conversion of CO_2 to methanol in the presence of amine-based capture solvents is an N-methylation, which is formed from a C–O cleavage of N-methyl formamide rather than C–N cleavage of amide to methanol. N-methylation leads to deactivation of the capture solvent by converting the 2° amine to a 3° amine, thus preventing further carbamate formation (CO_2 uptake) and thermal condensation of an ammonium formate salt to the formamide intermediate. Homogenous catalysts selective for hydrogenation of CO_2 to methanol have been reported in the literature (Rezayee et al., 2015; Kothandaraman et al., 2016a; Everett and Wass, 2017; Kar et al., 2018). However, from a separation standpoint, heterogenous catalysts are preferred for continuous flow operations. Additionally, their superior durability is needed for process conditions and impurities common in post-combustion CO_2 capture. While gas phase CO_2 catalysis in presence of a solid heterogenous catalysts were widely investigated, our understanding on low-temperature condensed phase CO_2 chemistry remains very limited.

To gain this knowledge we need to first study model systems to learn how to control the product selectivity in low-temperature CO_2 hydrogenation chemistry. Herein, N-formyl piperidine was chosen as a model substrate to understand the C–O vs. C–N bond cleavage selectivity during the amide hydrogenation to methanol step (Step 3b, Scheme 1). In the literature, the selection of the catalyst is often reported to be important for C–N cleavage selectivity and the majority of them are organometallic catalysts (Werkmeister et al., 2014; Cabrero-Antonino et al., 2020). We found that the presence of an additive with sufficient basicity plays a crucial role in switching the selectivity from C–O cleavage to C–N cleavage. For the first time such trend has been identified across different heterogenous catalysts. We also show selectivity as high as 86% for C–N cleavage to methanol, even in the presence of a Cu-based catalyst. It is also important to note that the findings derived from this research are also relevant to the selective synthesis of amines and alcohols from hydrogenation of amides—amide functionalities are common in pharmaceuticals, natural products, and agrochemicals.

2 Materials and methods

Materials: The $Cu/Zn/Al_2O_3$ (64wt%) was obtained from Alfa Aesar. Copper Chromite and 1,3,5-trimethoxybenzene (TMB) were purchased from Sigma Aldrich. Al_2O_3 (γ-Al_2O_3) was purchased from

TABLE 1 **Hydrogenation of N-formyl piperidine in the presence of $Cu/ZnO/Al_2O_3$ catalyst and different additives.**

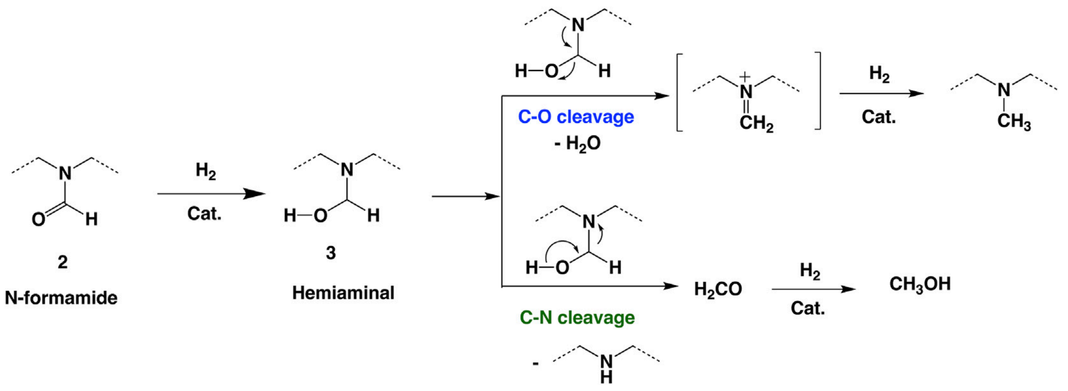


Entry	Catalyst	Conditions	Additives (Henderson et al., 2015)	Conversion (%)	CH_3OH selectivity (%)	N-Methyl piperidine selectivity (%)
1	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	–	94.2	4.9	95.1
2	$Cu/ZnO/Al_2O_3$	170°C, 3 h, THF	–	91.8	10.7	89.3
3	$Cu/ZnO/Al_2O_3$	170°C, 1 h, THF	–	78.6	12.2	87.8
4	$Cu/ZnO/Al_2O_3$	150°C, 1 h, THF	–	58.3	16.3	83.7
5	$Cu/ZnO/Al_2O_3$	170°C, 1 h, THF	Hunig's base (pKa = 10.75)	94.9	14.3	85.7
6	$Cu/ZnO/Al_2O_3$	170°C, 1 h, THF	KOH (pKa = 15.74)	3.2	88.6	11.4
7	$Cu/ZnO/Al_2O_3$	170°C, 1 h, THF	1-IPADM-2-BOL (pKa = 23)	40.7	12.7	87.3
8	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	KOH (pKa = 15.74)	47.1	51.0	49.0
9	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	KO^{t}Bu (pKa = 19.2)	48.8	49.9	50.1
10[a]	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	KO^{t}Bu (pKa = 19.2)	19.8	47.6	52.4
11	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	Piperidine (pKa = 11.22)	91.9	4.9	95.1
12	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	K_3PO_4 (pKa = 11.74)	77.1	12.3	87.7
13[b]	$Cu/ZnO/Al_2O_3$	120°C, 3 h	Formic acid	<1	0	traces

N-formylpiperidine = 5 g (44 mmol), THF = 5 mL, 64wt% $Cu/ZnO/Al_2O_3$ = 400 mg, KO^{t}Bu or Piperidine or KOH or 1-IPADM-2-BOL or Hunig's base or K_3PO_4 = 3.6 mmol, H_2 = 60 bar, t = 12 h, T = 170°C; [a]KO^{t}Bu = 7.2 mmol, [b]No hydrogen added. 87% formic acid in water = 2.5g; conversion and selectivity were determined by the ^1H NMR with TMB as an internal standard. pKa values of the bases are in water at 25°C.

Engelhard. Carbonylchlorohydrido[bis(2-(diphenylphosphinoethyl) amino]ruthenium (II) (also known as Ru-MACHO) was purchased from Strem chemicals. Unless otherwise mentioned, all other materials were obtained from commercial suppliers and used without further purification. All deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. All other catalysts (metal supported on metal oxides) were prepared by incipient wetness impregnation of nitrate metal precursors, followed by drying (8 h at 100°C) and calcination at 400°C (4 h under static air). TMB was used as an internal standard for NMR spectroscopy.

Standard experimental procedure for the hydrogenation of N-formyl piperidine: A Parr reactor (100 mL) equipped with a thermocouple, pressure transducer, turbine type impellor and reactor controller, was charged with a catalyst, base additive, and solvent, and sealed in a N_2-atmosphere glovebox. The reactor was then pressurized with H_2 (60 bar) and stirred at 170°C. The reactor



SCHEME 2
Proposed reaction mechanism for the hydrogenation for formamide.

was cooled to room temperature, and the gas in the reactor headspace was analyzed using a 2-channel Fusion MicroGC (Inficon). The remaining excess gas was slowly released after cooling the reactor to −78°C. TMB was added as an internal standard to the reaction mixture, and a small aliquot of the sample was analyzed by ^{1}H NMR experiments.

3 Results

First, the commercial methanol synthesis catalyst, $Cu/ZnO/Al_2O_3$, was studied to establish a baseline for the selective hydrogenation of N-formyl piperidine to methanol via C–N cleavage. Analogous to catalytic systems previously reported (Gredig et al., 1995; Gredig et al., 1996; 1997; Auer, 1999; Cui et al., 2014; Cabrero-Antonino et al., 2020), N-methyl piperidine formed with high conversion (93.2%) and selectivity (96%) via C–O cleavage of the N-formyl piperidine. In order to understand the reaction mechanism and conditions that favor the C–N cleavage over the C–O cleavage, the effect of reaction temperature, time and different additives on the selectivity and conversion was studied. As shown in entries 1–3, Table 1, the selectivity to methanol decreased with the increase in reaction time. The methanol yields for entries 1 (12 h), 2 (3 h) and 3 (1 h) were 4.6%, 9.8% and 9.6%, respectively. With the decrease in the reaction temperature from 170°C (entry 3, Table 1) to 150°C (entry 4, Table 1), the overall conversion decreased with some improvement in the methanol selectivity. These results show that the methanol acted as a N-methylating agent causing N-methylation of free amine with longer reaction time (Guillena et al., 2010). Thus, the methanol yield decreased while the N-methylation yield increased with increasing reaction time, as expected. To further confirm the role of methanol in N-methylation, piperidine was reacted with methanol under our typical reaction conditions ($Cu/ZnO/Al_2O_3$, under 60 bar H_2 at 170°C for 12 h), a quantitative conversion of piperidine to N-methyl formamide was observed. Thus, longer reaction time is detrimental to the reaction selectivity due to the reactive nature of methanol.

To further understand and improve the C–N cleavage selectivity, we examined the proposed reaction mechanism for the hydrogenation of formamide (Cantillo, 2011; Volkov et al., 2016; Cabrero-Antonino et al., 2020). Based on the literature, the initial hydrogenation of formamide forms a hemiaminal intermediat**e, 3** (Scheme 2), which then can undergo C–N cleavage to form methanol and free amine via hydrogenation of a formaldehyde intermediate. Alternatively, the hemiaminal intermediate can undergo dehydration to form an imine intermediate via C–O cleavage. The subsequent hydrogenation of the imine intermediate forms the N-methylated amine. From the reaction mechanism, we hypothesized that the addition of catalytic amounts of base additives could improve the C–N cleavage selectivity by deprotonation of the proposed hemiaminal intermediate in Scheme 2. The deprotonation of hemiaminal can prevent the dehydration and subsequent formation of the imine intermediate.

To validate this mechanism, we first tested bases with varying pKa and the results are shown in entries 5–11, Table 1. With the addition of Hünig's base (N,N-Diisopropylethylamine) (pKa = 10.75), there was some improvement in the methanol selectivity and conversion (entry 3 vs. 5, Table 1). The addition of KOH (pKa = 15.74) significantly improved the selectivity of methanol to 88.6% albeit with a low yield (3.2%) (entry 3 vs. 6, Table 1). The alkanolgaunidine based solvent additive, 1-IPADM-2-BOL (pKa = 23) (Zheng et al., 2016) significantly reduced the conversion with no change in the selectivity (entry 3 vs. 7, Table 1). This is because the amidinium based moieties are not stable under hydrogenation conditions in the presence of $Cu/ZnO/Al_2O_3$ catalyst. Longer reaction time improved the conversion to 47.1% (methanol yield = 24%) with a drop in selectivity to 51.0% (entry 8, Table 1), likely because the formed methanol became a methyl source to form N-methyl piperidine. The conversion and selectivity for the KO^{t}Bu (pKa = 19.2) added reaction performed similar to KOH (entry 9, Table 1). As the base additive content increased, the conversion decreased without significantly affecting selectivity because the excess base could block the active sites that are promoting hydrogenation (entry 10, Table 1). No significant change on the selectivity was observed with piperidine (pKa = 11.22; entry 1 vs. 11, Table 1), suggesting this additive is not strong enough to deprotonate the hemiaminal intermediate (**3**). There was some improved in the selectivity in the case of K_3PO_4 (pKa = 11.74; entry 1 vs. 12, Table 1) additive. Overall, base additives with

TABLE 2 Hydrogenation of N-formyl piperidine in the presence of different catalysts.

Entry	Catalyst	Conditions	Additives	Conversion (%)	CH_3OH selectivity (%)	N-Methyl piperidine selectivity (%)
1	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	–	94.2	4.9	95.1
2	$Cu/ZnO/Al_2O_3$	170°C, 12 h, THF	KO^tBu	48.8	49.9	50.1
3	$Cu/ZnO/Al_2O_3$	150°C, 12 h, THF	KO^tBu	4.3	83.0	17.0
4	Copper chromite	170°C, 12 h, THF	–	29.8	4.5	95.5
5	Copper chromite	170°C, 12 h, THF	KO^tBu	1.3	83	17
6	35wt% Cu/Al_2O_3	170°C, 12 h, THF	KO^tBu	10.7	63.8	36.2
7	5wt%Ag/Al_2O_3	170°C, 12 h, THF	–	5.0	9.5	90.5
8	5wt%Ag/Al_2O_3	170°C, 12 h, THF	KO^tBu	9.4	86.0	14.0
9	5wt%Pd/Al_2O_3	170°C, 12 h	–	5.4	21	79
10	5wt%Pd/Al_2O_3	170°C, 12 h, THF	KO^tBu	7	75	25
11	5wt%$Pd/ZnO/Al_2O_3$	170°C, 12 h, THF	–	72	2.0	98.0
12	5wt%$Pd/ZnO/Al_2O_3$	170°C, 12 h, THF	KO^tBu	5.4	76.8	23.3
13	5wt%Au/Al_2O_3	170°C, 12 h, THF	KO^tBu	0	–	–
14	35wt%Ni/Al_2O_3	170°C, 12 h, THF	KO^tBu	0.5	75.0	25.0
15[a]	5wt%Ru/Al_2O_3	170°C, 12 h, THF	–	84	–	–
16	Ru-MACHO	160°C, 3 h	–	17.6	33	67
17	Ru-MACHO	160°C, 3 h, THF	KO^tBu	72	94	6

N-formyl piperidine = 5 g (44 mol), THF, 5 mL, Ru-MACHO, 50 mg, Heterogenous catalysts = 400 mg, KO^tBu = 3.6 mmol, H_2 = 60 bar, 35wt% Cu/Al_2O_3 = 200 mg. [a]Methane formed with 84% yield (based on GC); Conversion and selectivity were determined by the ^1H NMR, with TMB, as an internal standard.

pKa >15.7 are effective in deprotonating the hemiaminal species, promoting the formation of formaldehyde intermediate and consequently improving the selectivity to methanol (Note the pKa values listed in Table 1 are in water, and the actual pKa will likely differ in the THF solvent). In addition, in the case of entries 8 and 9, the methanol yield was more than the amount of base added, suggesting sub-stoichiometric amount of base is sufficient for improved C-N cleavage selectivity. This study provides a first example for the switch in the selectivity of C–O cleavage to C–N cleavage in amide hydrogenation by using a co-catalyst or additive without changing the catalyst in heterogeneous systems. The use of formic acid in place of hydrogen formed a significant amount of H_2, CO and CO_2 in the gas phase (by decomposition of formic acid) with no appreciable reaction with the N-formyl piperidine (entry 13, Table 1).

Following this observation, we also tested other heterogenous catalysts to understand the effect of base additives (Table 2). Similar to $Cu/ZnO/Al_2O_3$ catalyst, the other Cu catalysts, copper chromite and Cu/Al_2O_3, also showed suppression in N-methylation upon the addition of a base. Even with the Ag/Al_2O_3, the first heterogenous catalyst reported in the literature for selective C–N cleavage, we noticed in the absence of a base additive, the C–O cleavage was predominant, and a base is necessary for the C–N cleavage selectivity (Xie et al., 2018; Cabrero-Antonino et al., 2020; Long et al., 2023). The following catalysts were also screened for the C–N cleavage selectivity: Pd/Al_2O_3 and $Pd/ZnO/Al_2O_3$. In both the cases, the addition of KO^tBu, switched the selectivity towards C–N cleavage. Au/Al_2O_3 was inactive for hydrogenation of N-formyl piperidine. Similar to previous reports (Kothandaraman et al., 2021; Koch et al., 2023), Ru/Al_2O_3 catalyst selectively formed methane after hydrogenation with no detectable amounts of methanol or N-methyl piperidine (Entry 15, Table 2).

Next, to understand if a similar switch in the selectivity can be observed in the presence of a homogenous catalyst, we tested the well-known low temperature methanol synthesis catalyst (from CO_2 hydrogenation), Ru-MACHO, for the hydrogenation of N-formyl piperidine (Kothandaraman et al., 2016a; Kar et al., 2018). Hydrogenation of CO_2 to methanol in the presence of Ru-MACHO has been widely demonstrated to proceed via a formamide intermediate. Entry 16, Table 2, to our surprise, in the absence of base addition and solvent, Ru-MACHO formed N-methyl piperidine with good selectivity. Notably, similar to heterogeneous catalysts, we observed a switch in the selectivity with Ru-MACHO catalyst with the addition of a base.

4 Conclusion

In summary, we studied the effect of reaction temperature, time and different additives on the C-O and C-N cleavage selectivity during catalytic hydrogenation of formamide. We show that in the absence of any additives, hydrogenation of N-formyl piperidine formed N-methyl piperidine by C–O bond cleavage with high selectivity (>90%). On the other hand, in the presence of a base additive, the selectivity switched to methanol formation by C–N bond cleavage. We also showed that the (*in situ* formed) product methanol can also act as a N-methylating agent upon longer residence time. Such reactivity trend has been identified for the first time across a range of heterogeneous catalysts and the homogeneous catalyst, Ru-MACHO. The strong base additive can deprotonate the hemiaminal intermediate, preventing the subsequent dehydration step to form N-methyl piperidine. The results from this study show the crucial role of base additives in determining the product selectivity. The ease of which the selectivity can be shifted from C–O cleavage to C–N cleavage provides a simple and effective means to suppress amine deactivation by N-methylation. This study provides new fundamental understandings on how to better design integrated capture and conversion systems to upcycle CO_2 into useful products like methanol.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher’s note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenrg.2023.1158499/full#supplementary-material

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