Supporting Information

Adsorptive Separation of Geometric Isomers of 2-Butene on Gallate-based Metal-organic Frameworks

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Calculation Procedures

Calculation of selectivity

The single-component adsorption isotherms of C_4 hydrocarbons were correlated by the Langmuir model at low pressure of 0-5 kPa because the Langmuir model worked well for linear isotherms. The Langmuir equation parameters for these isotherms are summarized in Table S2-S7.

$$q = \frac{q_m b p}{1 + b p} \qquad (1)$$

q, the adsorbed amount of the pure component i (mmol·g^{-1}); p, the pressure of the bulk gas at equilibrium (kPa); q_m, the saturated adsorption capacities (mmol·g^{-1}); b, the affinity parameters of the pure component (kPa^{-1}).

To estimate the separation selectivity of Ni-gallate, Mg-gallate and Co-gallate, Henry's selectivity (α_{ij}) were developed and applied, which reflected separation selectivity at low pressure about 0-5 kPa. The Henry's selectivity (α_{ij}) based on equilibrium alone can be calculated from the ratio of Henry's constants, $H=q_m \times b$. The values of q_{mi}, q_{mj}, b_i, b_j, H_i, H_j are showed in Table S2-S7.[1]

$$\alpha_{ij} = \frac{H_i}{H_j} = \frac{q_{mi} b_i}{q_{mj} b_j} \qquad (2)$$

Calculation of heat of adsorption

The slopes of linear van't Hoff plots (ln K vs. 1/T) allow us to determine the zero-coverage adsorption enthalpy. Langmuir equation was used to correlate the equilibrium isotherm data and to obtain the Henry constants. The adsorption enthalpies at zero coverage were calculated from Henry constants using the van't Hoff equation.[2]

$$\frac{d \ln K}{dT} = \frac{\Delta H}{R T^2} \qquad (3)$$

Figures

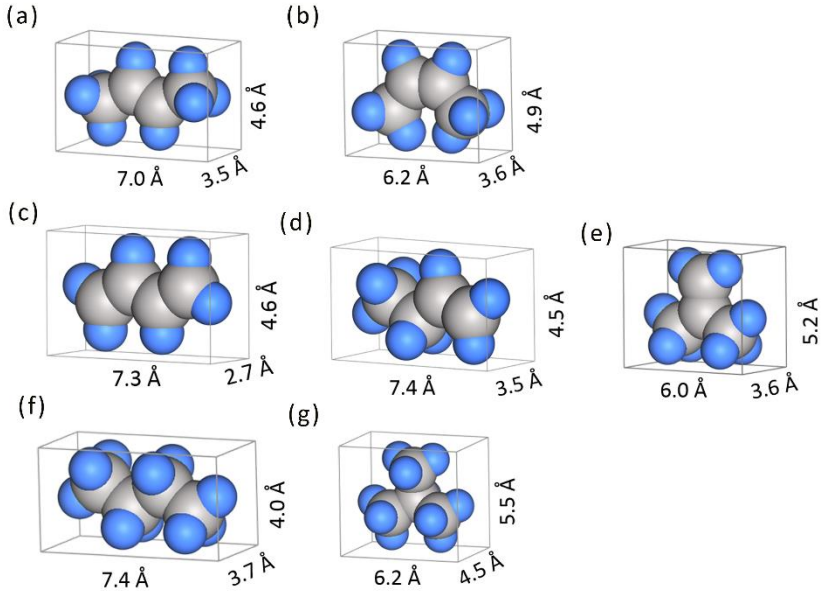

Figure S1. Van der Waals molecular dimensions of C_4 hydrocarbons: (a) *trans*-2-butene, (b) *cis*-2-butene. (c) 1,3-butadiene, (d) 1-butene, (e) *iso*-butene, (f) *n*-butane, (g) *iso*-butane.

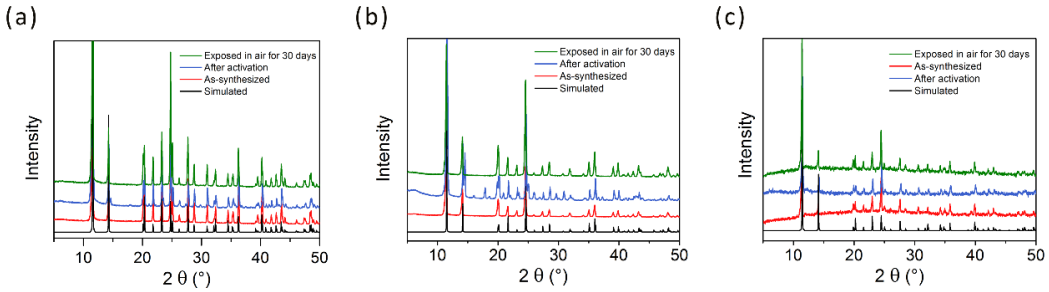

Figure S2. PXRD patterns of (a) Ni-gallate, (b) Mg-gallate, and (c) Co-gallate.

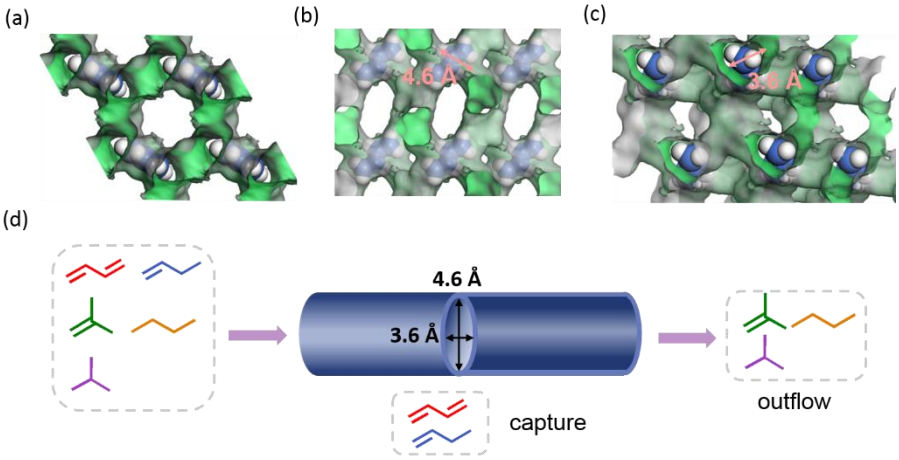

Figure S3. (a, b, c) Accessible Connolly surface calculated with a Connolly radius of 1.0 Å. The oval-shaped cages are restrained by a narrow window. The adsorbed molecule in the cages is 1,3-butadiene. Cross-section size of Mg-gallate measures 4.6×3.6 $Å^2$. The C atoms and H atoms in 1,3-butadiene are respectively presented in blue and white. (d) Schematic diagram of the shape-size selective separation of 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane based on the molecular cross-section size in Mg-gallate (3.6×4.6 $Å^2$).

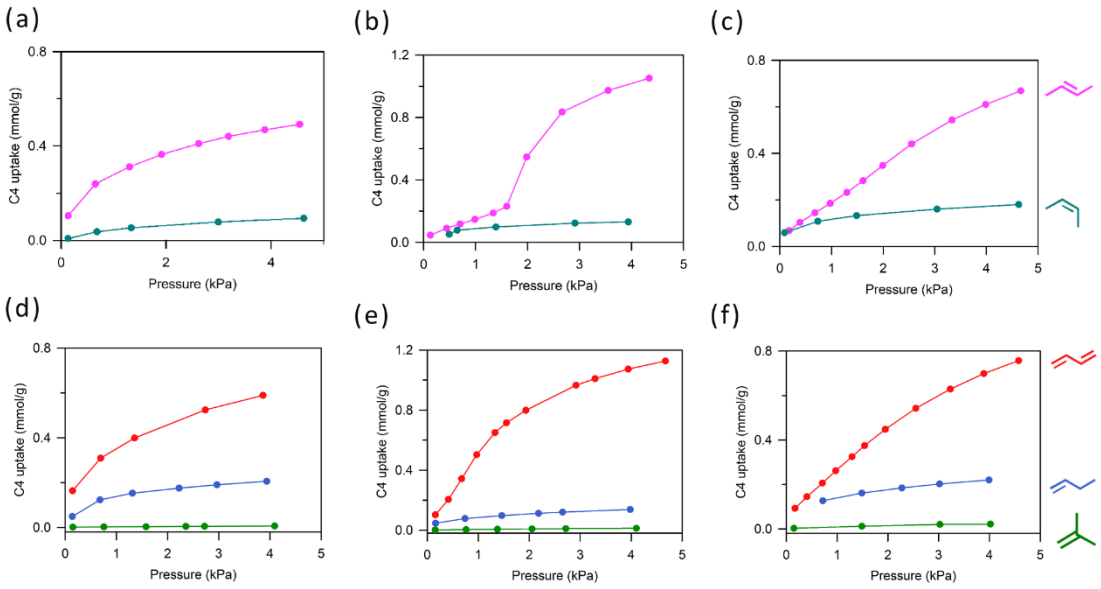

Figure S4. Adsorption isotherms of *trans*-2-butene (pink), *cis*-2-butene (cyan), 1,3-butadiene(red), 1-butene (blue), *iso*-butene (dark green) on Ni-gallate (a, d), Mg-gallate (b, e), Co-gallate (c, f) at 298 K, 0-5 kPa.

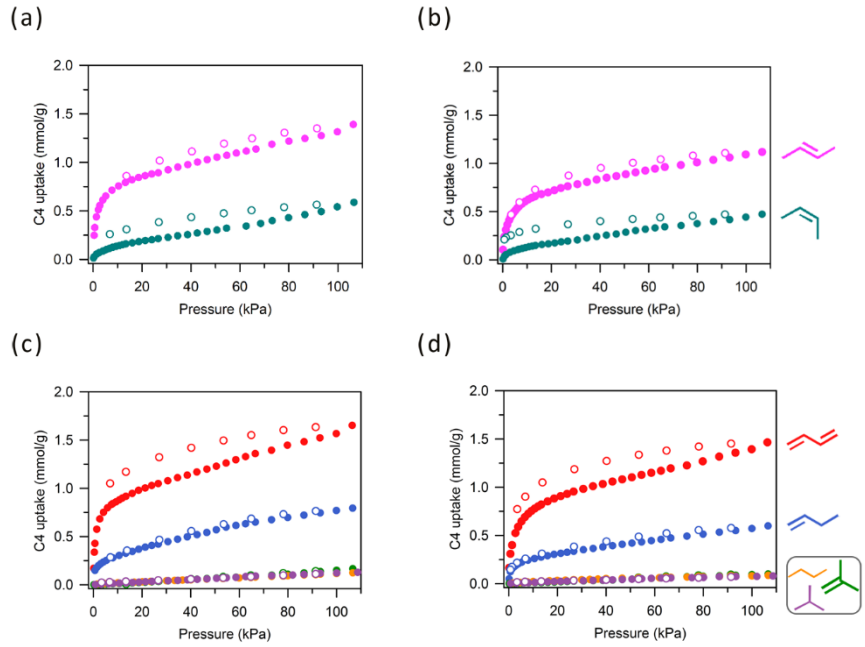

Figure S5. Adsorption isotherms of *trans*-2-butene (pink), *cis*-2-butene (cyan), 1,3-butadiene (red), 1-butene (blue), *iso*-butene (dark green), *n*-butane (orange), *iso*-butane (purple) on Ni-gallate, (a, c) 283K; (b,d) 298K.

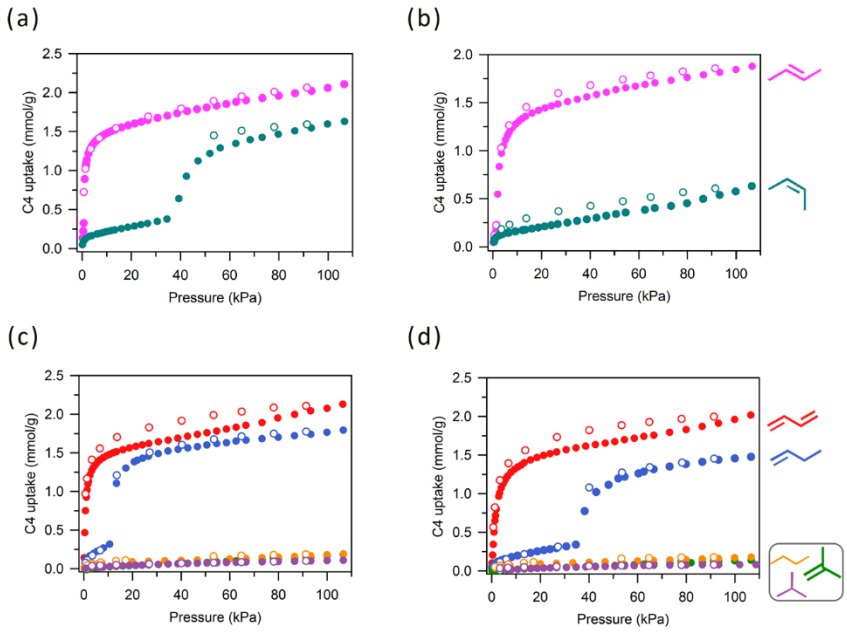

Figure S6. Adsorption isotherms of *trans*-2-butene (pink), *cis*-2-butene (cyan), 1,3-butadiene (red), 1-butene (blue), *iso*-butene (dark green), *n*-butane (orange), *iso*-butane (purple) on Mg-gallate, (a, c) 283K; (b, d) 298K..

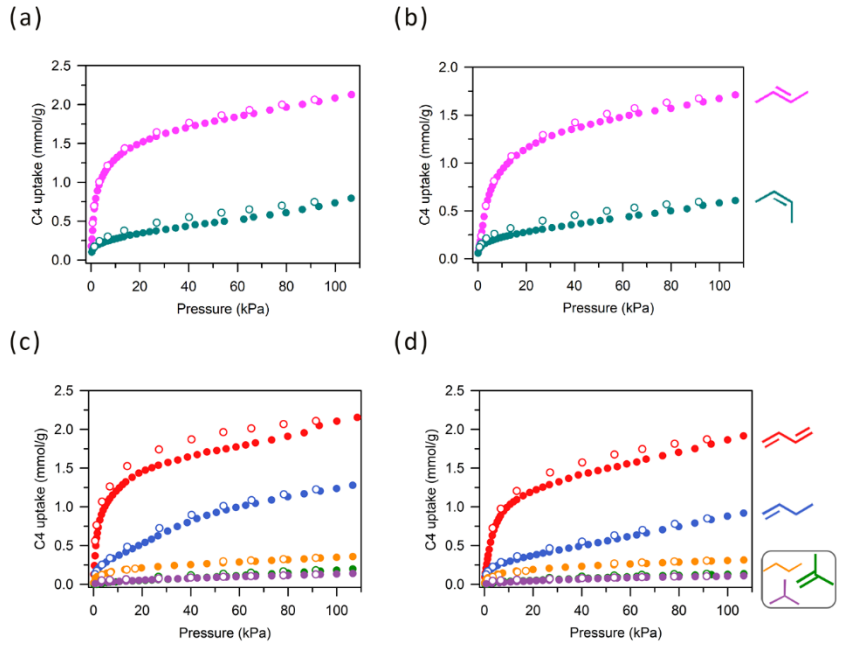

Figure S7. Adsorption isotherms of *trans*-2-butene (pink), *cis*-2-butene (cyan), 1,3-butadiene (red), 1-butene (blue), *iso*-butene (dark green), *n*-butane (orange), *iso*-butane (purple) on Co-gallate, (a, c) 283K; (b, d) 298K.

Tables

Table S1. Physical properties of C_4 hydrocarbons.[3-5]

Adsorbates	Molecular dimension (Å^3)	MIN-1×MIN-2 (Å^2)	Boiling point (K)	Polarizability (10^{-25} cm^3)	Dipole Moment (D)	Concentration in C_4 mixture (%)
trans-2-butene	3.5×4.6×7.0	3.5×4.6	274.03	7.501	0	5.1
cis-2-butene	3.6×4.9×6.2	3.6×4.9	276.87	7.367	0.253	4.0
1,3-butadiene	2.7×4.6×7.3	2.7×4.6	268.3	7.624	0	39.5
1-butene	3.5×4.5×7.4	3.5×4.5	266.92	7.351	0.359-0.438	13.0
iso-butene	3.6×5.2×6.0	3.6×5.2	266.25	7.347	0.550	27.2
n-butane	3.7×4.0×7.4	3.7×4.0	272.65	7.538-7.605	0	7.3
iso-butane	4.5×5.5×6.2	4.5×5.5	261.65	7.595	0.132	3.6

Table S2. Langmuir fit parameters for *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane in Ni-gallate at 283 K and 0-5 kPa.

Adsorbates	q_m (mmol·g^{-1})	b (kPa^{-1})	$q_m \times b$	R^2
trans-2-butene	0.74	1.15	0.8536	0.9936
cis-2-butene	0.11	0.75	0.0832	0.9945
1,3-butadiene	0.86	1.56	1.3526	0.9959
1-butene	0.27	1.62	0.4366	0.9459
iso-butene	8.23E11	1.72E-15	0.0014	0.9932
n-butane	0.03	0.13	0.0043	0.9798
iso-butane	0.08	0.03	0.0019	0.9943

Table S3. Langmuir fit parameters for *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane in Ni-gallate at 298 K and 0-5 kPa.

Adsorbates	q_m (mmol·g^{-1})	b (kPa^{-1})	$q_m \times b$	R^2
trans-2-butene	0.60	0.92	0.5499	0.9858
cis-2-butene	0.13	0.54	0.0694	0.9981
1,3-butadiene	0.73	1.07	0.7776	0.9736
1-butene	0.24	1.47	0.3522	0.9885
iso-butene	0.04	0.04	0.0014	0.9973
n-butane	0.04	0.09	0.0041	0.9930
iso-butane	0.04	0.04	0.0017	0.9914

Table S4. Langmuir fit parameters for *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane in Mg-gallate at 283 K and 0-5 kPa.

Adsorbates	q_m (mmol·g^{-1})	b (kPa^{-1})	$q_m \times b$	R^2
trans-2-butene	0.63	1.49	0.9388	0.9274
cis-2-butene	0.22	1.01	0.2271	0.9564
1,3-butadiene	1.61	1.21	1.9515	0.9935
1-butene	0.21	1.36	0.2878	0.9803
iso-butene	0.03	0.24	0.0072	0.9950
n-butane	0.07	0.82	0.0615	0.9791
iso-butane	0.03	0.17	0.0060	0.9789

Table S5. Langmuir fit parameters for *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane in Mg-gallate at 298 K and 0-5 kPa.

Adsorbates	q_m (mmol·g^{-1})	b (kPa^{-1})	$q_m \times b$	R^2
trans-2-butene	0.24	1.45	0.3516	0.9829
cis-2-butene	0.19	0.64	0.1184	0.9808
1,3-butadiene	1.73	0.42	0.7339	0.9950
1-butene	0.16	1.22	0.2003	0.9711
iso-butene	0.02	0.30	0.0069	0.9984
n-butane	0.08	0.69	0.0544	0.9921
iso-butane	0.03	0.22	0.0057	0.9906

Table S6. Langmuir fit parameters for *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane in Co-gallate at 283 K and 0-5 kPa.

Adsorbates	q_m (mmol·g^{-1})	b (kPa^{-1})	$q_m \times b$	R^2
trans-2-butene	0.97	1.11	1.0767	0.9455
cis-2-butene	0.27	1.37	0.3661	0.9413
1,3-butadiene	1.37	0.58	0.7997	0.9987
1-butene	0.30	1.16	0.3540	0.9668
iso-butene	0.06	0.12	0.0070	0.9877
n-butane	0.16	1.20	0.1952	0.9908
iso-butane	0.07	0.09	0.0064	0.9883

Table S7. Langmuir fit parameters for *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-butene, *iso*-butene, *n*-butane and *iso*-butane in Co-gallate at 298 K and 0-5 kPa.

Adsorbates	q_m (mmol·g^{-1})	b (kPa^{-1})	$q_m \times b$	R^2
trans-2-butene	0.33	1.24	0.4080	0.9848
cis-2-butene	0.23	1.01	0.2358	0.9434
1,3-butadiene	1.50	0.22	0.3331	0.9971
1-butene	0.32	0.66	0.2124	0.9486
iso-butene	0.08	0.07	0.0053	0.9971
n-butane	0.15	0.98	0.1492	0.9936
iso-butane	0.05	0.11	0.0053	0.9926

Table S8. Comparison of separation selectivity based on uptake ratio of various materials.

Adsorbents	Temperature (K)	Pressure (kPa)	Uptake (mmol·g^{-1})			Uptake selectivity			Ref.
			C_4H_6	*n*-C_4H_8	*i*-C_4H_8	C_4H_6/*n*-C_4H_8	C_4H_6/*i*-C_4H_8	*n*-C_4H_8/*i*-C_4H_8	
Mg-gallate	298	101	1.96	1.46	0.13	1.3	15.1	11.2	This work
Co-gallate	298	101	1.86	0.88	0.13	2.1	14.3	6.8	This work
Ni-gallate	298	101	1.39	0.57	0.09	2.4	15.4	6.3	This work
TIFSIX-2-Cu-i	298	101	4.05	3.67	2.90	1.1	1.4	1.3	[6]
SIFSIX-2-Cu-i	298	101	3.99	3.06	1.74	1.3	2.3	1.8	[6]
GeFSIX-2-Cu-i	298	101	3.67	3.3	1.25	1.1	2.9	2.3	[6]
NbFSIX-2-Cu-i	298	101	2.64	2.26	0.48	1.2	5.7	5.0	[6]
GeFSIX-14-Cu-i	298	101	2.67	0.57	0.42	4.7	6.4	1.4	[6]
SIFSIX-3-Ni	298	101	2.46	2.45	0.52	1.0	4.7	4.7	[6]
SIFSIX-1-Cu	298	101	6.75	6.43	6.28	1.1	1.1	1.0	[6]
AgY zeolite	343	101	1.45	1.25	-	1.2	-	-	[7]
5A zeolite	393	101	2.60	1.90	-	1.4	-	-	[7]
NaY	393	101	2.60	2.30	-	1.1	-	-	[7]
NaX	298	100	2.23	1.78	-	1.3	-	-	[3]
CuY	393	100	4.0	3.2	-	1.3	-	-	[8]
DD3R	303	101	0.83	-	-	-	-	-	[9]
ZJNU-30a	298	100	10.63	10.7	9.14	1.0	1.2	1.2	[10]
ZJNU-80a	298	101	8.35	8.35	6.80	1.0	1.2	1.2	[11]
NOTT-101a	298	101	9.28	9.28	9.15	1.0	1.0	1.0	[11]
Zn-ZIF-8	298	101	5.35	4.91	-	1.1	-	-	[3]
Al-MIL-53	298	101	4.46	3.57	-	1.3	-	-	[3]
SD-65	298	101	1.78	0.08	0.07	22.3	25.4	1.1	[3]
$Zn(Hmpba)_2$	303	100	3.10	2.80	2.80	1.1	1.1	1	[12]
$Cu4(m_4\text{-}O)(m_2\text{-}OH)_2(Me_2trz\text{-}pba)_4$	298	100	-	4.10	4.35	-	-	0.9	[13]
Mg-DOBDC	-	-	6.56	6.35	6.35	1.0	1.0	1.0	[14]
Co-DOBDC	-	-	5.90	5.60	5.60	1.1	1.1	1.0	[14]
Zn-EIM-RHO	-	-	5.00	5.25	5.25	1.0	1.0	1.0	[14]

Table S9. Comparison of Henry's selectivity (α_{ij}) of various materials.

Adsorbents	Temperature (K)	Pressure (kPa)	$\alpha_{C4H6/n\text{-}C4H8}$	$\alpha_{C4H6/i\text{-}C4H8}$	$\alpha_{n\text{-}C4H8/i\text{-}C4H8}$	Ref.
Mg-gallate	298	101	3.7	106	29	This work
Co-gallate	298	101	1.6	63	40	This work
Ni-gallate	298	101	2.2	148	67	This work
GeFSIX-14-Cu-i	298	101	85.8	111	1.3	[6]
GeFSIX-2-Cu-i	298	101	4.0	5.4	1.4	[6]
NbFSIX-2-Cu-i	298	101	1.0	142	138	[6]
SIFSIX-2-Cu-i	298	101	3.2	4.6	1.5	[6]
SIFSIX-1-Cu	298	101	0.5	1.6	3.4	[6]
AgY zeolite	343	101	1.5	-	-	[7]
5A zeolite	393	101	2.1	-	-	[7]
NaY zeolite	393	101	2.2	-	-	[7]
NaX zeolite	298	100	1.5	-	-	[3]
Zn-ZIF-8	298	101	0.7	-	-	[3]
Al-MIL-53	298	101	1.0	-	-	[3]
SD-65	298	101	3.4	3.7	1.1	[3]
$Zn(Hmpba)_2$	303	100	1.4	3.0	2.1	[12]

Table S10. C_4 uptakes ($mmol \cdot g^{-1}$) and Qst ($kJ \cdot mol^{-1}$) of Ni, Mg, Co-gallate at 298 K and 1.0 bar.

	Ni-gallate	Mg-gallate	Co-gallate
trans-2-butene uptake	1.09	1.85	1.67
cis-2-butene uptake	0.44	0.58	0.58
1,3-butadiene uptake	1.39	1.96	1.86
1-butene uptake	0.57	1.46	0.88
iso-butene uptake	0.09	0.13	0.13
n-butane uptake	0.08	0.17	0.31
iso-butane uptake	0.07	0.08	0.10
Qst of *trans*-2-butene	20.6	45.9	45.4
Qst of *cis*-2-butene	10.3	30.4	20.6
Qst of 1,3-butadiene	25.9	45.7	40.9
Qst of 1-butene	10.0	16.9	23.9
Qst of *iso*-butene	2.7	5.68	13.2
Qst of *n*-butane	1.7	1.77	12.6
Qst of *iso*-butane	0.008	1.66	8.3

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