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Short Communication

Transient kinetic analysis of CO oxidation over a Cu-SSZ-13 catalyst proves complete conversion of $ZCu^{2+}(OH)^-$ cations to binuclear Cu^{2+} species

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ABSTRACT

The nuclearity of Cu^{2+} species active in the low-temperature Reduction Half Cycle (RHC) of NOx Selective Catalytic Reduction with NH_3 over Cu-CHA catalysts is controversial. In the past, transient CO to CO_2 oxidation protocols have been used to titrate binuclear Cu^{2+} species, and identified NH_3-solvated $ZCu^{2+}(OH)^-$ ions as their precursors. However, the prior results relied on asymptotic extrapolation due to the very slow CO oxidation kinetics. We herein present the results from a prolonged (24 h) CO titration experiment under dry conditions over an industrial Cu-SSZ-13 catalyst: the results demonstrate the conversion of all $ZCu^{2+}(OH)^-$ ions to binuclear Cu^{2+} complexes and agree well with the extrapolation of a shorter (90 min) experiment, based on the assumption of the CO oxidation rate being second order in $ZCu^{2+}(OH)^-$. These outcomes confirm the adequacy of short CO oxidation tests to titrate $ZCu^{2+}(OH)^-$ ions and support a Cu^{2+} pair mediated RHC pathway.

1. Introduction

Substantial advancement has been achieved in the mechanistic understanding of the Selective Catalytic Reduction of NOx with NH_3 (NH_3-SCR) over Cu-exchanged small pore chabazite catalysts in the diesel exhaust environment. When in the low temperature regime (<250 °C), the Standard-SCR (STD-SCR) reaction

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

is associated with a redox pathway wherein the copper cations act as precursors of the catalytic active sites (Borfecchia et al., 2018; Kwak et al., 2012; Paolucci et al., 2017; Paolucci et al., 2016; Janssens et al., 2015; Marberger et al., 2018; Partridge et al., 2018; Liu et al., 2020; Lambert, 2019), and their formal oxidation state cycles between Cu^{2+} and Cu^+. Indeed, NO and NH_3 act as reducing agents in the Reduction Half Cycle ($Cu^{2+} \rightarrow Cu^+$, RHC) while O_2 re-oxidizes Cu in the Oxidation Half Cycle ($Cu^+ \rightarrow Cu^{2+}$, OHC). A variety of techniques (e.g.: DRIFTS, in situ FTIR, H_2-TPR, DFT calculations) have probed the existence of at least two initially segregated cations inside the zeolite crystalline structure, namely $ZCu^{2+}(OH)^-$ and Z_2Cu^{2+} (Z represents a zeolite Al site) (Paolucci et al., 2016; Gao and Szanyi, 2018; Kwak et al., 2012; Luo et al., 2015; Villamaina et al., 2019; Luo et al., 2017). These cationic species exhibit distinct positions, thermodynamic stability, and mobility within the CHA cage. Furthermore, several studies have identified the formation of NH_3-solvated Cu complexes (e.g., $Cu^{2+}(NH_3)_4$, $Cu^{2+}(OH)^-(NH_3)_3$, $Cu^+(NH_3)_2$) (Borfecchia et al., 2018; Paolucci et al., 2017; Paolucci et al., 2016; Partridge et al., 2018; Rizzotto et al., 2018). Ammonia, in fact, is believed to confer homogeneous catalytic traits to the system by detaching Cu cations from the zeolite framework and enabling them to diffuse within and across zeolite cages. A widely accepted proposal implies that the OHC step involves the oxygen-driven coupling of two $[Cu^+(NH_3)_2]$ structures, thus forming a Cu^{2+} oxo-dimer inside the zeolite pore (Paolucci et al., 2017; Paolucci et al., 2016; Rizzotto et al., 2018; Oda et al., 2020; Deka et al., 2022; Nasello et al., 2023). Conversely, the RHC pathway and the associated reaction intermediates remain less known. Single site mechanisms occurring on secluded cations have been typically proposed, based on DFT calculations and spectroscopic evidence (XAS, EPR, FTIR) (Paolucci et al., 2017; Paolucci et al., 2016; Janssens et al., 2015; Gao et al., 2017; Gao et al., 2014). Recent literature findings, however, have challenged such single-site proposals: transient response methods (TRMs), DFT calculations, as well as transient kinetic analysis suggest that formation of Cu^{2+} binuclear structures and their involvement in the RHC mechanism are

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also feasible (Nasello et al., 2023; Chen et al., 2020; Hu et al., 2021; Deka et al., 2022; Hu et al., 2021; Gramigni et al., 2021; Usberti et al., 2020).

In this context, transient CO oxidation serves as an effective probe reaction to investigate the presence of such binuclear complexes. In fact, CO oxidation to CO_2 requires a two-electron exchange whereas the reduction of each Cu^{2+} ion to Cu^{+} involves only one electron exchange, therefore it inherently detects adjacent Cu^{2+} cations (Hu et al., 2021; Da Costa et al., 2002; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020; Paolucci et al., 2020). The formation of multinuclear Cu^{2+} species due to Cu mobilization by NH_3 ligands, as well as the effects of catalyst formulation (Cu speciation, Cu loading), and of dynamic site interconversion in the presence of H_2O have been investigated with this methodology over model Cu-CHA samples (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020). Most importantly, CO titration tests under dry conditions suggest that only one of the two cation populations, namely $ZCu^{2+}(OH)^{-}$, serves as precursors of the binuclear catalyst active sites (Hu et al., 2021; Iacobone et al., 2023; Villamaina et al., 2020). A similar conclusion has been reported based on UV–vis observations (Paolucci et al., 2020). The conclusions from CO oxidation experiments referenced above, however, relied on asymptotic extrapolation of the Cu^{2+} reduction rate, as only an incomplete titration of the Cu^{2+} cations could be achieved in the 1.5 h long runs due to the very slow reaction kinetics.

In this study we have conducted an experiment with extended CO exposure (24 h) on a commercial Cu-SSZ-13 monolith catalyst in order to conclusively assess the share of the $ZCu^{2+}(OH)^{-}$ species involved in the dry CO oxidation mechanism, hence in the formation of binuclear Cu^{2+} species responsible for the RHC of Standard SCR. From a methodological perspective, we use the present results to establish whether shorter exposures to CO can be confidently extrapolated to count the dimeric Cu^{2+} species.

2. Experimental

CO titration experiments were carried out on a commercial Cu-SSZ-13 catalyst supplied by Cummins Inc. (USA) in the form of a washcoated honeycomb monolith, with a cell density of 600 cpsi and 2.2 % w/w as average Cu loading in the washcoat, measured by ICP analysis. The material was characterized and tested in two different experimental setups.

1) Powder rig: a powdered sample was obtained by scratching the washcoat off the monolith. The material was then sieved to obtain a particle size of ~90 μm. 32 mg of catalyst were diluted with cordierite up to 130 mg, and then loaded in a micro-flow quartz tubular reactor with an inner diameter of ~6 mm. This was placed in a vertical electrical oven, with a K-type thermocouple inserted into the catalytic bed. The inlet gas composition was set and controlled using Brooks mass flow controllers, with gases from bottles containing calibrated mixtures supplied by Sapio. The feed gas contained argon as a tracer, and helium as the carrier gas. Two 6-way pulse valves were used to change the feed gas composition during step change experiments (transient response methods, TRM). CO, CO_2, H_2O, NO, NO_2, N_2O, NH_3 and Ar concentrations were measured using an ABB Limas 11 W UV analyser in parallel with a Hiden Analytical QGA mass spectrometer. The gas hourly space velocity (GHSV) was 266,250 $cm^3/h/g_{cat}$ (STP). More details about the experimental apparatus can be found in (Usberti et al., 2020; Iacobone et al., 2022).
2) Monolith rig: a cylindrical honeycomb catalyst sample (45 cells) was core drilled and cut to a length of 2.9 cm. The catalyst was placed in a quartz tube, in turn placed inside a Lindberg Blue Mini-mite horizontal furnace with a K-type thermocouple pair, purchased from Omega, in direct contact with the upstream and downstream sections of the monolith. Nitrogen was used as the carrier gas and the inlet gas composition was set and controlled using MKS mass flow controllers. Gases were purchased from Praxair. Switches in gas composition were also achieved with a four-way valve installed upstream to the reactor. The total flow rate was set to ensure a GHSV of 60,000 1/h, and a MKS MultiGas 2030 FT-IR analyser was used to measure the reactor outlet concentrations of CO, CO_2, H_2O, NO, NO_2, N_2O and NH_3.

Prior to each experiment, a 1-h pre-oxidation step in 8% O_2 at 550°C was carried out to remove any adsorbates and oxidize all the Cu species to Cu^{2+} (Villamaina et al., 2019; Gramigni et al., 2021; Usberti et al., 2020; Iacobone et al., 2022).

3. Results and discussion

3.1. Transient characterization tests (Cu^{2+}, $ZCu^{2+}(OH)^{-}$)

A transient isothermal NO + NH_3 reduction was run at 150°C on the monolith catalyst to titrate the reducible Cu sites, following the experimental protocol described elsewhere (Gramigni et al., 2021). The monolith sample was initially exposed to 400 ppm NH_3, in 8% O_2 and balance N_2, until NH_3 saturation. NH_3 and O_2 were then removed from the feed stream, followed by a 5-minute N_2-only purge to ensure complete depletion of oxygen from the gas phase. The catalyst was then exposed to 400 ppm of both NO and NH_3, during which NO consumption was detected (Fig. 1(A)). This signals the Cu^{2+} reduction process, which proceeds according to an equimolar stoichiometry: Cu^{2+}:NO = 1:1 (Paolucci et al., 2017; Villamaina et al., 2019; Nasello et al., 2023; Deka et al., 2022; Gramigni et al., 2021; Usberti et al., 2020; Iacobone et al., 2022; Daya et al., 2022; Daya et al., 2021). Therefore, the integral amount of NO consumed until full reduction, 72 μmol, measures the overall content of reducible Cu^{2+} in the tested sample.

The $ZCu^{2+}(OH)^{-}$ population was estimated running a NO_2 adsorption/TPD protocol on the powdered catalyst (Villamaina et al., 2019; Hu et al., 2021; Gramigni et al., 2021; Iacobone et al., 2023; Colombo et al., 2012) in a dedicated rig which enabled NO_2 step feed and fast transients. The catalyst was first exposed to 500 ppm NO_2 at 150°C, until the reactor outlet concentration recovered the inlet value. Subsequently, a temperature programmed desorption (TPD) step, from 150 to 550°C at 10°C/min, was started. The decomposition of the nitrates formed during the adsorption phase and released as NO_2 during the TPD is correlated 1:1 to the $ZCu^{2+}(OH)^{-}$ cation fraction (Colombo et al., 2012; Negri et al., 2018). The quantification procedure has been reported in previous work (Villamaina et al., 2019). Combined with the Cu content from ICP, this sequence of experiments shows that 87% of the ion-exchanged Cu is present as $ZCu^{2+}(OH)^{-}$. The corresponding NO_2 profile during the TPD is shown in Fig. 1(B).

3.2. Transient CO oxidation tests

The isothermal CO oxidation protocol has been developed and applied in prior studies (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020). While previous tests were carried out at 200°C, a temperature of 150°C was adopted herein to extend the validity of the technique. The protocol consists of three steps: i) exposure of the catalyst sample to 400 ppm NH_3 for 1.5 h in the presence of 8% O_2, followed by removal of NH_3 and by a 5-min N_2-only purge; ii) exposure to 1000 ppm CO followed by a 30-min N_2-only purge phase; and iii) the same NO + NH_3 titration procedure described above, with 400 ppm each for 1 h. This protocol was executed in the monolith rig twice, with a CO exposure time first of 90-min and then of 24 h.

The results from step ii (CO exposure) of the two CO titration experiments over the Cu-SSZ-13 monolith catalyst are illustrated in Fig. 2.

Fig. 2(A) shows the transient CO_2 formation upon feeding CO to the reactor. Considering first the 90-min test (green curve), a sharp initial CO_2 peak is observed, followed by a monotonically decreasing trend,

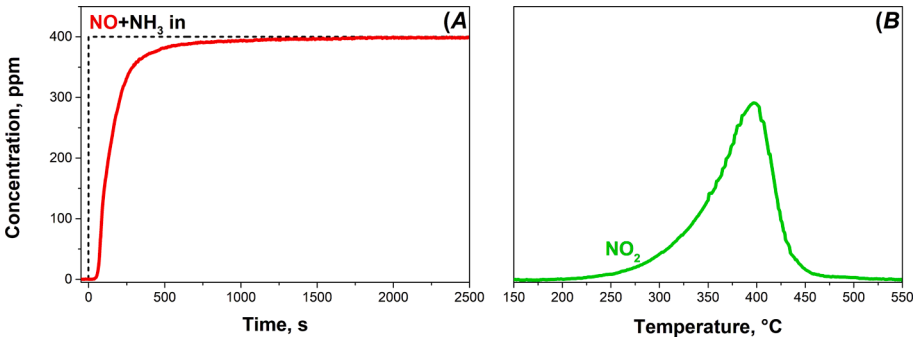

Fig. 1. Panel A - Transient NO release during exposure of the preoxidized Cu-SSZ-13 monolith catalyst to NO + NH_3 (the feed gas composition was 400 ppm for both NH_3 and NO, in balance N_2; GHSV = 60,000 1/h (STP) and T = 150°C). Panel B - NO_2 desorption during a TPD step (heating rate: 15 °C/min), following saturation of the powdered catalyst with NO_2 at 150°C (the TPD phase was carried out in N_2-only; GHSV = 266,250 $cm^3/h/g_{cat}$ (STP) and T = 150–550°C).

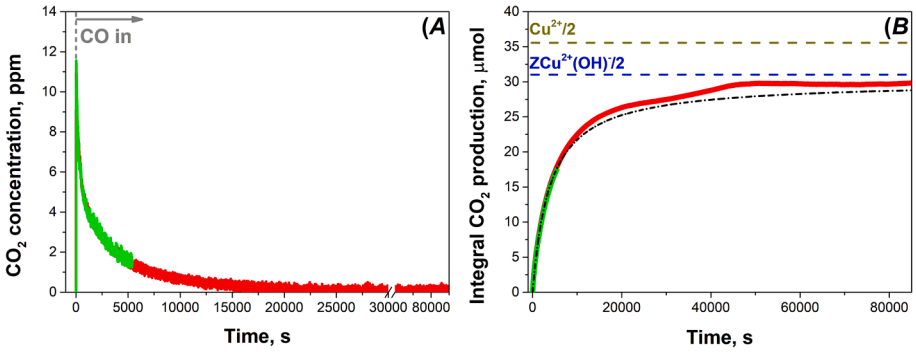

Fig. 2. Panel A - CO_2 evolution during the CO exposure phase (monolith catalyst). The 90-minute exposure data are in green while the 24-hour data are in red. Panel B - Integral production of CO_2. Also in panel B are the 2nd order model predictions, plotted as a black dash-dot line, and half of the Cu^{2+} and $ZCu^{2+}(OH)^-$ contents, plotted as dashed brown and blue horizontal lines, respectively. Feed gas composition = 1000 ppm CO in balance N_2. GHSV = 60,000 1/h and T = 150°C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which is consistent with previous reports (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020). This CO_2 formation is caused by the reduction of binuclear Cu^{2+} species according to a CO_2:Cu^{2+} = 1:2 molar ratio (Hu et al., 2021; Da Costa et al., 2002; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020; Paolucci et al., 2020). Upon exposure to NH_3, $Cu^{2+}(OH)^-(NH_3)_3$ and $Cu^{2+}(NH_3)_4$ complexes are formed, which are detached from the zeolite and mobile inside the zeolite crystalline structure (Paolucci et al., 2016; Villamaina et al., 2019; Hu et al., 2021). DFT calculations have suggested that two $Cu^{2+}(OH)^-(NH_3)_3$ species can form a thermodynamically favoured binuclear structure (Hu et al., 2021), herein labelled as Two-P. In agreement with this mechanistic picture, previous work has shown a net increase in the CO_2 production when the sample was saturated with NH_3 prior to the CO feed (Hu et al., 2021; Iacobone et al., 2022; Villamaina et al., 2020). Similarly, NO + NH_3 titration protocols, preceded by an NH_3 exposure step, showed more rapid reduction by CO with increasing NH_3 loading (Hu et al., 2021; Gramigni et al., 2021). The Two-P complex, $(Cu^{2+}(OH)(NH_3)_x)_2$, originating upon NH_3 coordination on two initially isolated $ZCu^{2+}(OH)$ ions, is viewed as the CO oxidation active site. The proposed overall reaction is (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020):

$$Two-P + CO \rightarrow CO_2 + 2Cu^{+}(NH_3)_x + H_2O \quad (2)$$

The 90-minute CO exposure is however insufficient to achieve complete reduction of the Cu^{2+} ions, as apparent from Fig. 2(A) and as already noted in prior work (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020). In the past, in order to quantify the overall amount of reducible binuclear species, a rate model 2nd order in $ZCu^{2+}(OH)^-$, i.e., consistent with a mechanism involving cation pairs, was fitted to the original CO_2 data and then extrapolated past the 90 min (Hu et al., 2021; Iacobone et al., 2023). Assuming isobaric and isothermal differential reactor conditions in view of the extremely low CO conversion, using a pseudo steady state assumption for the gas phase and considering a quadratic rate dependence on the $ZCu^{2+}(OH)^-$ fraction, the following expression for the temporal evolution of the integral CO_2 production can be derived (Hu et al., 2021; Iacobone et al., 2023):

$$CO_{2,integral} = \frac{[Cu^{2+}]_0}{2} * \frac{k_{app} * t}{1 + k_{app} * t} \quad (3)$$

In Eq. (3), t is the CO oxidation run time, k_{app} represents the apparent 2nd order rate constant while $[Cu^{2+}]_0$ is the initial $ZCu^{2+}(OH)^-$ population. This model was fitted to the integral CO_2 profile during the 90-minute CO exposure, as shown in Fig. 2(B) (black line), resulting in a close match with the experimental data (green line). The model can also be extrapolated to very long CO exposure times, until all binuclear Cu^{2+} sites are reduced and there is no more CO_2 formation. According to the reaction stoichiometry shown above, and to Eq. (3), the integral CO_2 formation should approach 50% of the available $ZCu^{2+}(OH)^-$ catalyst sites. The asymptote extrapolated from the 90-minute test in Fig. 2(B) (84% of the total Cu sites) is in fact in close agreement with the fraction

Table 1
Comparison of the $ZCu^{2+}(OH)^-$ site fraction estimated from the NO_2 TPD experiment, the $ZCu^{2+}(OH)^-$ site fraction predicted by extrapolation of the 90-min CO titration experiment and the $ZCu^{2+}(OH)^-$ site fraction determined by the 24 h CO titration experiment.

$ZCu^{2+}(OH)^-$, [%]	$[Cu^{2+}]_0$ from asymptote of 90-min. test, [%]	$[Cu^{2+}]_0$ from 24 h test, [%]
87	84	83

of $ZCu^{2+}(OH)^-$ cations independently measured by the NO_2 TPD experiment described above (87%), as reported in Table 1 below, in line with previous observations (Hu et al., 2021; Iacobone et al., 2023).

To challenge such an extrapolation, the same protocol was replicated running the CO oxidation step for 24 h. The corresponding CO_2 concentration profile is also shown in Fig. 2(A) as a red curve. The initial 90 min of the new CO_2 curve overlay the original 90-min experiment described above, confirming good reproducibility. The CO_2 production then further decreases and becomes negligible past about 14 h. The integral CO_2 profile is displayed in red in Fig. 2(B): the model prediction from extrapolation of the 90-min test matches reasonably well the experimental data of the long run. As discussed, the Cu^{2+} sites involved in the CO oxidation/titration can be counted as twice the integral amount of CO_2 released (Table 1) according to the stoichiometry in Eq. (2). Table 1 shows that the asymptotic titration result from the 24-hour experiment (83% of the total Cu sites) is consistent with the involvement of all the $ZCu^{2+}(OH)^-$ species as the active sites precursors in the formation of binuclear Cu species, in agreement with previous findings (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020). Moreover, the close match of the three independent estimates in Table 1 (83% – 87%) confirms that the 90-min CO oxidation experiment, combined with the 2nd order model extrapolated to very long times, is an effective method not only to titrate binuclear Cu^{2+} species (Hu et al., 2021; Iacobone et al., 2023), but also to count the $ZCu^{2+}(OH)^-$ cations. While this had been previously demonstrated at 200°C (Hu et al., 2021; Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020), the present results extend the operative temperature for such CO oxidation tests to 150°C.

The absence of significant fractions of CuOx species in the investigated catalyst can also be inferred *a posteriori*. In fact, in the case of previously studied model Cu-CHA catalysts, devoid of such species (Villamaina et al., 2019), comparable results for the titration of $ZCu^{2+}(OH)^-$ cations were obtained by NO_2-adsorption/TPD and by CO oxidation tests, similar to the results reported here (Hu et al., 2021; Iacobone et al., 2023). Furthermore, such results highlight how the methodology is independent of the experimental set-up, since the aforementioned protocols were executed on different rigs.

In both the short and the long tests, following the CO oxidation step, a final $NO + NH_3$ titration step was executed to close the Cu balance. The relevant quantitative results are listed in Table 2.

Adding the Cu^{2+} reduced during the CO oxidation phase, estimated as twice the integral CO_2 release, to the Cu^{2+} reduced by $NO + NH_3$, estimated as the integral NO consumption (see Table 2), the overall Cu count (~75 μmol) is similar to the overall Cu loading independently measured by ICP (Iacobone et al., 2022; Iacobone et al., 2023; Villamaina et al., 2020). Notice also that increasing the CO exposure time from 90-min to 24 h led, as expected, to a corresponding decrease in the NO consumption, since a higher Cu^{2+} fraction was reduced via CO oxidation during the long run.

4. Conclusions

Earlier research on powdered Cu-exchanged zeolites has shown that transient CO oxidation at 200°C can be used to probe binuclear Cu^{2+} structures, as well as to count such species. The integral CO_2 release corresponds to the amount of reducible binuclear Cu^{2+} sites, with a 1:1 CO_2:binuclear Cu species stoichiometry. Furthermore, prior work suggests that in Cu-CHA catalysts only mobile species, originated from $ZCu^{2+}(OH)^-$ ions when exposed to NH_3 in dry conditions, can form the active binuclear complexes. Here we have shown that the same CO oxidation/titration approach also works for a commercial Cu-SSZ-13 monolith catalyst, extending its viability to 150°C. Furthermore, we have shown that runs with shorter CO exposure times can be extrapolated, in conjunction with a 2nd order rate model of CO oxidation, to accurately predict the results of tests with much longer durations. From a mechanistic standpoint, the present results provide direct evidence that in the presence of adsorbed NH_3 all the $ZCu^{2+}(OH)^-$ ions are indeed activated to form reducible binuclear Cu^{2+} complexes.

Table 2
Cu balance for the two CO oxidation runs.

CO oxidation step duration	Cu total, [μmol]	CO_2 release, [μmol]	NO consumed, [μmol]	Cu bal. err., [%]
90 min.	72	17.8	40.2	5.3
24 h	72	29.8	15.6	4.4

CRediT authorship contribution statement

Umberto Iacobone: Writing – original draft, Investigation, Data curation. **William S. Epling:** Writing – review & editing, Validation, Supervision, Funding acquisition, Formal analysis. **Isabella Nova:** Visualization, Supervision, Formal analysis. **Enrico Tronconi:** Writing – review & editing, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: William Epling reports financial support was provided by National Science Foundation Grant CBET 2227016. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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