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Supporting Information for

Controlled Electropositive Catalytic Sites on Zeolites for Achieving High CH_3Cl Selectivity via Electrophilic CH_4 Chlorination using Cl_2

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Table S1. Standard Gibbs energies (ΔG_f°) of possible chlorination reactions depending on the Cl source

Reactant	Reaction	ΔG_f° (kJ mol^{-1})	Reference
Cl_2	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	–115.7	[1]
	$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$	–105	
	$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$	–87.8	
	$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	–62.5	
HCl	$CH_4 + HCl \rightarrow CH_3Cl + H_2$	83.5	
	$CH_3Cl + HCl \rightarrow CH_2Cl_2 + H_2$	94.2	
	$CH_2Cl_2 + HCl \rightarrow CHCl_3 + H_2$	111.4	
	$CHCl_3 + HCl \rightarrow CCl_4 + H_2$	136.7	

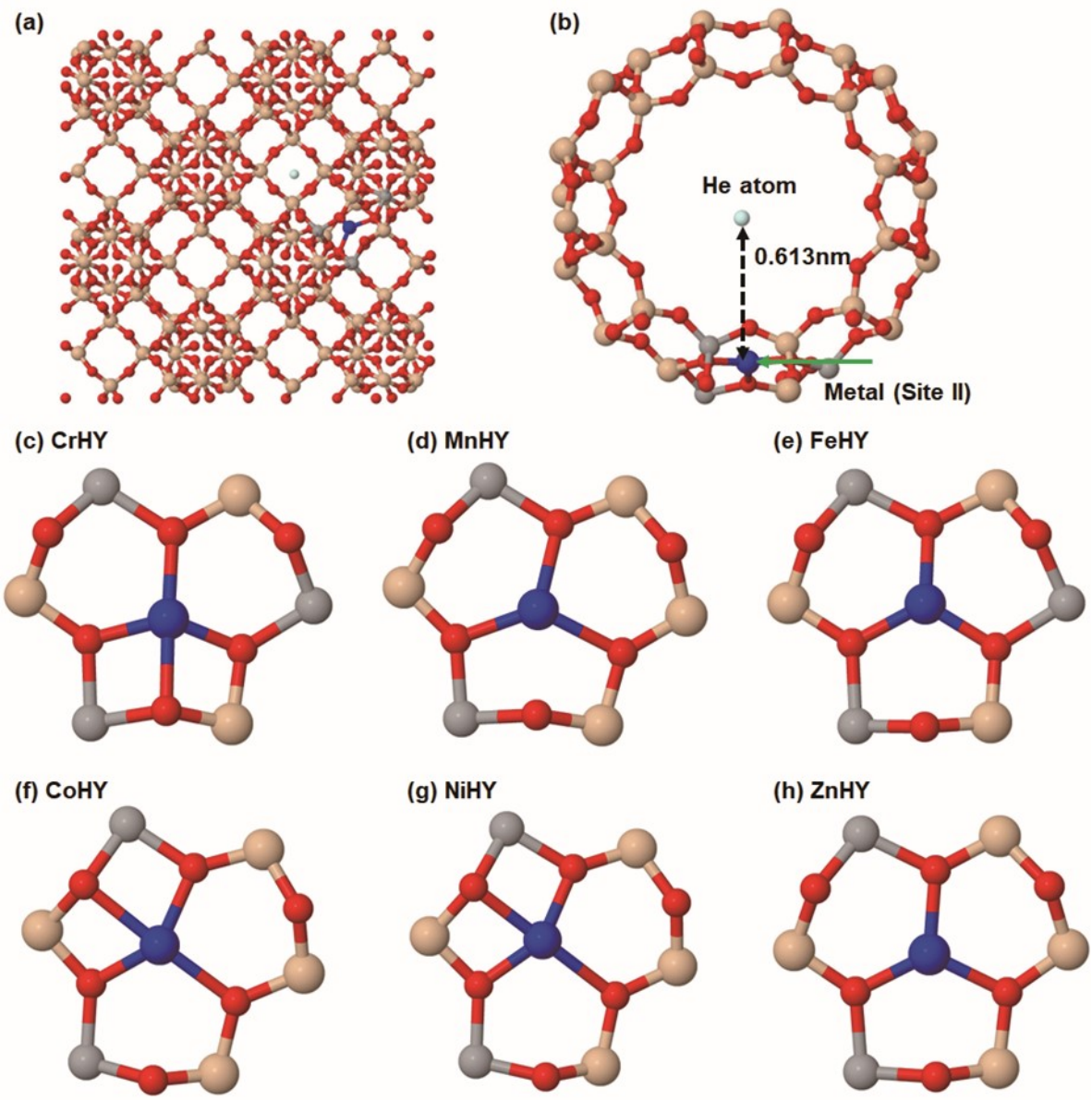

Fig. S1. Y zeolite models for p-DOS calculations. (a) Unit cell of the Y zeolite structure (b) He atom located in the middle of the Y zeolite pore to avoid additional interactions (c–h) Y zeolite pore interacting with metal cations bound to Site II (He, white; O, red; Si, ivory; Al, gray; transition metal atoms, blue).

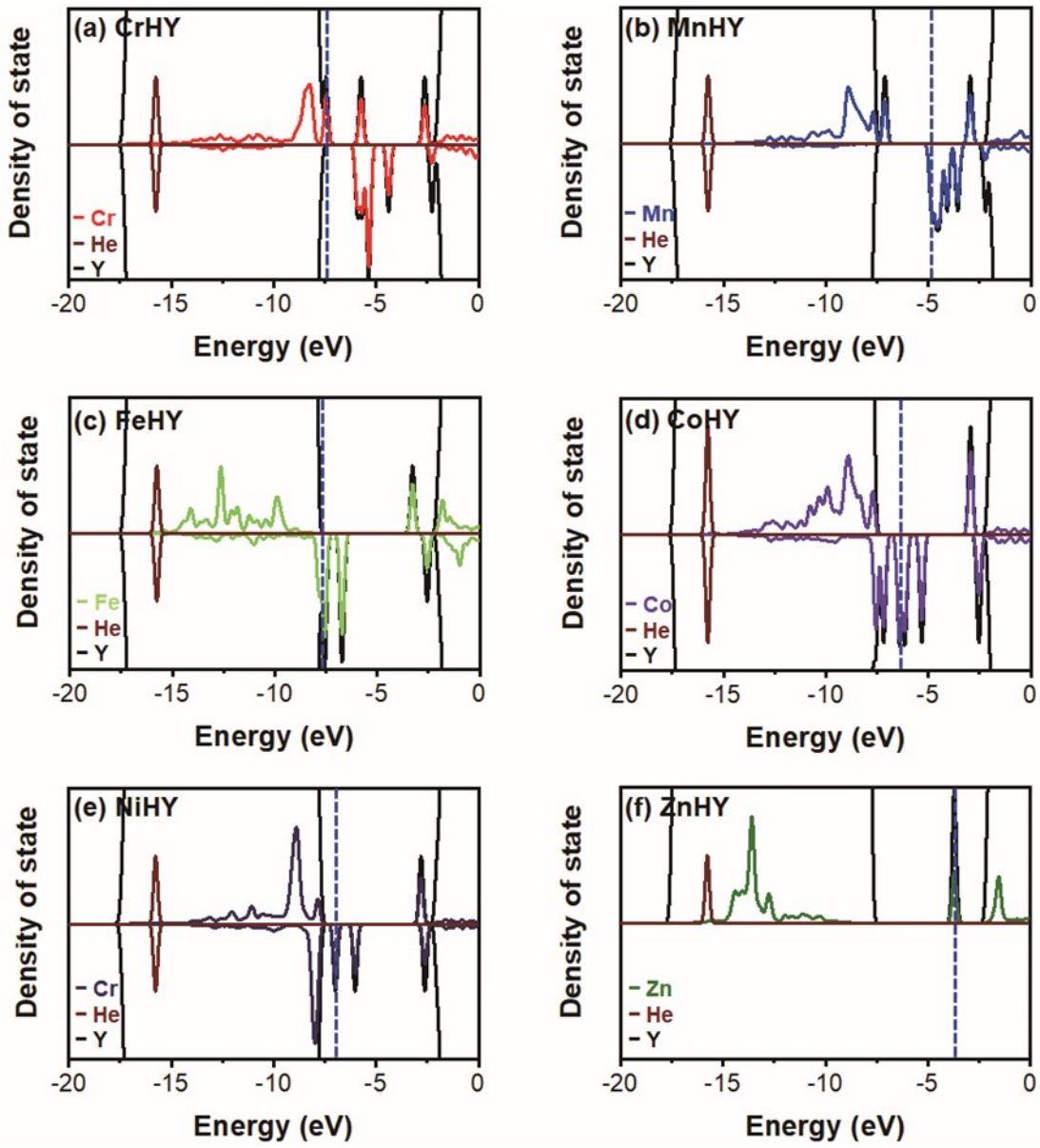

Fig. S2. Calculated atom-projected partial density of states for (a) CrHY, (b) MnHY, (c) FeHY, (d) CoHY, (e) NiHY, and (f) ZnHY. For comparison, the He 1s orbital energy level is set as a reference at −15.77 eV. The blue dashed line indicates the LUMO energy level of each Y zeolite model.

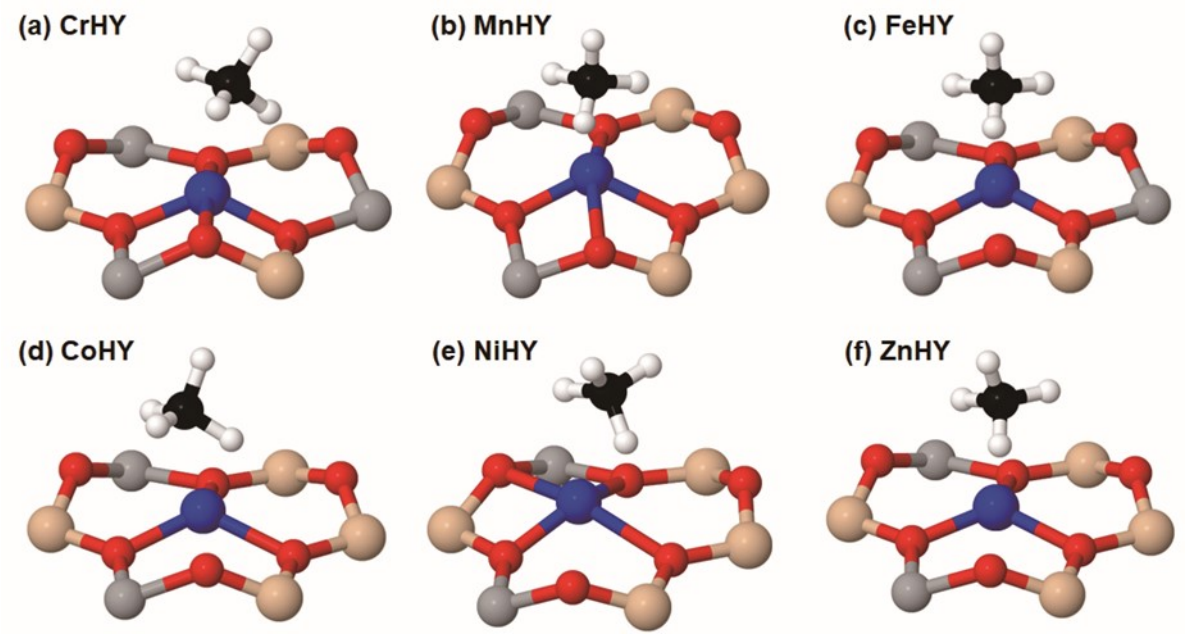

Fig. S3. CH_4 adsorption models in (a) CrHY, (b) MnHY, (c) FeHY, (d) CoHY, (e) NiHY, and (f) ZnHY used to calculate the theoretical CH_4 adsorption energy (H, white; C, black; O, red; Si, ivory; Al, gray; and transition metal atoms, blue).

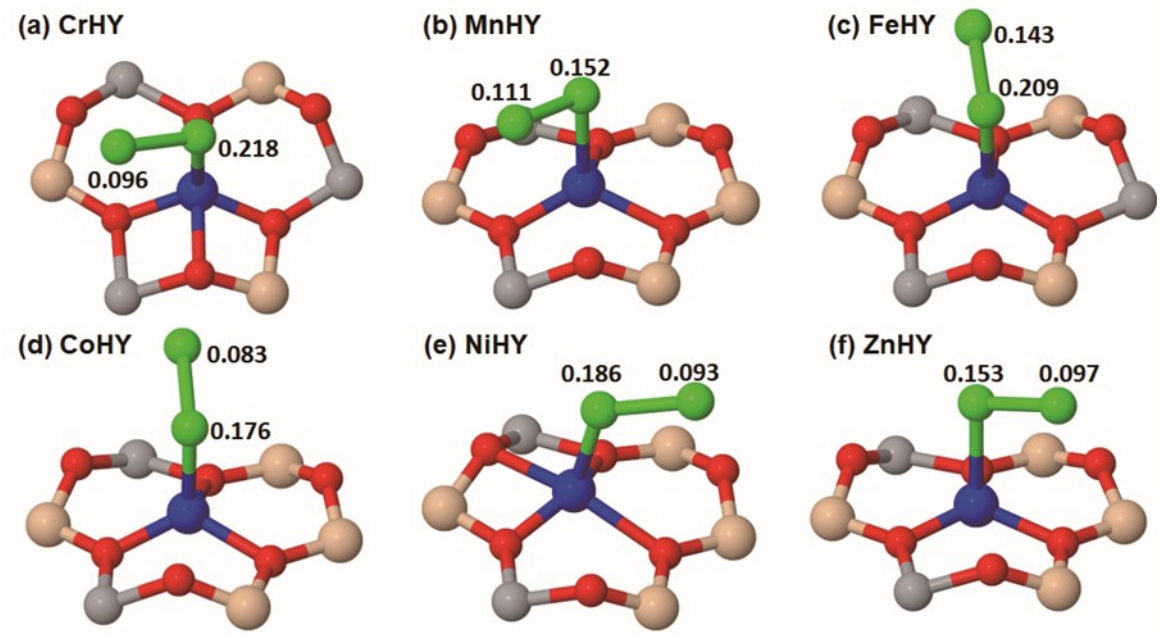

Fig. S4. Cl_2 adsorption models in (a) CrHY, (b) MnHY, (c) FeHY, (d) CoHY, (e) NiHY, and (f) ZnHY used to calculate the theoretical Cl_2 adsorption energy (Cl, green; O, red; Si, ivory; Al, gray; and transition metal atoms, blue). The numbers in the vicinity of Cl atoms indicate the charge values affected by Cl_2 polarization on electropositive transition metal cations.

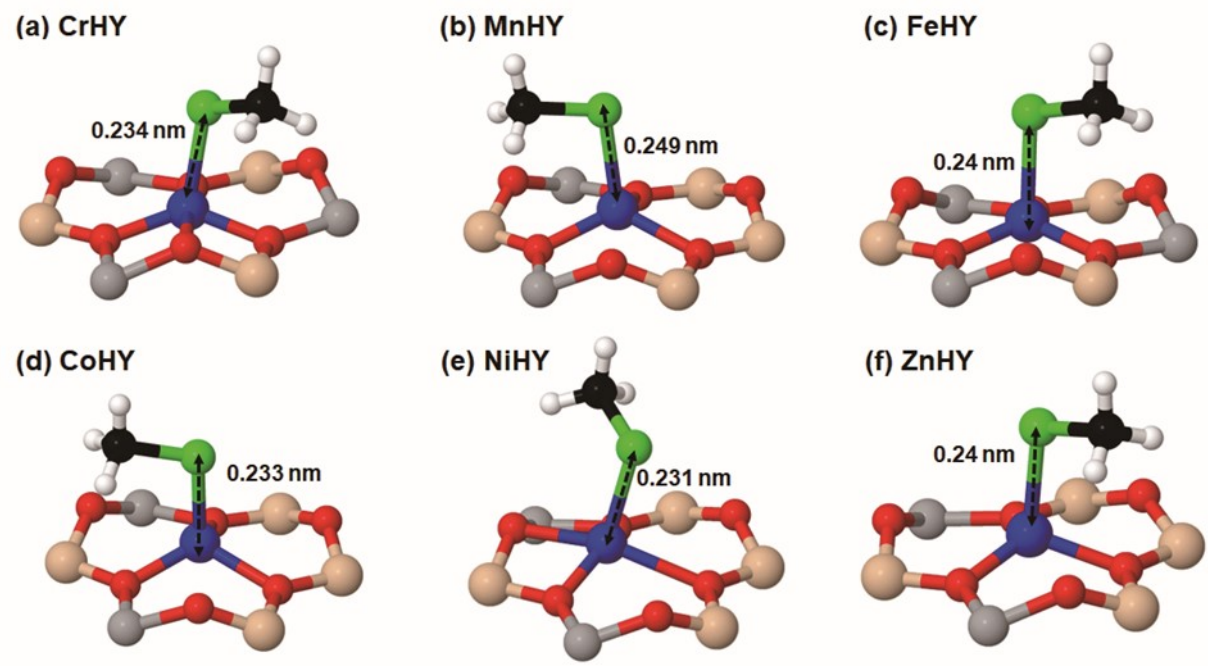

Fig. S5. CH_3Cl adsorption models in (a) CrHY, (b) MnHY, (c) FeHY, (d) CoHY, (e) NiHY, and (f) ZnHY used to calculate the theoretical CH_3Cl adsorption energy (H, white; C, black; Cl, green; O, red; Si, ivory; Al, gray; and transition metal atoms, blue).

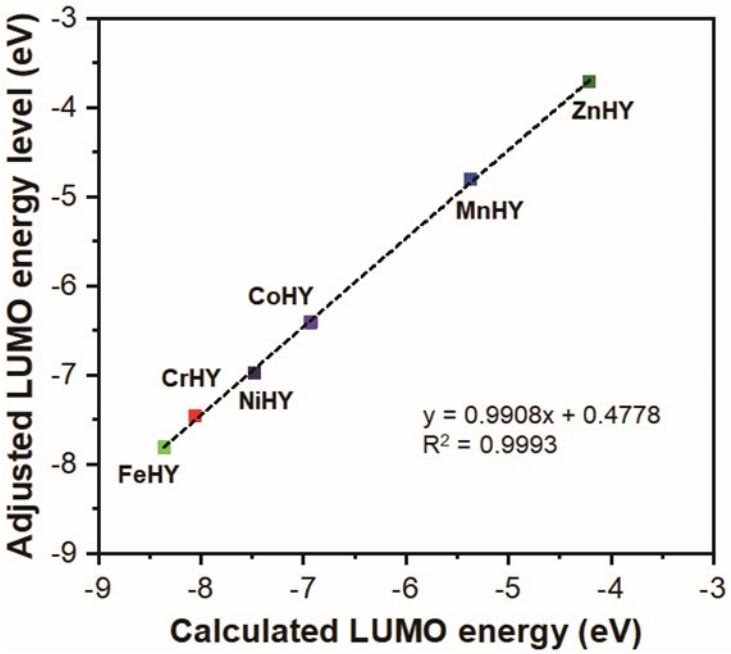

Fig. S6. Correlation between calculated LUMO and adjusted LUMO energy levels using an He atom

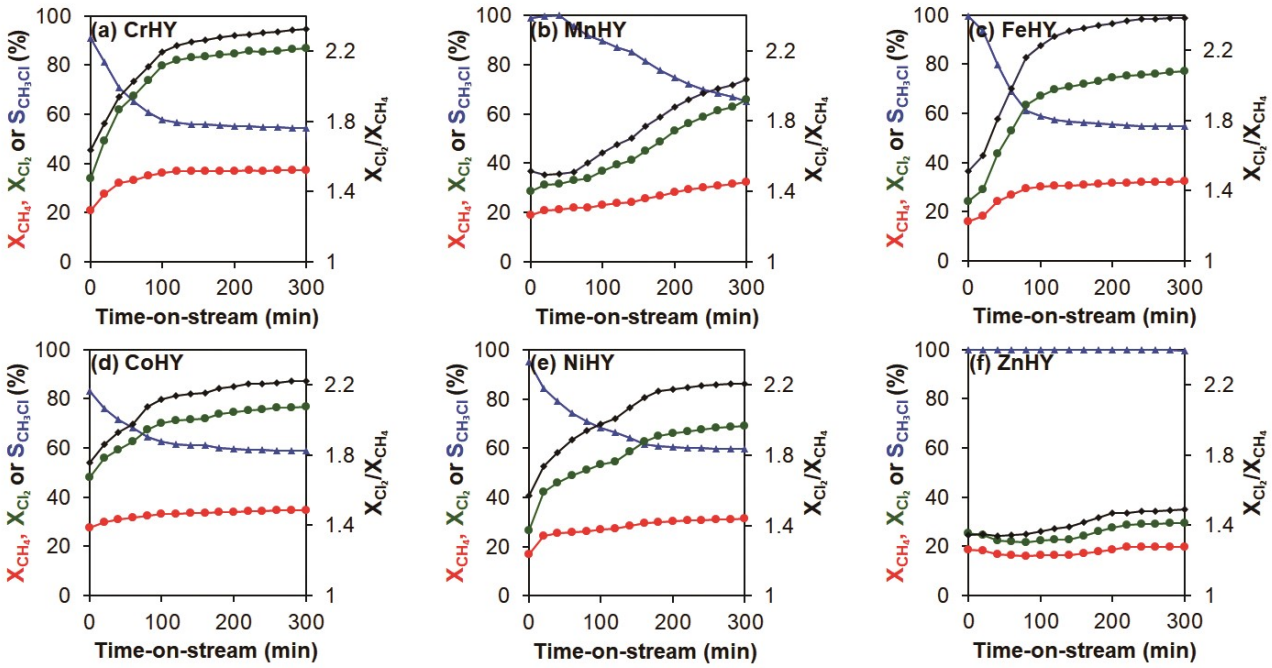

Fig. S7. Reaction profiles showing CH_4 conversion (X_{CH_4}, red circles), Cl_2 conversion (X_{Cl_2}, green circles), CH_3Cl selectivity (S_{CH_3Cl}, blue triangles), and conversion ratio of Cl_2/CH_4 (X_{Cl_2}/X_{CH_4}, black rhombus) as a function of time-on-stream (min).

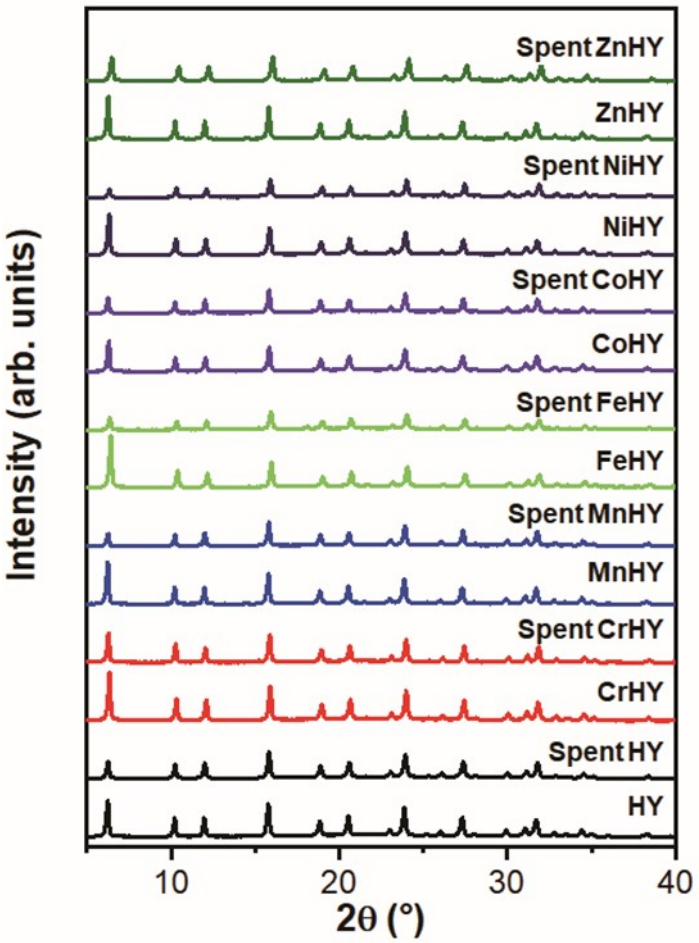

Fig. S8. XRD diffraction patterns of HY zeolites partially exchanged with Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, and Cr^{3+} ions before and after the reaction, in comparison with those of pristine HY.

References

[1] D. W. Oxtoby, H. P. Gillis, A. Campion, Principle of Modern Chemistry, 7th ed., Cengage learning, 2014.