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Reactivity of borohydride incorporated in coordination polymers toward carbon dioxide[†]

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Borohydride (BH₄⁻)-containing coordination polymers converted CO_2 into HCO_2^- or $[BH_3(OCHO)]^-$, whose reaction routes were affected by the electronegativity of metal ions and the coordination mode of BH_4^- . The reactions were investigated using thermal gravimetric analysis under CO_2 gas flow, infrared spectroscopy, and NMR experiments.

Conversion of carbon dioxide (CO₂) into valuable chemicals is a key to realize a sustainable society.^{1,2} In particular, it is essential to establish chemical reactions that transform CO₂ into various types of chemical moieties under mild conditions.³ However, the inherent inertness of CO₂ has hampered the utilization of CO₂ in transformation reactions. To overcome the inertness, various catalytic and stoichiometric reactions have been widely studied in both solution and the solid-state, including metals, metal oxides,⁴ metal complexes,^{5,6} and metal-free organic molecules.⁷

Borohydride (BH₄⁻), a hydride-based complex anion, has been commonly utilized as a reducing agent. In the solution phase, metal borohydrides (MBHs) stoichiometrically react with CO₂ at ambient temperatures and pressures.^{8–11} BH₄⁻ in solution is able to convert CO₂ into chemical species such as formate (HCO₂⁻) and formylhydroborate ([BH_{4-x}(OCHO)_x]⁻, x = 1, 2 and 3) depending on the reaction conditions, *e.g.* counter cations, temperatures,

^a Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan solvents, and pressures.^{8,9,12} The solid-state reactivity of BH_4^- toward CO_2 is also interesting from the viewpoint of heterogeneous catalysts and CO_2 scrubbers. Nevertheless, limited studies have been performed on the solid-state reactivity of MBHs toward CO_2 .^{13,14} This is because slow diffusion of CO_2 in dense MBHs results in low reactivity under mild conditions.¹⁴ Although porous structures are advantageous for the diffusion of CO_2 , MBHs with the porous structure are limited except for a few examples, *e.g.* γ -Mg(BH₄)₂.^{14,15}

Coordination polymers (CPs) and metal-organic frameworks (MOFs) are crystalline solids constructed from metal ions and bridging organic linkers.¹⁶⁻¹⁸ Their open structures have offered an attractive platform for various gas-solid reactions, such as CO₂ sorption¹⁹⁻²¹ and post-synthetic modification.^{22,23} In addition, rich structural and chemical tunability of CPs demonstrated the controlled reactivity of reactive species, e.g. radicals,24,25 imines,26 and photoactive metal complexes.²⁷ CPs are a promising platform for solidgas reactions between BH₄⁻ and CO₂. BH₄⁻-containing CPs are constructed from metal ions (e.g. Mg²⁺, Ca²⁺, Mn²⁺, Zn²⁺, and Th⁴⁺) and N-based neutral linkers show various types of the chemical environment of $BH_4^{-.28-30}$ Here, we investigate the reactivity of BH₄⁻-containing CPs to convert CO₂ into HCO₂⁻ or [BH₃(OCHO)]⁻ under mild conditions depending on their structures.

 $[M(BH_4)_2(pyz)_2]$ (**M-pyz**, M = Mg²⁺, Ca²⁺, pyz = pyrazine)^{28,29} were selected to investigate the influence of metal ions on the reactivity of BH₄⁻ toward CO₂. The metal ion center shows an octahedral geometry and the two BH₄⁻ ions coordinate in the axial positions (Fig. 1A). The extended structure of **M-pyz** comprises a 2D square grid constructed by $[M_4pyz_4]$ units (Fig. 1B). The electronic properties and reactivity of BH₄⁻ are influenced by the electronegativity of counter metal ions.^{31,32} Attempts at the synthesis of isostructural **M-pyz** were made using a Mn²⁺-based MBH precursor. $[Mn(BH_4)_2.3THF]\cdotNaBH_4$ was prepared following the literature methods.³³ The general synthetic method involves mechanochemical milling of the MBH precursor and pyz under Ar. **Mg-pyz** was previously

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Fig. 1 (A) Local coordination geometry of M-pyz (M = Mg²⁺, Ca²⁺, Mn²⁺). (B) ABAB stacking structure of the extended 2D layers of M-pyz (M = Mg²⁺, Ca²⁺, Mn²⁺). (C) IR spectra of **Ca-pyz** before and after CO₂ adsorption at 25 °C.

synthesized in the solution phase, whereas the solvent-free conditions afford a highly crystalline product as well (Fig. S1, ESI[†]). The powder X-ray diffraction (PXRD) pattern of **Mn-pyz** shows a good agreement with that of **Mg-pyz** (Fig. S1, ESI[†]).

The solid-state synthesis of M-pyz proceeds without solvents at 25 °C within 30 min. The fast reaction kinetics in the solidstate is ascribed to the low melting point of pyz (52 °C). The lower melting point of reactants leads to higher molecular mobility, enhancing the reactivity in the solid-state.³⁴ Mechanical milling is useful to synthesize CPs from MBHs because most of the MBHs are poorly soluble in common organic solvents. The thermal properties were characterized by thermal gravimetric analysis (TGA) under N2 (Fig. S2, ESI⁺). Each compound exhibits a weight loss at relatively low temperatures; 50, 70, and 70 °C for Mg-, Mn-, and Ca-pyz due to the low boiling point of pyz (115 °C). Isothermal TGA measurements at 40 °C under N₂ indicate that Ca-pyz shows higher thermal stability than Mn-pyz (weight loss after 6 hours; 0.2 vs. 3.2 wt%, Fig. S3, ESI⁺). In the case of MBHs, electropositive metal ions construct MBHs with higher thermal stability.35 Meanwhile, in the case of BH₄⁻-containing CPs, the strength of the coordination bonds is also essential. The Hard and Soft Acids and Bases (HSAB) theory reveals that electropositive metal ions (hard acids) form weaker coordination bonds with nitrogen-based linkers (soft bases) such as pyz. Therefore, the trend of thermal stability for M-pyz does not simply follow the electronegativity of metal ions (thermal stability: Mg < Mn < Ca, Pauling electronegativity: Ca < Mg < Mn).

To characterize the chemical environment of BH_4^- in the CP, solid-state ¹¹B magic angle spinning (MAS) nuclear magnetic resonance (NMR) was carried out on non-paramagnetic **Ca-pyz**. The ¹¹B NMR spectrum of **Ca-pyz** displays a peak at -36 ppm corresponding to the signal of BH_4^- (Fig. S4, ESI†). The total charge on BH_4^- is correlated with the chemical shift of ¹¹B NMR: electron-rich BH_4^- shows a peak in a lower frequency.³¹ The low-frequency shift of the ¹¹B peak indicates that BH_4^- in **Ca-pyz** is more electron-rich than $Ca(BH_4)_2$. In the framework of **Ca-pyz**, the Lewis acidity of Ca^{2+} was reduced by electron donation from the coordinating pyz molecules, which leads to the formation of electron-rich BH_4^- .²⁹

 CO_2 adsorption measurement was carried out to evaluate the reactivity of Ca-pyz in gas-solid equilibrium. The CO_2



Fig. 2 Isothermal TGA profiles of M-pyz (M = Mg²⁺, Ca²⁺, Mn²⁺) under CO₂ flow (0.1 MPa, 30 mL min⁻¹) at 40 °C.

isotherm at 25 °C displays irreversible adsorption (7 mL g⁻¹ at 100 kPa), which is characteristic of chemisorption behavior (Fig. S5, ESI[†]).³⁶ The IR spectrum of **Ca-pyz** after CO₂ adsorption displays a new peak at 1600 cm⁻¹, corresponding to C=O stretching (Fig. 1C). The solid-state ¹H-¹³C cross-polarization (CP) MAS NMR spectrum of **Ca-pyz** after CO₂ adsorption shows peaks at 170 and 145 ppm. The peaks correspond to the signals of HCO₂⁻ and pyz, respectively (Fig. S6, ESI[†]). The results indicate that BH₄⁻ in **Ca-pyz** reduces CO₂ to HCO₂⁻ with the release of diborane (B₂H₆) as a by-product.¹⁰

The kinetic reactivity of M-pyz toward CO₂ was evaluated using isothermal TGA under CO2 flow. Fig. 2 displays the TGA profiles of each powder sample (10 mg) under CO₂ flow (0.1 MPa, 30 mL min⁻¹) at 40 °C. Mg-pyz and Ca-pyz exhibit higher weight increases than Mn-pyz (25.5, 21.9, and 3.2 wt% after 400 min, respectively). Ca-pyz was amorphous after the CO₂ reaction, as confirmed by PXRD (Fig. S7, ESI[†]). To identify the chemical species after the CO₂ reaction, solution NMR was carried out on Ca-pyz dissolved in DMSO- d_6 . The solution ¹³C NMR spectrum of Ca-pyz after the CO₂ reaction displays peaks at 167, 146, 53, 50, 47 and 44 ppm (Fig. S8, ESI†). The peaks at 167 and 146 ppm correspond to the ¹³C signals of HCO₂⁻ and pyz, respectively. The peak at 47 ppm is assigned to piperazine formed by the reduction of pyz by B₂H₆, whereas the rest of the peaks are not able to be assigned.^{29,37} The higher reactivity of Ca-pyz toward CO₂ is attributed to the preferable electronic interaction between Ca^{2+} (hard acid) and HCO_2^- (hard base) rather than BH_4^- (soft base).

The formation of $[BH_{4-x}(OCHO)_x]^-$ from BH_4^- and CO_2 was investigated at a BH_4^- -containing CP. Given that $[BH_{4-x}(OCHO)_x]^$ is bulky than HCO_2^{-} , $[Mn(BH_4)_2(dpe)_{1,5}]$ (Mn-dpe, dpe = dipyridylethane) having voids was selected. 28 The two BH_4^- ions coordinate to the Mn²⁺ center in a bidentate manner, which was confirmed by single-crystal X-ray diffraction (SC-XRD) in Fig. 3A. The extended structure of Mn-dpe comprises a 1D ladder constructed from [Mn4dpe4] units (Fig. 3B). The coordination mode of BH_4^- was confirmed by IR spectroscopy as well. The IR spectrum of Mn-dpe displays two stretching peaks in the B-H stretching region at 2378 and 2127 cm⁻¹, respectively (Fig. 4B). The peak at 2378 cm⁻¹ corresponds to the B-H bond coordinating to the Mn²⁺ center, whereas the peak at 2127 cm⁻¹ corresponds to the noncoordinating B-H.³⁸ In contrast to the broadened B-H stretching peak of Ca-pyz (Fig. 1C), Mn-dpe displays distinct two peaks of B-H stretching, which is originated from a stronger binding interaction between Mn^{2+} (soft acid) and BH_4^{-} (soft base).

The kinetic curve of the CO₂ reaction with Mn-dpe was collected using the same procedure as M-pyz (Fig. 3B). Mn-dpe demonstrates a weight increase of 26.2 wt% after 600 min at 40 °C, which corresponds to a value of the 1.1:1 molar ratio of reacted CO₂ per BH₄⁻. After the CO₂ reaction, Mn-dpe shows small diffraction peaks different from the original peaks (Fig. S9, ESi[†]). Solution ¹¹B NMR measurement was carried out to determine the chemical species after the CO₂ reaction. The ¹¹B ^{1}H NMR spectrum of digested **Mn-dpe** after the CO₂ reaction displays the peaks at -33, -11, and 2.2 ppm in Fig. 4A. The broad peaks were observed due to the paramagnetic effect of Mn^{2+} . The ¹¹B peaks correspond to BH_4^{-} , $[BH_3(OCHO)]^-$ and $[BH_2(OCHO)_2]^-$, respectively.^{9,39} Successive CO_2 insertions into the B-H bond of BH_4^- produce $[BH_{4-x}(OCHO)_x]^-$, and the number of reacted CO₂ molecules is affected by the reaction conditions such as pressure and temperature in the solution phase.^{8,9} The reaction of NaBH₄ in acetonitrile with 0.1 MPa of CO₂ for 10 minutes produces [BH(OCHO)₃]⁻ as a major product, and [BH₃(OCHO)]⁻ is not observed.⁹ This is because all the hydrogen atoms of BH₄⁻ dissociated in acetonitrile are available for the reaction with CO₂. On the other hand, in the case of **Mn-dpe**, two of the hydrogen atoms of BH₄⁻ are pinned with the Mn²⁺ center by



Fig. 4 (A) Solution ¹¹B{¹H} NMR of digested Mn-dpe after CO₂ reaction.
(B) IR spectra of Mn-dpe before and after the CO₂ reaction.

a coordination bond as confirmed by SC-XRD and IR spectroscopy. After the CO₂ reaction, a non-coordinating B–H stretching peak was not observed, and this is because of the reaction with CO₂ to form $[BH_3(OCHO)]^-$ and $[BH_2(OCHO)_2]^-$ in Fig. 4B. The coordinating B–H stretching peak is preserved after the CO₂ reaction, indicating the coordinating bonds between Mn²⁺ and $[BH_3(OCHO)]^-$ or $[BH_2(OCHO)_2]^-$. A sluggish kinetics of dense NaBH₄ in the solid-state toward CO₂ indicates that the open structure of **Mn-dpe** is essential for the diffusion of CO₂ (Fig. 3C). Based on the results, the reaction between **Mn-dpe** and CO₂ to produce $[BH_3(OCHO)]^-$ and $[BH_2(OCHO)_2]^-$ is proposed (Fig. S11, ESI†). The results indicate that the anisotropic coordination geometry of BH_4^- in **Mn-dpe** affects the reaction route with CO₂.



Fig. 3 (A) Local coordination geometry of Mn-dpe. (B) Packing structure of the extended 1D ladders of Mn-dpe. (C) Isothermal TGA profiles of Mn-dpe and NaBH₄ under CO₂ flow (0.1 MPa, 30 mL min⁻¹) at 40 °C.

In conclusion, we demonstrated the reactivity of BH₄⁻ toward CO₂ which is correlated with the crystal structures of BH₄⁻-containing coordination polymers. The reactivity of $[M(BH_4)_2(pyrazine)_2]$ (M = Mg²⁺, Mn²⁺, Ca²⁺) and $[Mn(BH_4)_2(dipyridylethane)_{1.5}]$ toward CO₂ at 40 °C was investigated by using isothermal TGA under CO₂ flow, IR and NMR. BH₄⁻ in $[Ca(BH_4)_2(pyrazine)_2]$ converted CO₂ into HCO₂⁻. The BH₄⁻ pinned by coordination bonds with Mn²⁺ in $[Mn(BH_4)_2(dipyridylethane)_{1.5}]$ regulated the successive CO₂ insertion reaction and produced $[BH_3(OCHO)]^-$ as a major species. The structural diversity of coordination polymers provides a new approach to regulate the reaction routes between BH₄⁻ and CO₂ in the solid-state.

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Conflicts of interest

The authors declare no conflict of interest.

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