

Electronic property of alkoxo-bridged tetranuclear Fe(II) cluster and CO₂ hydrogenation reactivity

Hyoyi Yang¹ | Jihyun Kim¹ | Wonjung Lee¹ | Junseong Lee²  | Junhyeok Seo¹ 

¹Department of Chemistry, Gwangju Institute of Science and Technology, Gwangju, Republic of Korea

²Department of Chemistry, Chonnam National University, Gwangju, Republic of Korea

Correspondence

Junhyeok Seo, Department of Chemistry, Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea.
Email: seojh@gist.ac.kr

Funding information

GIST Research Institute; National Research Foundation of Korea, Grant/Award Number: 2020R1C1C1007106

Abstract

Here we report on the synthesis of tetranuclear Fe(II) cluster [Fe₄I₂(O₂C₁₄H₁₁)₆] (**1**) derived from a benzoin-based scaffold. The Fe centers displayed a rhombus-like core structure, including two types of coordination environments: trigonal bipyramid and trigonal prism. The binding energy of the trigonal prismatic Fe(II) 2p electron appeared ~1.43 eV higher than that of the trigonal bipyramidal Fe(II) 2p electron because of more Fe–O bonds. The trigonal bipyramidal Fe site exhibited stoichiometric CO₂ hydrogenation reactivity with the assistance of an external Lewis basic agent.

KEYWORDS

CO₂ hydrogenation, Fe cluster, Fe-alkoxo, tetranuclear Fe(II), trigonal bipyramid

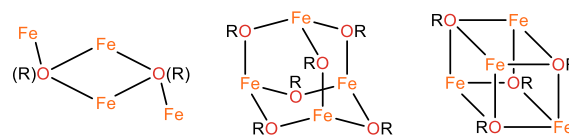
Multinuclear complexes have structural and functional significance in biological systems.¹ Iron–sulfur (FeS) clusters are prominent near the active sites of metalloenzymes^{2,3} while involved in electron-transfer steps.⁴ In 2003, Zhou and Holm⁵ reported the synthesis of a single cubane-type cluster of [Fe₄S₄(PR₃)₄]⁺ by reacting [Fe₄S₄Cl₄]^{2−} with phosphine and the chemical reactivities with small molecules. Lee et al.⁶ synthesized [3Fe–3(μ-H)] cluster supported by tris(β-diketiminato) cyclophane, of which Fe–(μ-H) exhibited the CO₂ reactivity. Sánchez et al.⁷ showed that multidentate amino/phosphine could support Fe clusters with high nuclearity, such as [(^{tr}enL)₂Fe₈(PMe₂Ph)₂]ⁿ (*n* = 0, −1). Coordination environment of each nuclear center in multinuclear clusters determined the physical property of the overall cluster⁸ as well as the chemical reactivity of the electronically localized metal site.^{9,10}

Multinuclear Fe–O moieties are found in the metalloprotein structures such as hemerythrin and ferritin core.¹¹ The structural relevance with biological systems has motivated syntheses of various cluster structures, featuring butterfly, adamantane-like, and cubane Fe–O cores (Figure 1a).^{12–16} However, the reactivity studies were limited to several oxidative reactions by highly oxidized ferric centers.^{16–21} Albeit rare, ferric centers in multinuclear coordination conditions have shown CO₂ reactivity.^{22–23} Thus, we became interested in the CO₂ reactivity of a ferric center in Fe–O cluster. Herein, we report the structural

and electronic characteristics of a novel Fe(II)-alkoxo cluster and the CO₂ hydrogenation reaction.

The [Fe₄I₂(O₂C₁₄H₁₁)₆] Cluster (**1**) was synthesized by decarbonylation of Fe₂(CO)₄ in the presence of K⁺(benzoin) in tetrahydrofuran (THF) at room temperature, where the carbonyl ligands were completely dissociated with evolving CO gas and KI precipitate. The reaction product was filtered through a Celite pad to

(a) Synthetic tetranuclear Fe clusters with oxo, hydroxo, alkoxo bridges



(b) This work: Conversion of CO₂ to formate by Fe-alkoxo cluster

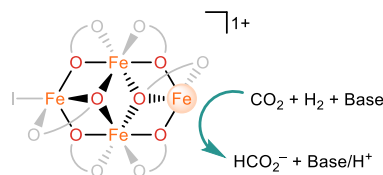


FIGURE 1 Structural features of (a) synthetic tetranuclear Fe clusters with oxo, hydroxo, and alkoxo bridges, and (b) [Fe₄I₂(O₂C₁₄H₁₁)₆] (**1**) cluster for this work

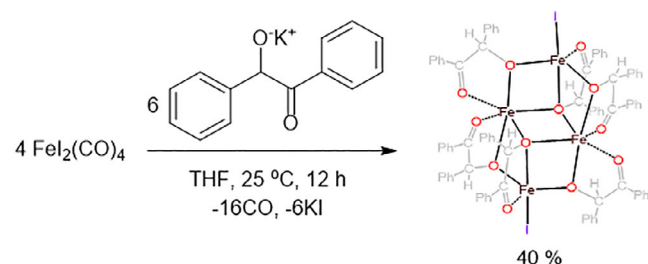


FIGURE 2 Synthetic procedure of $[\text{Fe}_4\text{I}_2(\text{O}_2\text{C}_{14}\text{H}_{11})_6]$ (**1**) cluster

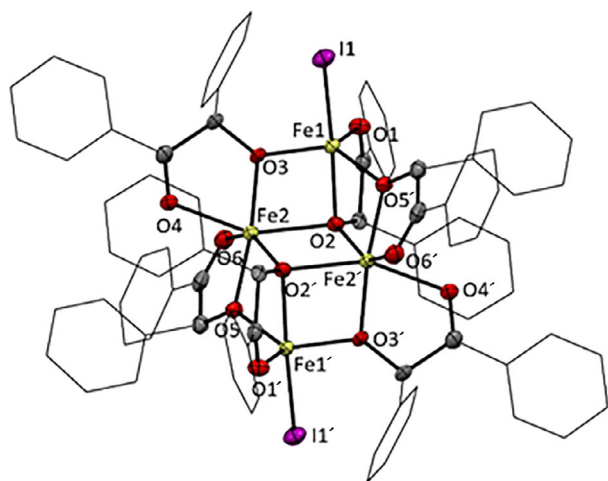


FIGURE 3 X-ray crystal structure of $[\text{Fe}_4\text{I}_2(\text{O}_2\text{C}_{14}\text{H}_{11})_6]$ (**1**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Fe1–I1 2.7404(6), Fe1–O1 2.115(2), Fe1–O2 2.250(2), Fe1–O3 1.962(2), Fe1–O5' 1.957(2), Fe1–Fe2 3.128(6), Fe2–O2 2.163(2), Fe2–O2' 2.174(2), Fe2–O3 2.002(2), Fe2–O4 2.220(2), Fe2–O6 2.292(2), Fe2'–O5' 2.013(2). Selected bond angles (°): I1–Fe1–O2 172.31(6), O1–Fe1–O3 95.85(9), O1–Fe1–O5' 113.42(9), O2–Fe2–O3 80.04(9), O2–Fe2–O4 153.33(8), O3–Fe2–O5 172.75(9), O2–Fe2–O2' 76.52(8), Fe2–O2–Fe2' 103.48(9), O3–Fe1–O2 78.76(9), O3–Fe1–O5' 136.47(9), O3–Fe2–O2 80.04(9), O3–Fe2–O2' 105.12(9), O5'–Fe1–O2 77.88(9), O5'–Fe2'–O2 78.57(9), O5'–Fe2'–O2' 107.02(9), Fe2–O2–Fe2' 103.48(9), Fe1–O3–Fe2 104.2(1), Fe1–O5'–Fe2' 104.4(1), O2–Fe2–O2' 76.52(8)

produce a dark violet solution. Crystallization of the product in dichloromethane/hexane provided single crystals suitable for x-ray crystallography. Infrared (IR) spectroscopy showed the $\text{C}=\text{O}$ vibration peak ($\nu(\text{C}=\text{O})$) of the deprotonated benzoin ligand at 1637 cm^{-1} and the extinction of the $\nu(\text{OH})$ peak of free benzoin.

Free benzoin has a higher $\nu(\text{C}=\text{O})$ frequency at 1679 cm^{-1} (Figure S1), but the $\text{Fe}\cdots\text{O}=\text{CR}_2$ bond interaction decreased the $\nu(\text{C}=\text{O})$ by 42 cm^{-1} because of the π -back donation. The spectral observation was consistent with the x-ray crystal structure of the Fe cluster, having multiple coordinate bonds with the deprotonated benzoin ligand (Figure 2).

The cluster has a rhombus-like structure with tetranuclear Fe(II) centers, supported by six benzoin-derived ligands and two iodides (Figure 3). The four Fe centers are connected through the bridging $\mu_3\text{-O}$ and $\mu_2\text{-O}$ bonds, where two

Fe(II) centers show the distorted trigonal prismatic coordination, and the other two Fe(II) centers have the bridging O-bonds and one iodide in the distorted trigonal bipyramidal coordination. The equatorial plane of $[\text{Fe}_2\text{-O}_2\text{-Fe}_2'\text{-O}_2']$ has angles of $103.48(9)^\circ$ for $\text{Fe}_2\text{-O}_2\text{-Fe}_2'$ and $76.52(8)^\circ$ for $\text{O}_2\text{-Fe}_2\text{-O}_2'$. The $\mu_3\text{-O}$ bond to Fe centers remains $\sim 2.2\text{ Å}$ (Fe1–O2, 2.250(2) Å; Fe2–O2, 2.163(2) Å; Fe2–O2', 2.174(2) Å). The $\mu_2\text{-O}$ binding to Fe centers (Fe1 and Fe2) results in relatively short bond distances of $\sim 2.0\text{ Å}$ (Fe1–O3, 1.962(2) Å; Fe2–O3, 2.002(2) Å). The $\text{Fe-O}=\text{CR}_2$ bond additionally stabilized the Fe coordination. The four Fe(II) centers make no direct bond with one another, retaining the long distance between Fe1–Fe2 (3.128 Å) and Fe2–Fe2' (3.402 Å). In addition, we obtained the powder x-ray diffraction of the cluster complex, which showed a well-matching pattern with the simulation and confirmed the purity of the sample (Figure S2).

The presence of Fe(II) centers in the two different coordination environments was detected by x-ray photoelectron spectroscopy (XPS) (Figure 4a). Because of more Fe–O bonds, the trigonal prismatic Fe center (Fe2) will have higher binding energy than the trigonal bipyramidal Fe center (Fe1). Thus, the spin-orbit doublet peaks of Fe $2p_{3/2}$ and $2p_{1/2}$ at 708.97 and 722.46 eV were assigned to be of the trigonal prismatic Fe(II) center, and the other peaks at 710.40 and 723.89 eV were accordingly of the trigonal bipyramidal Fe(II) center. The relative areas of the Fe 2p fragment peaks were measured to be the same, consistent with the even number of Fe(II) centers in the two coordination conditions. In addition, the O 1s region peak appeared to fit well with three fragment peaks (Figure 4b). The areas of the three O 1s fragment peaks show a ratio of 1:2:3 at the binding energies of 533.10, 532.23, and 531.30 eV, consistent with the numbers of two $\mu_3\text{-O}$, four $\mu_2\text{-O}$, and six non-bridging O, respectively.

We calculated atomic charges to ensure the assignment of XPS data. Although the atomic partial charge is not considered the oxidation state of an element, the charge value should relate to the binding energy of the Fe(II) electron. Thus, we compared the atomic charges of Fe(II) centers obtained from the Mulliken, Löwdin, CHELPG, and Hirshfeld schemes (Table 1). The Fe2 and Fe2' sites consistently had more significant atomic charges than Fe1 and Fe1'. Therefore, the trigonal prismatic Fe(II) site could be assigned to have larger binding energy than the trigonal bipyramidal Fe(II) site.

Cluster **1** showed two reduction peaks at -1.83 and -2.61 V vs. $\text{Fc}^{0/+}$ (ferrocene/ferrocenium) and three oxidation peaks at -1.12 , -1.67 , and -2.26 V vs. $\text{Fc}^{0/+}$ (Figure S3). A new reduction current peak appeared at a large negative potential of -2.87 V vs. $\text{Fc}^{0/+}$ under CO_2 atmosphere, which is likely due to direct CO_2 reduction at a glassy carbon electrode surface. We next examined CO_2 hydrogenation reactivity of **1** under CO_2/H_2 gas mixture with interest in the chemical reactivity of a trigonal bipyramidal Fe center.^{18,20}

The trigonal bipyramidal Fe site was activated by the iodide abstraction with AgClO_4 in THF. UV-vis absorption spectroscopy of **1** in THF showed the maximum absorbance

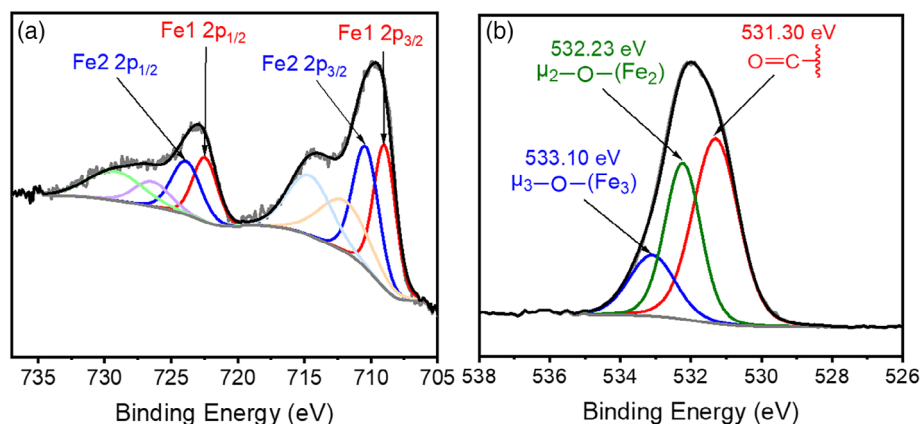
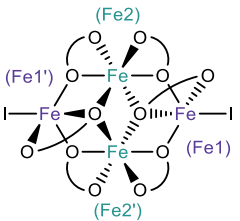


FIGURE 4 High-resolution x-ray photoelectron spectra of cluster **1** in the region of (a) Fe 2p fitting with two types of Fe1 (red), Fe2 (blue) coordination environments, and (b) O 1s fitting with three types of oxygen conditions

TABLE 1 Atomic charge analysis of Cluster **1**



$$\text{Fe}-\text{O} = \text{Fe}-\text{O}-\text{C}(\text{Ph})_2$$

	Fe1	Fe1'	Fe2	Fe2'
Mulliken	0.633	0.633	0.716	0.716
Löwdin	−0.471	−0.471	−0.343	−0.343
CHELPG	0.540	0.528	0.551	0.549
Hirshfeld	0.269	0.269	0.286	0.286

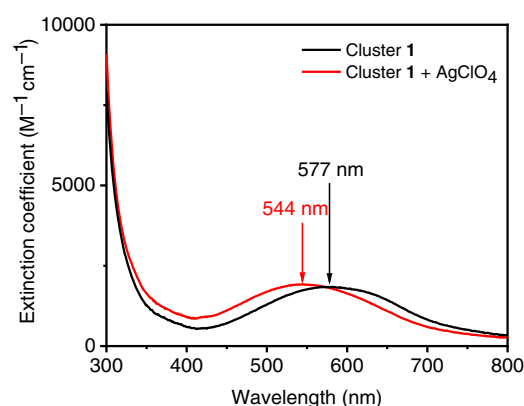


FIGURE 5 UV-vis absorption spectra of $[\text{Fe}_4\text{I}_2(\text{O}_2\text{C}_{14}\text{H}_{11})_6]$ (**1**) (black) and **1** + AgClO_4 (red) in THF solution

(λ_{max}) at 577 nm ($\epsilon = 1.84 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 5). The elimination of the π -donating iodide ligand from **1** slightly shifted λ_{max} to 544 nm ($\epsilon = 1.93 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Initially, the injection of H_2 and CO_2 gas into **1** + AgClO_4 solution in THF did not give a CO_2 hydrogenation product, but the addition of 1,8-diazabicycloundec-7-ene (DBU) into the reaction solution afforded formate/DBUH⁺ product with 36% yield per cluster (Table 2). Additional use of the Lewis basic agent was critical to obtain formate product, which denotes the Lewis acidic Fe(II) center conducts the CO_2 hydrogenation with the assistance of the external Lewis basic agent.²⁴ Another reaction of **1** without the iodide abstraction did not give the CO_2 hydrogenation product even in the presence of the same additives, which excludes a possible substitution of iodide by acetonitrile solvent. Additional use of lithium trifluoromethanesulfonate (LiOTf) significantly increased the formate yield up to 100%. The formate production was confirmed by detecting $\text{Li}[\text{HCO}_2]$ peak with NMR spectroscopy, 8.46 ppm in the ^1H NMR spectrum (Figure S4) and 171.6 ppm in the ^{13}C NMR spectrum (Figure S5). DBU could capture a free proton generated from the H_2 splitting through the Lewis acid/base interaction at the

Fe(II) site, and the formation of $\text{Li}[\text{HCO}_2]$ salt improved the yield of the CO_2 hydrogenation.

Quantum mechanical calculations of the Gibbs free energies were used to propose a reaction mechanism. As expected, an iodide abstraction of **1** to **2** is facile with the free energy difference (ΔG) of -18.8 kcal/mol . The role of DBU was critical to capturing a proton released after the H_2 splitting. The reaction was thermodynamically unfavorable without DBU, with a large ΔG value of 32.8 kcal/mol . The H_2 splitting step would be a concerted fashion because of the essential role of the external Lewis basic agent. Plausible generation of Fe–H is likely a prior step for CO_2 reaction, and the Fe-formate intermediate (**4**) could be formed through the **3-TS** transition state with 8.58 kcal/mol energy (Figure 6). The low barrier energy indicates the high reactivity of the Fe center in the trigonal bipyramidal coordination. Liberation of formate product to give back **2** is, however, energetically prohibited because of the large stabilization energy of **4** with a strong Fe–OCHO bond. Therefore, the current CO_2 hydrogenation reaction was observed as a stoichiometric process rather than a catalytic cycle, although additional Li^+ cation could obtain formate from the Fe site at the

TABLE 2 Hydrogenation of CO₂ to formate in the presence of additives^a

Entry	Additive	CO ₂ :H ₂	Yield ^b (%)
1	DBU (10 eq.)/LiOTf (5 eq.)	1:1	100
2	DBU (10 eq.)/LiOTf (5 eq.)	1:0	-
3	DBU (10 eq.)	1:1	36
4	LiOTf (5 eq.)	1:1	-

^aReaction conditions: CO₂ (~1 atm, balloon), H₂ (~1 atm, balloon). Amount of DBU (10 eq.)/LiOTf (5 eq.) was optimized.

^bYield: conversion yield per cluster, analyzed by ¹H NMR spectroscopy through DMF calibration method (see Data S1 for details).

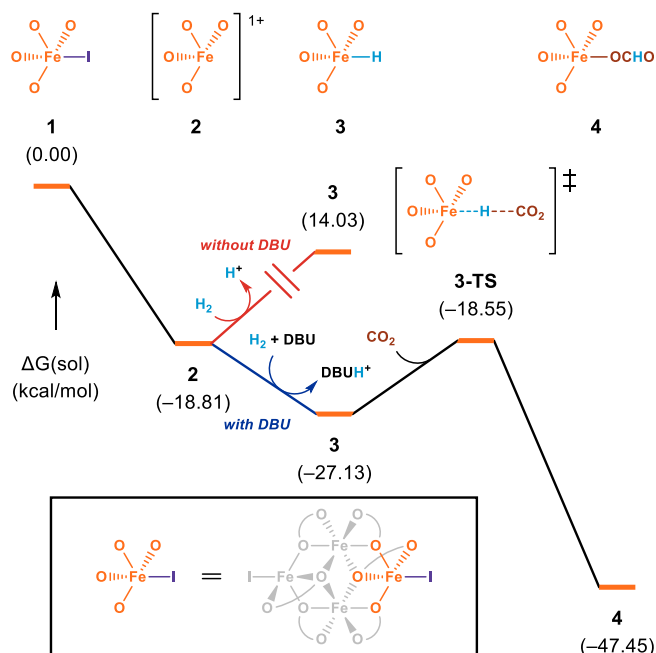


FIGURE 6 Gibbs free energy profile for CO₂ hydrogenation by the Fe cluster

final step. In other pathways, intramolecular or intermolecular hydrogen transfer from sp^3 C–H of benzoin ligand would be considered to generate Fe–H species. However, those reaction pathways appeared to be highly uphill procedures, thus, mechanistically irrelevant (see Figure S6).

In summary, we synthesized a tetranuclear Fe(II) cluster supported by benzoin-derived ligands and demonstrated the CO₂ hydrogenation reactivity. The x-ray crystal structure presented a rhombus-like shape of the Fe cores, of which Fe centers possessed the two different coordination environments of trigonal bipyramid and trigonal prism. The two types of Fe(II) centers and the ligand's O elements exhibited distinct electronic properties according to the coordination conditions. The Lewis acidic Fe(II) of the trigonal bipyramidal site conducted the CO₂ hydrogenation in the presence of an external Lewis basic agent. In this work, we could describe the first example of the CO₂ hydrogenation reactivity of the Lewis acidic Fe(II) supported in an Fe-alkoxo cluster.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (no. 2020R1C1C1007106) and GIST Research Institute grant funded by the GIST in 2022.

ORCID

Junseong Lee <https://orcid.org/0000-0002-5004-7865>

Junhyeok Seo <https://orcid.org/0000-0002-9436-6964>

REFERENCES

- [1] H. Shomar, G. Bokinsky, *Molecules* **2021**, 26, 6930.
- [2] Y. Khodour, L. S. Kaguni, J. Stiban, *The Enzymes* **2019**, 45, 225.
- [3] C. Andreini, I. Bertini, G. Cavallaro, R. J. Najmanovich, J. M. Thornton, *J. Mol. Biol.* **2009**, 388, 356.
- [4] L. Liu, S. Chakraborty, P. Hosseinzadeh, Y. Yu, S. Tian, I. Petrik, A. Bhagi, Y. Lu, *Chem. Rev.* **2014**, 114, 4366.
- [5] H. C. Zhou, R. H. Holm, *Inorg. Chem.* **2003**, 1, 11.
- [6] Y. Lee, K. J. Anderton, F. T. Sloane, D. M. Ermert, K. A. Abboud, R. García-Serres, L. J. Murray, *J. Am. Chem. Soc.* **2015**, 137, 10610.
- [7] R. H. Sánchez, A. M. Willis, S. L. Zheng, T. A. Betley, *Angew. Chem., Int. Ed.* **2015**, 54, 12009.
- [8] H. Weihe, H. U. Güdel, *J. Am. Chem. Soc.* **1997**, 119, 6539.
- [9] L. Haim, F. Robert, L. Peres, P. Lecante, K. Philippot, R. Poteau, M. Respaud, C. Amiens, *Nanoscale Adv.* **2021**, 3, 4471.
- [10] G. Rousse, J. Rodriguez-Carvajal, S. Patoux, C. Masquelier, *Chem. Mater.* **2003**, 15, 4082.
- [11] A. J. Jasniewski, L. Que, *Chem. Rev.* **2018**, 118, 2554.
- [12] I. P. Lorenze, W. Pohl, H. Nöth, *Angew. Chem., Int. Ed.* **1997**, 36, 55.
- [13] K. H. Lii, Y.-F. Huang, *Chem. Commun.* **1997**, 839.
- [14] H. Li, Z. J. Zhong, W. Chen, X. Z. You, *Dalton Trans.* **1997**, 463.
- [15] J. Choi, S. Yoon, *Bull. Korean Chem. Soc.* **2022**, 43, 299.
- [16] B. M. Pires, D. M. Silva, L. C. Visentin, V. Drago, N. M. F. Carvalho, R. B. Faria, O. A. C. Antunes, *Inorg. Chim. Acta* **2013**, 407, 69.
- [17] J. Trettenhahn, M. Nagl, N. Neuwirth, V. B. Arion, W. Jary, P. Pöchlauer, W. Schmid, *Am. Ethnol.* **2006**, 45, 2794.
- [18] J. Deutscher, T. Corona, K. Warm, X. Engelmann, S. Sobottka, B. Braun-Cula, B. Sarkar, K. Ray, *Eur. J. Inorg. Chem.* **2018**, 2018, 4925.
- [19] G. de Ruiter, N. B. Thompson, M. K. Takase, T. Agapie, *J. Am. Chem. Soc.* **2016**, 138, 1486.
- [20] M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata, S. Masaoka, *Nature* **2016**, 530, 465.
- [21] B. Das, B. L. Lee, E. A. Karlsson, T. Åkermarck, A. Shatskiy, S. Demeshko, R. Z. Liao, T. M. Laine, M. Haukka, E. Zeglio, A. F. Abdel-Maged, P. E. M. Siegbahn, F. Meyer, M. D. Kärkäs, E. V. Johnston, E. Nordlander, B. Åkermarck, *Dalton Trans.* **2016**, 45, 13289.
- [22] A. Taheri, C. R. Carr, L. A. Berben, *ACS Catal.* **2018**, 8, 5787.
- [23] Y. J. Wnag, H. J. Wang, F. Luo, S. Yao, T. B. Lu, Z. M. Zhang, *Appl. Catal. B.* **2022**, 300, 120487.
- [24] Y. Zhang, A. D. MacIntosh, J. L. Wong, E. A. Bielinski, P. G. Williard, B. Q. Mercado, N. Hazari, W. H. Bernskoetter, *Chem. Sci.* **2015**, 6, 4291.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: H. Yang, J. Kim, W. Lee, J. Lee, J. Seo, *Bull. Korean Chem. Soc.* **2022**, 43(11), 1236. <https://doi.org/10.1002/bkcs.12617>