Supporting Information of

Direct methylation of benzene with methane over Co/MFI catalysts generated by self-dispersion of $Co(OH)_2$

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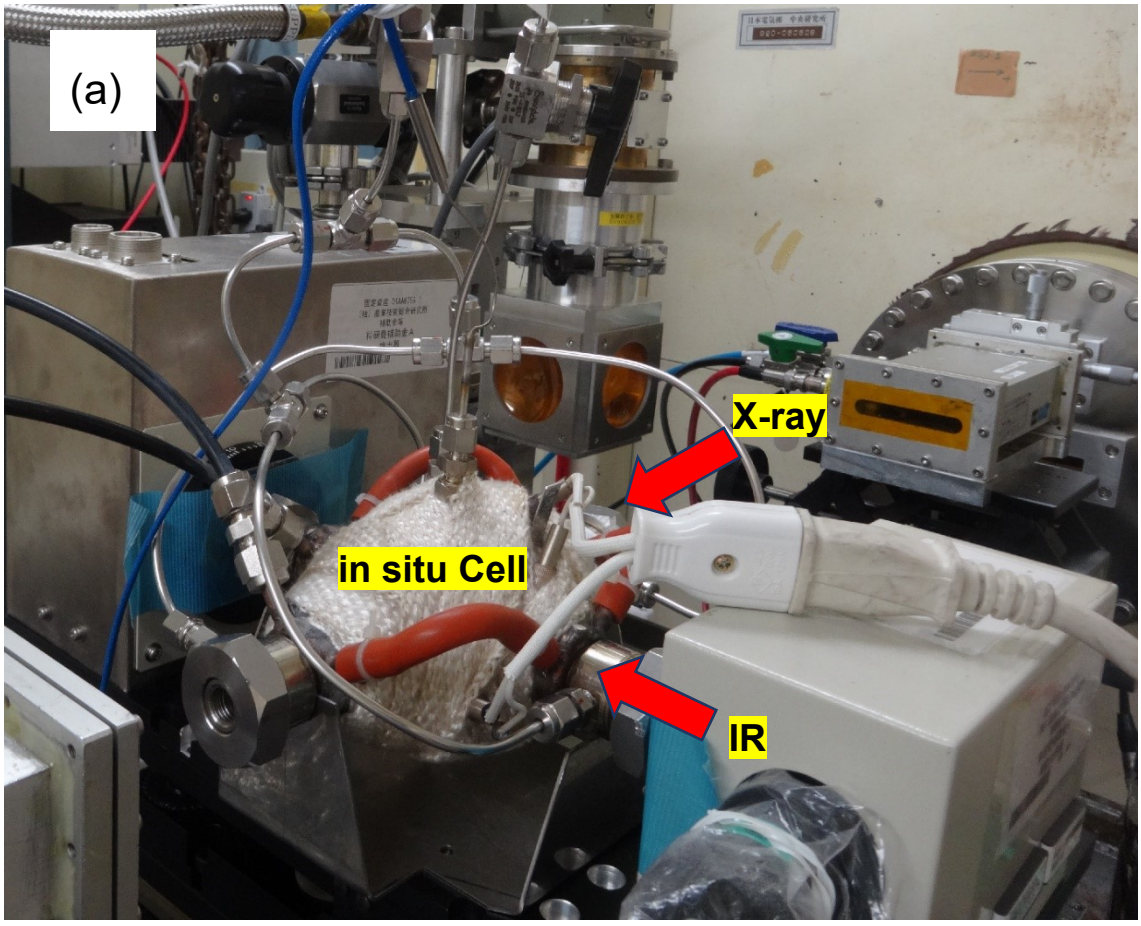
Table S1. Total, internal, and external Al content determined with NH_3 TPD and AA

Sample name	Total Al / mmol g^{-1} [a]	Internal Al / mmol g^{-1} [b]	External Al / mmol g^{-1} [c]
822N	1.11	0.74	0.37
822N-AT6h	1.28	0.65	0.63
822N-AT16h	1.53	0.29	1.24

[a] determined with AA, [b] determined with NH_3 TPD (h-peak), [c] calculated by subtracting the amount of Al in the framework (desorbed amount of NH_3) from the total amount of Al.



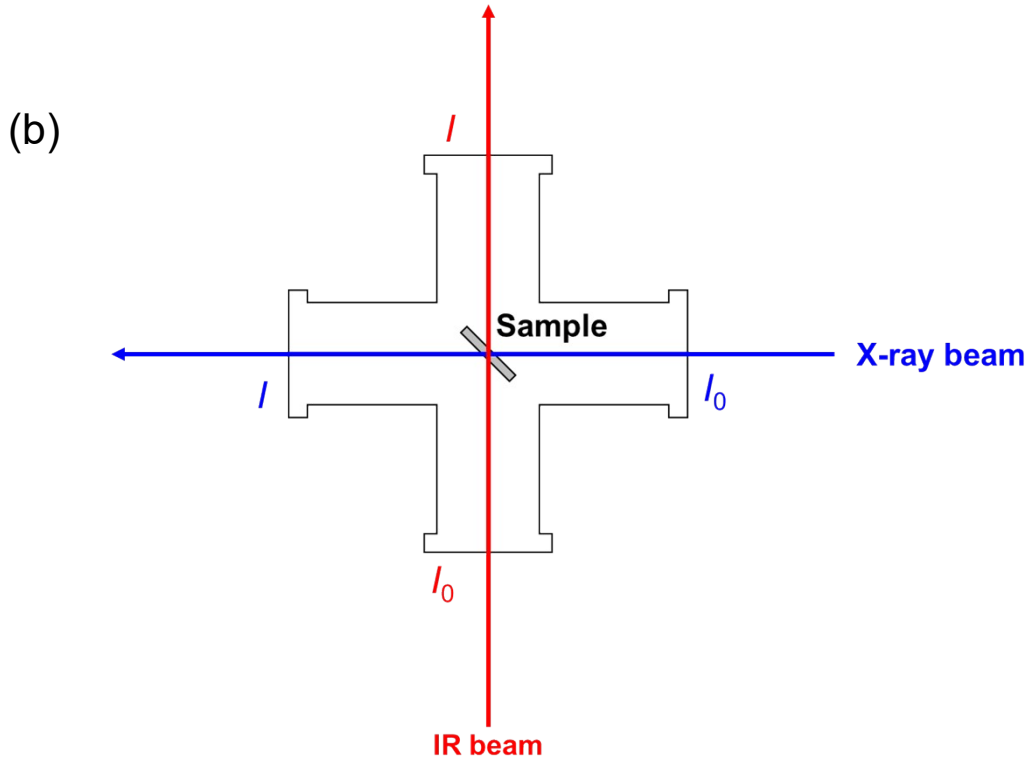


Figure S1. (a) The photograph (b) schematic (top) view of KEK-PF BL-9C setup for operando FT-IR and XAFS measurements.

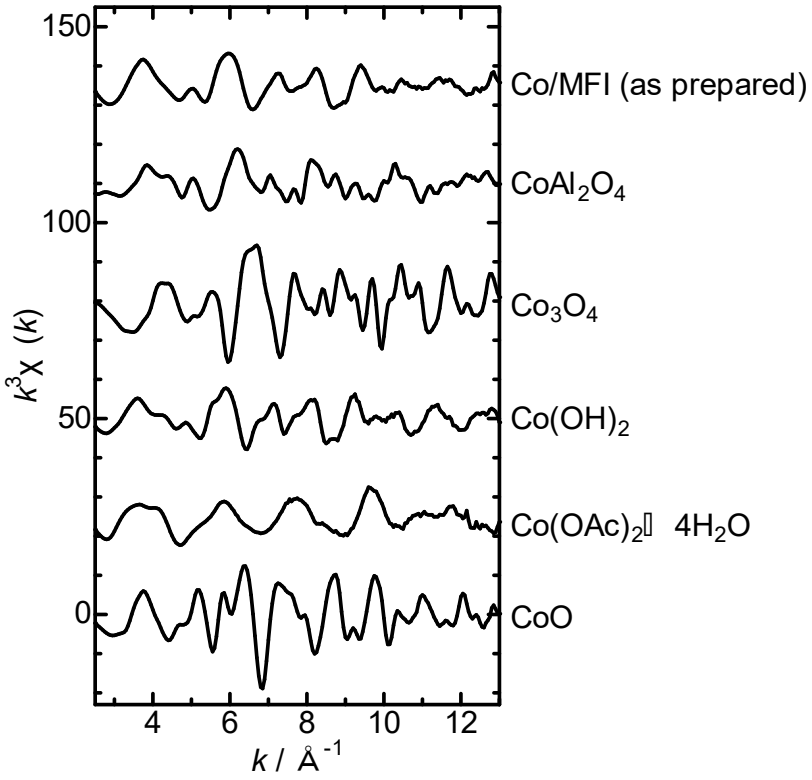


Figure S2. $k^3\chi(k)$ of Co K-edge EXAFS for Co/MFI(52N, as prepared) and reference samples. Co loading of the Co/MFI was 0.5 mmol g^{-1}.

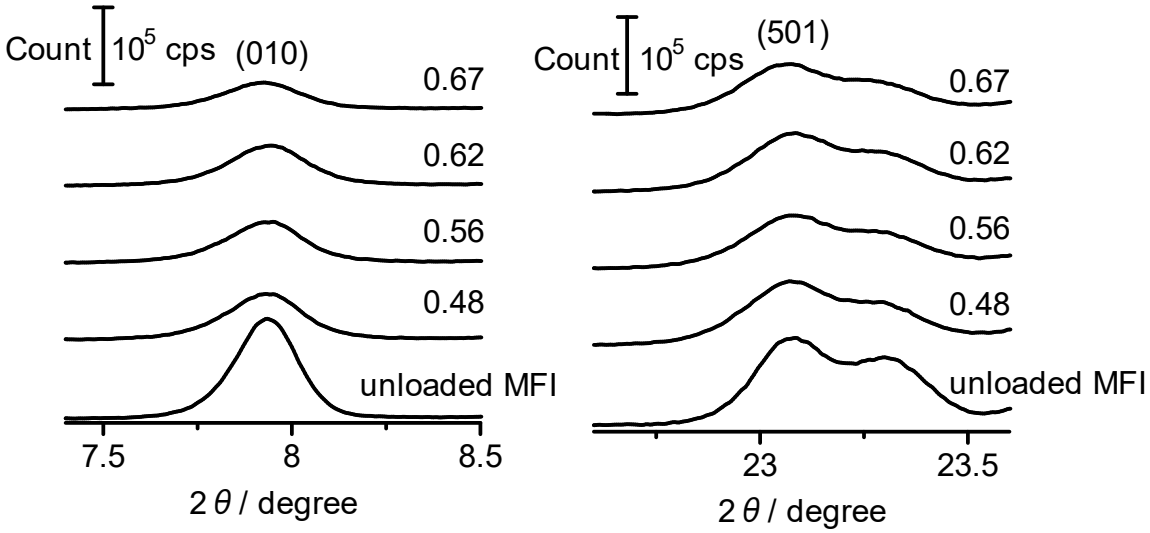


Figure S3. XRD patters of Co-unloaded MFI and Co/MFI corresponding to Figure 6(a). The X-axis was adjusted with the diffraction of MgO as an internal standard.

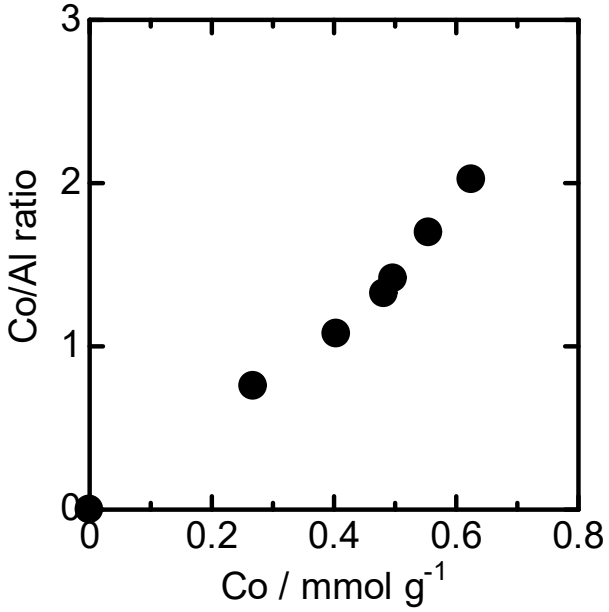


Figure S4. The Co/Al ratio of Co/MFI(52N) plotted as a function of Co loading.

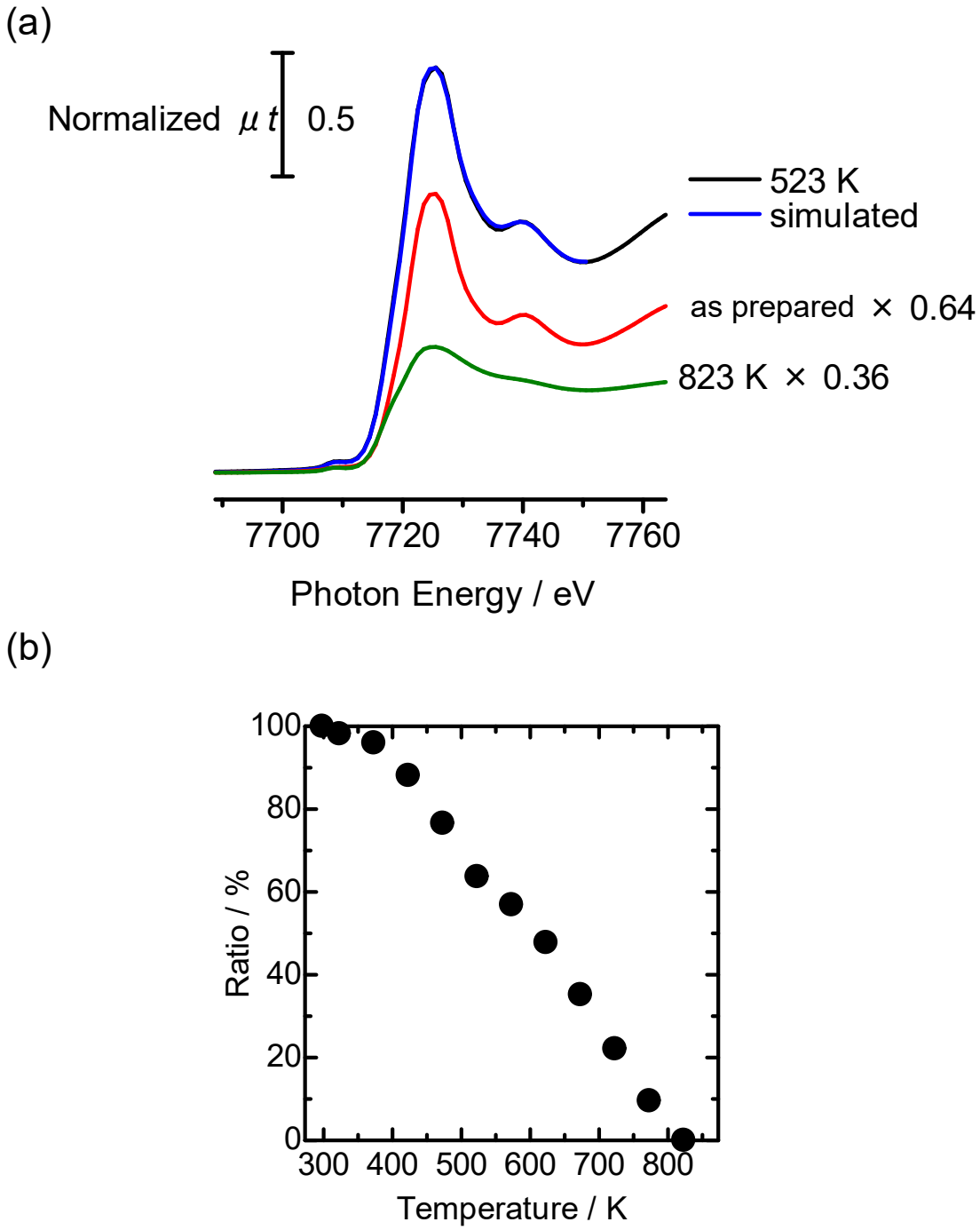


Figure S5. (a) An example of the liner combination fitting of Co K-edge XANES of 523 K-Co/MFI(52N) using those of as prepared and 823 K-samples. (b) Ratio of the as prepared component calculated with a linear combination of Co K-edge XANES of as received and 823 K-treated Co/MFI(52N). Co loading: 0.5 mmol g^{-1}.

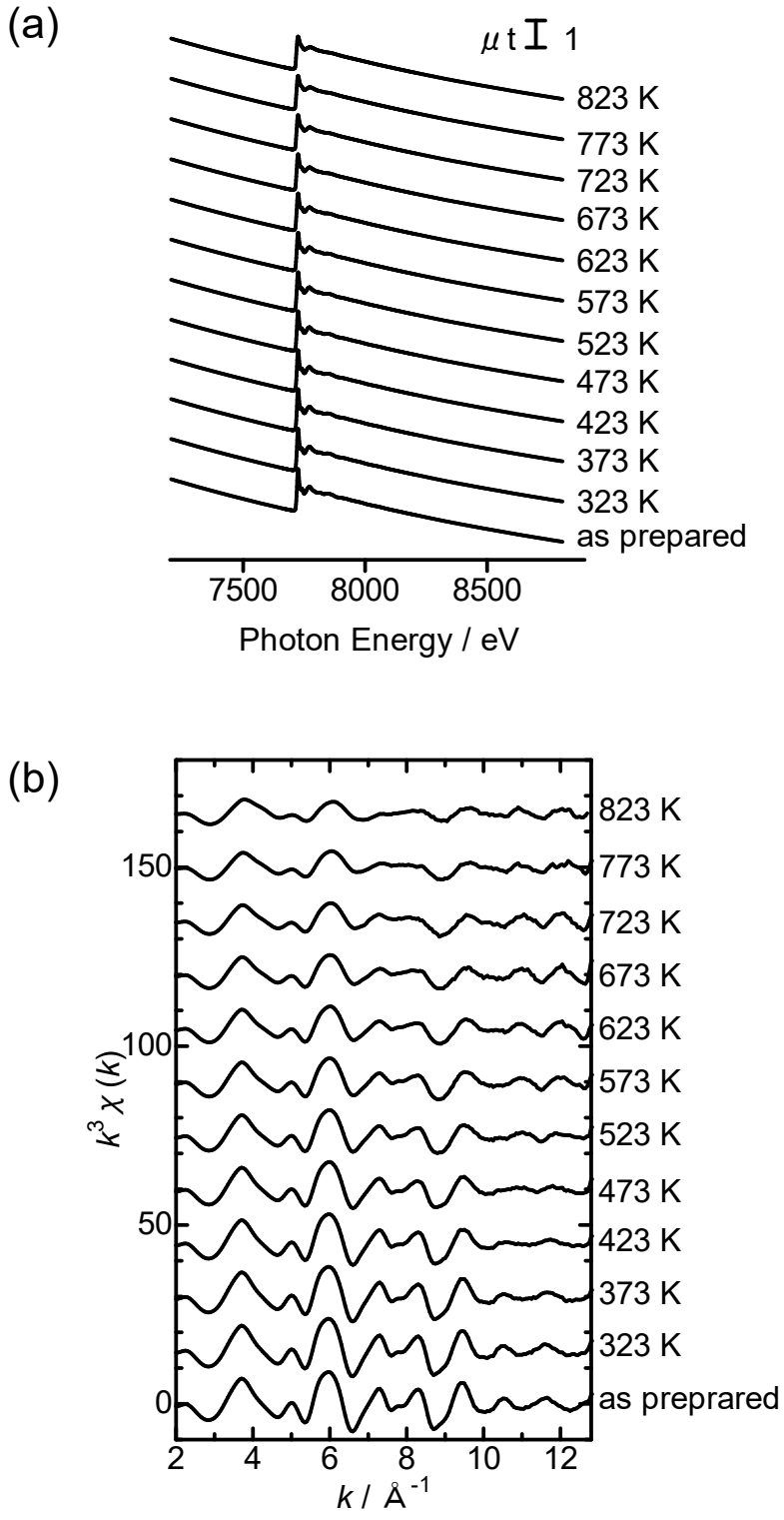


Figure S6. (a) Raw XAFS and (b) $k^3\chi(k)$ of Co K-edge EXAFS for Co/MFI(52N) measured in an N_2 flow under in situ conditions corresponding to the EXAFS-FT of Figure 4(a). Co loading: 0.5 mmol g^{-1}.

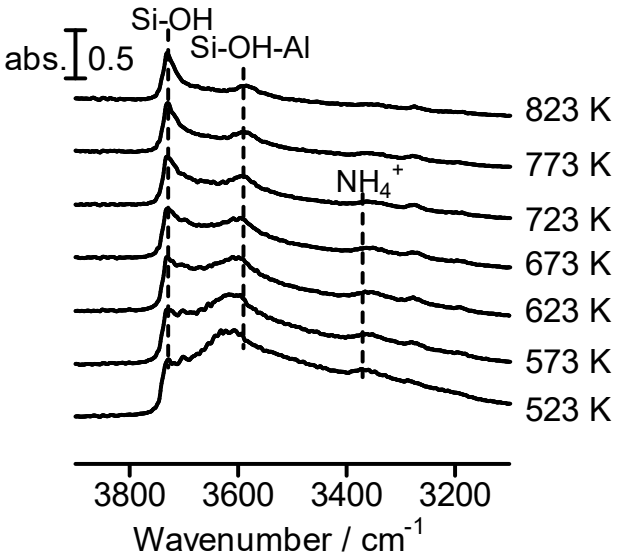


Figure S7. FT-IR spectra of Co/MFI(52N) (Co: 0.5 mmol g^{-1}) measured under N_2 flow from 523 to 823 K under in situ conditions.

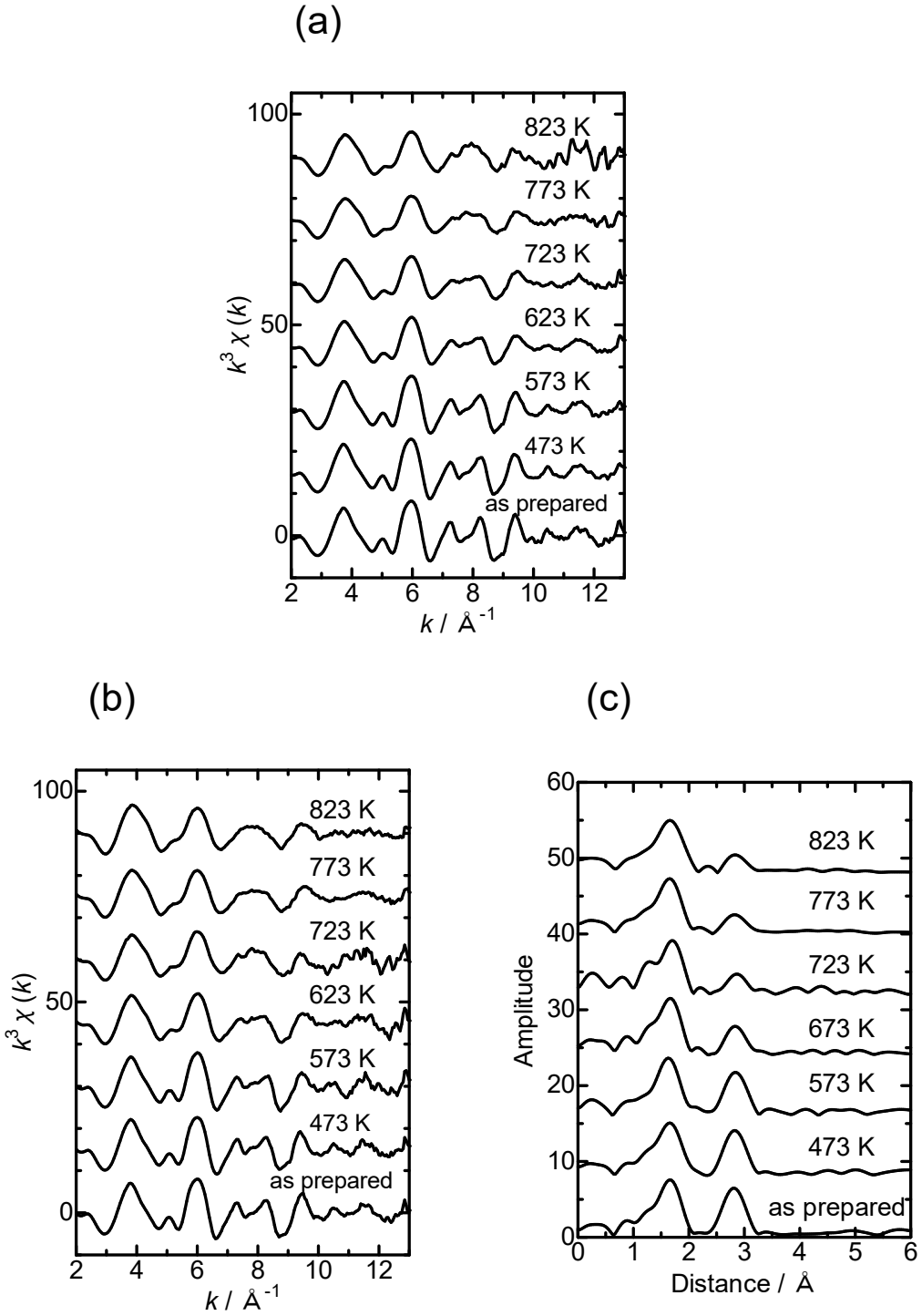


Figure S8. (a) Co K-edge EXAFS Fourier transforms for 0.5 mmol g^{-1}-Co/MFI(52N) corresponding to Figure 4(b) measured after treatment at different temperatures in an N_2 flow. Co K-edge EXAFS (b) $k^3\chi(k)$ and (c) FTs for 0.3 mmol g^{-1}-Co/MFI(52N) measured at 298 K after thermal treatment in an N_2 flow.

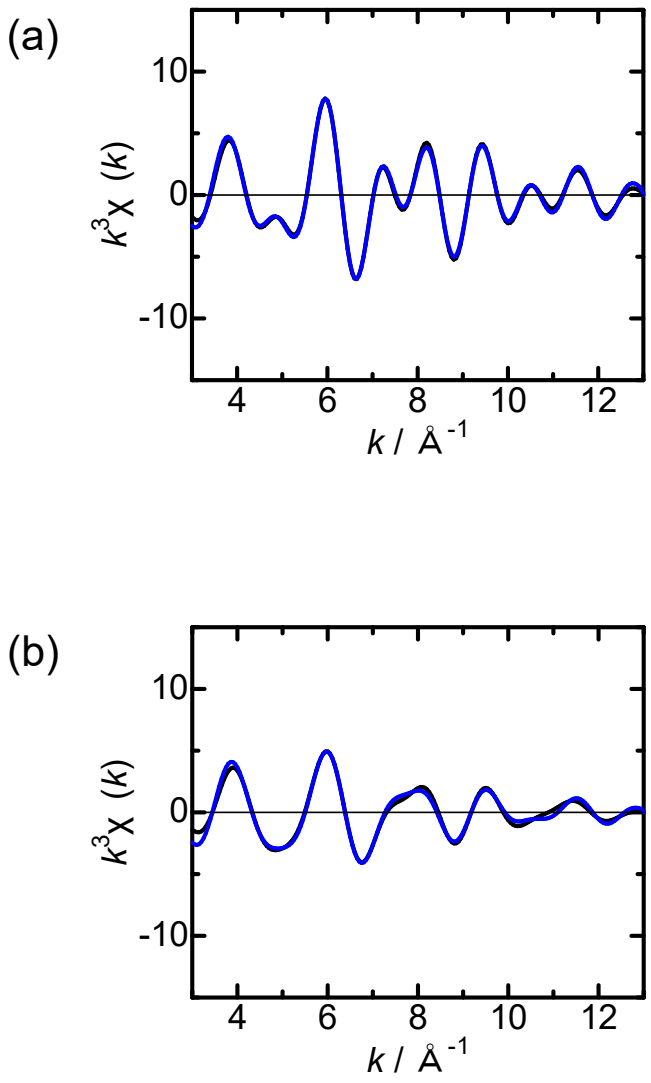


Figure S9. $k^3\chi(k)$ (black lines) and simulated (blue lines) Co K-edge EXAFS oscillations of (a) as prepared Co/MFI(52N) and (b) Co/MFI(52N) treated at 773 K. Co loading: 0.5 mmol g^{-1}.

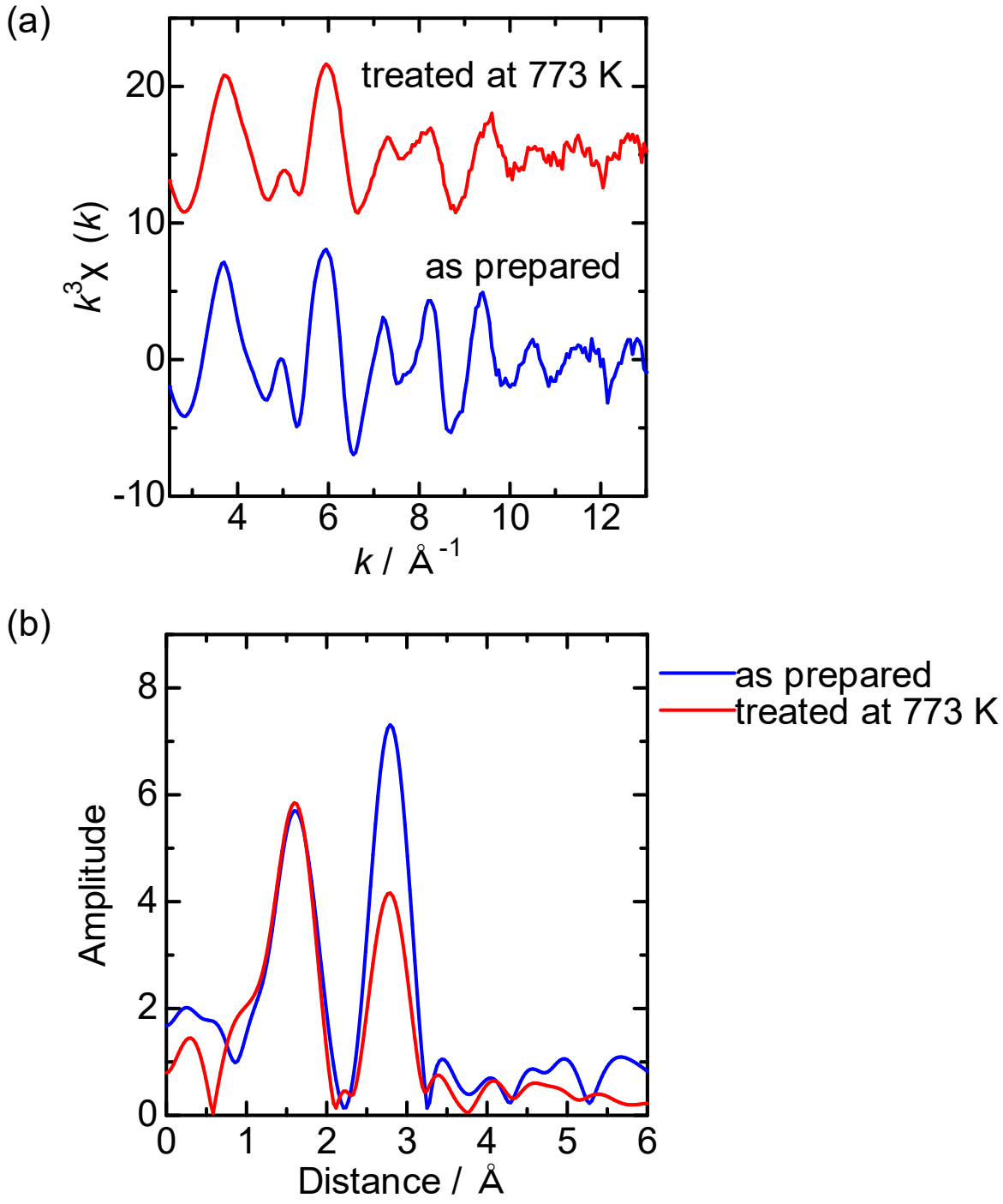


Figure S10. Co K-edge EXAFS (a) $k^3\chi(k)$, and (b) EXAFS-FTs of as prepared and 773 K-treated Co/SiO_2. Co loading: 0.5 mmol g^{-1}.

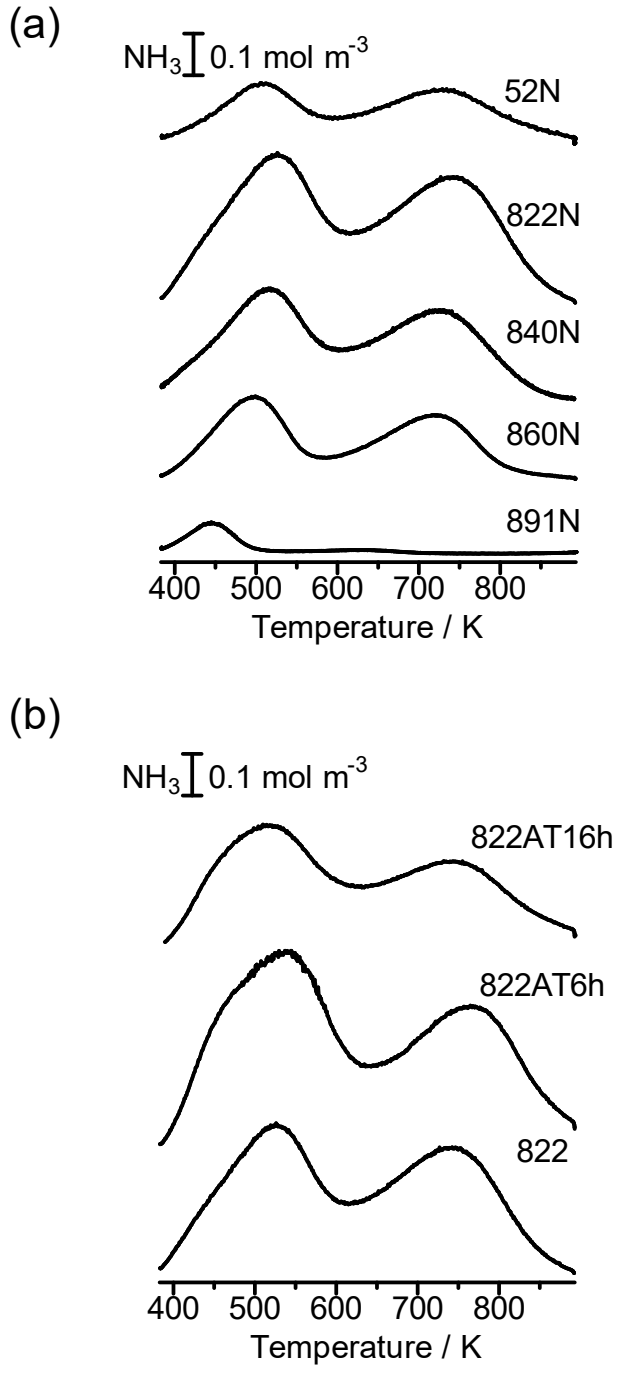


Figure S11. NH_3 TPD profiles of (a) MFI zeolites employed as the support for Co, and (b) MFI(822N) and those treated with an aqueous solution of NaOH for 6 and 16 h.

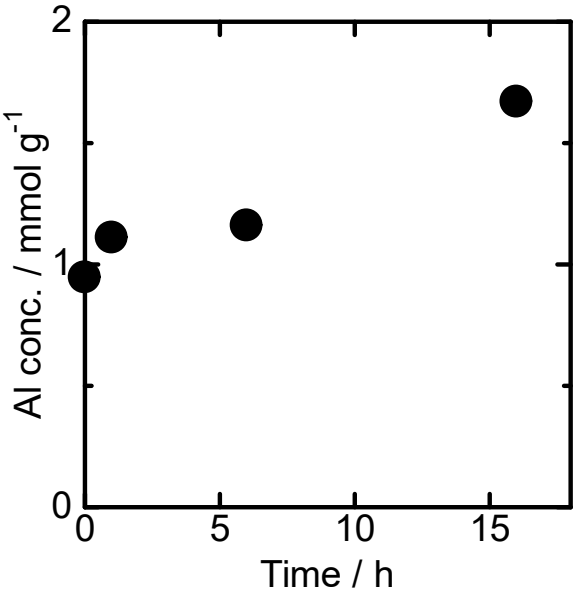


Figure S12. Dependence of the Al concentration on the treatment time with a 0.7 mol L^{-1} NaOH solution. Temperature: 313 K. MFI(822N) was used for the treatment.

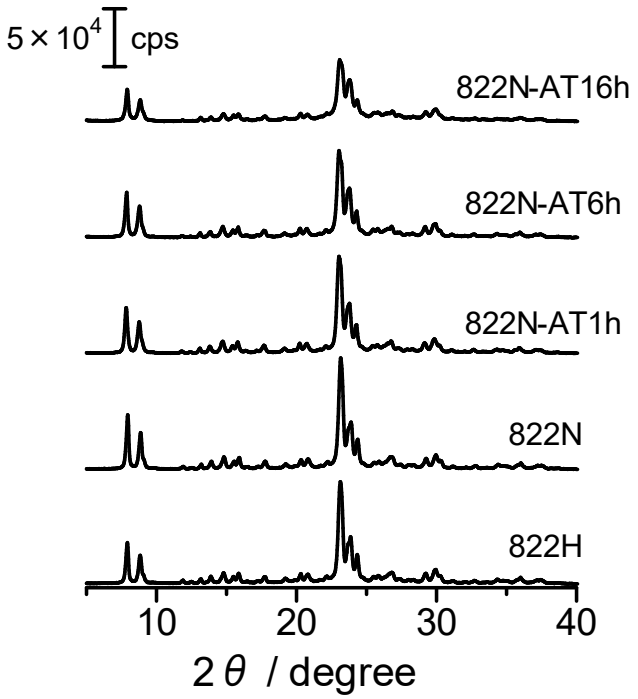


Figure S13. XRD patterns of untreated MFI (822H, 822N) and treated MFI(822N) with a 0.7 mol L^{-1} aqueous NaOH solution for 1, 6, and 16 h.

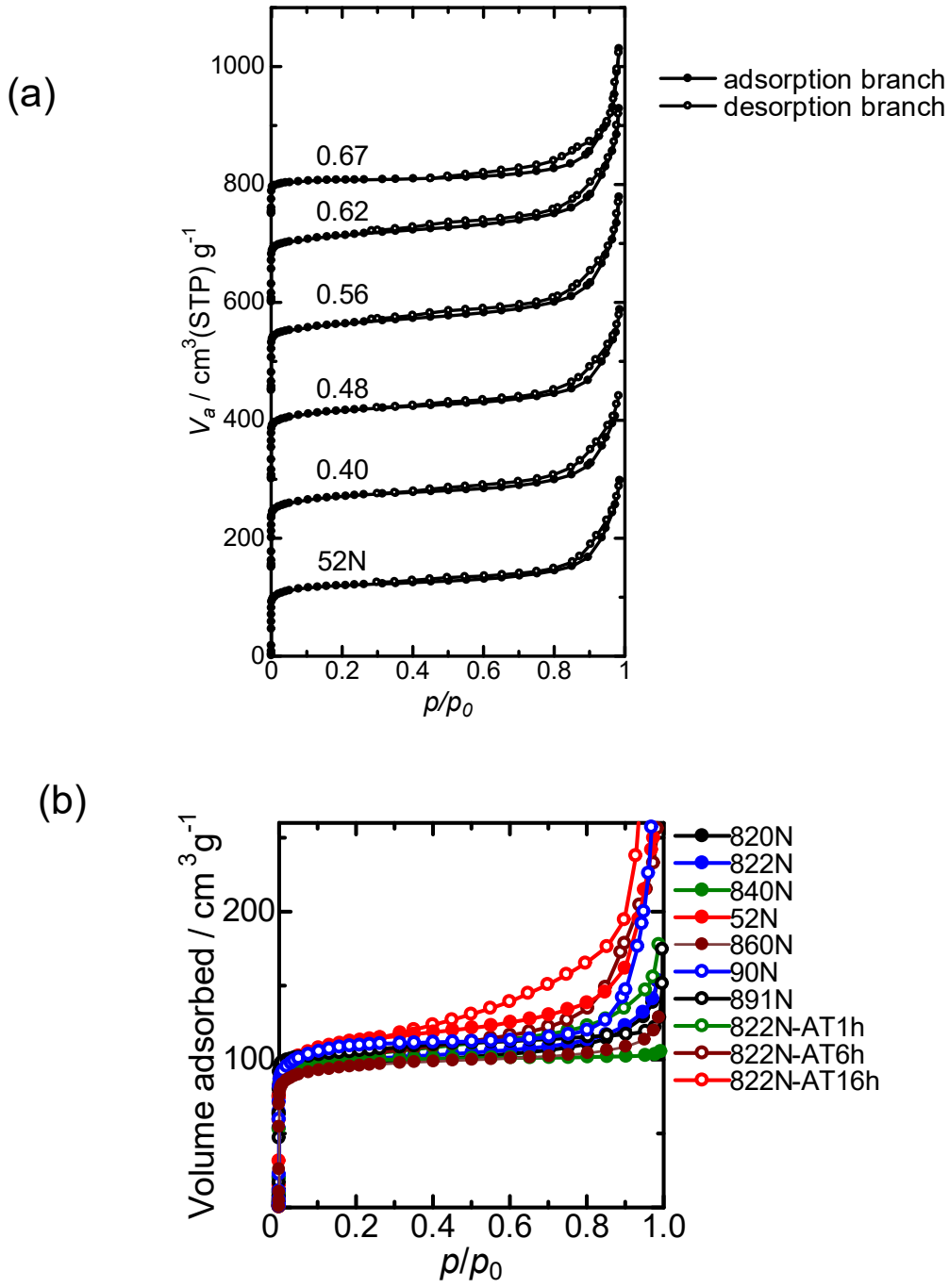


Figure S14. (a) N_2 adsorption isotherms of unloaded MFI(52N) and the Co/MFI(52N) with different Co loadings. The numbers indicate the Co loadings (mmol g^{-1}). (b) N_2 adsorption isotherms of employed MFI zeolites.

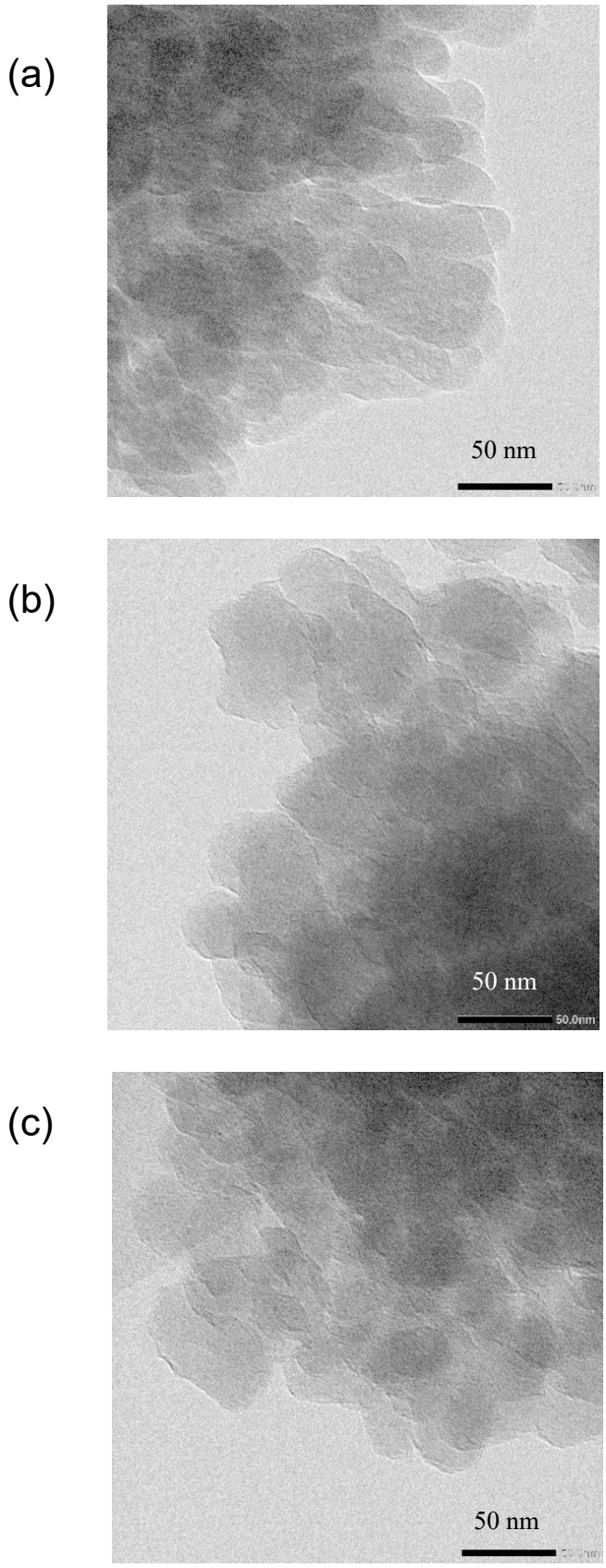


Figure S15. TEM images of (a) Co-unloaded MFI(52N), (b) as prepared Co/MFI(52N), and (c) Co/MFI(52N) treated at 773 K. The Co loading of Co/MFI was 0.5 mmol g^{-1}.