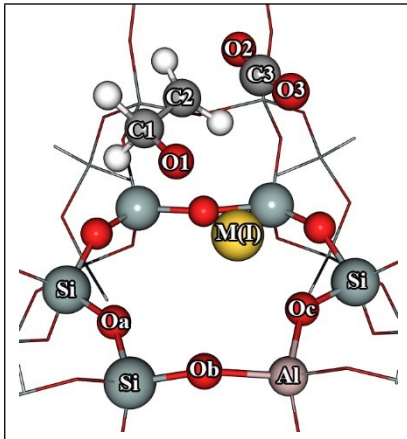
Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Effects of Lewis acid strength of monovalent coinage metals and zeolite frameworks on catalytic CO_2 cycloaddition with ethylene oxide: A DFT study

Winyoo Sangthong[a,b] and Jakkapan Sirijaraensre[b,c*]

[a.] *Research Network of NANOTEC–KU on NanoCatalysts and NanoMaterials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand*
[b.] *Center for Advanced Studies in Nanotechnology for Chemical, Food, and Agricultural Industries, Kasetsart University Institute for Advanced Studies, Kasetsart University, Bangkok 10900, Thailand*
[c.] *Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand. E-mail: fscijkp@ku.ac.th*

Table S1. Optimized geometrical parameters and NBO charge for the species involved in the CO_2 cycloaddition with EO on Cu(I)-, Ag(I)-, and Au(I)-FAU zeolites with the atomic labels based on the TS structure in the inset figure.

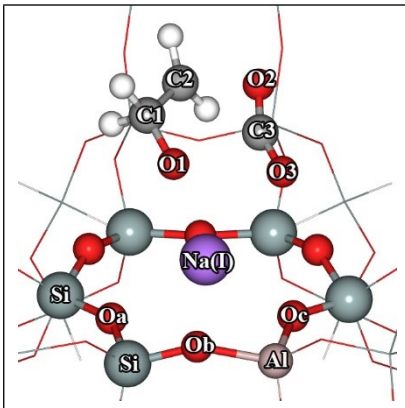


Parameters	Cu(I)-FAU				Ag(I)-FAU				Au(I)-FAU			
	Isolated	EO_ADS	TS	PROD	Isolated	EO_ADS	TS	PROD	Isolated	EO_ADS	TS	PROD
Distances (Å)												
C1-C2	1.46	1.46	1.45	1.52	1.46	1.46	1.44	1.53	1.46	1.46	1.45	1.52
C1-O1	1.42	1.44	1.35	1.44	1.42	1.43	1.33	1.44	1.42	1.46	1.36	1.45
C2-O1	1.42	1.43	2.37	2.32	1.42	1.43	2.33	2.32	1.42	1.45	2.38	2.33
C2-O2	-	-	1.93	1.44	-	-	2.04	1.44	-	-	1.98	1.44
C3-O1	-	-	2.43	1.34	-	-	2.30	1.34	-	-	2.44	1.32
C3-O2	1.17	-	1.20	1.33	1.17	-	1.20	1.33	1.17	-	1.20	1.33
C3-O3	1.17	-	1.16	1.22	1.17	-	1.16	1.21	1.17	-	1.16	1.23
M-O1	-	2.05	1.91	-	-	2.37	2.22	-	-	2.15	2.07	-
M-O3	-	-	-	1.99	-	-	-	2.39	-	-	-	2.14
Metal-zeolite distances (Å)												
M-Al	2.86	2.88	2.89	2.81	3.18	3.19	3.15	3.17	3.09	3.04	3.15	3.17
M-Oa	2.11	2.37	2.66	2.40	2.38	2.51	2.57	2.51	2.34	3.26	3.25	3.30
M-Ob	2.46	2.46	2.55	2.26	2.75	2.74	2.67	2.71	2.81	2.93	3.03	3.07
M-Oc	2.02	2.04	1.99	2.12	2.28	2.33	2.38	2.35	2.21	2.14	2.18	2.16
Angle (°)												
C2-O2-C3	-	-	117.2	108.9	-	-	113.0	109.3	-	-	117.2	108.8
C2-C1-O1	59.1	59.3	115.6	102.9	59.1	59.4	114.1	103.0	59.1	59.9	116.4	102.9
O1-C3-O2	-	-	93.4	112.7	-	-	94.9	112.2	-	-	92.6	113.6
O1-C3-O3	-	-	102.2	124.3	-	-	100.9	123.1	-	-	100.4	125.1
O2-C3-O3	-	-	164.1	123.0	-	-	164.2	124.7	-	-	167.0	121.3
M-O3-C3	-	-	-	126.8	-	-	-	111.2	-	-	-	129.3
NBO charge (*e*)												
M	+0.73	+0.69	+0.60	+0.68	+0.76	+0.74	+0.72	+0.72	+0.61	+0.56	+0.46	+0.59
EO	0.00	+0.06	+0.02	-	0.00	+0.05	–0.01	-	0.00	+0.15	+0.11	-
CO_2	0.00	-	+0.13	-	0.00	-	+0.09	-	0.00	-	+0.14	-
EC	0.00	-	-	+0.09	0.00	-		+0.07	0.00	-	-	+0.15

Table S2. Calculated Wiberg bond order for the species involved in the CO_2 cycloaddition with EO on Cu(I)-, Ag(I)-, and Au(I)-FAU zeolites.

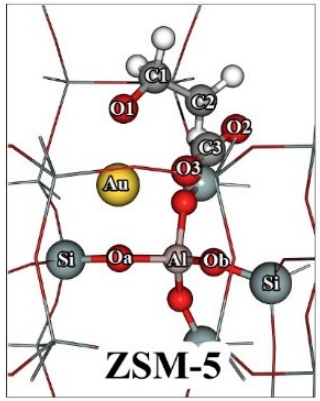
Parameters	Cu(I)-FAU				Ag(I)-FAU				Au(I)-FAU			
	Isolated	**EO_ADS**	**TS**	**PROD**	**Isolated**	**EO_ADS**	**TS**	**PROD**	**Isolated**	**EO_ADS**	**TS**	**PROD**
Wiberg bond order												
C1-C2	1.022	1.025	1.138	1.012	1.022	1.025	1.163	1.010	1.022	1.031	1.156	1.011
C1-O1	0.928	0.866	1.062	0.863	0.928	0.882	1.093	0.864	0.928	0.849	1.037	0.852
C2-O1	0.928	0.874	0.153	0.015	0.928	0.885	0.188	0.014	0.928	0.849	0.133	0.014
C2-O2	-	-	0.333	0.867	-	-	0.266	0.869	-	-	0.301	0.865
C3-O1	-	-	0.112	1.051	-	-	0.122	1.026	-	-	0.093	1.089
C3-O2	1.888	-	1.593	1.062	1.888	-	1.633	1.054	1.888	-	1.630	1.081
C3-O3	1.888	-	1.995	1.565	1.888	-	1.976	1.626	1.888	-	2.001	1.509
M-O1	-	0.152	0.316	-	-	0.102	0.176	-	-	0.274	0.438	-
M-O3	-	-	-	0.196	-	-	-	0.111	-	-	-	0.260
Wiberg bond order (Metal-zeolite)												
M-Al	0.032	0.031	0.037	0.033	0.018	0.020	0.021	0.020	0.033	0.044	0.034	0.033
M-Oa	0.138	0.085	0.056	0.085	0.085	0.062	0.056	0.069	0.158	0.018	0.018	0.017
M-Ob	0.061	0.076	0.079	0.118	0.051	0.052	0.060	0.059	0.050	0.034	0.029	0.031
M-Oc	0.189	0.172	0.211	0.157	0.129	0.111	0.089	0.104	0.263	0.329	0.276	0.311

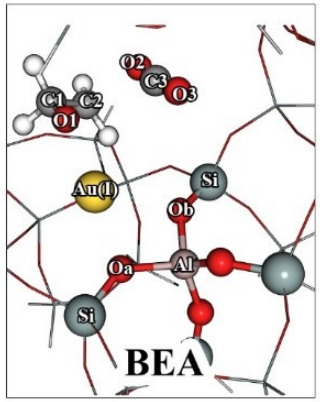
Table S3. Optimized geometrical parameters and NBO charge for the species involved in the CO_2 cycloaddition with EO on Na-FAU zeolite with the atomic labels based on the TS structure in the inset figure.



Parameters	Isolated	EO_ADS	TS	PROD
Distances (Å)				
C1-C2	1.46	1.46	1.43	1.52
C1-O1	1.42	1.43	1.32	1.44
C2-O1	1.42	1.43	2.33	2.32
C2-O2	-	-	2.11	1.44
C3-O1	-	-	2.07	1.35
C3-O2	1.17	-	1.20	1.34
C3-O3	1.17	-	1.18	1.21
Na-O1	-	2.31	2.25	-
Na-O3	-	-	-	2.30
Na-zeolite distances (Å)				
Na-Al	3.12	3.12	3.09	3.09
Na-Oa	2.34	2.40	2.47	2.45
Na-Ob	2.64	2.63	2.58	2.60
Na-Oc	2.24	2.27	2.31	2.27
Angle (°)				
C2-O2-C3	-	-	108.1	109.2
C2-C1-O1	59.1	59.4	115.8	102.9
O1-C3-O2	-	-	101.6	112.0
O1-C3-O3	-	-	102.2	123.1
O2-C3-O3	-	-	156.2	124.9
Na-O3-C3	-	-	-	116.9
NBO charge (*e*)				
Na	+0.95	+0.94	+0.93	+0.94
EO	0.00	+0.01	+0.04	-
CO_2	0.00	-	–0.03	-
EC	0.00	-	-	+0.01

Table S4. Optimized geometrical parameters and NBO charge for the species involved in the CO_2 cycloaddition with EO on Au(I)-ZSM-5 and Au(I)-BEA zeolites with the atomic labels based on TS structure in the inset figure.





Parameters	Au(I)-ZSM-5				Au(I)-BEA			
	Isolated	EO_ADS	TS	PROD	Isolated	EO_ADS	TS	PROD
Distances (Å)								
C1-C2	1.46	1.45	1.46	1.52	1.46	1.46	1.45	1.52
C1-O1	1.42	1.46	1.36	1.44	1.42	1.45	1.35	1.45
C2-O1	1.42	1.46	2.40	2.30	1.42	1.46	2.39	2.31
C2-O2	-	-	1.94	1.45	-	-	1.95	1.45
C3-O1	-	-	2.52	1.32	-	-	2.63	1.33
C3-O2	1.17	-	1.20	1.32	1.17	-	1.19	1.33
C3-O3	1.17	-	1.16	1.23	1.17	-	1.16	1.23
Au-O1	-	2.16	2.06	-	-	2.16	2.07	-
Au-O3	-	-	-	2.19	-	-	-	2.16
Au-zeolite distances (Å)								
Au-Al	3.15	3.11	3.09	3.07	3.08	3.09	3.17	3.15
Au-Oa	2.30	2.15	2.18	2.18	2.40	2.15	2.17	2.16
Au-Ob	2.35	2.69	3.19	2.75	2.36	2.78	2.98	2.90
Angle (°)								
C2-O2-C3	-	-	118.3	107.7	-	-	116.4	108.1
C2-C1-O1	59.1	60.1	116.9	101.9	59.1	60.1	116.9	102.3
O1-C3-O2	-	-	92.2	113.4	-	-	88.7	113.4
O1-C3-O3	-	-	97.9	123.1	-	-	99.0	123.9
O2-C3-O3	-	-	169.4	123.5	-	-	172.1	122.7
Au-O3-C3	-	-	-	106.9	-	-	-	118.2
NBO charge (*e*)								
Au	+0.72	+0.57	+0.46	+0.61	+0.72	+0.56	+0.45	+0.58
EO	0.00	+0.15	+0.11	-	0.00	+0.15	+0.10	-
CO_2	0.00	-	+0.16	-	0.00	-	+0.17	-
EC	0.00	-	-	+0.15	0.00	-	-	+0.15

Table S5. Relative energies with respect to the reactants of the CO_2 cycloaddition with EO on Au(I)-exchanged zeolites calculated with the M06-L/6-31G(d,p) level of theory.

	Relative energy (kcal/mol)					
	Au(I)-FAU		Au(I)-ZSM-5		Au(I)-BEA	
Systems	**30T (Optimized)**	**6T (Single point)**	**34T (Optimized)**	**5T (Single point)**	**38T (Optimized)**	**5T (Single point)**
ADS	−24.1	−19.0	−34.5	−29.0	−32.7	−29.3
TS	10.0	19.5	−8.7	−0.1	−4.6	3.6
PROD	−38.2	−28.8	−47.5	−41.9	−49.6	−41.2
E_a	34.1	38.5	25.8	28.9	28.1	32.9
E_{des}	27.5	18.2	36.8	31.2	39.0	30.6