Supporting information for

Reactivity of Borohydride Incorporated in Coordination Polymers toward Carbon Dioxide

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Materials and general methods

All chemicals and solvents used in the syntheses were of regent grade and used without any further purification. LiBH₄, NaBH₄, Mg(BH₄)₂ and Ca(BH₄)₂ were purchased from Sigma-Aldrich. Anhydrous MnCl₂ was purchased from Strem Chemicals, Inc. Pyrazine and dipyridylethane were purchased from Tokyo Chemical Industry Co., Ltd. Super dehydrated acetonitrile (MeCN), super dehydrated diethyl ether (Et₂O) and deoxidized tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries, Ltd.

Mechanical milling: mechanical milling was performed using a planetary ball-milling apparatus with zirconia vessel and balls (Fritsch, Pulverisette 7) under Ar atmosphere. The volumetric capacity of the pot was 20 mL and 10 balls with a diameter of 10 mm were used for the milling. The ball mill vessel was previously oven dried.

Powder X-ray diffraction (PXRD): PXRD patterns were collected on a Rigaku SmartLab with CuK_{α} anode.

Fourier transform infrared (IR): IR spectra were collected using a Bruker Optics ALPHA FT-IR spectrometer with Universal ATR accessory under Ar.

Thermogravimetric analysis (TGA): TGA profiles were collected using a Rigaku Thermo plus TG 8121 apparatus in the temperature range of 40 to 500 °C at a heating rate of 10 °C min⁻¹ under flowing N₂.

Gas adsorption: Gas adsorption isotherms were collected by a BELSORP-mini. The powder sample was packed in an Ar-filled glovebox.

Solution nuclear magnetic resonance (NMR): ${}^{11}B{}^{1}H}$ and ${}^{13}C$ NMR spectra were obtained using JEOL A-500 and spectrometers operating at 500 MHz. For ${}^{11}B{}^{1}H$ NMR measurement a quartz based NMR sample tube was utilized.

Solid-state magic angle spinning (MAS) NMR: Solid-state NMR spectroscopy was performed using a Bruker Biospin, ADVANCE III 400 NMR spectrometer. ¹¹B and ¹³C magic angle spinning (MAS) NMR spectra were recorded at a spinning rate of 10 kHz at the magic angle. The powder sample was packed in an Ar-filled glovebox.

Synthesis of [Mg(BH₄)₂(pyz)₂] (Mg-pyz, pyz = pyrazine).

 $Mg(BH_4)_2$ (54.0 mg, 1.0 mmol) and pyz (240.3 mg, 3.0 mmol) were mixed and transferred to a ball mill vessel inside Ar-filled glove box. The ball mill vessel was taken outside the glovebox, and the reaction mixture was milled at 200 rpm for 30 min (5 min of milling and 5 min of rest × 6 cycles). The resultant powder was washed with super dehydrated Et₂O (10 mL × 3) and dried at 298 K for 3 hours inside Ar-filled glove box.

Synthesis of [Mn(BH₄)₂(pyz)₂] (Mn-pyz).

Mn-pyz was synthesized according to the method of **Mg-pyz** using $[Mn(BH_4)_2 \cdot 3THF] \cdot NaBH_4^1$ instead of $Mg(BH_4)_2$.

Synthesis of [Ca(BH₄)₂(pyz)₂] (Ca-pyz).

Ca-pyz was synthesized according to the literature.²

Synthesis of [Mn(BH₄)₂(dpe)_{1.5}] (Mn-dpe, dpe = dipyridylethane).

Mn-dpe was synthesized according to the literature.²



Figure S1. PXRD patterns of **M-pyz** ($M = Mg^{2+}$, Ca^{2+} , Mn^{2+}) under Ar.



Figure S2. TGA profiles of **M-pyz** ($M = Mg^{2+}$, Ca^{2+} , Mn^{2+}) under N₂.



Figure S3. Isothermal TGA profiles of **M-pyz** ($M = Ca^{2+}$, Mn^{2+}) at 40 °C under N₂.



Figure S4. Solid-state ¹¹B MAS NMR spectra of Ca-pyz and Ca(BH₄)₂ under Ar.



Figure S5. CO₂ adsorption isotherm for Ca-pyz at 25 °C.



Figure S6. Solid-state ¹³C MAS NMR spectrum of Ca-pyz after CO₂ adsorption.



Figure S7. PXRD patterns of **Ca-pyz** before and after CO_2 reaction under Ar.



Figure S8. Solution ¹³C NMR spectrum of **Ca-pyz** after CO₂ reaction.



Figure S9. PXRD patterns of **Mn-dpe** before and after CO₂ reaction under Ar.



Figure S10. IR spectra of **Mn-dpe** before and after CO₂ reaction under Ar.



Figure S11. Reaction between **Mn-dpe** and CO₂.

References

- 1. V. D. Makhaev, A. P. Borisov, T. P. Gnilomedova, É. B. Lobkovskii and A. N. Chekhlov, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1987, **36**, 1582-1586.
- 2. K. Kadota, N. T. Duong, Y. Nishiyama, E. Sivaniah, S. Kitagawa and S. Horike, *Chem. Sci.*, 2019, **10**, 6193-6198.