Antioxidant-driven activity and stability enhancement in multiphase bicarbonate hydrogenation catalysis with a Ru-PNP pincer complex

Hirano, Makoto; Wada, Kazuhito; Matsuda, Hirokazu; Pidko, Evgeny A.

DOI
10.1016/j.jcou.2024.102718

Publication date
2024

Document Version
Final published version

Published in
Journal of CO2 Utilization

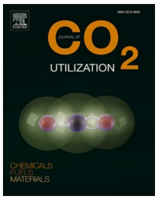
Citation (APA)
Hirano, M., Wada, K., Matsuda, H., & Pidko, E. A. (2024). Antioxidant-driven activity and stability enhancement in multiphase bicarbonate hydrogenation catalysis with a Ru-PNP pincer complex. *Journal of CO2 Utilization*, *81*, Article 102718. https://doi.org/10.1016/j.jcou.2024.102718

Journal of CO2 Utilization 81 (2024) 102718

Contents lists available at ScienceDirect

Journal of CO2 Utilization

journal homepage: www.elsevier.com/locate/jcou



Antioxidant-driven activity and stability enhancement in multiphase bicarbonate hydrogenation catalysis with a Ru-PNP pincer complex

Makoto Hirano [a,*], Kazuhito Wada [a], Hirokazu Matsuda [a], Evgeny A. Pidko [b,*]

[a] Core Technology Research Center Nitto Denko Corporation, 1-1-2 Ibaraki, Osaka 567–8680, Japan
[b] Inorganic Systems Engineering Group, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Van der Maasweg 9, Delft 2629Hz, the Netherlands

ARTICLE INFO

Keywords:
Bicarbonate hydrogenation
Pincer complexes
Multiphase system
Antioxidant
Catalyst Stabilization

ABSTRACT

Herein, we present a practical strategy to enhance the performance of a multiphase system for bicarbonate hydrogenation based on a molecular Ru-PNP pincer catalyst. This study demonstrates that the use of organic antioxidants not only mitigates catalyst degradation but also significantly boosts its intrinsic activity. This enables efficient catalyst recycling at ultra-low concentrations. Systematic screening and optimization of a range of organic antioxidants has identified TDTBP (tris(2,4-di-tert-butylphenyl) phosphite) as being exceptionally efficient in stabilizing and enhancing the performance of the Ru-PNP catalyst. With the optimized system an unprecedented integral turnover frequency (TOF) of 115,000 h^{-1} and a total turnover number (TTON) of 9.43×10^6 across four recycling tests were demonstrated, conducted at a reaction temperature of 90 °C and H_2 pressure of 50 bar. These findings represent a substantial advancement in sustainable formate/formic acid production, offering a scalable and highly efficient method suitable for industrial-scale application.

1. Introduction

Concerns over CO_2 emissions and their environmental implications giving rise to global climate change have accelerated the quest for efficient technologies to capture and utilize carbon dioxide [1–3]. One of the promising strategies is the exploitation of CO_2 as a versatile and abundant C1 building block for chemical conversions [4,5] to produce such base chemicals as formic acid/formate [6,7], methanol [8,9], and methane [10,11]. Most of the promising routes for CO_2 valorization begin with a reduction step that takes place either electrochemically [12,13] or catalytically with gaseous H_2 [14,15]. Furthermore, reductive valorization of CO_2 can be integrated within a carbon capture utilization concept [16–18], in which gaseous CO_2 is first captured from lower-concentration sources (including atmosphere), followed by the reductive conversion of the resulting adduct to some valuable chemical or energy storage materials. In this context, alkali solutions, which are characterized by low vapor pressure, high abundance, nontoxic and reactive nature, appear ideal for scrubbing CO_2 even from low-concentration sources (e.g. ambient air) to form bicarbonate, which is then hydrogenated in the presence of a catalyst to a formate salt [19,20]. Formate salts and formic acid itself [21] are gaining attention for their application as C1 source alternative to syngas within green chemical conversion processes [22,23] as well as promising molecular hydrogen carriers. [24–26]. To realize these potential applications, there is a critical need for new sustainable and efficient way to produce formic acid/formate on an industrial scale, ensuring that they are economically viable.

Remarkable progress has been observed in the field of catalytic CO_2 hydrogenation to formate in the last decades [27–34]. A summary of the most active catalyst system reported to date is provided in Table S1 of the Supporting Information. The early example of a highly efficient iridium pincer catalyst for CO_2 hydrogenation was reported in 2009 by Nozaki and coworkers [27]. Using an iridium complex with a PNP-pincer ligand ([Ir(PNP)H_3]) high turnover frequency (TOF) and turnover number (TON) were achieved, reaching values up to 150,000 h^{-1} and 3500,000, respectively. We have developed an alternative catalyst system based on a Ru-PNP pincer complex ([RuHCl(CO)(PNP)] or Ru-PNP **1** (Fig. 1a), with which reversible hydrogenation of CO_2 was demonstrated in the presence of the organic DBU base in DMF solvent, with TOF^0 and TON values of 1100,000 h^{-1}and 206,000, respectively, achieved for the hydrogenation step [28,29].

From an industrialization standpoint, a successful catalyst system suitable for implementation in a bulk chemical process for CO_2 hydrogenation should meet several critical requirements besides showing

---

* Corresponding authors.
E-mail addresses: makoto.hirano@nitto.com (M. Hirano), e.a.pidko@tudelft.nl (E.A. Pidko).

https://doi.org/10.1016/j.jcou.2024.102718
Received 21 December 2023; Received in revised form 19 February 2024; Accepted 20 February 2024

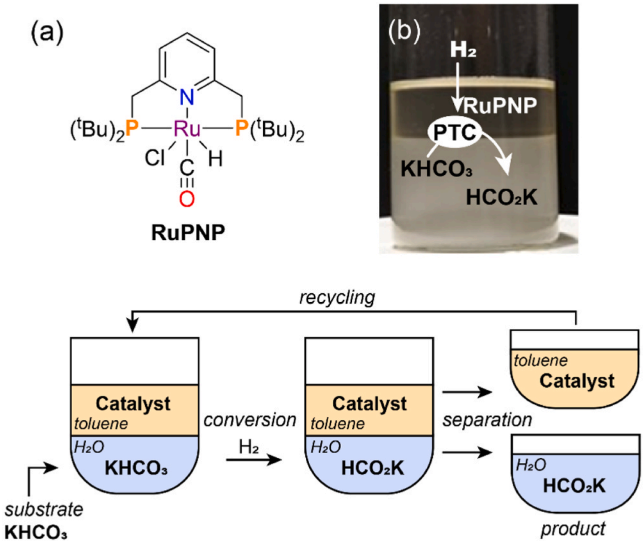


Fig. 1. (a) Ru-PNP **1** (b) Biphasic system with an aqueous phase containing $KHCO_3$ and an organic phase containing complex **1** and PTC. PTC facilitates the transfer of $KHCO_3$ and HCO_2K between organic phase and aqueous phase. Schematic illustrating the repeated utilization of **1** under the biphasic system. After the hydrogenation reaction, the organic and aqueous phases are separated, and the organic phase is reused for subsequent reactions.

excellent performance characteristics within an ideal setting of an organometallic chemistry lab. First, the expensive organometallic catalyst should be easily separable from the product, formate, after the hydrogenation reaction to enable product purification and catalyst recycling. Recently, several groups reported on the use of biphasic catalyst systems to address the challenge of catalyst separation [30,31]. We successfully employed Ru-PNP **1** for hydrogenation of a saturated bicarbonate slurry in a biphasic toluene/water system showing stability for up to 474,000 turnovers (Fig. 1b) [32]. Beller and coworkers have demonstrated a successful recycling of a Mn-pincer catalyst in THF/H_2O biphasic CO_2 hydrogenation system to provide a total turnover number (TTON) of 2,000,000 over several consecutive catalytic runs [33]. The realization of a process that enables the separation of catalysts from formate and the recycling of catalysts, through the development of a biphasic system, represents a significant advancement towards industrialization.

Second, the prevention of catalyst deactivation and reducing the amount of catalyst used are crucial for demonstrating their economic advantages [35,36]. A significant obstacle to the practical implementation of homogeneous transition metal catalysis, particularly when employing precious metals, is the high catalyst loadings often required to achieve satisfactory product yields [37]. For instance, a catalyst with a 1% loading suggests a TON of about 100, whereas a minuscule loading of 1 ppm indicates a TON in the vicinity of 10^6, markedly more favorable under similar conditions. Notably, even a slight decrease in the deactivation to productive catalysis rate ratio can substantially improve catalyst efficiency. Addressing this challenge necessitates ongoing research into the mechanisms behind the very complex deactivation chemistry [38–40].

The cost-effectiveness of the formic acid production process based on CO_2 hydrogenation compared to the established syngas-based technology has been a subject of a comprehensive economic analysis by Pérez-Fortes et al. [41] The detailed cost breakdowns for the emerging technology were presented in the work by Jarvis and Samsatli [42]. These studies underscore the necessity of diminishing material costs via enhanced catalyst activity in CO_2 to formic acid conversion. To improve the efficiency of the catalyst, it is critically important to minimize the effects of deactivation even when operating at minimal catalyst loading to improve TON. Catalyst deactivation can be categorized into internal factors, which originate from the catalytic reactions themselves, and external factors, arising from industrial manufacturing processes. In industrial applications, the influence of these external operational factors becomes significantly pronounced. Even in lab research aimed at applications, it is posited that the incursion of oxygen and other impurities from external sources during operations can lead to catalyst deactivation [43,44]. However, the scope of research on these homogeneous catalysts is somewhat limited in comparison to their heterogeneous counterparts, especially when it comes to studying catalyst degradation due to external operational factors [45–47]. Thus, improving the robustness of catalyst activity to withstand external operational factors, thereby enhancing TON, emerges as a critical initiative for validating the economic feasibility of CO_2 conversion into formate/formic acid.

In our study aimed at practical carbon dioxide to formate conversion for industrial use, we faced the challenge of creating a system that not only separates the catalyst from the product but also achieves high TON. Herein we report on the optimization of biphasic catalyst system based on **1** suitable for cyclic operation within an industrial setting providing and meeting the performance criteria enabling further industrialization of the catalytic process. We demonstrate that catalyst degradation initiated by ligand oxidation is the key mechanism for catalyst loss within the cyclic process (Fig. 1). To minimize the oxidative catalyst degradation, we studied the effect of various common organic antioxidants and revealed their positive effect not only on the longevity but also on the activity of catalyst **1**. The resulting catalyst system allowed us to reach unprecedented productivities and stabilities.

2. Experimental

The details of the relevant chemicals, and analysis methods, as well as details of supporting computational studies and experimental screening tests are provided in the Supporting Information.

2.1. Catalytic reactions

Complex **1** was prepared according to a literature procedure [48]. Under a nitrogen gas atmosphere, the following steps were carried out for the catalytic hydrogenation of potassium bicarbonate: 50 mL of water, 0.25 moles of potassium bicarbonate, 50 mL of toluene, the specified amount of **1**, 2.7 mmol of methyltrioctylammonium chloride, and the designated type and quantity of antioxidants were added to a reaction vessel. In this paper, the molar concentration of potassium bicarbonate is adjusted based on the volume of the aqueous solution. Similarly, the molar concentrations of **1**, methyltrioctylammonium chloride, and antioxidants are set based on the volume of the organic phase within toluene. For the initial reaction, hydrogen gas was introduced up to the specified pressure, and the mixture was heated to 90°C while being stirred at 800 rpm. After the desired reaction time, the mixture was cooled to room temperature, and the pressure was released. The following separation and collection procedure were also carried out in the inert atmosphere. The aqueous phase was separated from the organic phase, and quantified formate by ^1H NMR measurement using D_2O as deuterated solvent and dimethyl sulfoxide (DMSO) as internal standard. To assess the state of **1** in the organic phase, a portion of organic phase was diluted threefold with acetonitrile, followed by LC/MS analysis.

2.2. Catalyst recycling tests

Under an inert gas atmosphere, to adjust the separated and collected organic phase to a volume of 50 mL, toluene was added. Subsequently, the adjusted organic phase (50 mL), along with 50 mL of water and 0.25 moles of potassium bicarbonate, was introduced into a reactor. Following this, a catalyst recycling reaction was conducted under the specified reaction conditions. Unless otherwise specified, the time between the end of a reaction and the next recycling reaction is within 24 h. Post-reaction, the reaction mixture was taken out from the reactor under an inert gas atmosphere, and the organic and aqueous phases were separated. TON of the catalyst and the yield of formate for the second reaction were calculated using the same approach as the first reaction.

3. Results and discussion

3.1. *Effect of catalyst concentration on Ru-PNP recycling*

The stability optimization and catalyst recycling experiments were carried out at a 100 mL scale, which is a 50-fold increase compared to our earlier catalyst development studies [32]. The progress of catalytic runs was monitored by tracking the consumption of hydrogen during the reaction. These data were used to construct the kinetic profiles. The initial recycling tests have been conducted at two concentrations, namely, 120 and 60 μM of catalyst **1** and the catalytic results are summarized in Fig. 2.

For all 4 runs a similar initial rate TOF^0 of 7.7–9.6 s^{-1} was observed suggesting the operation within the kinetic regime and close intrinsic activity upon recycling for both catalyst concentrations. Nevertheless, the kinetic profiles reveal a pronounced loss in performance upon recycling of the catalytic mixture containing a lower concentration of **1** (60 μM, #2). The reuse of the organic (toluene) phase of the catalytic system containing 120 μM of catalyst **1** yielded a similar amount of potassium formate product (ca. 72% yield) and an identical kinetic trace to that observed in the initial run. The total TON (TTON) over these two runs was 5.1×10^4. For the experiments with the twice lower concentration of 60 μM, the kinetic trace of the #2 recycle run deviates strongly from the primary #1 run with reaction time evidencing the in situ catalyst degradation resulting in the decline of both the rate and formate yield (65%). The TTON for the recycling experiment with a twice lower concentration of **1** was therefore only 9.8×10^4.

3.2. *Ru-PNP stabilization with antioxidants*

Previous studies suggested that ligand oxidation is one of the common causes for the deactivation of phosphine-based transition metal catalyst [43]. Phosphine oxidation can even occur under reducing conditions of catalytic reactions even though stringent efforts were made to eliminate dioxygen. Herein, we hypothesized that the oxygen contamination and oxidative degradation of catalyst **1** could be the reason for the observed activity loss during the recycling preventing further optimization of the performance in terms of TTON. Such a deactivation mechanism could be readily mitigated by using antioxidants. Antioxidants are widely used as additives for the stabilization of food, pharmaceuticals, and polymers [49,50].

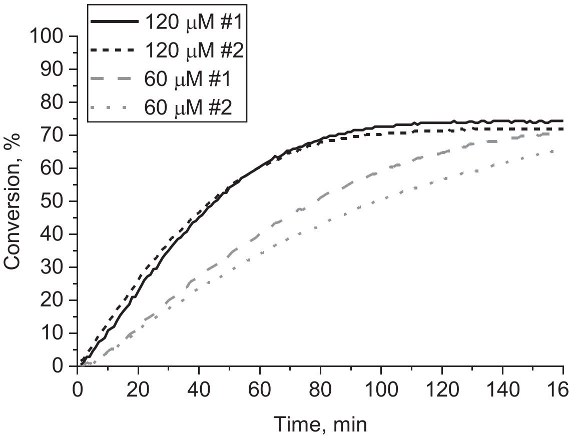


Fig. 2. The effect of catalyst **1** (S/C = 3.5 $\times10^4$ and 7.0 $\times10^4$) loading on the kinetics of the biphasic $KHCO_3$ hydrogenation in the recycling tests. #1 indicates the first reaction, and #2 indicates the second reaction. (Conditions: 100 mL solvent (toluene/H_2O = 1/1), T = 90 °C, p_{H2} = 40 bar, stirring speed = 800 rpm, 120 μM or 60 μM catalyst **1**, 4.2 M $KHCO_3$, 54 mM PTC).

To test this hypothesis, we evaluated whether the addition of a common organic antioxidant - 2,6-di-tert-butyl-*p*-cresol (BHT, Scheme 1) - to the reaction system could enhance the stability of **1**. To enhance the oxidative degradation and thus emphasize the potential impact of the antioxidant, we have aged the catalytic toluene phase initially containing 60 μM **1** obtained after the first catalytic run for 5 days in a closed under nitrogen prior to the second run.

Fig. 3 compares the kinetic traces of the recycling tests with the aged catalyst mixture in the presence and in the absence of the BHT antioxidant. The prolonged storage of the toluene catalyst phase gives rise to a much more pronounced activity decline than the direct recycling (#2 and #2 aged traces in Fig. 3): the initial rate decreased by a factor of 2.1 (8.8 and 4.1 s^{-1}, respectively) and the reaction yield was only 36% after 160 min reaction time. When BHT was added to the catalyst system, no signs of deactivation could be observed under the current conditions. The kinetic traces for both the primary and recycle runs of biphasic $KHCO_3$ hydrogenation with 60 μM catalyst **1** stabilized with 500 eq. BHT coincided perfectly with the benchmark test. A closer inspection of the catalytic data revealed that the presence of BHT resulted in a ca. 15% higher TOF^0 for both runs (10.8–10.9 s^{-1}).

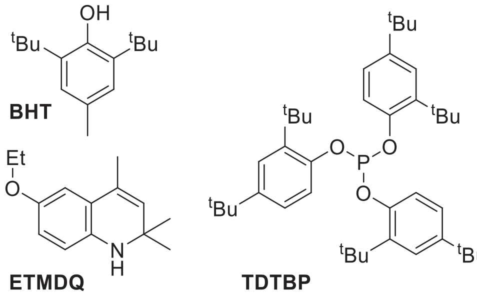
3.3. *Stabilizing effect of BHT*

To shed light onto the stabilizing effect of BHT antioxidant, the post-catalytic reaction mixtures were next analyzed by LC-MS, which revealed the presence of oxidized catalyst **1** species as well as the free oxidized ligand in the post-catalytic reaction mixture. The possible structures of the identified species (Table 1) were proposed based on the detected *m/z* values and density functional theory calculations (see Supporting Information for details). The results obtained suggest that the observed deactivation of **1** proceeds via a gradual oxidation process as proposed in Scheme 2, which ultimately results in the decomposition of the Ru complex, the elimination of the free oxidized PNP ligand (**4**$^+$), and irreversible catalyst deactivation. Semi-quantitative analysis of the LC-MS data reveals that although the addition of BHT results in the decreased relative abundance of all oxidized species, the most notable effect is seen for the concentration of species **4**$^+$ (Table 1).

A super-stoichiometric concentration of the BHT antioxidant is necessary to retain the performance over several recycle runs. Nevertheless, we found that BHT concentration could be decreased to 6 mM for the catalytic reactions with 60 μM **1** to reach the maximal $KHCO_2$ yield in 2.5 h reaction for 3 consecutive recycle runs (Figure S4).

3.4. *Antioxidants screening*

Next, a screening campaign (Figure S5) has been carried out using smaller scale lower pressure reactor to evaluate alternative antioxidants



Scheme 1. Selection of organic antioxidants.

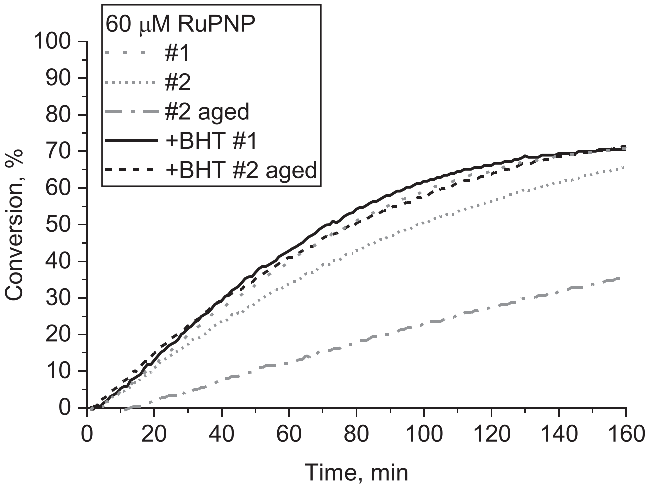
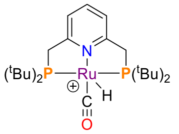
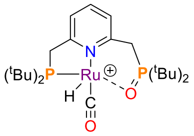
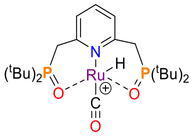
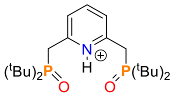


Fig. 3. The stabilizing effect of BHT antioxidant on the performance of catalyst **1** in the biphasic $KHCO_3$ hydrogenation. The recycling experiment carried out using the catalyst-containing organic phase stored under inert gas conditions in a closed vial for 5 days (#2 aged). The kinetic trace of a direct recycle experiment (#2) with catalyst **1** in the absence of the antioxidant is shown for comparison. (Conditions: 100 mL solvent (toluene/H_2O = 1/1), T = 90 °C, p_{H2} = 40 bar, t = 160 min, stirring speed = 800 rpm, 60 μM catalyst **1**, 4.2 M $KHCO_3$, 54 mM PTC, 30 mM BHT).

Table 1
The results of LC-MS analysis (identified Ru-containing species with the proposed structure and the respective *m/z* as well as the peak areas relative to that of the intact complex **1**) of the toluene phase of the post-catalytic mixture after the second hydrogenation run with and without the BHT antioxidant, corresponding to the experiments in Fig. 3.

Species	*m/z*	Proposed structure	Peak area ratio [i]/[1]	
			Ru-PNP	Ru-PNP+BTH
1^+	526.20		1	1
2^+	542.21		0.68	0.41
3^+	558.18		1.8	1.3
4^+	428.29		2.9	0.68

and identify most promising systems for further process optimization. The results are summarized in Figure S5 of the Supporting Information, which point to 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMDQ) and tris(2,4-di-tert-butylphenyl) phosphite (TDTBP) as the most promising antioxidant catalyst stabilizers.

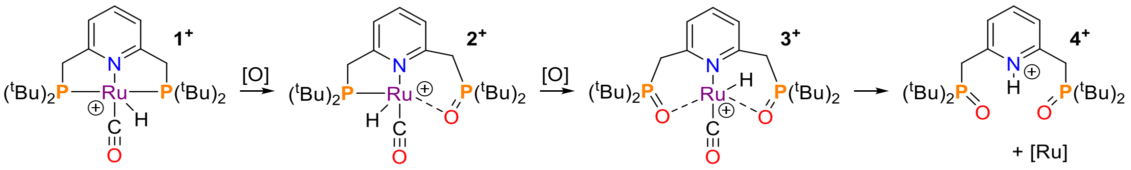
To better asses the stabilizing effect of the selected antioxidants (Scheme 1), the S/C ratio was further reduced to the value of 333'333 corresponding to the initial concentration of catalyst **1** of only 15 μM. The kinetic trances of 3 consecutive catalytic runs in the absence and in the presence of BHT, ETMDQ, and TDTBP stabilizers are presented in Fig. 4. The catalytic tests at such a low concentration without any antioxidant reveal some loss of activity already in the initial run, which becomes detrimental upon recycling ($TOF^0 = 6.1, 4.0, 1.7\ s^{-1}$, for #1, #2 and #3 catalytic runs, Fig. 4a). Although the addition of BHT in the first run recovers the intrinsic activity recorded at higher catalyst concentration ($TOF^0 = 11.4\ s^{-1}$), the stabilizing effect is not sufficient to ensure an efficient recycling (Fig. 4b). The 2nd and 3rd runs with BHT stabilizer show TOF^0 values of only 7.5 and 3.0 s^{-1}, respectively. Much better results are obtained with ETMDQ and TDTBP antioxidants, which allowed, under the current conditions, to fully recover the initial performance in 2 and 3 consecutive runs, respectively (Fig. 4c,d). Remarkably, the antioxidant addition not only increased the catalyst stability, but had also an apparent promoting effect on the intrinsic activity observed. The estimated initial rates - TOF^0 were ca. 16 s^{-1} and 23–30 s^{-1} for the stable catalytic runs in the presence of ETMDQ and TDTBP, respectively. The origin of the rate enhancement observed is however beyond the scope of the current study.

3.5. *Enhanced performance of 1 with TDTBP*

To further evaluate the potential of TDTBP as the catalyst stabilizer and push the performance of **1** to the levels that could be relevant for a practical commercial process for catalytic hydrogenation of bicarbonate, the catalytic tests were conducted with only 2.0 μM **1** and 7.0 M $KHCO_3$ substrate. The conversion curves for four consecutive hydrogenation runs are presented in Fig. 5. Despite some loss of activity could be seen upon the 4th recycle, it allowed reaching the maximal conversion within 20 h reaction time, providing thus an impressive cumulative TTON of 9.43×10^6. As far as we are aware, this value surpasses any other reported TTON under comparable reaction conditions, as summarized in the Supporting Information Table S1. The productivity of the catalyst expressed as the integral TOF was >115'000 h^{-1} in all runs.

Interestingly, under these conditions, a much higher intrinsic activity of **1** was observed, characterized by TOF^0 of 90–130 s^{-1}. A consistently higher initial TOF^0 of 133 and 129 s^{-1} was recorded for the #2 and #3 runs, compared to the value of 93 s^{-1} in run #1. In the 4th run, TOF^0 drops to "only" 83 s^{-1}, due to the catalyst loss. The increased reaction rate upon recycling may imply a lag in formation of the active species in the reaction system. However, the more detailed mechanistic analysis of the associated transformations is outside the scope of the current work and, furthermore, beyond our current experimental abilities. We hope to be able to shed lighter onto the origin of the observed condition- and oxidant-dependent activity enhancements in our further studies.

To evaluate these performance data from an economic standpoint, we employed the dimensionless parameter known as 'Catalyst Price Normalized to TON' (CON), a method for normalizing catalyst cost based on TON as proposed by Chatterjee and coworkers [51]. The CON



Scheme 2. A proposal on the oxidative degradation of catalyst **1**.

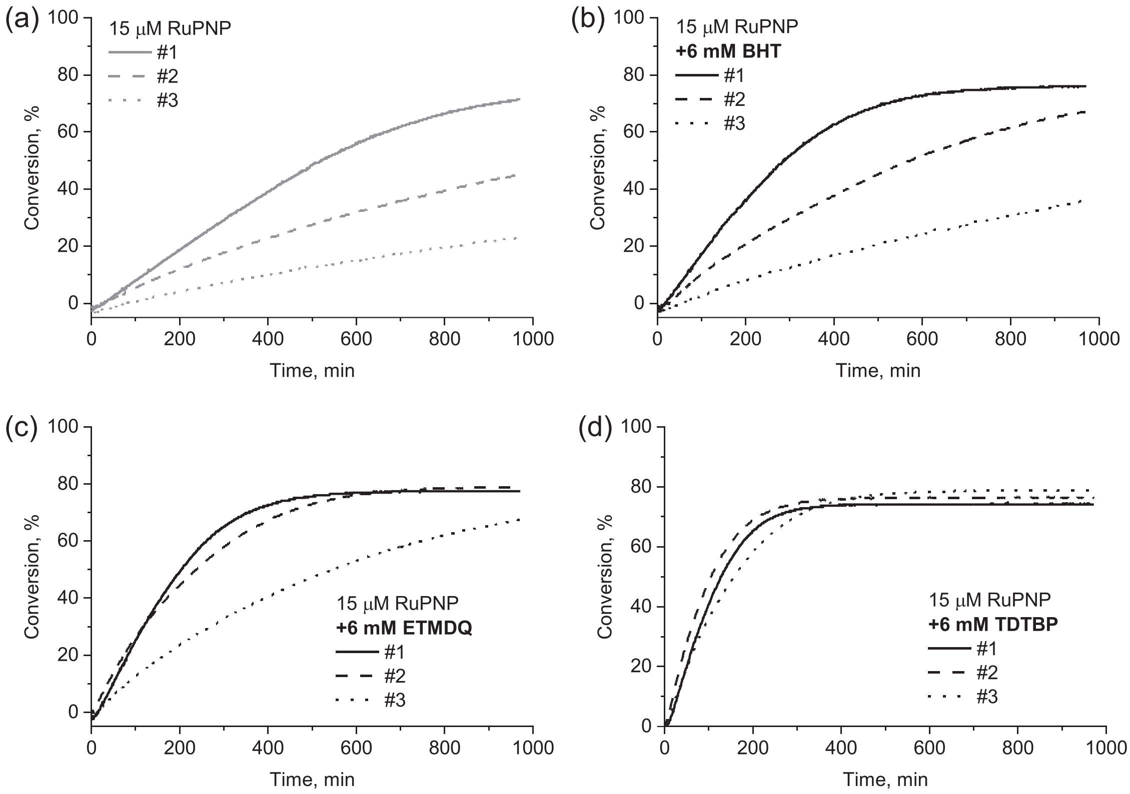


Fig. 4. Recycle experiments of potassium bicarbonate hydrogenation with catalyst **1** (S/C = 333'333) in the (a) absence and the presence of (b) BHT, (c) ETMDQ, (d) TDTBP antioxidants (Conditions: 100 mL solvent (toluene/H_2O = 1/1), T = 90 °C, p_{H2} = 50 bar, t = 16 h, stirring speed = 800 rpm, 15 μM catalyst **1**, 6.0 mM antioxidant, 5.0 M $KHCO_3$, 54 mM PTC).

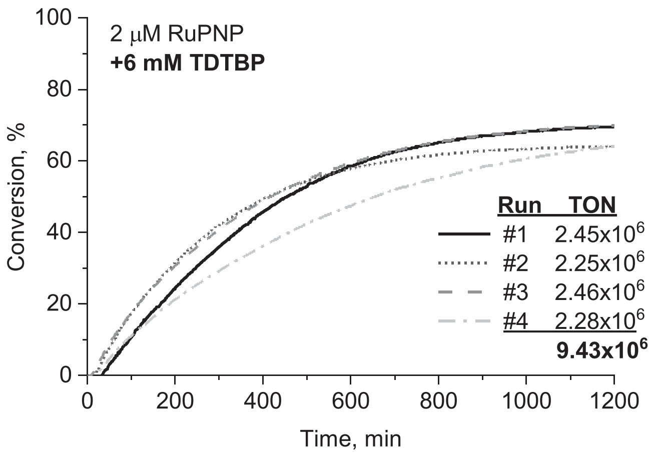


Fig. 5. Recycle experiments of $KHCO_3$ hydrogenation with TDTBP antioxidant. (Conditions: 100 mL solvent (toluene/H_2O = 1/1), T = 90 °C, p_{H2} = 50 bar, stirring speed = 800 rpm, 2.0 μM catalyst **1**, 6.0 mM TDTBP, 7.0 M $KHCO_3$, 54 mM PTC).

represents the contribution of the catalyst to the overall cost of the formic acid produced. The remarkably high TTON value of 9.43×10^6, achieved in the presence of TDTBP with catalyst **1**, translates to a CON of 0.037, significantly lower than any value previously reported. Moreover, according to the report by Chatterjee and coworkers, the commercial price of catalyst **1** is $97,000 per mol, whereas that of the TDTBP antioxidant can be estimated based on the openly available data to be only $82 per mol [52]. This suggests that the use of TDTBP to improve the stability of **1** is economically advantageous, although a deeper and more detailed economic analysis is necessary to comprehensively evaluate this characteristics of the process. Pérez-Fortes have discussed the potential and challenges of formic acid production via catalytic hydrogenation of CO_2, underscoring the pivotal role of R&D in enhancing catalyst performance. Such advancements are essential for reducing manufacturing costs and overcoming economic barriers to the commercialization of formic acid production. Therefore, our findings do not simply represent a new benchmark; they mark a substantial advance in addressing the critical challenge of cost-efficiency in formic acid manufacturing.

3.6. *Conclusion*

Herein we have investigated the potential of common organic antioxidants for boosting the stability and performance of multiphase catalyst systems for the direct hydrogenation of potassium bicarbonate to formate based on molecularly-defined Ru-PNP pincer complex **1**. Through a detailed optimization and analysis campaign specifically focusing on understanding and combatting the catalyst deactivation, we aimed at reaching the performance metrics necessary for further scale up towards a more sustainable and practical industrial bulk conversion process as a part of future carbon capture and utilization technology. We have systematically evaluated the stabilizing effect of a wide range of common organic antioxidant, analyzed the nature of deactivated catalyst species and optimized the reaction conditions to drastically improve the recyclability of our biphasic catalyst system. We discovered that the addition of antioxidants such as BHT, ETMDQ, and TDTBP significantly improved the stability and activity of **1**. Notably, TDTBP stood out by allowing us to achieve and maintain unprecedented productivities (TOF) of over 10^5 h^{-1} and stabilities (TON) over multiple reaction cycles with sub-ppm concentrations of catalyst **1**. Our results point to the impact of the antioxidant additive and the selection of the specific catalytic conditions on the intrinsic activity of **1**, which warrant further more detailed mechanistic analysis, which is beyond the scope of the current study. The use of TDTBP enabled a remarkable cumulative TTON of 9.43×10^6 over four consecutive runs under optimized conditions, which represents a significant milestone in the field.

We have used the 'Catalyst Price Normalized to TON' (CON) parameter to assess the economic potential of the presented system for the practical utilization in carbon capture utilization technologies. We demonstrated that our multiphase catalyst system, especially when stabilized by TDTBP, attains a CON value of 0.037, which is substantially lower than the values for any other bicarbonate hydrogenation catalyst system reported to date. This finding underlines the potential of our catalyst system to be economically viable for a more sustainable industrial-scale formic acid production technology based on CO_2 as the circular carbon source.

CRediT authorship contribution statement

Makoto Hirano: Conceptualization, Formal analysis, Methodology, Project administration, Validation, Writing – original draft. **Kazuhito Wada:** Methodology, Validation, Formal analysis, Investigation, Visualization. **Hirokazu Matsuda:** Supervision, Project administration. **Evgeny A. Pidko:** Conceptualization, Supervision, Investigation, Formal analysis, Visualization, Writing – review & editing.

Declaration of Generative AI and AI-assisted technologies in the writing process

Generative AI (ChatGPT-4, OpenAI) has been used for minor language editing during the preparation of the manuscript. All generated text was reviewed and edited by the authors.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hirano Makoto has patent pending to Nitto Denko. Hirano Makoto has patent #US 2023/0312448A1 filed to Nitto Denko. 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.

Acknowledgments

The authors wish to thank Masaya Seriu for contributions to the experimental work, and E.N. and H.N. at Nitto Analytical Techno-Center for their support in LC-MS analysis.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2024.102718.

References

[1] A.J. Hunt, E.H.K. Sin, R. Marriott, J.H. Clark, Generation, capture, and utilization of industrial carbon dioxide, ChemSusChem 3 (2010) 306–322, https://doi.org/10.1002/cssc.200900169.

[2] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T.E. Müller, Worldwide innovations in the development of carbon capture technologies and the utilization of CO_2, Energy Environ. Sci. 5 (2012) 7281–7305, https://doi.org/10.1039/c2ee03403d.

[3] H. De Coninck, S.M. Benson, Carbon dioxide capture and storage: Issues and prospects, Annu. Rev. Environ. Resour. 39 (2014) 243–270, https://doi.org/10.1146/annurev-environ-032112-095222.

[4] W.G. Cui, G.Y. Zhang, T.L. Hu, X.H. Bu, Metal-organic framework-based heterogeneous catalysts for the conversion of C1 chemistry: CO, CO_2 and CH_4, Coord. Chem. Rev. 387 (2019) 79–120, https://doi.org/10.1016/j.ccr.2019.02.001.

[5] Q. Liu, L. Wu, R. Jackstell, M. Beller, Using carbon dioxide as a building block in organic synthesis, Nat. Commun. 6 (2015) 5933, https://doi.org/10.1038/ncomms6933.

[6] A. Álvarez, A. Bansode, A. Urakawa, A.V. Bavykina, T.A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneously catalyzed CO_2 hydrogenation processes, Chem. Rev. 117 (2017) 9804–9838, https://doi.org/10.1021/acs.chemrev.6b00816.

[7] W. Leitner, Carbon dioxide as a raw material: the synthesis of formic acid and its derivatives from CO_2, Angew. Chem. Int. Ed. 34 (1995) 2207–2221, https://doi.org/10.1002/anie.199522071.

[8] L.C. Grabow, M. Mavrikakis, Mechanism of methanol synthesis on Cu through CO_2 and CO hydrogenation, ACS Catal. 1 (4) (2011) 365–384, https://doi.org/10.1021/cs200055d.

[9] S. Kattel, P.J. Ramírez, J.G. Chen, J.A. Rodriguez, P. Liu, Active sites for CO_2 hydrogenation to methanol on Cu/ZnO catalysts, Science 355 (2017) 1296–1299, https://doi.org/10.1126/science.aal3573.

[10] D. Pakhare, J. Spivey, A review of dry (CO_2) reforming of methane over noble metal catalysts, Chem. Soc. Rev. 43 (2014) 7813–7837, https://doi.org/10.1039/c3cs60395d.

[11] P. Frontera, A. Macario, M. Ferraro, P.L. Antonucci, Supported catalysts for CO_2 methanation: a review, Catalysts 7 (2017) 59, https://doi.org/10.3390/catal7020059.

[12] N.S. Spinner, J.A. Vega, W.E. Mustain, Recent progress in the electrochemical conversion and utilization of CO_2, Catal. Sci. Technol. 2 (2012) 19–28, https://doi.org/10.1039/c1cy00314c.

[13] J.P. Jones, G.K.S. Prakash, G.A. Olah, Electrochemical CO_2 reduction: recent advances and current trends, Isr. J. Chem. 54 (2014) 1451–1466, https://doi.org/10.1002/ijch.201400081.

[14] T.A. Atsbha, T. Yoon, P. Seongho, C.J. Lee, A review on the catalytic conversion of CO_2 using H_2 for synthesis of CO, methanol, and hydrocarbons, J. CO_2 Util. 44 (2021) 101413, https://doi.org/10.1016/j.jcou.2020.101413.

[15] W. Wang, S. Wang, X. Ma, J. Gong, Recent advances in catalytic hydrogenation of carbon dioxide, Chem. Soc. Rev. 40 (2011) 3703–3727, https://doi.org/10.1039/c1cs15008a.

[16] R. Sen, A. Goeppert, S. Kar, G.K.S. Prakash, Hydroxide based integrated CO_2 capture from air and conversion to methanol, J. Am. Chem. Soc. 142 (2020) 4544–4549, https://doi.org/10.1021/jacs.9b12711.

[17] S. Kar, R. Sen, A. Goeppert, G.K.S. Prakash, Integrative CO_2 capture and hydrogenation to methanol with reusable catalyst and amine: toward a carbon neutral methanol economy, J. Am. Chem. Soc. 140 (2018) 1580–1583, https://doi.org/10.1021/jacs.7b12183.

[18] S. Kar, A. Goeppert, V. Galvan, R. Chowdhury, J. Olah, G.K.S. Prakash, A carbon-neutral CO_2 capture, conversion, and utilization cycle with low-temperature regeneration of sodium hydroxide, J. Am. Chem. Soc. 140 (2018) 16873–16876, https://doi.org/10.1021/jacs.8b09325.

[19] D. Wei, X. Shi, P. Sponholz, H. Junge, M. Beller, Manganese promoted (Bi) carbonate hydrogenation and formate dehydrogenation: toward a circular carbon and hydrogen economy, ACS Cent. Sci. 8 (2022) 1457–1463, https://doi.org/10.1021/acscentsci.2c00723.

[20] S. Kar, A. Goeppert, G.K.S. Prakash, Integrated CO_2 capture and conversion to formate and methanol: connecting two threads, Acc. Chem. Res. 52 (2019) 2892–2903, https://doi.org/10.1021/acs.accounts.9b00324.

[21] M. Ramdin, A.R.T. Morrison, M. De Groen, R. Van Haperen, R. De Kler, E. Irtem, A. T. Laitinen, L.J.P. Van Den Broeke, T. Breugelmans, J.P.M. Trusler, W. De Jong, T. J.H. Vlugt, High-pressure electrochemical reduction of CO_2 to formic acid/formate: effect of pH on the downstream separation process and economics, Ind. Eng. Chem. Res. 58 (2019) 22718–22740, https://doi.org/10.1021/acs.iecr.9b03970.

[22] R. Sang, P. Kucmierczyk, K. Dong, R. Franke, H. Neumann, R. Jackstell, M. Beller, Palladium-catalyzed selective generation of CO from formic acid for carbonylation of alkenes, J. Am. Chem. Soc. 140 (2018) 5217–5223, https://doi.org/10.1021/jacs.8b01123.

[23] H.J. Lee, D.C. Kang, E.J. Kim, Y.W. Suh, D.P. Kim, H. Han, H.K. Min, Production of H_2-free carbon monoxide from formic acid dehydration: the catalytic role of acid sites in sulfated zirconia, Nanomater 12 (2022) 3036, https://doi.org/10.3390/nano12173036.

[24] M. Iguchi, M. Chatterjee, N. Onishi, Y. Himeda, H. Kawanami, Sequential hydrogen production system from formic acid and H_2/CO_2 separation under high-pressure conditions, Sustain. Energy Fuels 2 (2018) 1719–1725, https://doi.org/10.1039/c8se00087e.

[25] J. Eppinger, K.W. Huang, Formic acid as a hydrogen energy carrier, ACS Energy Lett. 2 (2017) 188–195, https://doi.org/10.1021/acsenergylett.6b00574.

[26] A. Bahuguna, Y. Sasson, Formate-bicarbonate cycle as a vehicle for hydrogen and energy storage, ChemSusChem 14 (2021) 1258–1283, https://doi.org/10.1002/cssc.202002433.

[27] R. Tanaka, M. Yamashita, K. Nozaki, Catalytic hydrogenation of carbon dioxide using Ir(III)-pincer complexes, J. Am. Chem. Soc. 131 (2009) 14168–14169, https://doi.org/10.1021/ja903574e.

[28] G.A. Filonenko, R. Van Putten, E.N. Schulpen, E.J.M. Hensen, E.A. Pidko, Highly efficient reversible hydrogenation of carbon dioxide to formates using a ruthenium PNP-pincer catalyst, ChemCatChem 6 (2014) 1526–1530, https://doi.org/10.1002/cctc.201402119.

[29] G.A. Filonenko, E.J.M. Hensen, E.A. Pidko, Mechanism of CO_2 hydrogenation to formates by homogeneous Ru-PNP pincer catalyst: from a theoretical description to performance optimization, Catal. Sci. Technol. 4 (2014) 3474–3485, https://doi.org/10.1039/c4cy00568f.

[30] M. Scott, B. Blas Molinos, C. Westhues, G. Franciò, W. Leitner, Aqueous biphasic systems for the synthesis of formates by catalytic CO_2 hydrogenation: integrated reaction and catalyst separation for CO_2-scrubbing solutions, ChemSusChem 10 (2017) 1085–1093, https://doi.org/10.1002/cssc.201601814.

[31] C. Guan, Y. Pan, E.P.L. Ang, J. Hu, C. Yao, M.H. Huang, H. Li, Z. Lai, K.W. Huang, Conversion of CO_2 from air into formate using amines and phosphorus-nitrogen PN^3P-Ru(II) pincer complexes, Green. Chem. 20 (2018) 4201–4205, https://doi.org/10.1039/c8gc02186d.

[32] C. Rebreyend, E.A. Pidko, G.A. Filonenko, Homogeneous hydrogenation of saturated bicarbonate slurry to formates using multiphase catalysis, Green. Chem. 23 (2021) 8848–8852, https://doi.org/10.1039/d1gc02246f.

[33] D. Wei, R. Sang, P. Sponholz, H. Junge, M. Beller, Reversible hydrogenation of carbon dioxide to formic acid using a Mn-pincer complex in the presence of lysine, Nat. Energy 7 (2022) 438–447, https://doi.org/10.1038/s41560-022-01019-4.

[34] S. Kushwaha, J. Parthiban, S.K. Singh, Recent developments in reversible CO_2 hydrogenation and formic acid dehydrogenation over molecular catalysts, ACS Omega 8 (2023) 38773–38793, https://doi.org/10.1021/acsomega.3c05286.

[35] H.U. Blaser, A. Indolese, A. Schnyder, Applied homogeneous catalysis by organometallic complexes, Curr. Sci. 78 (2000) 1336–1344. ⟨https://www.jstor.org/stable/24104040⟩.

[36] G.W. Parshall, S.D. Ittel. Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, 2nd Edition, Wiley-Interscience, 1992.

[37] R.H. Crabtree, Deactivation in homogeneous transition metal catalysis: Causes, avoidance, and cure, Chem. Rev. 115 (2015) 127–150, https://doi.org/10.1021/cr5004375.

[38] P.W.N.M. Van Leeuwen, Decomposition pathways of homogeneous catalysts, Appl. Catal. A: Gen. 212 (2001) 61–81, https://doi.org/10.1016/S0926-860X(00)00844-9.

[39] K. Köhnke, N. Wessel, J. Esteban, J. Jin, A.J. Vorholt, W. Leitner, Operando monitoring of mechanisms and deactivation of molecular catalysts, Green. Chem. 24 (2022) 1951–1972, https://doi.org/10.1039/d1gc04383h.

[40] W. Yang, G.A. Filonenko, E.A. Pidko, Performance of homogeneous catalysts viewed in dynamics, Chem. Commun. 59 (2023) 1757–1768, https://doi.org/10.1039/d2cc05625a.

[41] M. Pérez-Fortes, J.C. Schöneberger, A. Boulamanti, G. Harrison, E. Tzimas, Formic acid synthesis using CO_2 as raw material: techno-economic and environmental evaluation and market potential, Int. J. Hydrog. Energy 41 (2016) 16444–16462, https://doi.org/10.1016/j.ijhydene.2016.05.199.

[42] S.M. Jarvis, S. Samsatli, Technologies and infrastructures underpinning future CO_2 value chains: a comprehensive review and comparative analysis, Renew. Sust. Energy Rev. 85 (2018) 46–68, https://doi.org/10.1016/j.rser.2018.01.007.

[43] P.B. Webb, M.F. Sellin, T.E. Kunene, S. Williamson, A.M.Z. Slawin, D.J. Cole-Hamilton, continuous flow hydroformylation of alkenes in supercritical fluid-ionic liquid biphasic systems, J. Am. Chem. Soc. 125 (2003) 15577–15588, https://doi.org/10.1021/ja035967s.

[44] M. Solinas, A. Pfaltz, P.G. Cozzi, W. Leitner, Enantioselective hydrogenation of imines in ionic liquid/carbon dioxide media, J. Am. Chem. Soc. 126 (2004) 16142–16147, https://doi.org/10.1021/ja046129g.

[45] J.A. Moulijn, A.E. Van Diepen, F. Kapteijn, Catalyst deactivation: is it predictable?: What to do?, Appl. Catal. A: Gen. 212 (2001) 3–16, https://doi.org/10.1016/S0926-860X(00)00842-5.

[46] C.H. Bartholomew, Mechanisms of catalyst deactivation, Appl. Catal. A: Gen. 212 (2001) 17–60, https://doi.org/10.1016/S0926-860X(00)00843-7.

[47] A.J. Martín, S. Mitchell, C. Mondelli, S. Jaydev, J. Pérez-Ramírez, Unifying views on catalyst deactivation, Nat. Catal. 5 (2022) 854, https://doi.org/10.1038/s41929-022-00842-y.

[48] B. Gnanaprakasam, J. Zhang, D. Milstein, Direct synthesis of imines from alcohols and amines with liberation of H_2, Angew. Chem. Int. Ed. 49 (2010) 1468–1471, https://doi.org/10.1002/anie.200907018.

[49] W.A. Yehye, N.A. Rahman, A. Ariffin, S.B. Abd Hamid, A.A. Alhadi, F.A. Kadir, M. Yaeghoobi, Understanding the chemistry behind the antioxidant activities of butylated hydroxytoluene (BHT): A review, Eur. J. Med. Chem. 101 (2015) 295–312, https://doi.org/10.1016/j.ejmech.2015.06.026.

[50] M.S. Dopico-García, J.M. López-Vilariñó, M.V. González-Rodríguez, Antioxidant content of and migration from commercial polyethylene, polypropylene, and polyvinyl chloride packages, J. Agric. Food Chem. 55 (2007) 3225–3231, https://doi.org/10.1021/jf070102+.

[51] S. Chatterjee, I. Dutta, Y. Lum, Z. Lai, K.W. Huang, Enabling storage and utilization of low-carbon electricity: power to formic acid, Energy Environ. Sci. 14 (2021) 1194–1246, https://doi.org/10.1039/d0ee03011b.

[52] Sigma-Aldrich. Tris(2,4-di-tert-butylphenyl) Phosphite. 2024. Online information, available at: ⟨https://www.sigmaaldrich.com/JP/ja/product/aldrich/441791⟩ [last accessed February 15, 2024].