Supporting Information:

A DFT study on the adsorption of H_2S and other Claus process tail gas components on Cu- and Ag- exchanged Y zeolites

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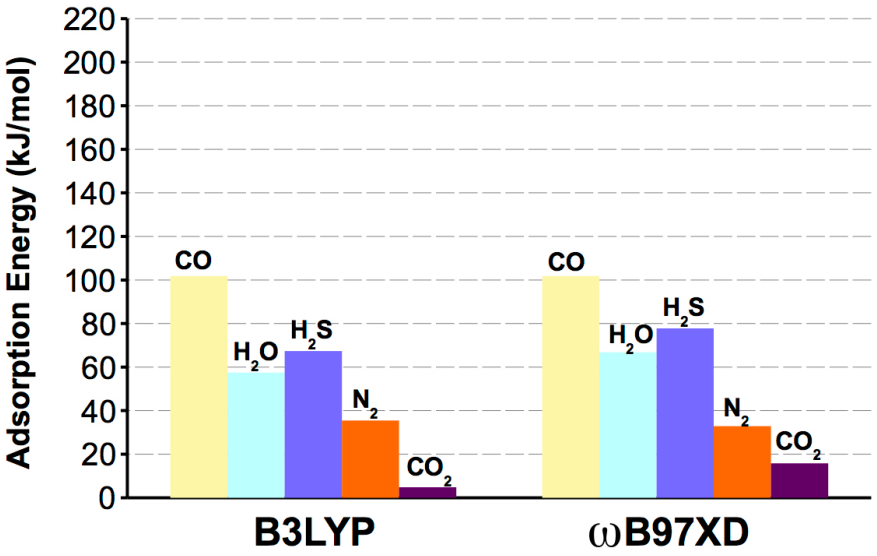
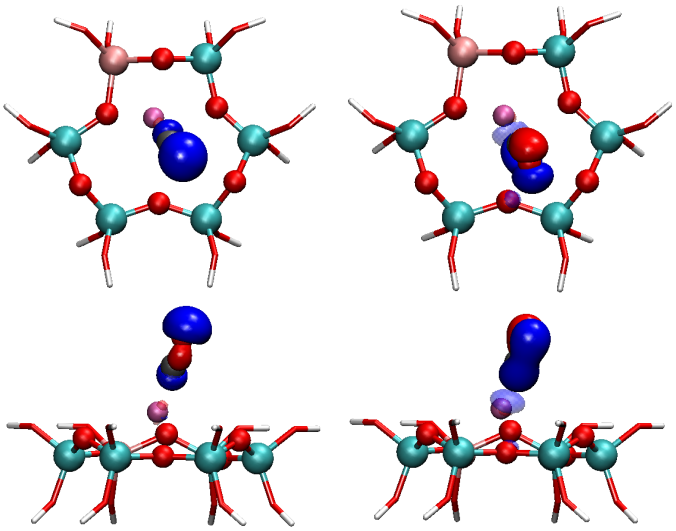


Figure S1: Adsorption energies of CO, H_2O, H_2S, N_2, and CO adsorbed on CuY zeolite cluster calculated with B3LYP and ωB97X-D functionals. Color version available online.



(a) (b)

Figure S2: Top and side views of significant COVPs between CO and CuY cluster that contribute (a) 11.6 kJ/mol (21.5 % of ΔE_{CT}) and (b) 8.9 kJ/mol (16.5 % of ΔE_{CT}) to ΔE_{CT}. Occupied orbitals are represented with glossy surfaces, and virtual orbitals are represented with transparent surfaces. Isovalue surface of 0.1 a.u. Atomic representations can be referred to Figure 1. Color version available online.

0.1 Natural bond orbital (NBO) charge analysis

The NBO charges and electronic configurations of Cu and Ag cations are listed in Table 1. When the Cu cation is embedded in the zeolite cluster, it receives electrons in the 4s and 4p orbitals from the zeolite, and loses electrons from the 3d orbitals to the zeolite. Upon adsorption, Cu cation attracts extra electrons in the 4s and 4p orbitals and loses some more electrons from the 3d orbitals. In the presence of the zeolite cluster, this loss is larger than when Cu is isolated, but the most significant change is the occupation in p orbitals. However, more electrons are retrieved in the 4s and 4p orbitals than lost in the 3d orbital, which leads to the overall lowering of the positive charge of the Cu cation in the presence of the zeolite cluster. The same phenomena were observed for the 5s, 5p, and 4d orbitals of Ag cation.

In contrast to Cu and Ag containing systems, alkali metals were only observed to gain electrons on valence s and p orbitals as shown in Table 2. For example, Li cation retrieves electrons from the cluster mainly in the 2p orbital. Upon adsorption, Li cation attracts more electrons in the 2s and 2p orbitals in the presence of the zeolite cluster than when isolated with the 2p orbital undergoing the most significant change, which leads to the lowering of the charge of Li cation. The above features were observed for Na and K cations as well. The decrease of the charge of the cation follows this order: Li > Na > K.

Table S1: Distances (Å) between the cation M and three O(2) atoms in the S6R[1], and the height (Å) of the cation from the plane formed by three O(2) atoms in the S6R at different level of theories.

	Cation M														
Distances (Å)	Cu			Ag			Li			Na			K		
M - O(2)	1.95	2.05	2.20	2.29	2.50	2.64	1.86	2.00	2.57	2.19	2.31	2.50	2.56	2.76	2.92
M - O(2) plane	0.02			1.34			0.51			1.05			1.78		

[1] The interatomic distances between the cation and three O(2) atoms are listed from the framework O(2) atom next to Al atom to the other two O(2) atoms clockwise in the S6R.

Table S2: Selected geometric parameters of CO, H_2O, H_2S, N_2, and CO_2 adsorbed on MY zeolite cluster (M = Cu, Ag, Li, Na, or K). The atom labels are defined in Figure 3.

	distance (Å)				angle (°)
CO	C-O			M-C	M-C-O
gas phase	1.14				
CuY	1.14			1.81	178
AgY	1.14			2.04	180
LiY	1.13			2.28	175
NaY	1.13			2.66	168
KY	1.14			3.19	179
H_2O	O-H1	O-H2	H1-O_z	M-O	H1-O-H2
gas phase	0.97	0.97			105
CuY	0.98	0.97	1.98	1.97	106
AgY	0.98	0.97	2.00	2.30	106
LiY	0.98	0.97	1.93	1.97	106
NaY	0.99	0.97	1.89	2.32	105
KY	1.00	0.97	1.82	2.79	103
H_2S	S-H1	S-H2	H1-O_z	M-S	H1-S-H2
gas phase	1.35	1.35			92.9
CuY	1.36	1.35	2.39	2.22	93.5
AgY	1.35	1.35	2.59	2.49	93.4
LiY	1.35	1.35	3.03	2.58	93.4
NaY	1.37	1.35	2.16	3.03	92.9
KY	1.38	1.35	1.90	3.36	92.5
N_2	N1-N2			M-N1	M-N1-N2
gas phase	1.11				
CuY	1.11			1.85	177
AgY	1.11			2.24	178
LiY	1.10			2.19	175
NaY	1.10			2.57	174
KY	1.10			3.07	164
CO_2	O1-C	O2-C		M-O1	M-O1-C
gas phase	1.17	1.17			
CuY	1.17	1.17		2.66	129
AgY	1.18	1.16		2.59	129
LiY	1.18	1.16		2.07	131
NaY	1.18	1.16		2.41	131
KY	1.18	1.16		2.86	138

Table S3: Selected geometric parameters of CO, H_2O, H_2S, N_2, and CO_2 in the gas phase and adsorbed on cation M (M = Cu, Ag, Li, Na, or K). The atom labels are defined in Figure 4.

	distance (Å)			angle (°)
CO	C-O		M-C	M-C-O
gas phase	1.14			
Cu^+	1.13		1.89	180
Ag^+	1.13		2.17	180
Li^+	1.13		2.17	180
Na^+	1.13		2.56	180
K^+	1.13		3.06	180
H_2O	O-H1	O-H2	M-O	H1-O-H2
gas phase	0.97	0.97		105
Cu^+	0.97	0.97	1.94	108
Ag^+	0.97	0.97	2.23	108
Li^+	0.97	0.97	1.83	106
Na^+	0.97	0.97	2.21	105
K^+	0.97	0.97	2.61	105
H_2S	S-H1	S-H2	M-S	H1-S-H2
gas phase	1.35	1.35		92.9
Cu^+	1.36	1.36	2.22	94.3
Ag^+	1.35	1.35	2.50	94.0
Li^+	1.35	1.35	2.40	94.4
Na^+	1.35	1.35	2.78	94.1
K^+	1.35	1.35	3.26	94.1
N_2	N1-N2		M-N1	M-N1-N2
gas phase	1.11			
Cu^+	1.10		1.92	180
Ag^+	1.10		2.28	177
Li^+	1.10		2.04	180
Na^+	1.10		2.45	180
K^+	1.10		2.94	180
CO_2	O1-C	O2-C	M-O1	M-O1-C
gas phase	1.17	1.17		
Cu^+	1.18	1.15	1.95	178
Ag^+	1.18	1.15	2.28	180
Li^+	1.19	1.15	1.84	180
Na^+	1.18	1.15	2.23	180
K^+	1.18	1.16	2.67	180

Table S4: ALMO EDA results for CO, H_2O, H_2S, N_2, and CO_2 adsorbed on bare cation M (M = Cu, Ag, Li, Na, and K). All terms are in kJ/mol.

Cu	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.7	-0.8	-0.3	0.0	-2.9
FRZ	-42.2	63.5	6.4	-49.1	-11.2
POL	108.1	73.1	100.9	93.5	81.0
CT(M→X)	33.4	3.9	14.9	19.9	6.4
CT(X→M)	57.5	33.0	85.1	33.3	20.9
HO-CT	6.5	0.9	1.6	3.6	1.1
Total	162.6	173.7	208.7	101.3	95.3
Ag	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.8	-0.5	-0.5	0.0	-2.1
FRZ	-47.8	56.8	-5.7	-24.3	1.3
POL	71.8	40.4	63.1	48.7	43.5
CT(M→X)	18.9	3.0	8.0	7.1	3.3
CT(X→M)	58.4	26.0	93.0	23.6	13.1
HO-CT	4.4	0.6	-1.9	1.5	0.7
Total	104.8	126.4	156.0	56.7	59.7
Li	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.6	-0.1	-0.1	0.0	-3.2
FRZ	20.5	99.8	35.0	7.6	22.8
POL	40.4	37.6	47.0	40.5	54.4
CT(M→X)	0.1	0.2	0.0	0.1	0.2
CT(X→M)	7.5	9.5	19.2	6.1	10.4
HO-CT	0.3	0.4	0.6	0.5	0.3
Total	68.2	147.2	101.7	54.9	85.0
Na	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.4	-0.1	-0.1	0.0	-2.0
FRZ	17.7	82.8	31.6	8.4	22.0
POL	23.8	20.0	30.6	23.1	31.2
CT(M→X)	-0.1	0.0	-0.1	-0.1	0.1
CT(X→M)	1.6	-0.5	5.9	0.8	1.6
HO-CT	0.1	-0.1	0.2	0.1	0.1
Total	42.7	102.3	68.0	32.4	52.9
K	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.2	-0.1	0.0	0.0	-1.3
FRZ	10.1	58.5	19.9	4.4	14.2
POL	12.7	12.4	16.6	12.3	18.1
CT(M→X)	0.1	0.1	0.1	0.1	0.2
CT(X→M)	1.9	3.0	4.2	1.4	2.5
HO-CT	0.1	0.2	0.3	0.2	0.1
Total	22.6	74.1	41.1	18.4	33.7

Table S5: ALMO EDA results for CO, H_2O, H_2S, N_2, and CO_2 adsorbed on bare cation M (M = Cu, Ag, Li, Na, and K). The cations and the adsorbates were held at their positions from the cluster calculations. All terms are in kJ/mol.

Cu	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-1.3	-1.3	-0.4	-2.4	-1.4
FRZ	-85.4	50.7	6.6	-76.4	13.1
POL	120.2	72.2	100.9	105.4	23.6
CT(M→X)	46.5	3.1	14.9	26.9	0.5
CT(X→M)	67.9	40.2	85.2	39.1	9.8
HO-CT	7.6	0.4	1.5	4.6	0.6
Total	155.5	165.3	208.7	97.2	46.2
Ag	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.7	-0.9	-0.2	-1.3	-2.5
FRZ	-97.9	45.8	-4.7	-31.6	7.8
POL	85.9	37.8	64.3	51.9	26.5
CT(M→X)	30.4	1.9	7.8	8.5	0.9
CT(X→M)	73.3	32.3	91.0	25.7	12.2
HO-CT	6.3	0.1	-2.1	1.7	0.7
Total	97.3	117.0	156.1	54.9	45.6
Li	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.3	-1.3	-0.2	-1.0	-1.5
FRZ	21.4	71.9	34.6	12.4	17.7
POL	36.7	31.6	41.9	34.7	40.5
CT(M→X)	0.0	0.1	0.0	0.0	0.0
CT(X→M)	6.6	10.8	17.9	4.7	8.1
HO-CT	0.4	0.4	0.6	0.4	0.3
Total	64.8	113.5	94.8	51.2	65.1
Na	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.3	-1.3	-0.8	-1.1	-2.2
FRZ	16.0	51.9	28.8	9.8	13.4
POL	22.1	18.6	26.9	20.8	24.6
CT(M→X)	-0.1	0.0	-0.1	-0.1	-0.1
CT(X→M)	1.7	1.9	5.7	0.8	2.5
HO-CT	0.1	0.1	0.2	0.1	0.2
Total	39.5	71.2	60.7	30.3	38.4
K	CO	H_2O	H_2S	N_2	CO_2
GD(X)	-0.6	-2.7	-1.9	-1.1	-3.6
FRZ	10.1	39.9	13.9	5.5	9.3
POL	11.4	10.6	16.6	10.6	14.2
CT(M→X)	0.1	0.0	0.1	0.1	0.1
CT(X→M)	1.5	3.3	4.7	1.0	2.3
HO-CT	0.1	0.2	0.3	0.1	0.2
Total	22.6	51.3	33.7	16.2	22.5

Table S6: ALMO EDA results for CO, H_2O, H_2S, N_2, and CO_2 adsorbed on MY zeolite cluster (M = Cu, Ag, Li, Na, and K). All terms are in kJ/mol.

CuY	CO	H_2O	H_2S	N_2	CO_2
GD(MY)	-38.8	-52.8	-48.4	-35.6	-1.8
GD(X)	-1.3	-1.3	-0.4	-2.4	-1.4
FRZ	-103.7	10.1	-22.9	-100.3	-2.8
POL	95.3	59.4	60.5	76.2	6.6
CT(MY→X)	96.3	11.5	24.5	64.2	2.5
CT(X→MY)	52.3	28.0	52.0	30.0	2.3
HO-CT	1.4	1.3	4.1	2.3	-0.1
Total	101.5	56.2	69.4	34.4	5.3
AgY	CO	H_2O	H_2S	N_2	CO_2
GD(MY)	-9.1	-12.1	-11.6	-4.8	-1.6
GD(X)	-0.7	-0.9	-0.3	-1.3	-2.5
FRZ	-107.9	3.6	-26.4	-45.4	-1.0
POL	69.6	33.7	36.6	31.3	12.9
CT(MY→X)	56.8	8.7	14.7	18.1	3.3
CT(X→MY)	57.4	20.6	55.2	18.2	5.4
HO-CT	7.5	0.6	2.3	2.9	0.5
Total	73.6	54.2	70.5	19.0	17.0
LiY	CO	H_2O	H_2S	N_2	CO_2
GD(MY)	-1.4	-12.9	-3.0	-0.6	-2.5
GD(X)	-0.3	-1.3	-0.2	-1.0	-1.5
FRZ	4.1	33.1	12.7	-0.7	6.7
POL	9.6	22.1	10.5	8.2	12.0
CT(MY→X)	1.0	8.8	0.5	0.8	0.5
CT(X→MY)	4.5	5.1	6.5	3.0	3.6
HO-CT	-0.1	0.7	0.2	-0.1	-0.2
Total	17.4	55.6	27.2	9.6	18.6
NaY	CO	H_2O	H_2S	N_2	CO_2
GD(MY)	-0.4	-5.5	-4.9	0.1	-1.3
GD(X)	-0.4	-1.3	-0.8	-1.1	-2.3
FRZ	6.5	39.2	12.5	4.6	12.3
POL	7.3	18.0	15.9	5.1	11.6
CT(MY→X)	1.2	8.9	10.6	-0.2	1.3
CT(X→MY)	1.0	-0.7	1.6	0.6	0.8
HO-CT	0.0	0.4	0.5	-0.1	-0.4
Total	15.2	59.0	35.4	9.0	22.0
KY	CO	H_2O	H_2S	N_2	CO_2
GD(MY)	-0.4	-6.2	-2.5	-0.3	-0.9
GD(X)	-0.6	-2.7	-1.9	-1.1	-3.7
FRZ	2.0	32.1	-0.9	1.8	11.3
POL	6.7	20.2	20.8	4.3	10.6
CT(MY→X)	3.1	16.5	20.6	0.5	3.9
CT(X→MY)	1.1	1.8	2.6	0.7	1.5
HO-CT	0.1	0.7	1.1	-0.4	0.2
Total	12.0	62.4	39.8	5.5	22.9