Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Hierarchical Metal-Organic Frameworks constructed from intergrowth for light hydrocarbons adsorption

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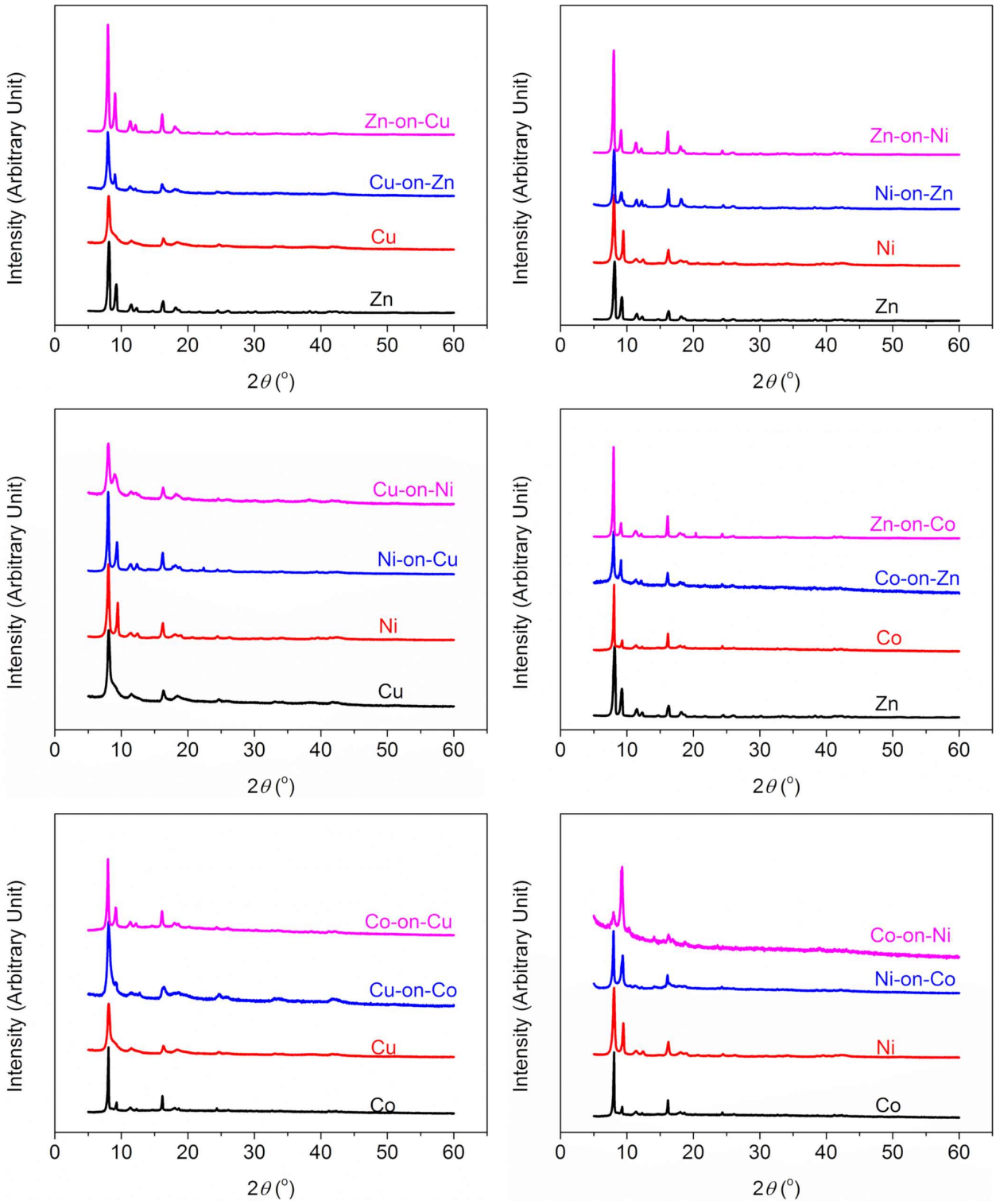
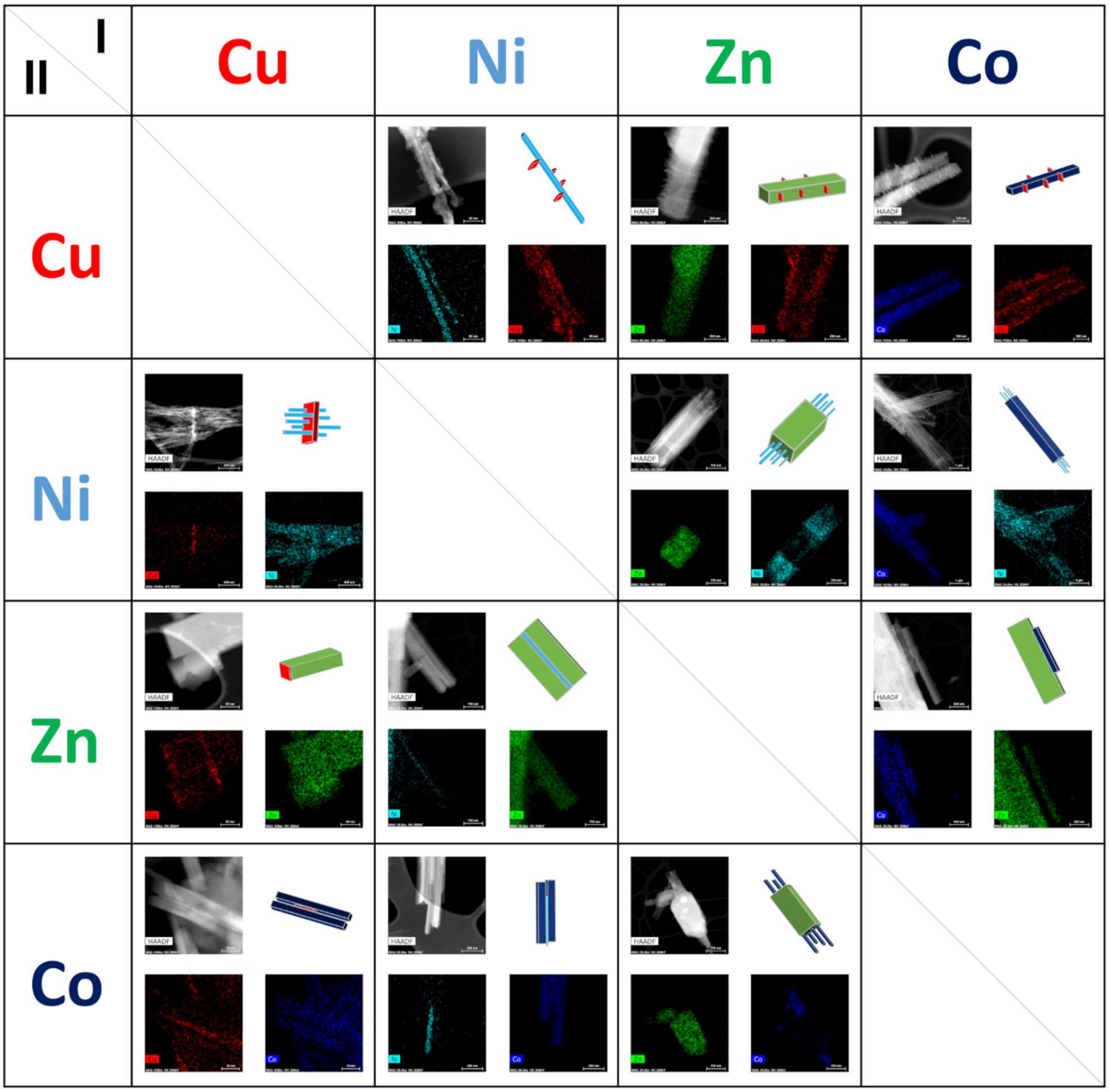


Figure S1. Powder XRD patterns of intergrowth MOFs $M^{II}_2(ndc)_2(dabco)$ on $M^{I}_2(ndc)_2(dabco)$ (M^{II} and M^{I} = Cu, Zn, Ni, Co)



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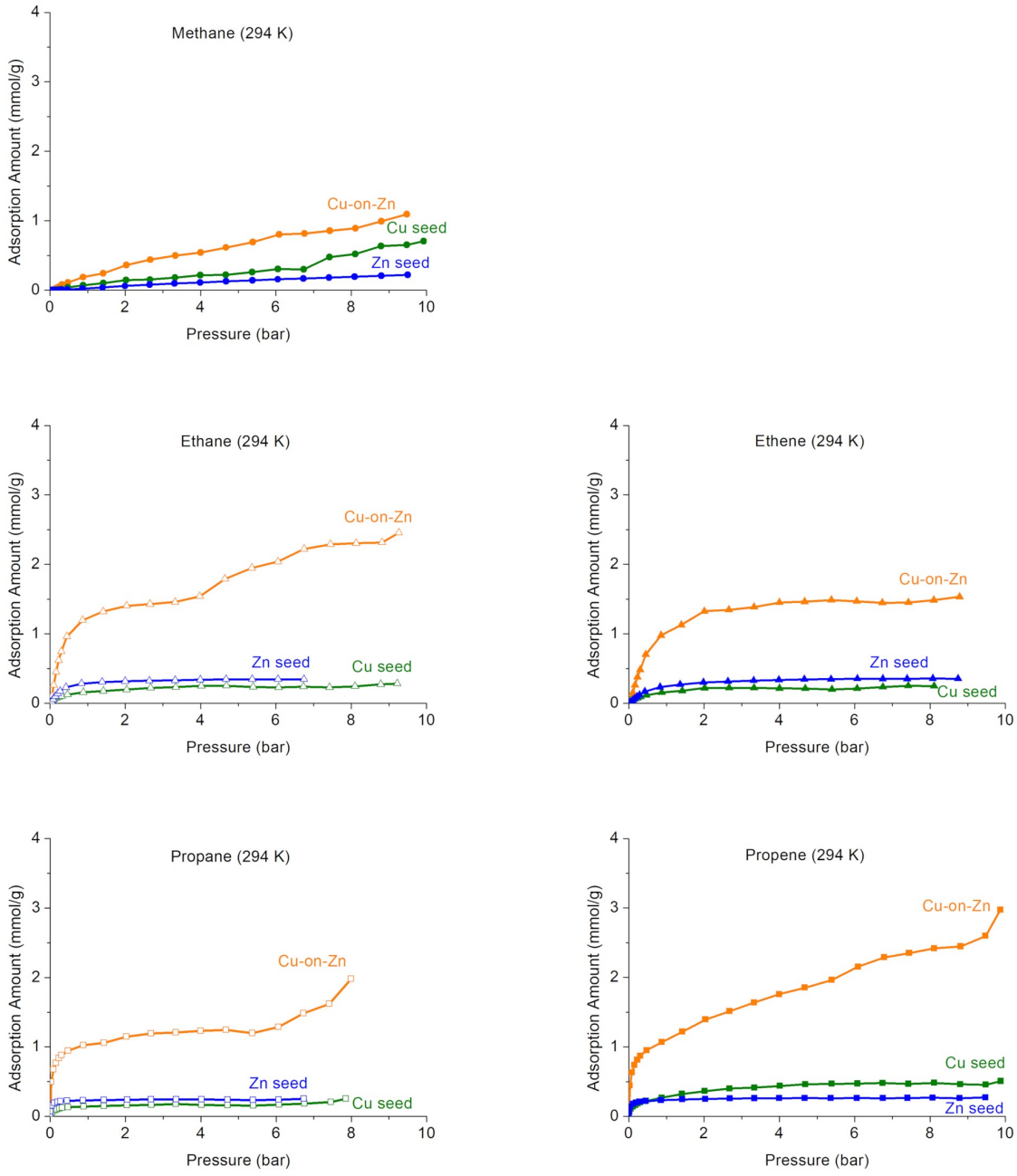


Figure S3. Adsorption isotherms of methane, ethane, ethene, propane, and propene on Cu seed, Zn seed and Cu-on-Zn intergrowth

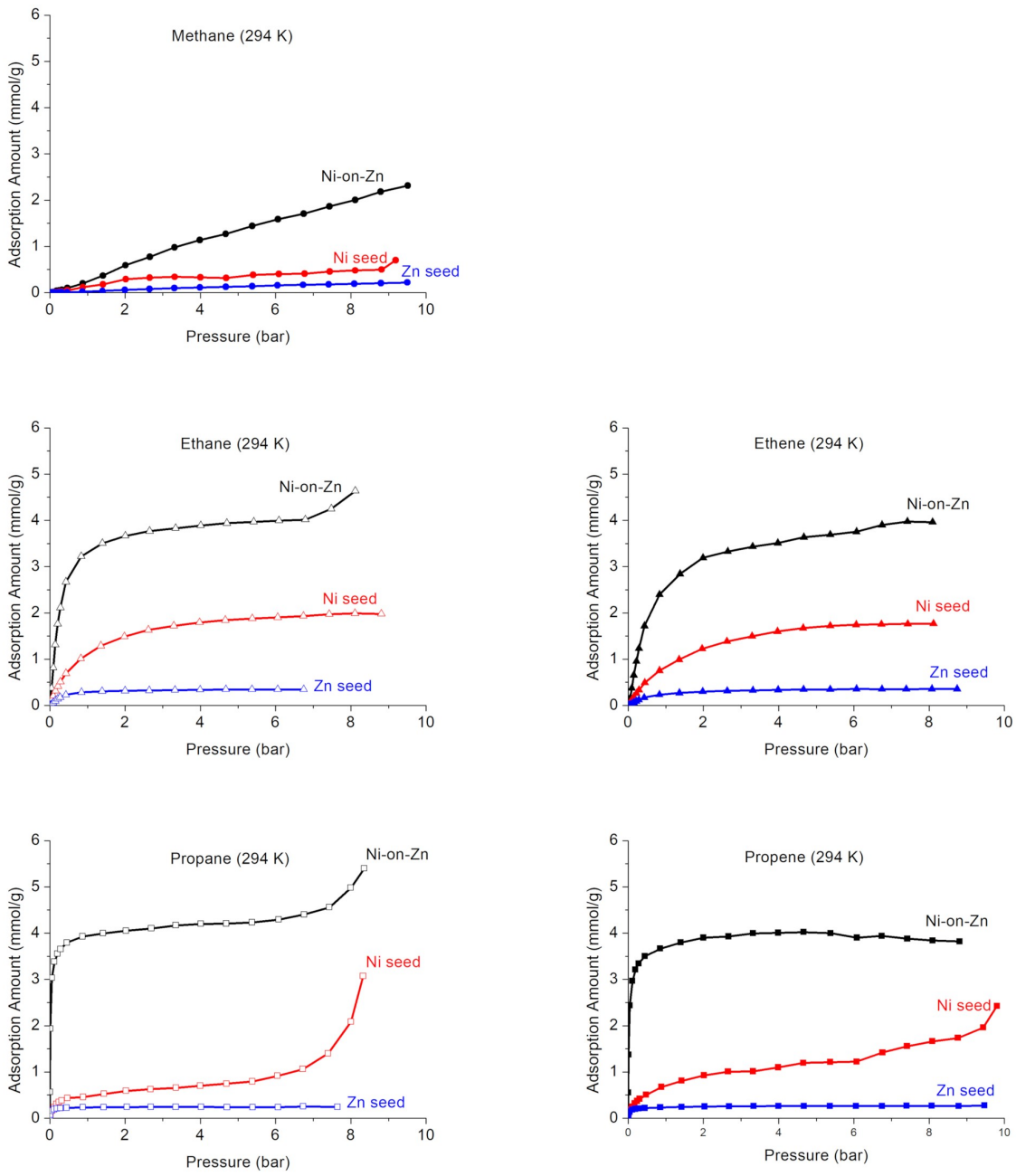


Figure S4. Adsorption isotherm of methane, ethane, ethene, propane, and propene on Ni seed, Zn seed and Ni-on-Zn intergrowth

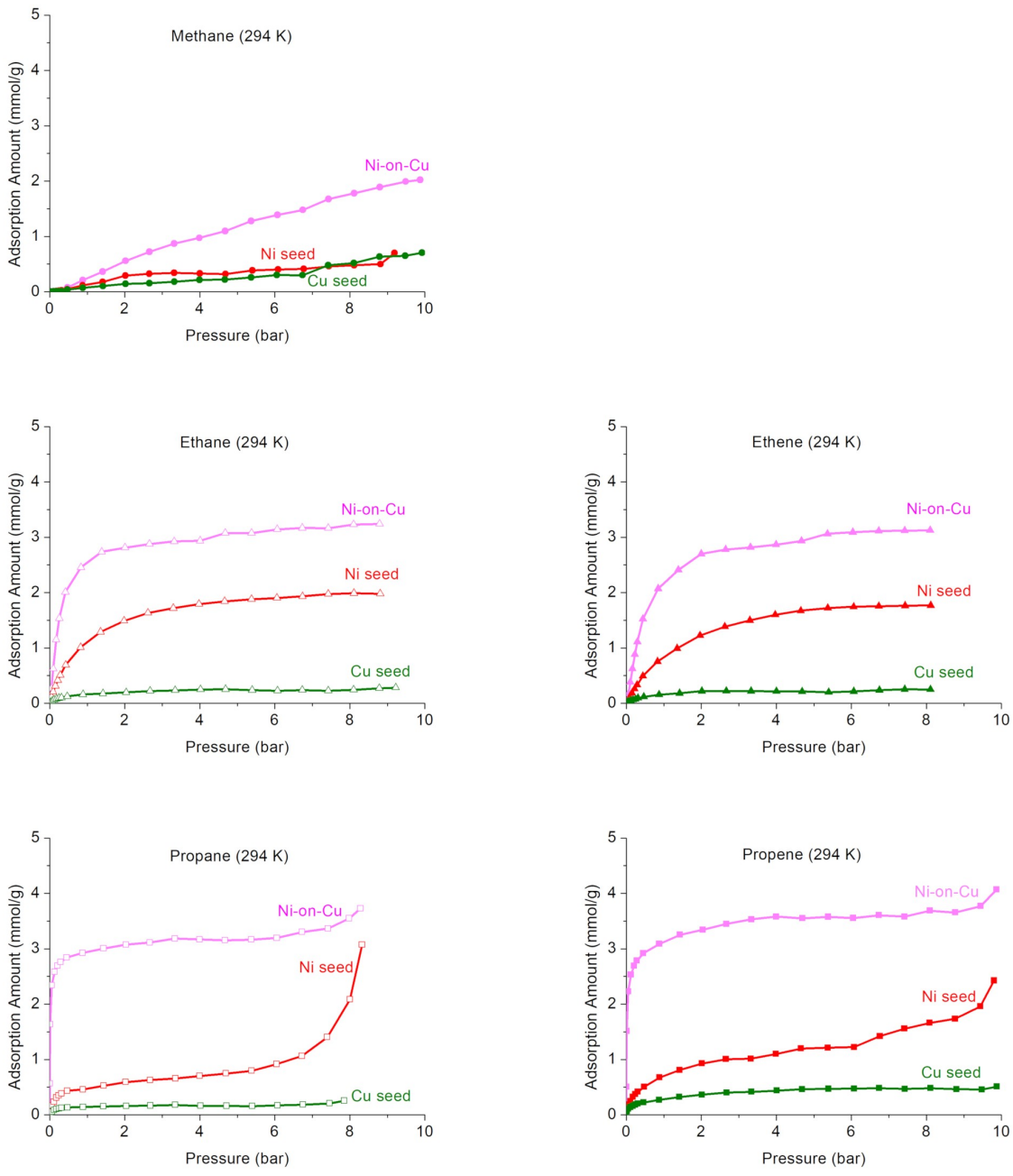
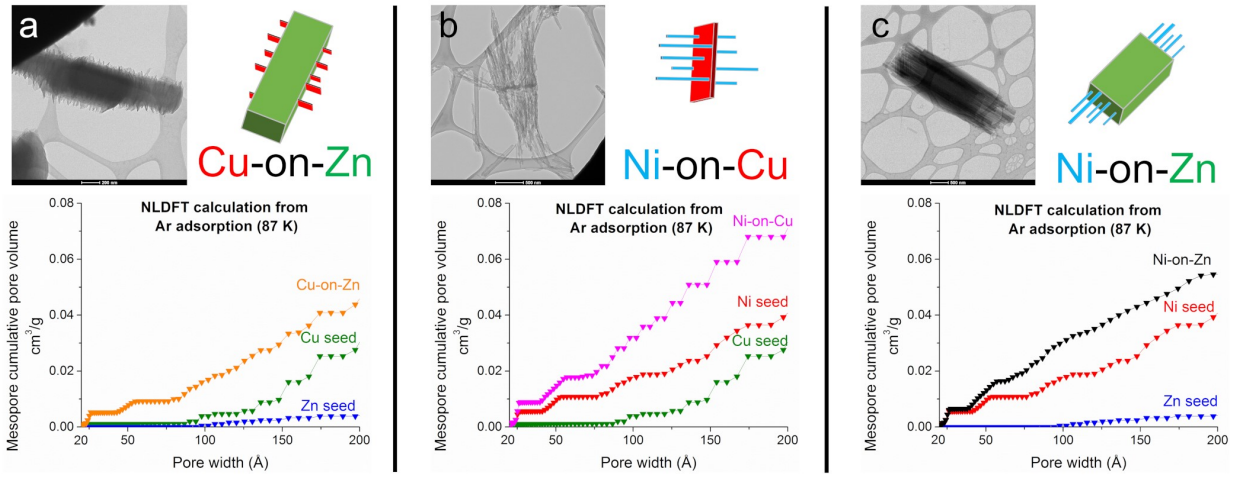


Figure S5. Adsorption isotherm of methane, ethane, ethene, propane, and propene on Ni seed, Cu seed and Ni-on-Cu intergrowth



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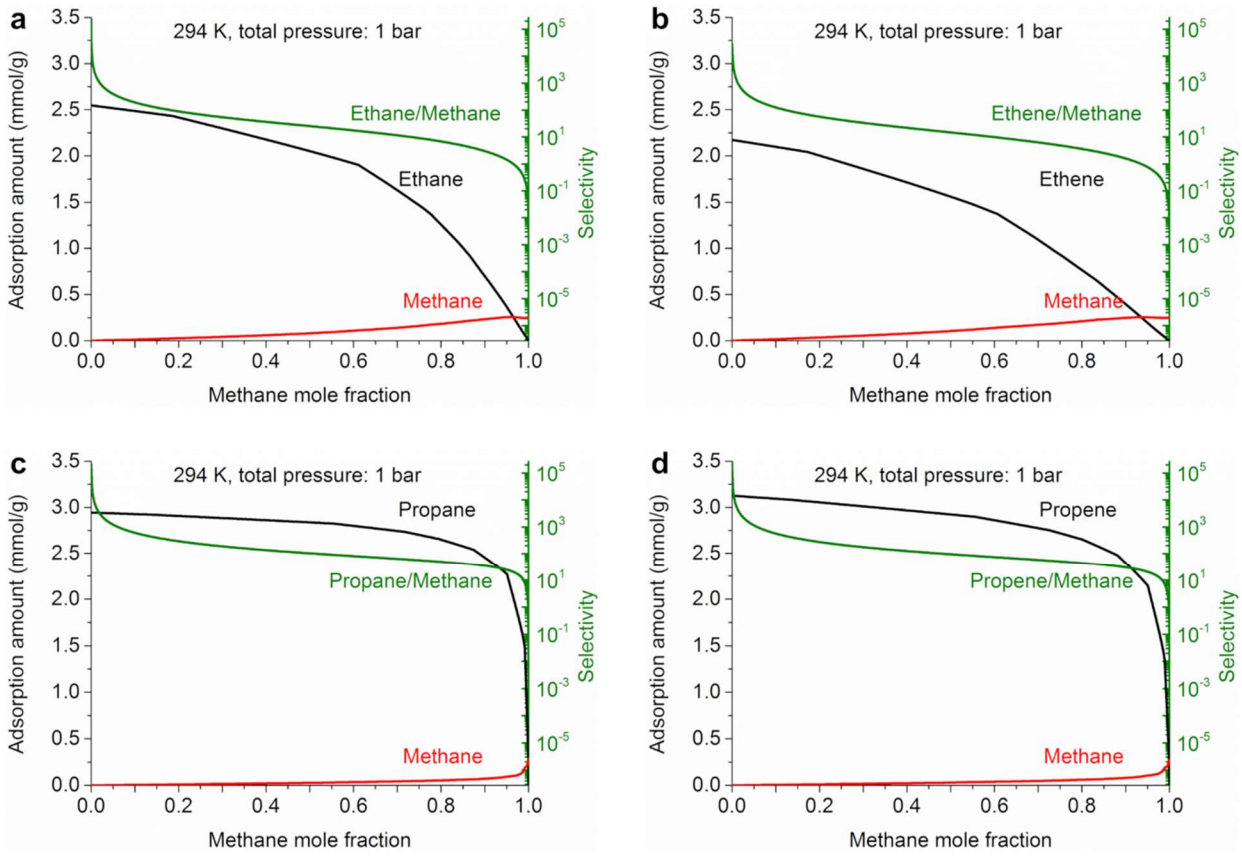

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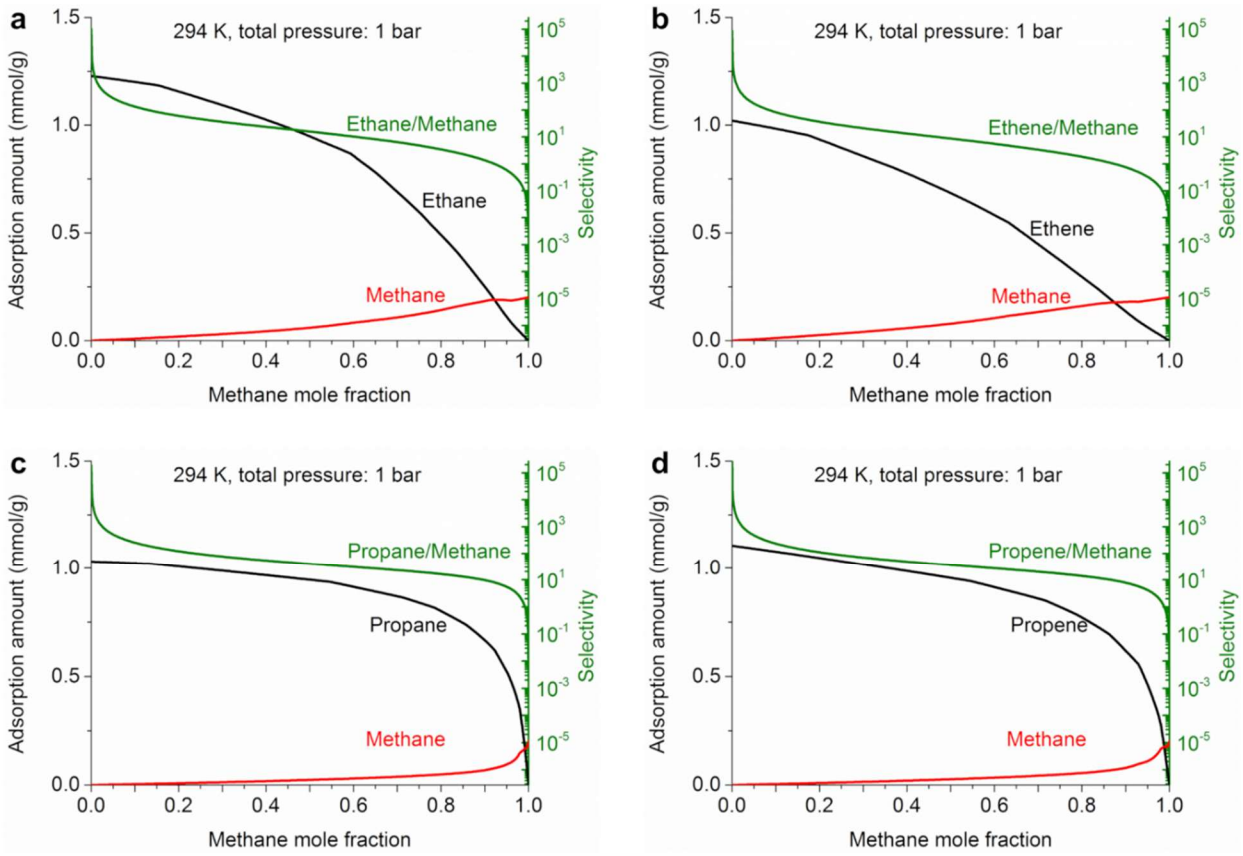

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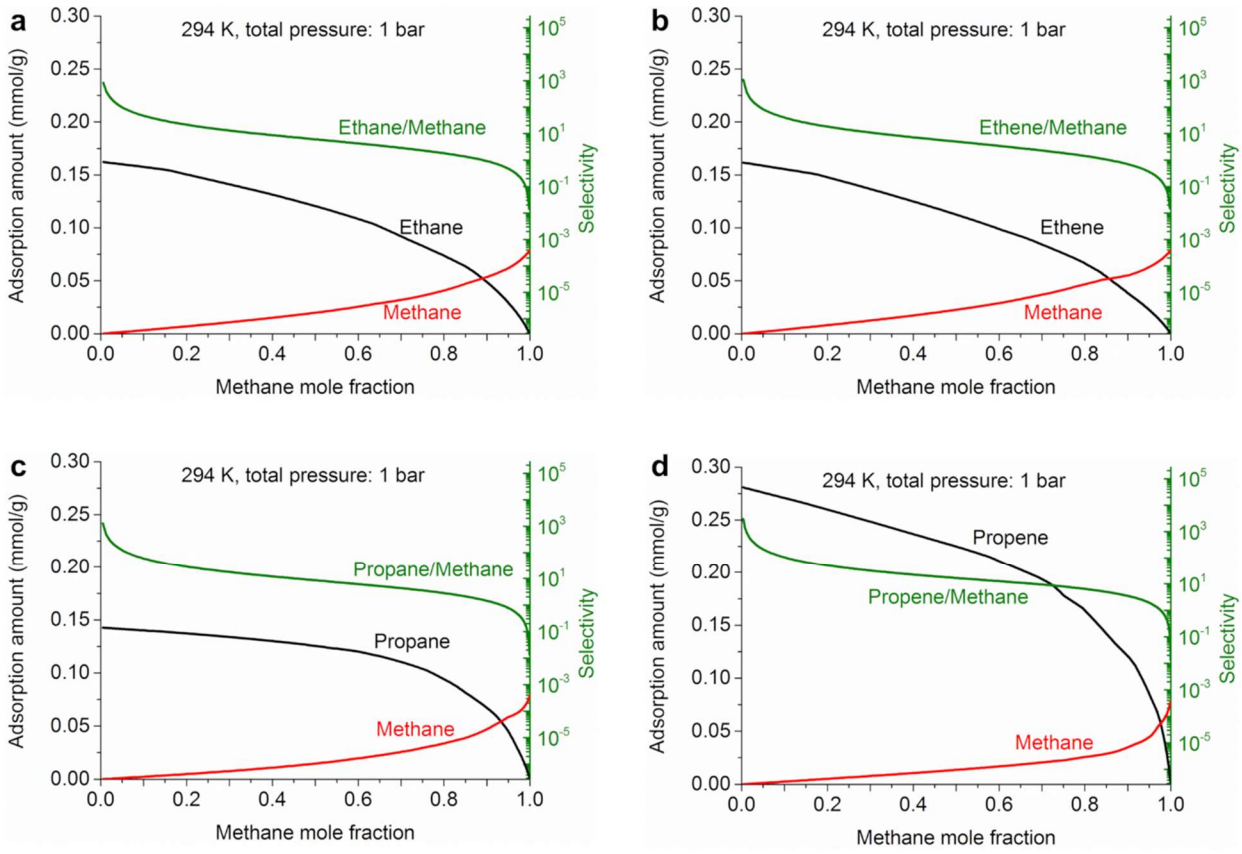

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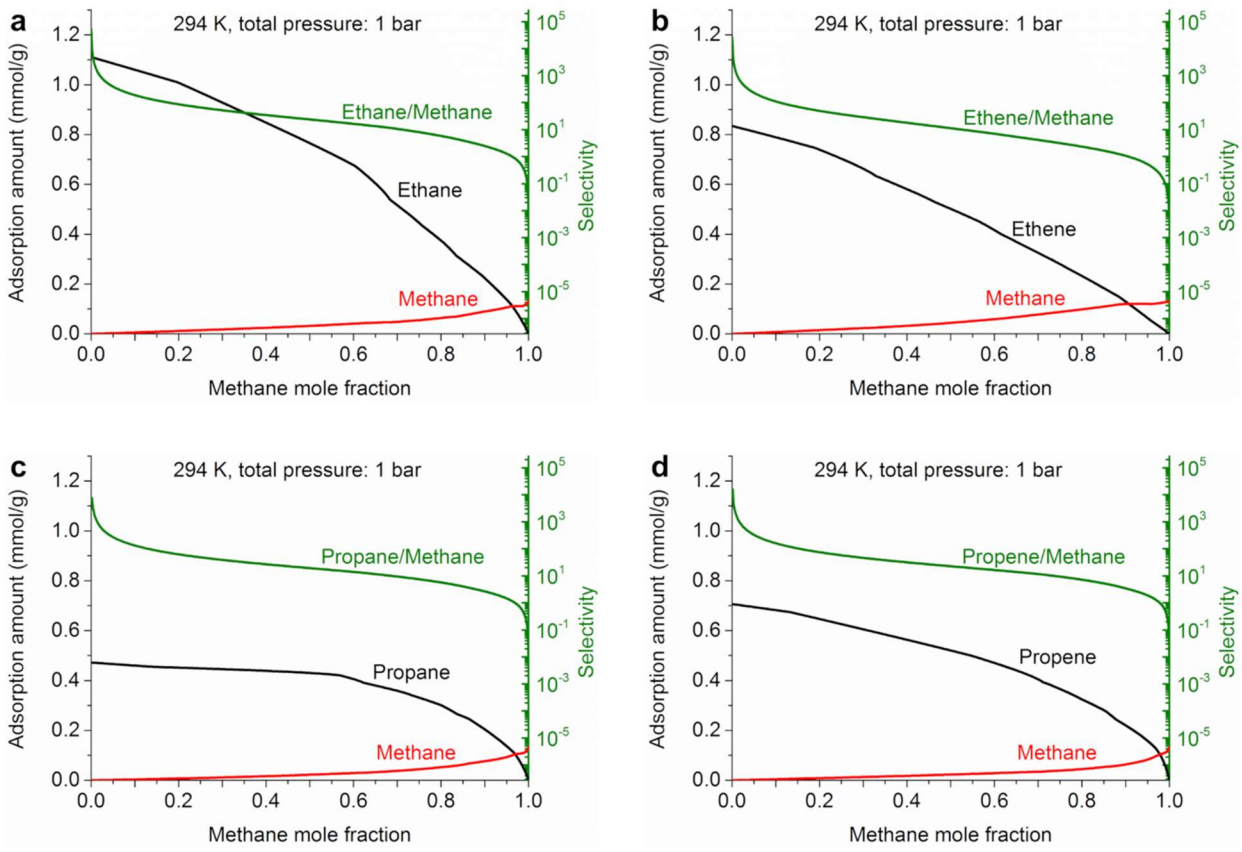
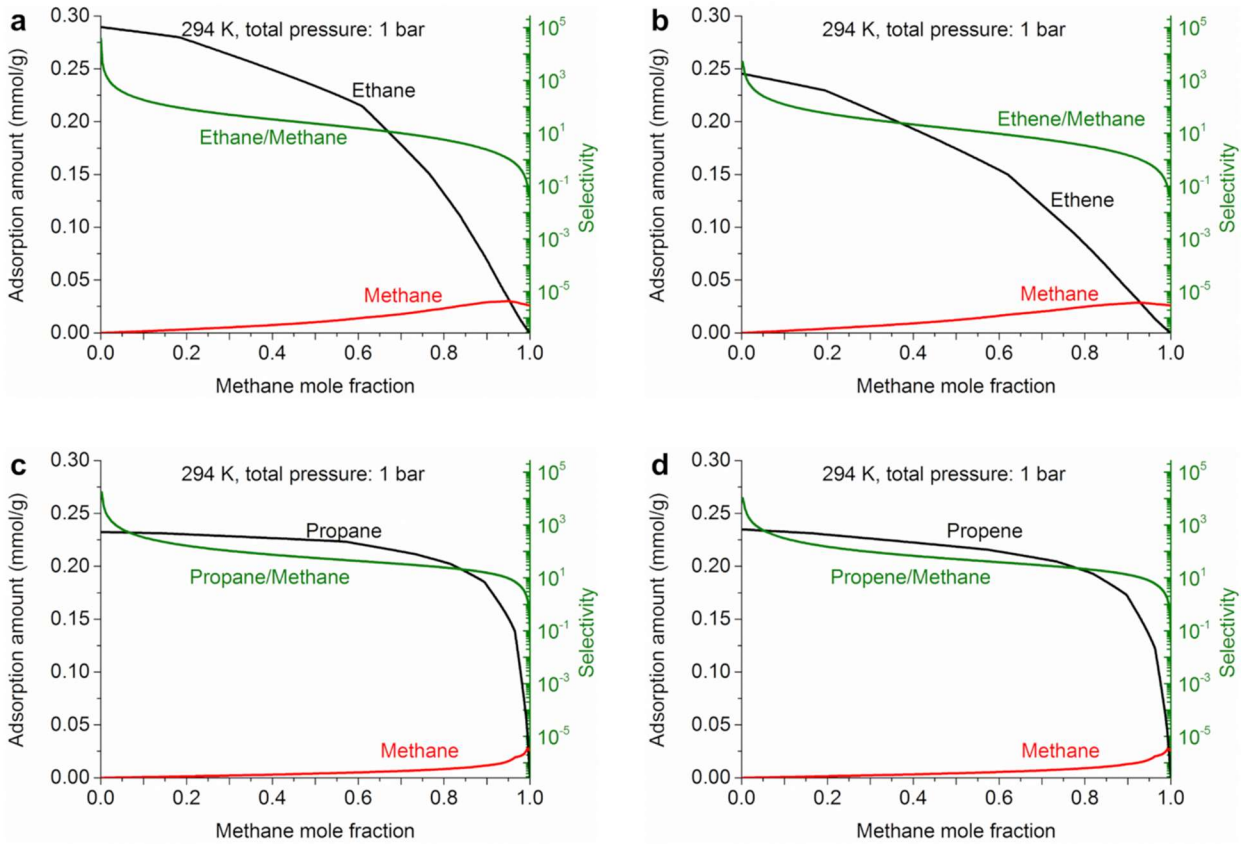


Figure S10. IAST-predicted adsorption amount and selectivity of mixed gases on Ni seed: a). Ethane and methane; b). Ethene and methane; c). Propane and methane; d). Propene and methane



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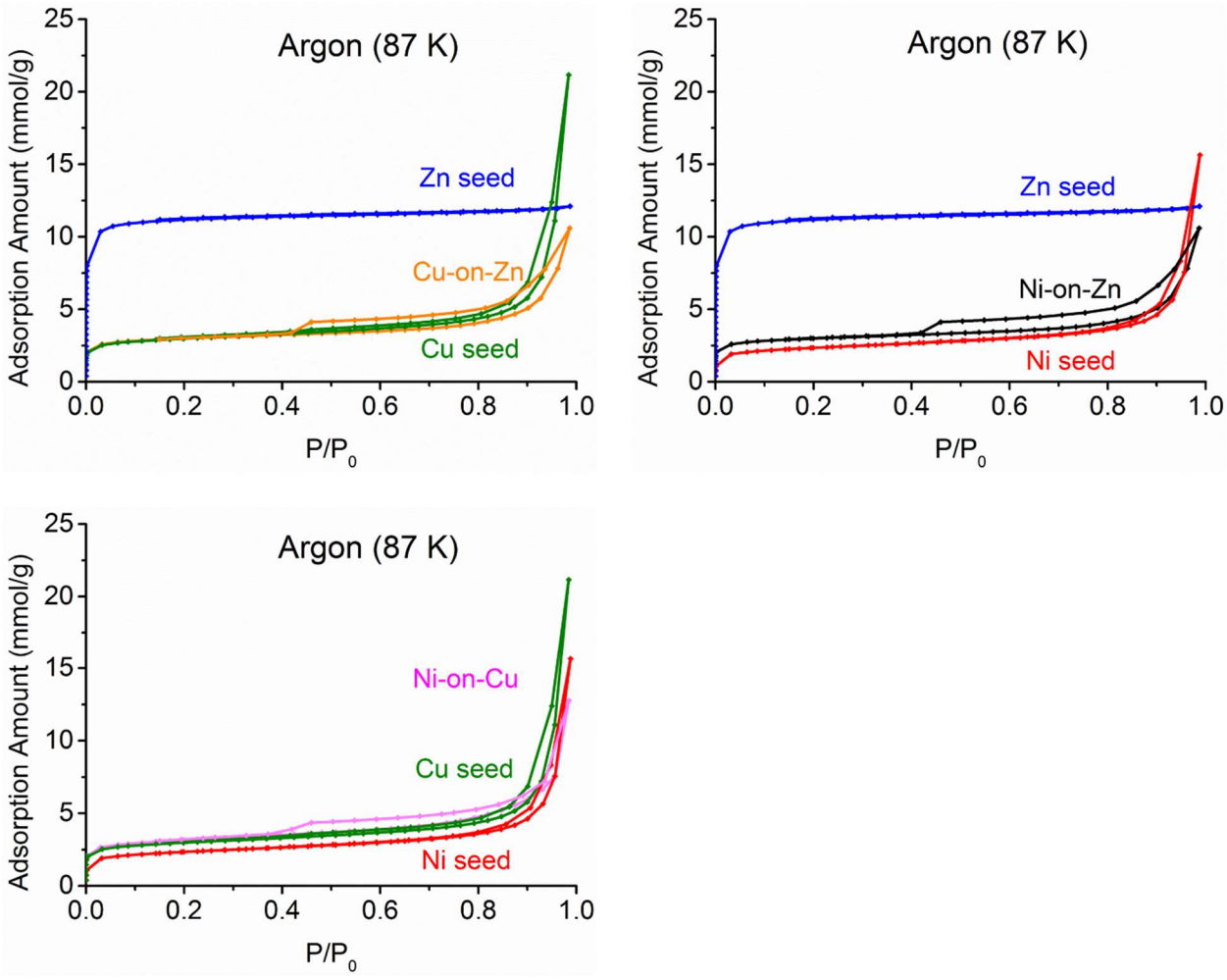
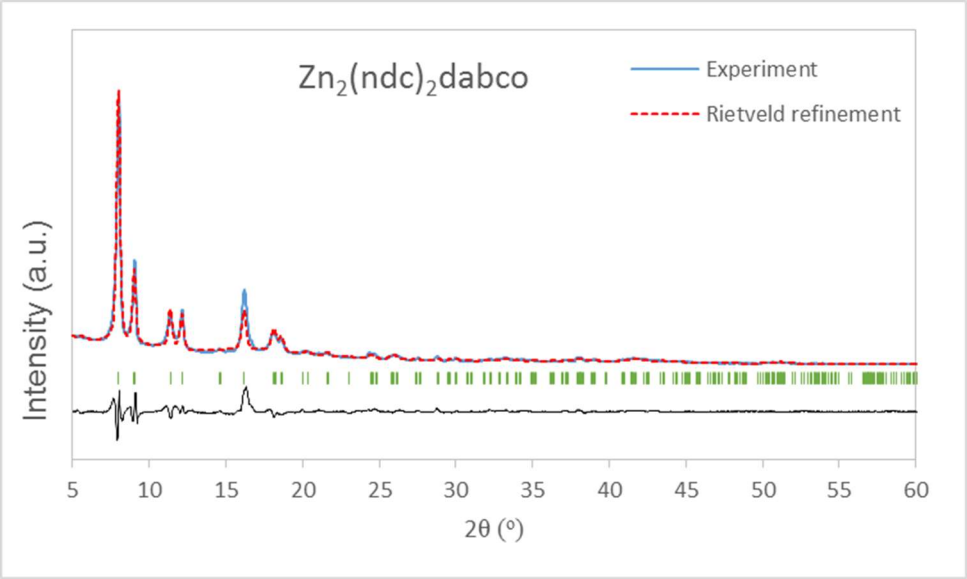
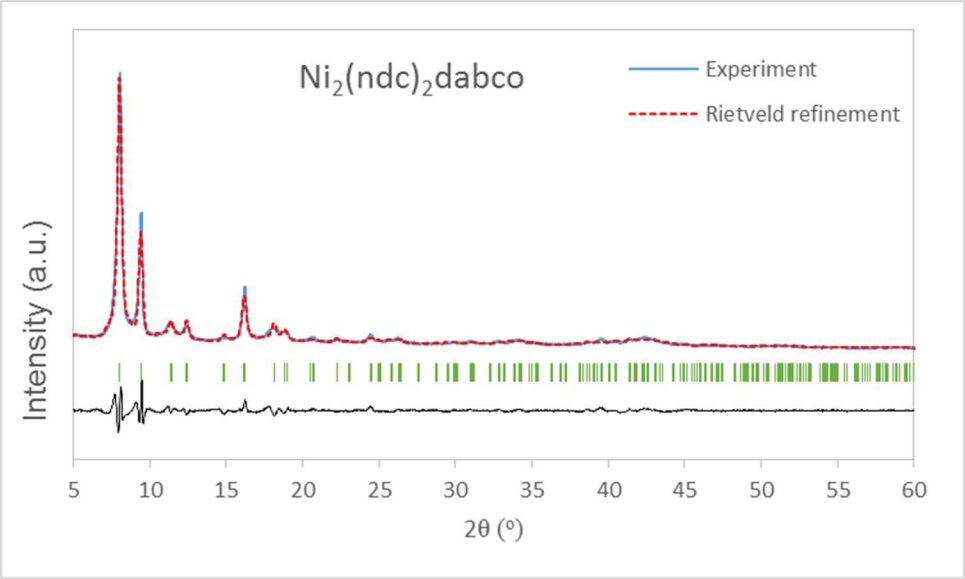


Figure S12. Adsorption isotherm of Argon on Zn seed, Cu seed and Cu-on-Zn intergrowth, Zn seed, Ni seed and Ni-on-Zn intergrowth, Ni seed, Cu seed and Ni-on-Cu intergrowth



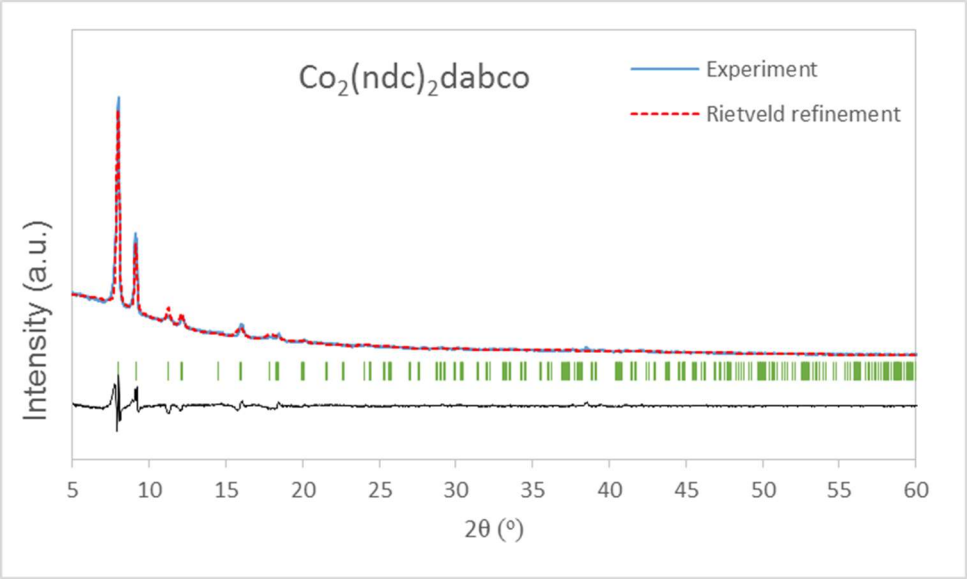
Rwp=9.07%		Rp=6.49%			
a=1.0847(3) nm		c=0.9631(3) nm		P4/mmm	
Atom	Multiplicity	Occupancy	x/a	y/b	z/c
Zn1	2	1	0	0	0.138(1)
C2	4	1	0	0.805(1)	0
C3	4	1	0	0.3756	0
C4	16	0.5	0.086(1)	0.4413(1)	0.0835(1)
C5	8	0.25	0	0.88597	0.359(3)
C6	16	0.25	0.09874	0.94299	0.362(3)
N7	2	1	0	0	0.262(3)
O8	8	1	0	0.863(1)	0.12213
C9	16	0.25	0.1714(7)	0.3752(5)	0.168(1)
C10	16	0.25	0.259(2)	0.441(2)	0.252(2)
H10	16	0.25	0.16014	0.92734	0.33525
H11	16	0.25	0.1023	0.85691	0.33525
H12	16	0.25	0.17506	0.98285	0.33525
H13	16	0.25	0.18064	0.28619	0.15671
H14	16	0.25	0.32475	0.39681	0.29825
H15	16	0.25	0.14817	0.39681	0.13548

Figure S13. Rietveld refinement for $Zn_2(ndc)_2dabco$ (powder XRD patterns and atomic coordinates)



Rwp=5.04%		Rp=3.52%			
a=1.0872(3) nm		c=0.9287(3) nm		P4/mmm	
Atom	Multiplicity	Occupancy	x/a	y/b	z/c
Ni1	2	1	0	0	0.1672(1)
C2	4	1	0	0.2239	0
C3	4	1	0	0.36489	0
C4	16	0.5	0.084(1)	0.4288(1)	0.0826(9)
C5	8	0.25	0	0.11078	0.4202(1)
C6	16	0.25	0.05539	0.09593	0.4227(4)
N7	2	1	0	0	0.152(5)
O8	8	1	0	0.1689(6)	0.1209(1)
C9	16	0.25	0.1665(7)	0.3646(5)	0.167(1)
C10	16	0.25	0.252(2)	0.428(2)	0.249(2)
H10	16	0.25	0.07059	0.15558	0.39643
H11	16	0.25	0.13901	0.09938	0.39643
H12	16	0.25	0.01666	0.17007	0.39643
H13	16	0.25	0.17549	0.27803	0.15512
H14	16	0.25	0.31549	0.38549	0.29523
H15	16	0.25	0.14394	0.38549	0.1341

Figure S14. Rietveld refinement for $Ni_2(ndc)_2dabco$ (powder XRD patterns and atomic coordinates)



Rwp=4.72%		Rp=3.20%			
a=1.1115(1) nm		c=0.9693(2) nm		P4/mmm	
Atom	Multiplicity	Occupancy	x/a	y/b	z/c
Co1	2	1	0	0	0.0936(3)
C2	4	1	0	0.22643	0
C3	4	1	0	0.36902	0
C4	16	0.5	0.085(1)	0.4336(1)	0.0827(9)
C5	8	0.25	0	0.11203	0.4206(1)
C6	16	0.25	0.05602	0.09701	0.4231(4)
N7	2	1	0	0	0.323(5)
O8	8	1	0	0.1699(6)	0.1210(1)
C9	16	0.25	0.1684(7)	0.3687(5)	0.167(1)
C10	16	0.25	0.255(3)	0.434(2)	0.249(2)
H10	16	0.25	0.07139	0.15734	0.39678
H11	16	0.25	0.14059	0.1005	0.39678
H12	16	0.25	0.01685	0.17199	0.39678
H13	16	0.25	0.17748	0.28117	0.15526
H14	16	0.25	0.31906	0.38985	0.29549
H15	16	0.25	0.14557	0.38985	0.13422

Figure S15. Rietveld refinement for $Co_2(ndc)_2dabco$ (powder XRD patterns and atomic coordinates)

Table S1. Selectivity between alkane and methane, alkene and methane at 294 K for a mixture of 0.8 bar CH_4 and 0.2 bar C_2 or C_3.

Gas	Cu seed	Zn seed	Ni seed	Cu-on-Zn	Ni-on-Zn	Ni-on-Cu
Ethane/Methane	1.8	5.7	5.9	3.5	3.1	6.9
Ethene/Methane	1.4	3.4	2.4	1.8	3.7	3.6
Propane/Methane	2.8	24.6	5.7	16.5	52.9	49.8
Propene/Methane	6.4	21.6	7.2	14.0	42.6	44.5

Synthesis

Materials Synthesis

Cu(NO3)2·3H2O (Fisher Science Education), Zn(NO3)2·6H2O (Alfa Aesar), Ni(NO3)2·6H2O (Sigma Aldrich), Co(NO3)2·6H2O (Acros Organics), naphthalene-1,4-dicarboxylic acid (Alfa Aesar), 1,4-Diazabicyclo[2.2.2]Octane (Sigma Aldrich), Nitroterephthalic Acid (Alfa Aesar), Acetone (Fisher Science Education), N,N-Dimethylformamide (VWR BDH Chemicals) were used without further purification.

Seed particles MI2(ndc)2(dabco) (MI=Cu, Zn, Ni, Co, ndc =naphthalene-1,4-dicarboxylate, dabco=1,4-Diazabicyclo[2.2.2]Octane) were synthesized using conventional solvent-based method. In a typical synthesis, base linker dabco (0.0125 g) was added into Cu(NO3)2·3H2O (0.0376 g) (or alternatively Zn(NO3)2·6H2O, Ni(NO3)2·6H2O, Co(NO3)2·6H2O) Acetone (9.36 g) solution. DTBP(2,6-Di-tert-butylpyridine) (62.4 μL) was added with micropipette into acid linker (0.0240 g) ndc Acetone (10.00g) solution. Once linkers and metal salt were completely dissolved, acid linkers solution was added into metal salt solution. The final mixture has a molar ratio of Metal salt : ndc : dabco : DTBP : Acetone = 2.8 : 2 : 2 : 5 : 6000 and was shaken on an orbital shaker at 200 rpm for 48 hours. The solid in the resulting suspension was separated using centrifugation (4000 RCF). After 3 times washing with Acetone, the last precipitation was dispersed in 2 g of Acetone.

Intergrowth MII2(ndc)2(dabco) on MI2(ndc)2(dabco) (noted as MII-on-MI) was synthesized by conventional seeded growth method. In a typical procedure, MII = Cu(NO3)2·3H2O, (0.0188 g) (or alternatively Zn(NO3)2·6H2O, Ni(NO3)2·6H2O, Co(NO3)2·6H2O) was dissolved in Acetone (4.00 g). Acid Linker ndc (0.0120 g) was dissolved in Acetone (22.20 g). DTBP(2,6-Di-tert-butylpyridine) (124.7 μL) was added with micropipette into base linker dabco (0.0062 g) Acetone (22.20 g) solution. 66 μL seed dispersion was added into DTBP solution. Once linkers and metal salt were completely dissolved, acid linkers and metal solutions were added into seed solution. The final mixture has a molar ratio of Metal salt : ndc : dabco : DTBP : Acetone = 2.8 : 2 : 2 : 20 : 30000 and was shaken on an orbital shaker at 200 rpm for 48 hours. The solid in the resulting suspension was separated using centrifugation (4000 RCF).

Material characterization

Powder XRD patterns were obtained using PANalytical Empreyean diffractometer (40 mA, 45 kV), Cu Kα radiation (λ=1.54Å). TEM, STEM, and STEM-EDS micrographs were collected on FEI Talos F200X at 200 kV, and FEI Titan3 G2 at 300 kV. Bruker Esprit software was used to collect the element maps. SEM images of the synthesized pillared MOF were taken using FEI Helios NanoLab 660 FESEM and Thermo Fisher Scios 2 at 2 kV.

Physical adsorption of hydrocarbons was measured on a fixed-volume, vacuum/high-pressure barometric adsorption system at 295 K. Before each isotherm measurement, the samples were evacuated in a chamber under dynamic vacuum (6x10-7 mBar) at 373 K for 12 h with a Pfeiffer HiCube 80 turbomolecular pump. The samples were then cooled down to 295 K under vacuum (6x10-7 mBar). Adsorbate (methane, ethane, ethene, propane, propene) with known amount was injected into the sample chamber, and the pressure change after steady state was measured for the calculation of amount of gas adsorbed. The cumulative gas amount adsorbed was used to plot gas adsorption isotherms at 295 K.

Physical adsorption of Ar at 87 K was performed on a Micromeritics ASAP 2000 with same activation procedure mentioned above.