Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Cation-exchanged SAPO-34 for adsorption-based hydrocarbon separations: Predictions from dispersion-corrected DFT calculations

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A) DFT-optimised geometries for preferred cation sites

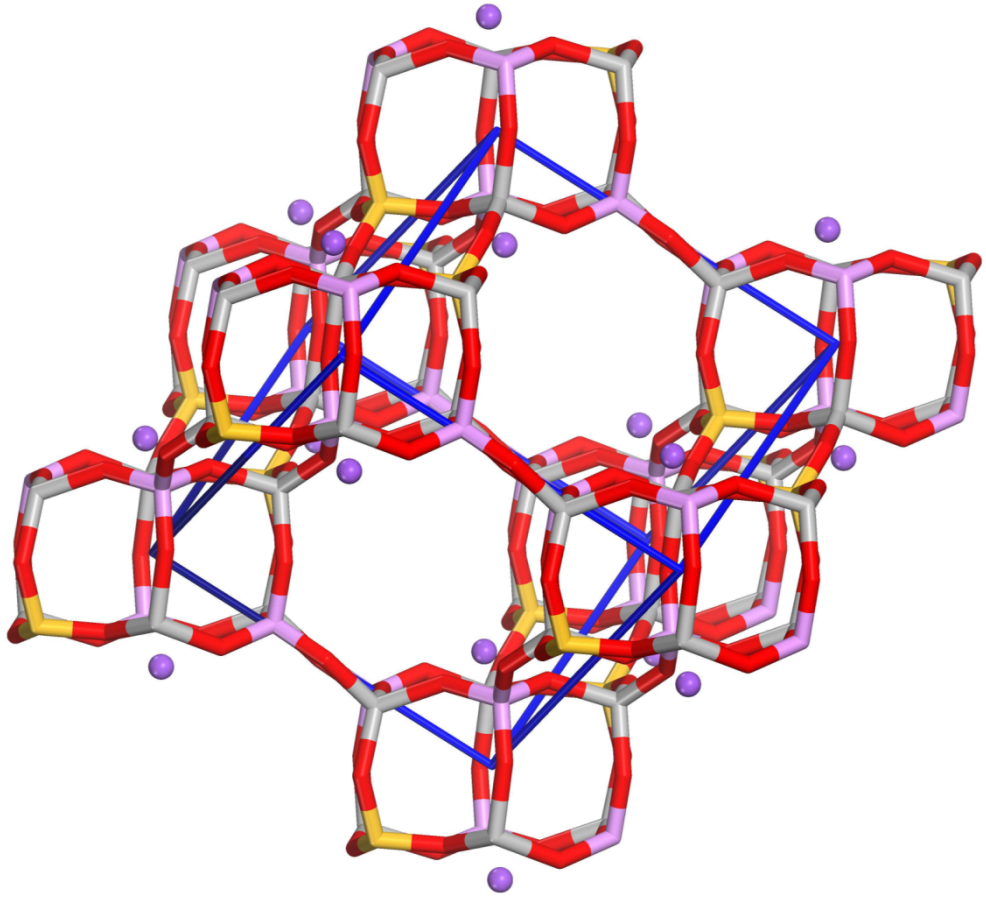

Figure S1: Full unit cell of Na-SAPO-34 as used in the DFT calculations.

Table S1: Energy difference *ΔE(SII-SIII')* obtained from DFT calculations assuming the cations at either of the two sites. The energy difference is given per cation, rather than per unit cell. The ionic radius r_{ion} for octahedral coordination is also given.

	ΔE(SII-SIII') / kJ mol^{-1}	r_{ion} / Å
Li^+	-39.0	0.76
Na^+	-17.5	1.02
K^+	14.3	1.38
Rb^+	29.3	1.52
Mg^{2+}	-106.6	0.72
Ca^{2+}	-38.8	1.00
Sr^{2+}	4.7	1.18
Cu^+	-82.1	0.77
Ag^+	-20.5	1.15
Fe^{2+}	-130.9	0.61

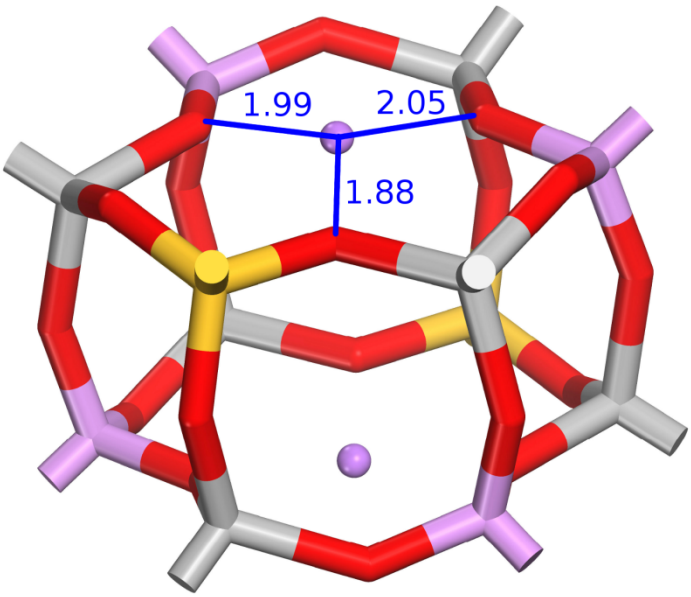

Figure S2: DFT-optimised geometry of the environment of lithium in Li-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given. The distance between the two lithium cations amounts to 4.27 Å.

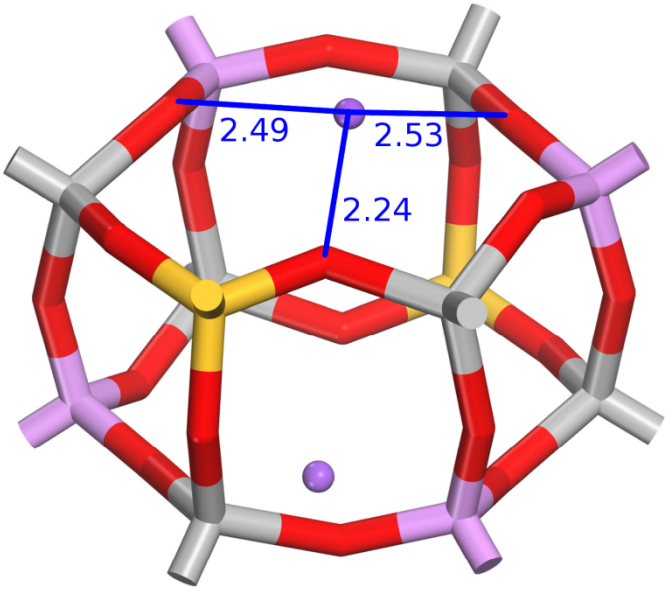

Figure S3: DFT-optimised geometry of the environment of sodium in Na-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given. The distance between the two sodium cations amounts to 5.35 Å.

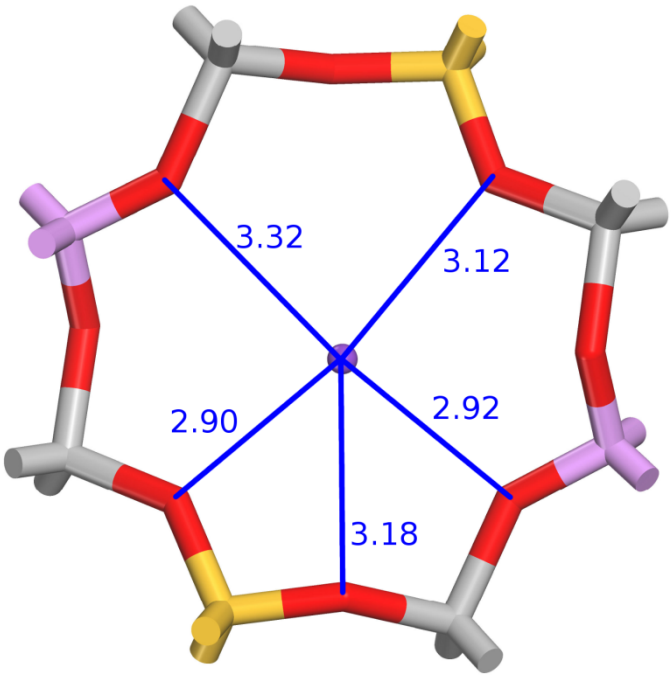

Figure S4: DFT-optimised geometry of the environment of potassium in K-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given.

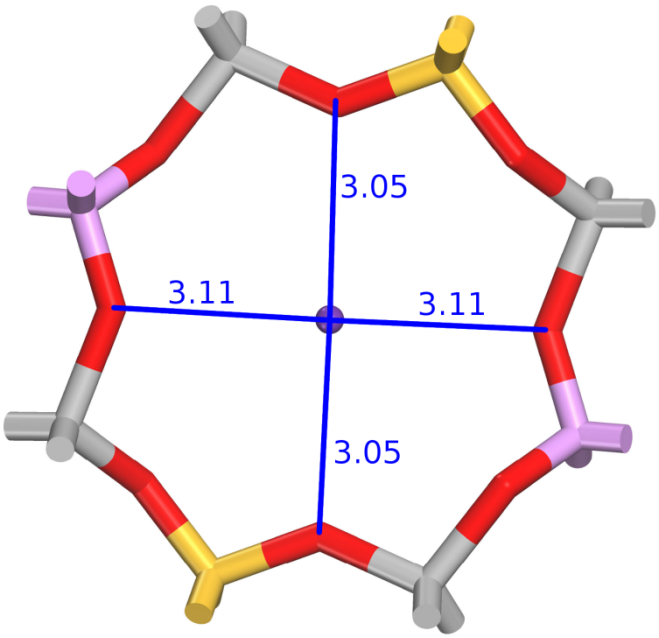

Figure S5: DFT-optimised geometry of the environment of rubidium in Rb-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given.

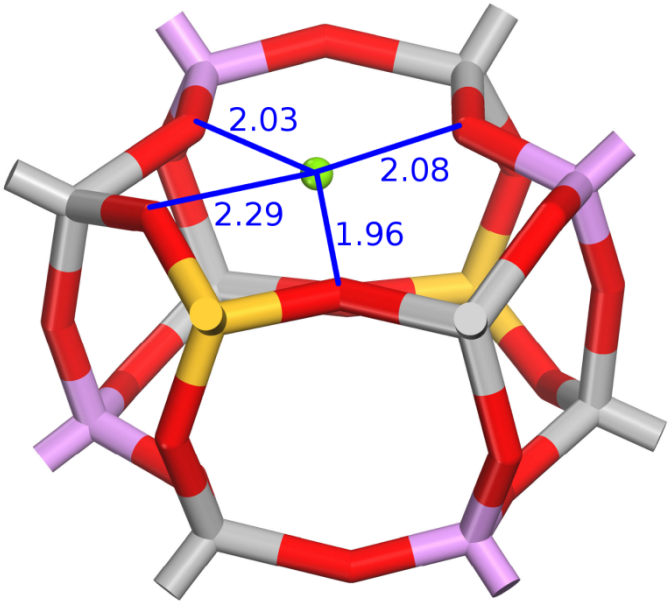

Figure S6: DFT-optimised geometry of the environment of magnesium in Mg-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given.

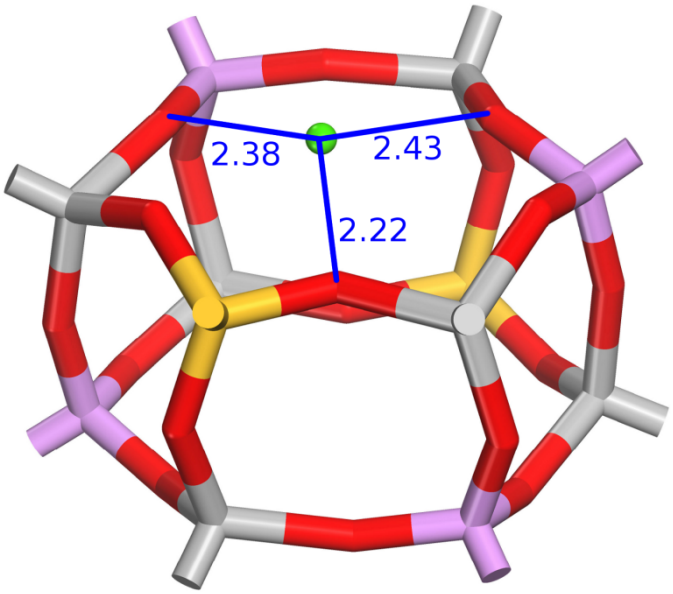

Figure S7: DFT-optimised geometry of the environment of calcium in Ca-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given.

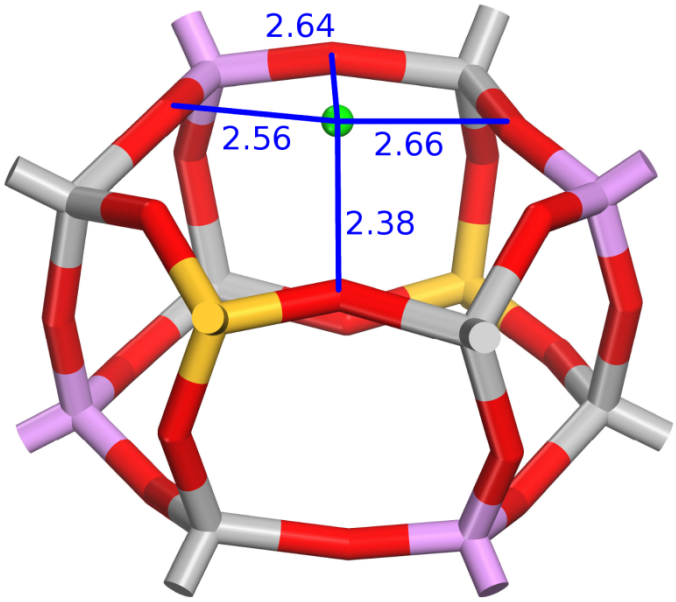

Figure S8: DFT-optimised geometry of the environment of strontium in Sr-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given.

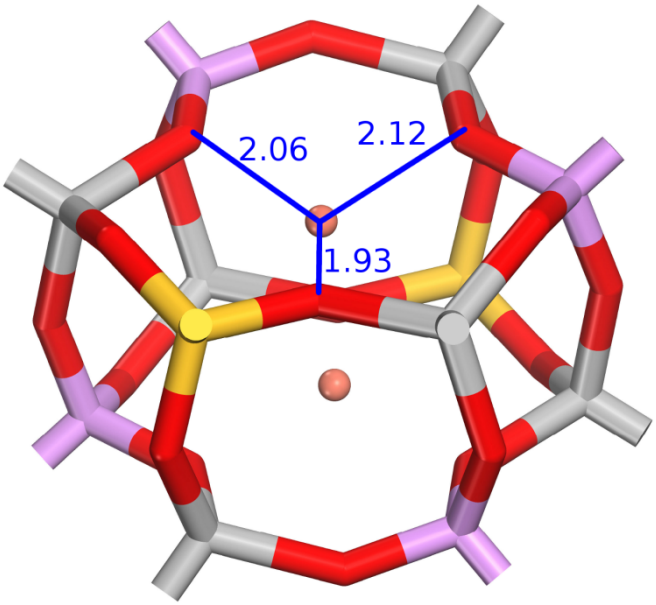

Figure S9: DFT-optimised geometry of the environment of copper in Cu-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given. The distance between the two copper cations amounts to 2.55 Å.

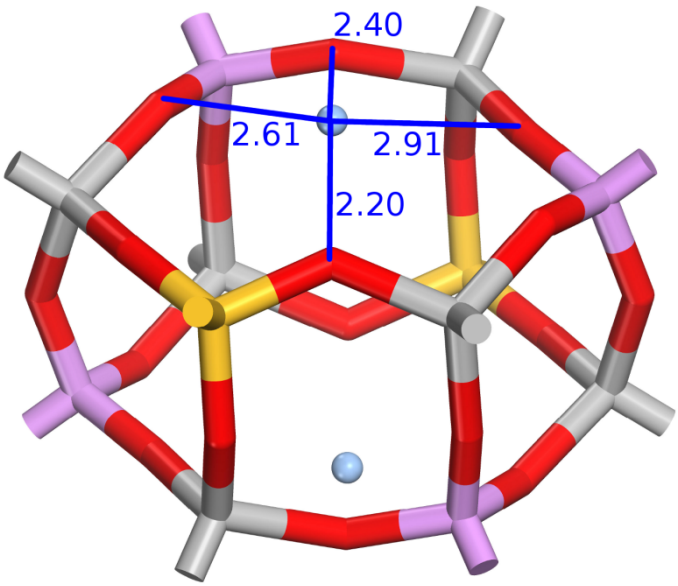

Figure S10: DFT-optimised geometry of the environment of silver in Ag-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given. The distance between the two silver cations amounts to 5.50 Å.

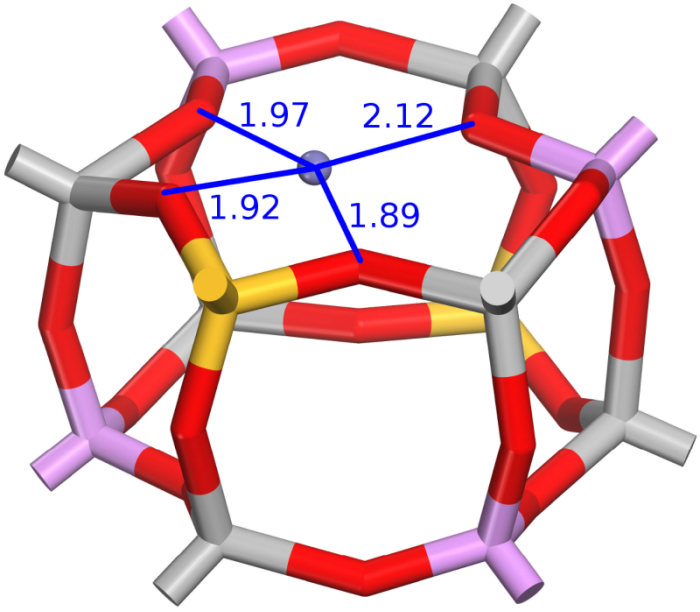

Figure S11: DFT-optimised geometry of the environment of iron in Fe-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given.

B) DFT calculations for Cu/Na-SAPO-34

The calculations for Cu/Na-SAPO-34 considered a total of five distributions of the two cations. Scenario 1 was found to be the energetically preferred combination. For the other four scenarios X, the energy difference $\Delta E(1\text{-}X)$ is given (per unit cell) .

1 = Cu and Na at site SII

2 = Cu at site SII, Na at site SIII' $\Delta E(1\text{-}2)$ = -27.3 kJ mol^{-1}

3 = Cu at site SIII', Na at site SII $\Delta E(1\text{-}3)$ = -68.2 kJ mol^{-1}

4 = Cu at site SI, Na at site SIII' $\Delta E(1\text{-}4)$ = -33.4 kJ mol^{-1}

5 = Cu at site III', Na at site SI $\Delta E(1\text{-}5)$ = -53.7 kJ mol^{-1}

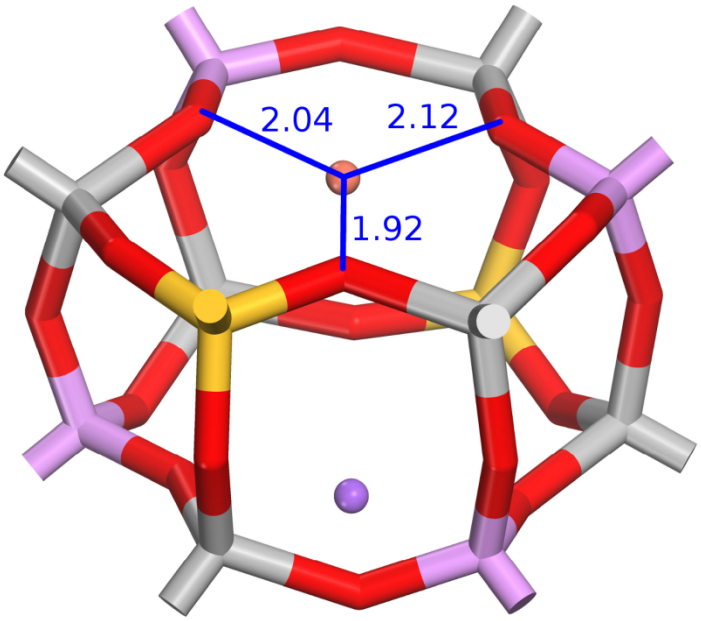

Figure S12: DFT-optimised geometry of the environment of copper in Cu/Na-SAPO-34. The distances to the closest framework oxygens (in Ångström) are given. The distance between the copper and the sodium cation amounts to 4.42 Å.

C) Comparison of DFT-D interaction energy and pure DFT interaction energy

Table S2: DFT interaction energies E_{int} , which include the Grimme-type dispersion correction, and "DFT-only" interaction energy E_{nodisp}, which is obtained by subtracting the dispersion correction term, for ethane, ethylene, and acetylene. All values in kJ mol^{-1}.

	C_2H_6		C_2H_4		C_2H_2	
	E_{int}	E_{nodisp}	E_{int}	E_{nodisp}	E_{int}	E_{nodisp}
Li-SAPO-34	-57.9	-5.2	-66.6	-24.4	-65.1	-30.1
Na-SAPO-34	-57.2	-12.0	-61.6	-29.5	-57.3	-32.3
Mg-SAPO-34	-72.0	-27.4	-102.0	-63.2	-98.2	-67.7
Ca-SAPO-34	-72.3	-34.4	-84.9	-55.4	-82.6	-59.1
Sr-SAPO-34	-67.2	-30.9	-80.5	-52.8	-75.5	-53.9
Cu/Na-SAPO-34	-39.5	-2.2	-165.7	-136.4	-151.7	-128.4
Ag-SAPO-34	-49.6	-13.7	-128.4	-101.5	-106.5	-86.3
Fe-SAPO-34	-37.7	-0.3	-168.0	-118.4	-149.5	-115.4

Table S3: DFT interaction energies E_{int} , which include the Grimme-type dispersion correction, and "DFT-only" interaction energy E_{nodisp}, which is obtained by subtracting the dispersion correction term, for propane and propylene. All values in kJ mol^{-1}.

	C_3H_8		C_3H_6	
	E_{int}	E_{nodisp}	E_{int}	E_{nodisp}
Li-SAPO-34	-65.5	-0.5	-84.2	-22.0
Na-SAPO-34	-69.3	-12.4	-81.7	-31.2
Mg-SAPO-34	-86.4	-35.4	-127.5	-68.6
Ca-SAPO-34	-88.3	-35.5	-111.3	-60.9
Sr-SAPO-34	-85.7	-36.1	-112.4	-61.0
Cu/Na-SAPO-34	-52.3	0.0	-175.9	-129.3
Ag-SAPO-34	-66.0	-16.3	-145.0	-97.8
Fe-SAPO-34	-50.0	0.2	-182.4	-109.5

D) Additional electron density plots

1) Ethane

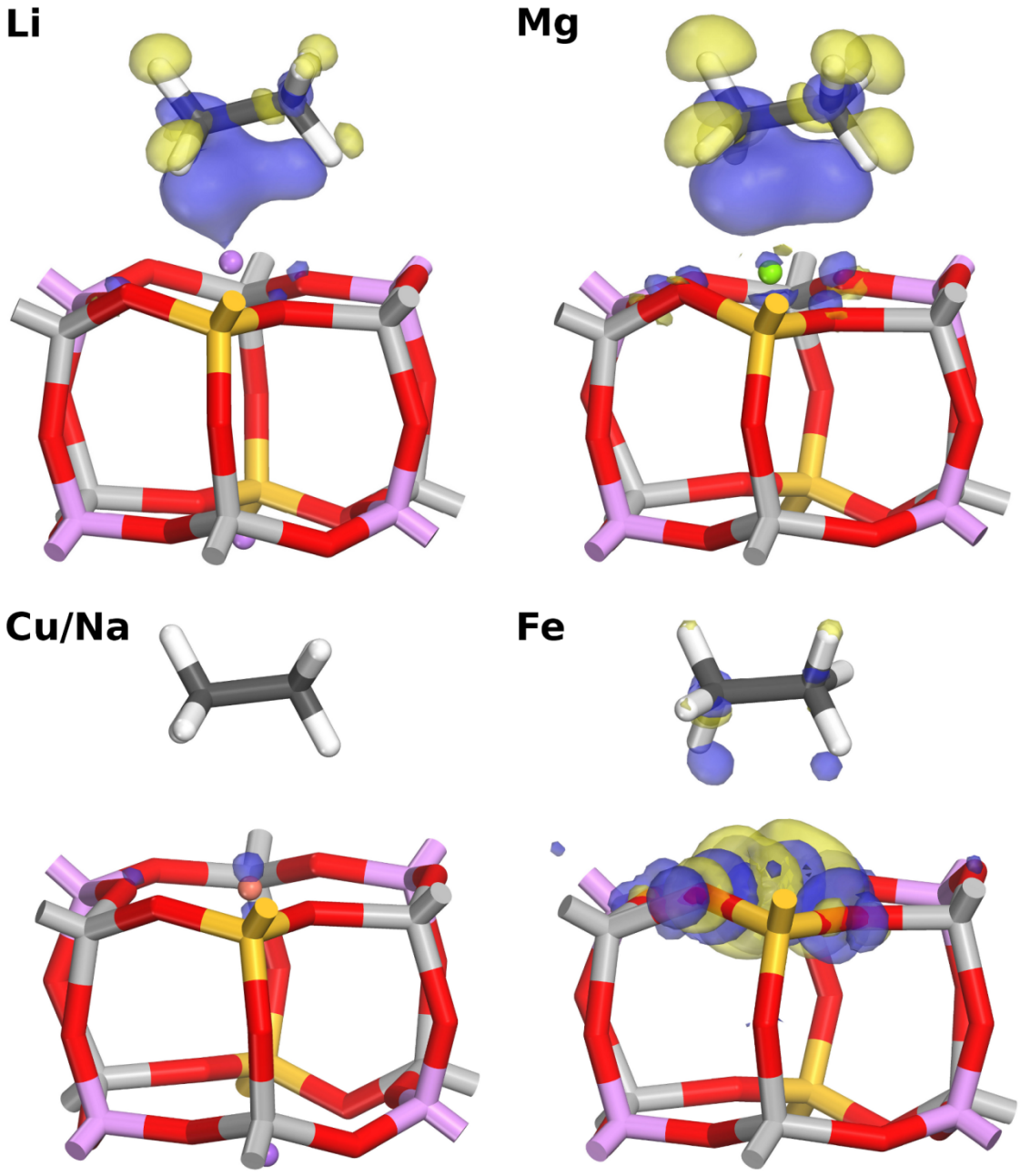

Figure S13: Isosurface of the electron density difference for ethane adsorbed in Li-, Mg-, Cu/Na-, and Fe-SAPO-34. The isosurfaces were created for an isodensity value of 0.01 e $Å^{-3}$. Blue designates regions of charge accumulation, and yellow designates regions of charge depletion.

2) Propylene

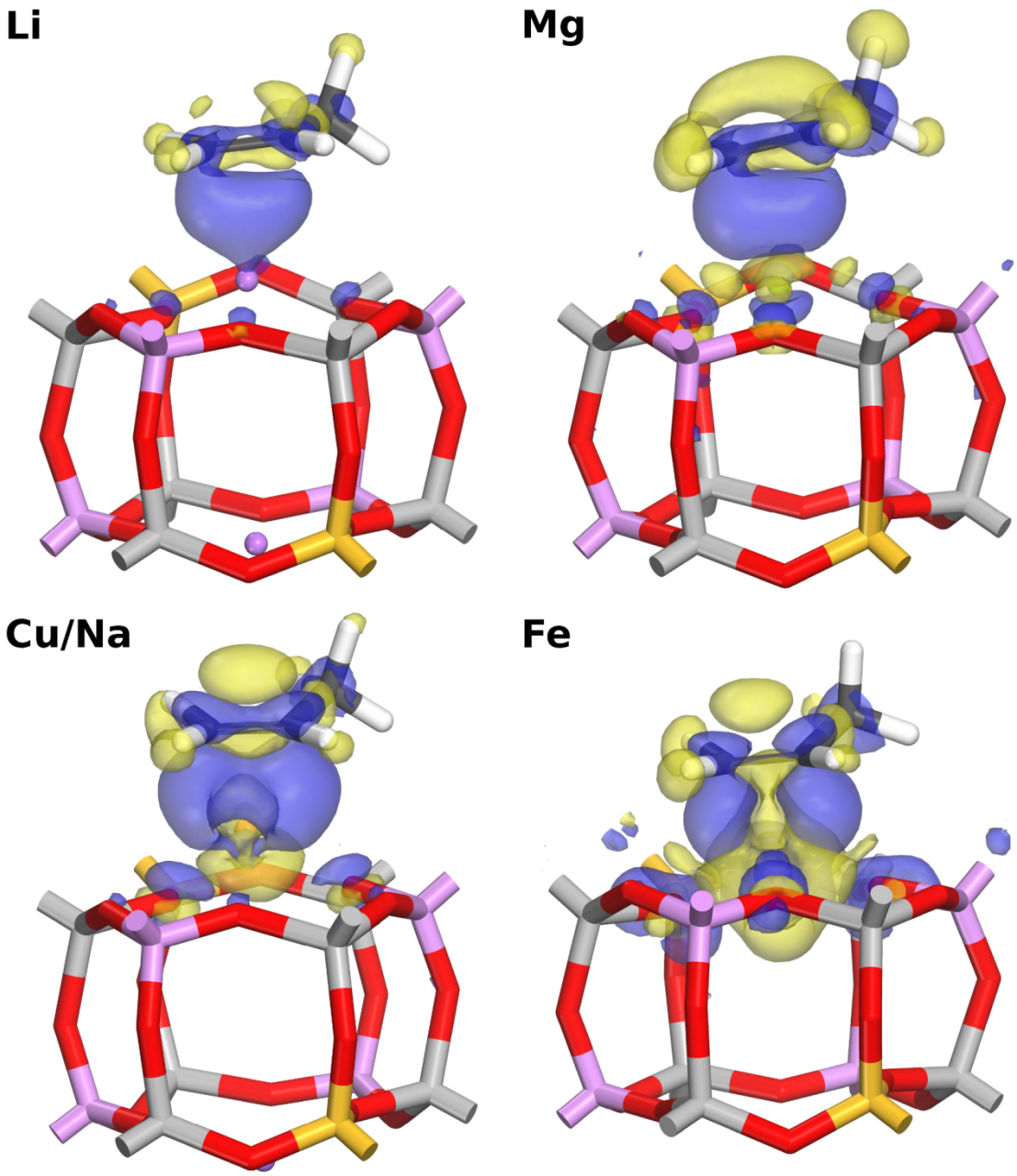

Figure S14: Isosurface of the electron density difference for propylene adsorbed in Li-, Mg-, Cu/Na-, and Fe-SAPO-34. The colour scheme and the isodensity value are the same as in figure S12.

3) Acetylene

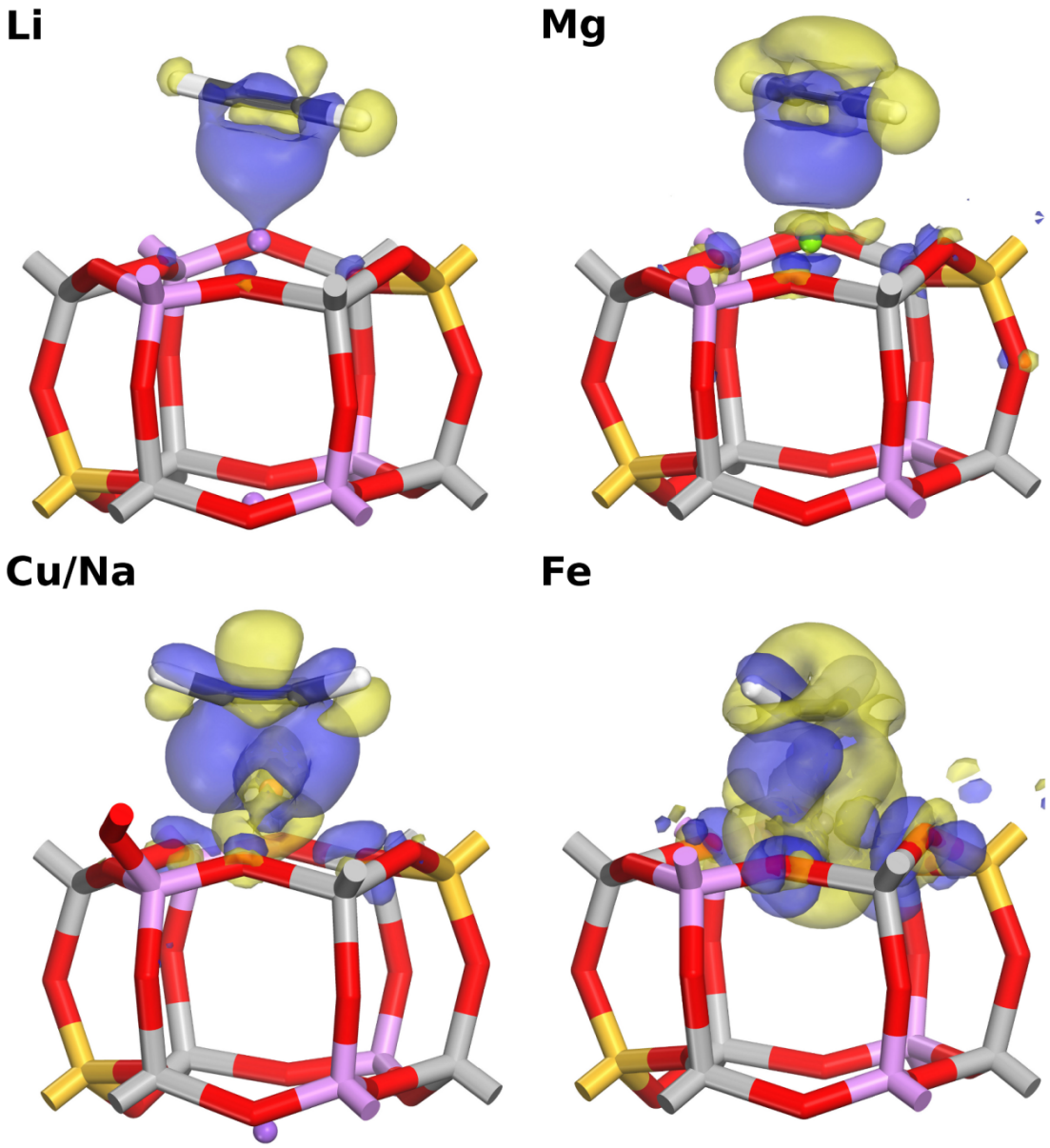

Figure S15: Isosurface of the electron density difference for acetylene adsorbed in Li-, Mg-, Cu/Na-, and Fe-SAPO-34. The colour scheme and the isodensity value are the same as in figure S12.

4) Unsaturated hydrocarbons in Ag-SAPO-34

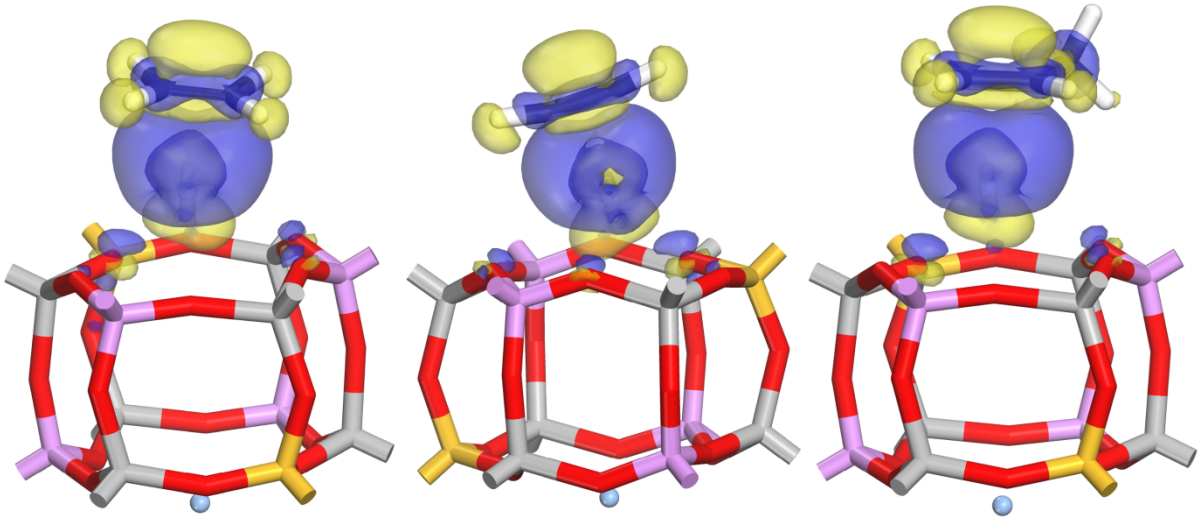

Figure S16: Isosurface of the electron density difference for ethylene, acetylene, and propylene adsorbed in Ag-SAPO-34. The colour scheme and the isodensity value are the same as in figure S12.