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Mesoporous alumina-zirconia-organosilica composites for CO_2 capture at ambient and elevated temperatures

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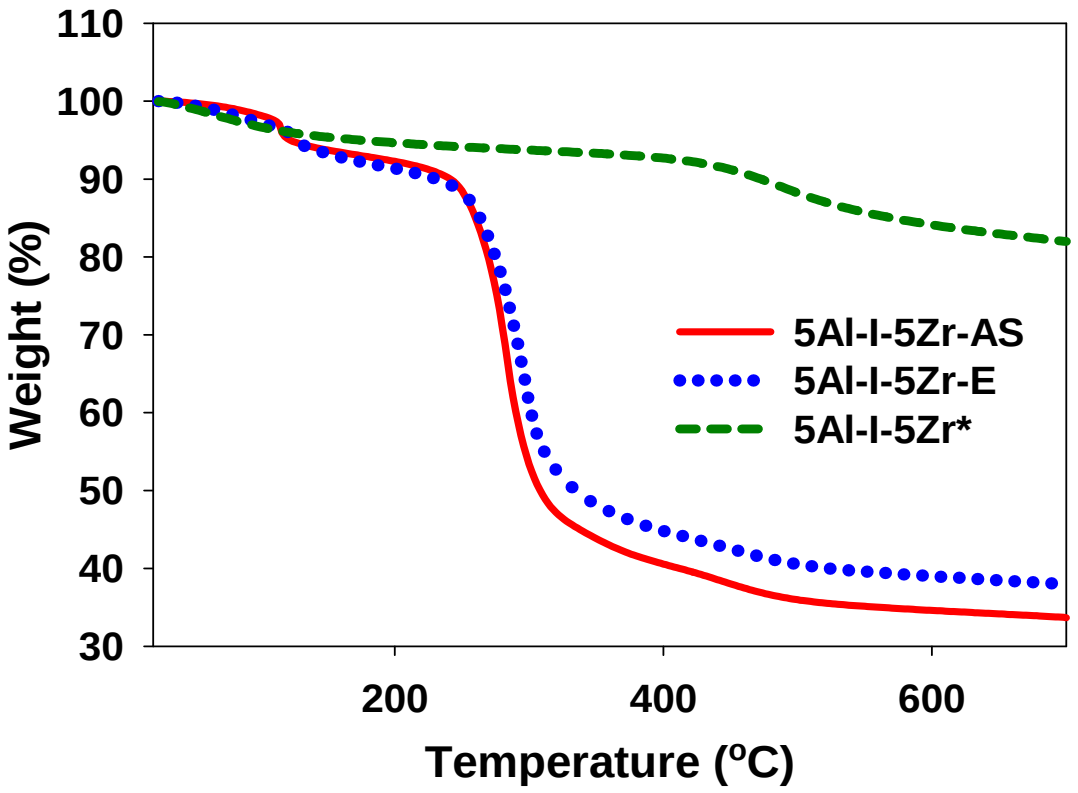

Figure S1. TG profiles of the as-synthesized (AS), extracted (E), and thermally treated (*)samples.

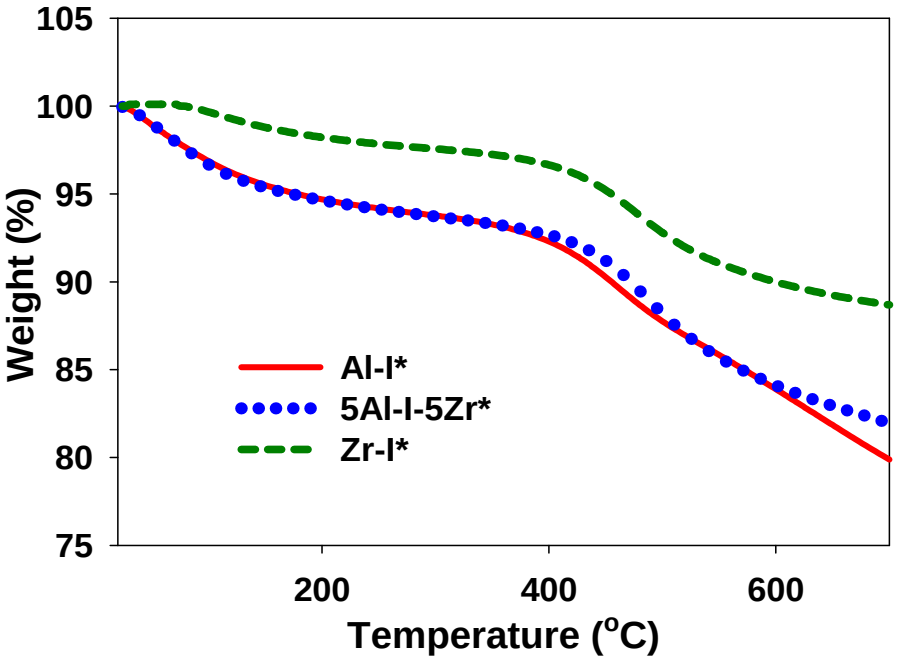

Figure S2. TG profiles of the extracted-thermally treated (*) samples.

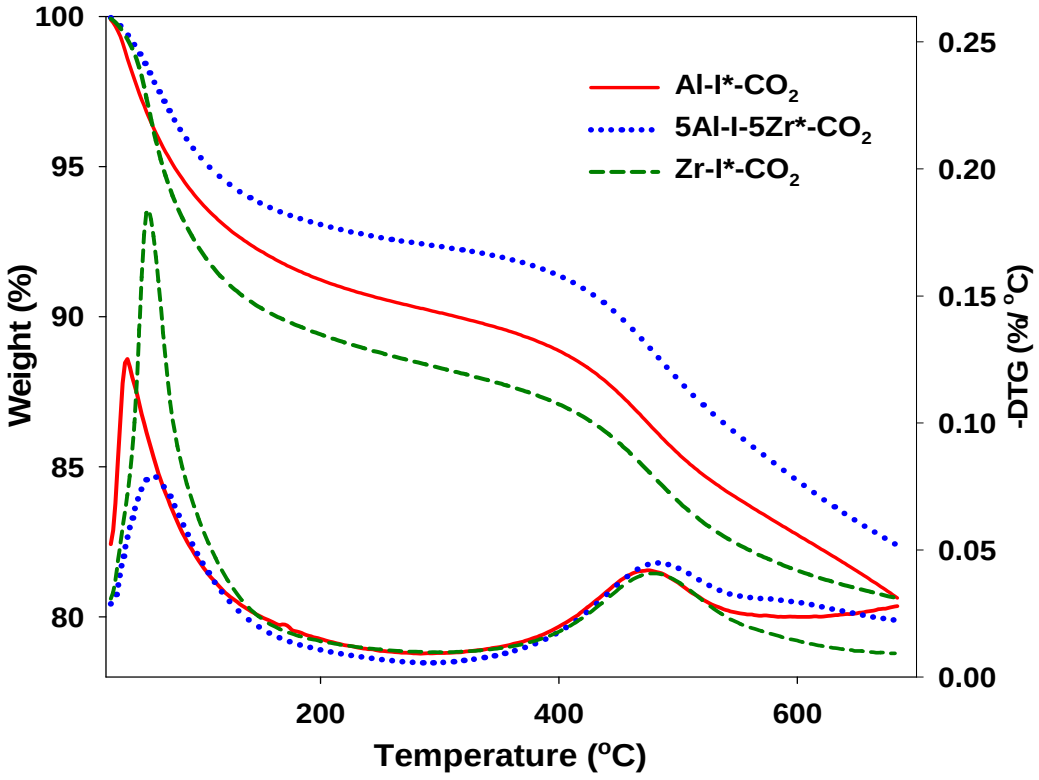

Figure S3. TG and DTG profiles of the samples with chemisorbed CO_2.

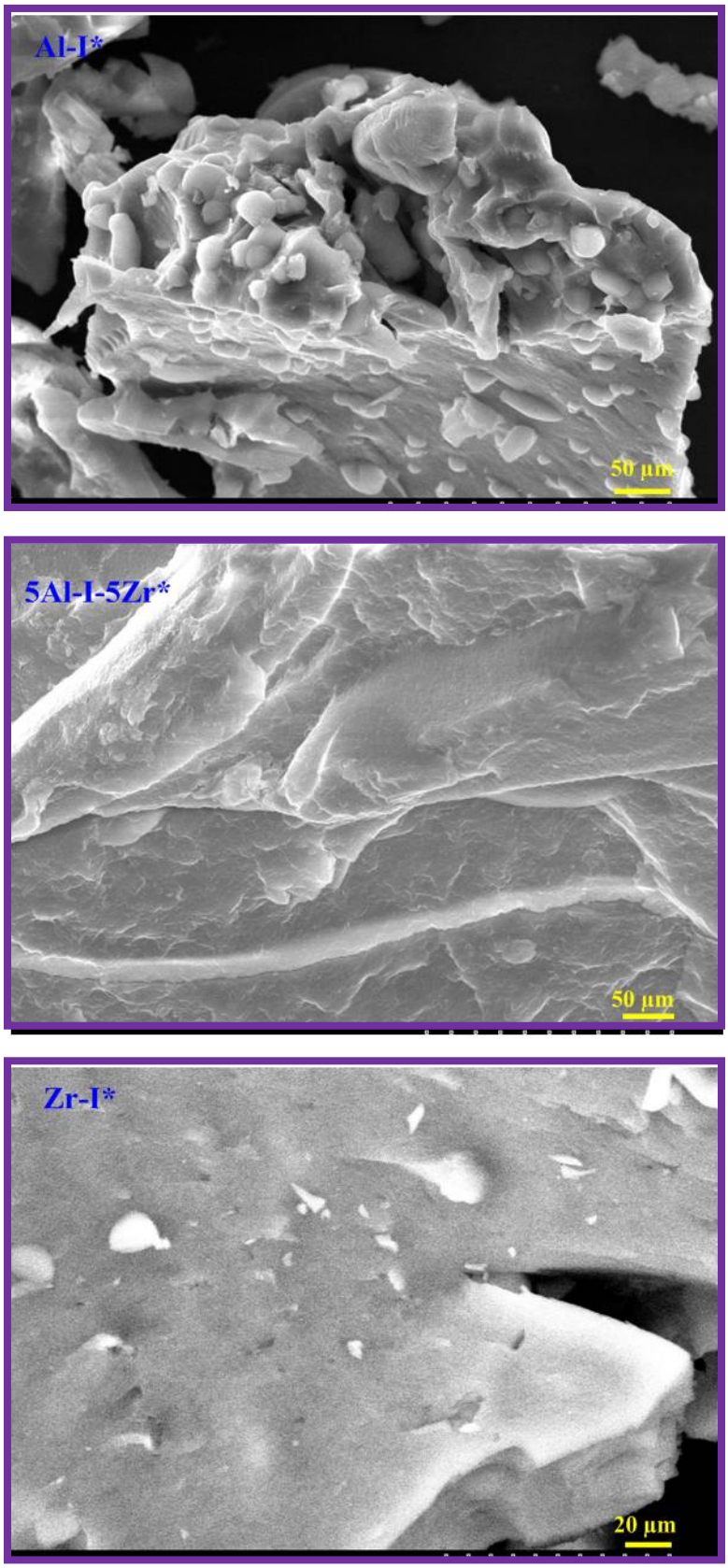

Figure S4. SEM images of the Al-I* (top), 5Al-I*-5Zr (middle), and Zr-I * (bottom) samples.

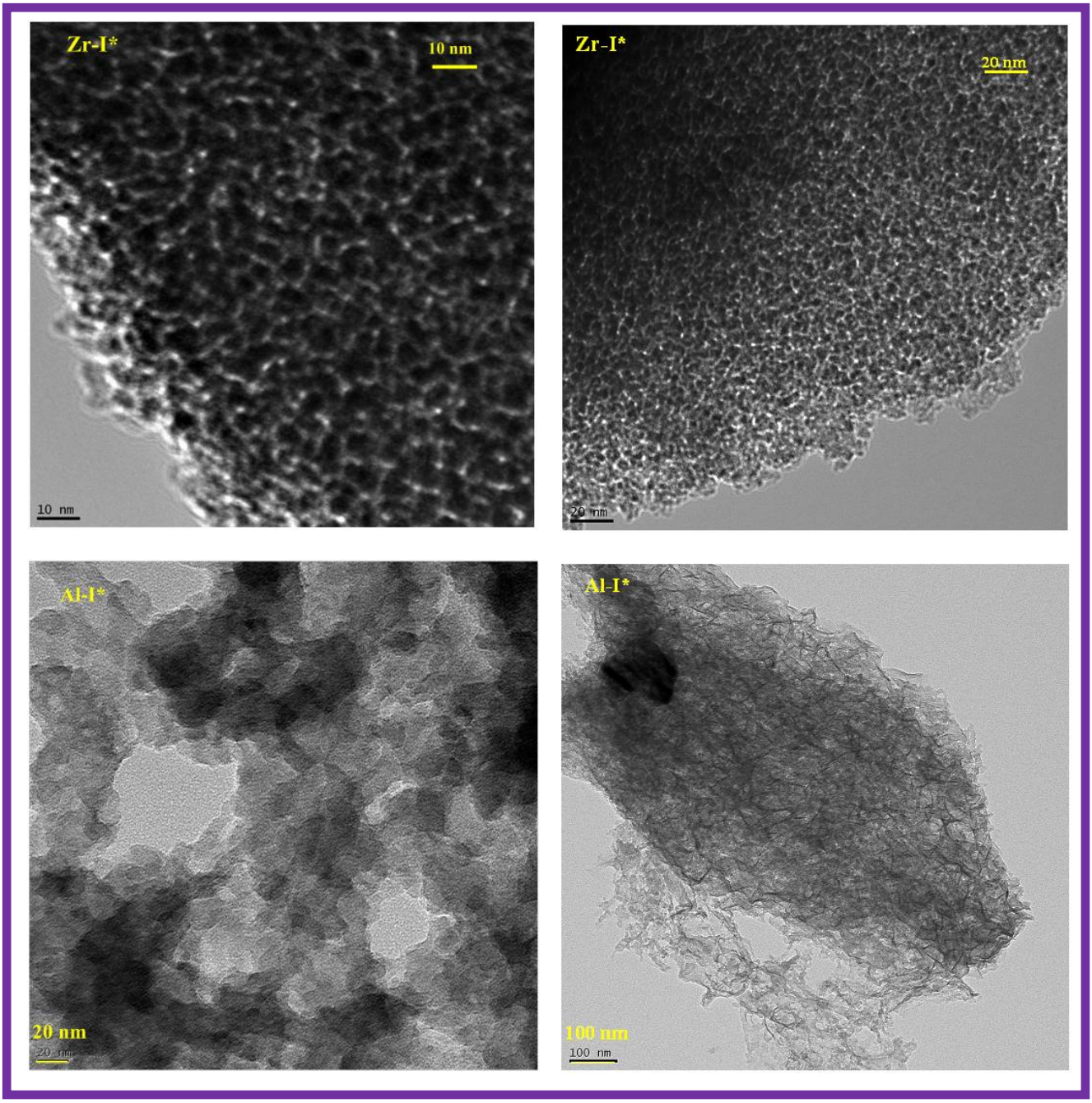

Figure S5. TM images of the Zr-I* (top left and right panel) and Al-I * (bottom left and right panel) samples.

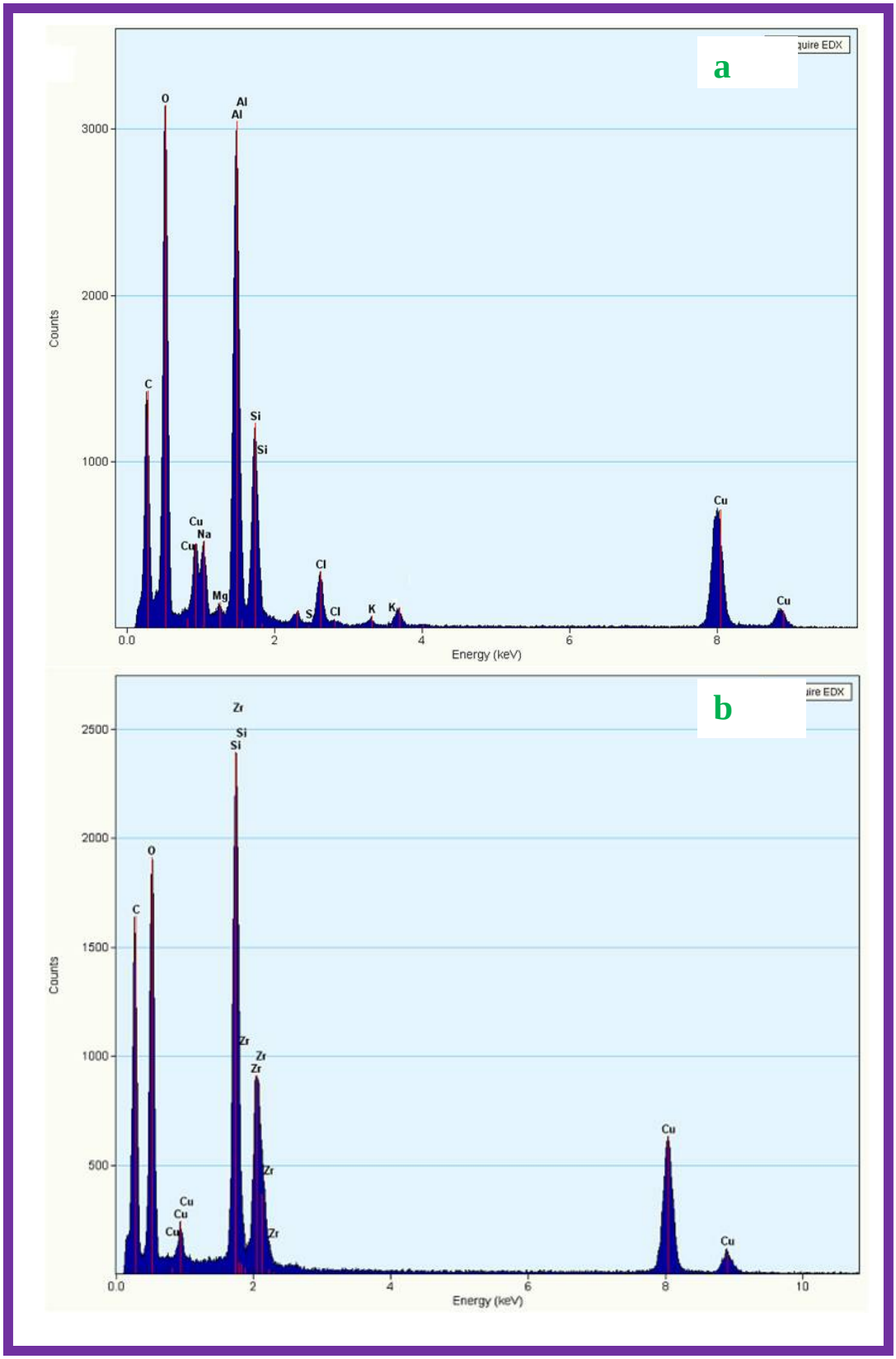

Figure S6. EDX spectra of the **a**) Al-I* (top) and **b**) Zr-I * (bottom) samples.

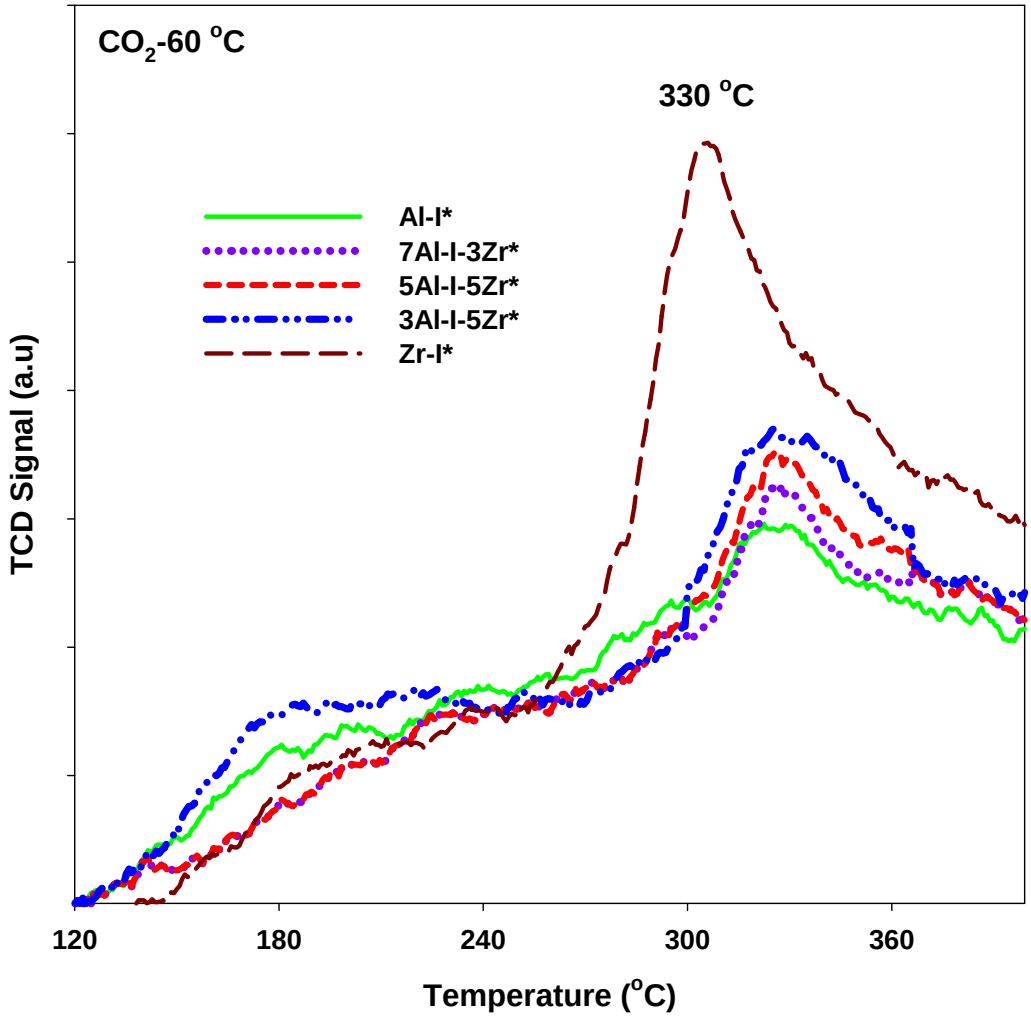

Figure S7. CO_2 TPD profiles recorded for the samples studied; pulse at 60 °C.

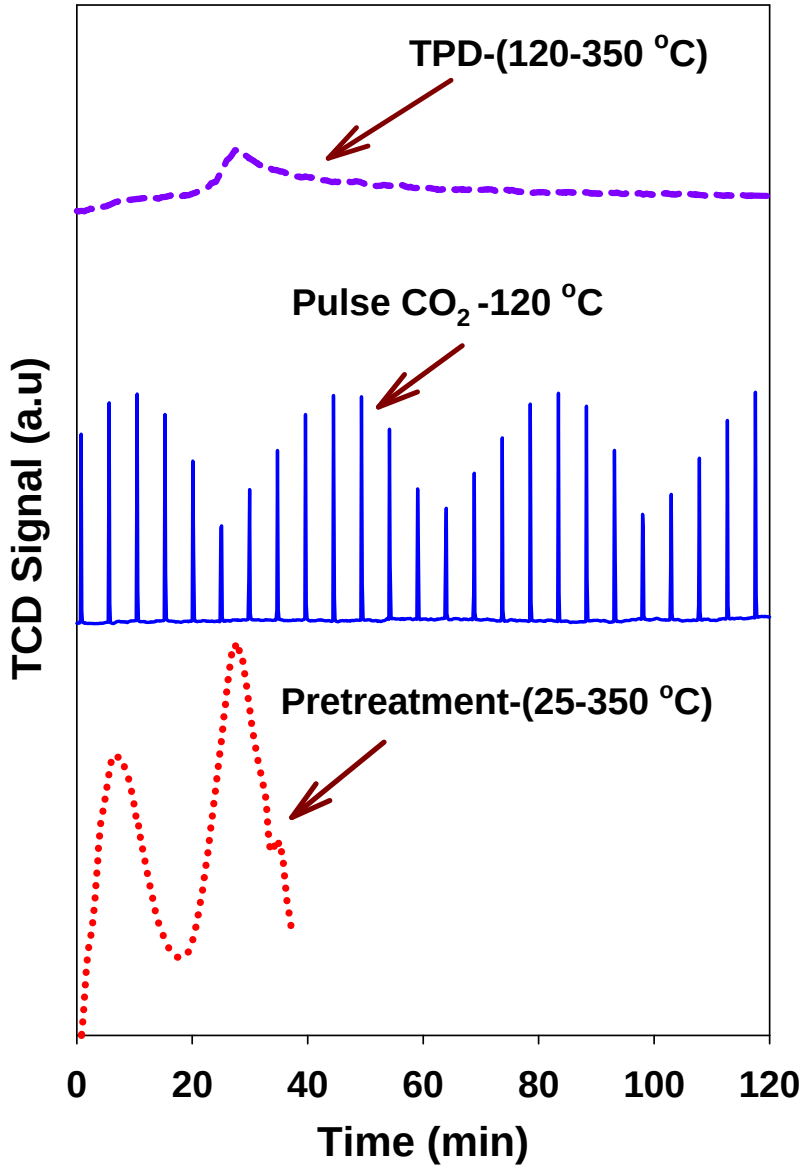

Figure S8. Pretreatment, pulse, and CO_2 TPD profiles of the Zr-I* sample.

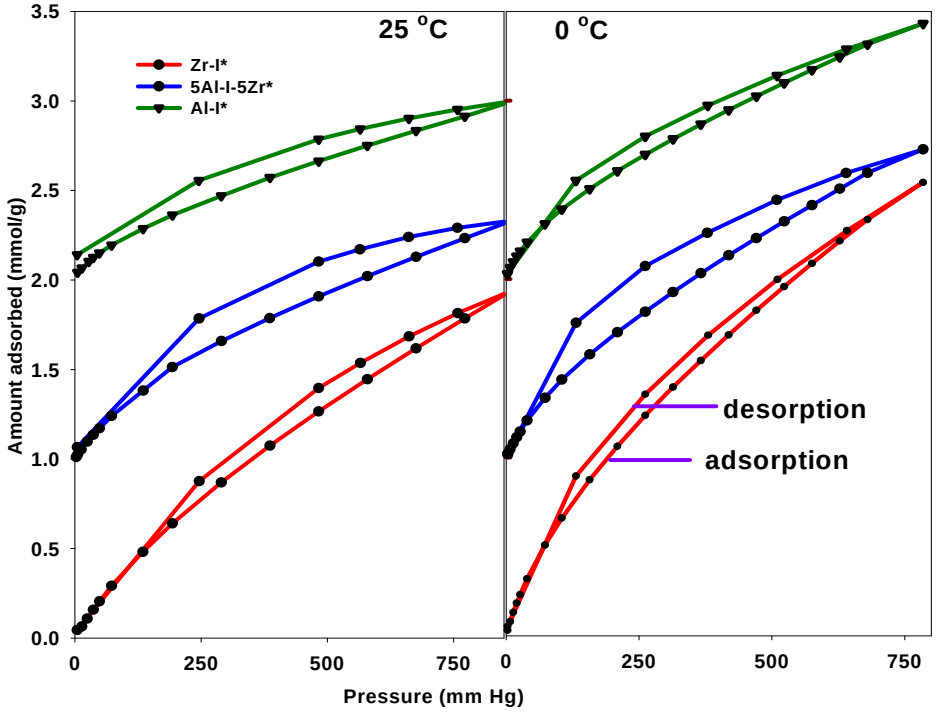

Figure S9. CO_2 adsorption-desorption isotherms at 25 °C (left panel) and 0 °C (right panel) measured on the Al-I*, 5Al-I-5Zr*, and Zr-I * samples. The second & third isotherm curves on each panel are respectively shifted by 1 mmol/g and 2 mmol/g in relation to the first isotherm curve.

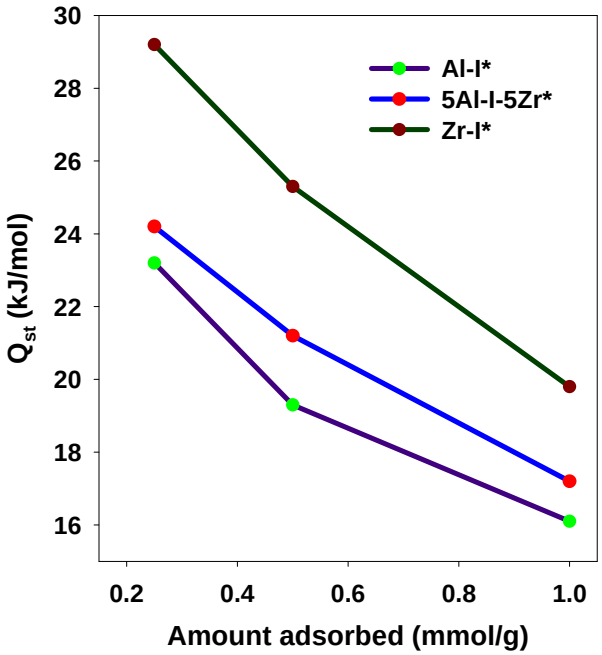

Figure S10. Variation of the isosteric heat of adsorption (Q_{st}) on the surface coverage for the Al-I*, 5Al-I*-5Zr, and Zr-I * samples.

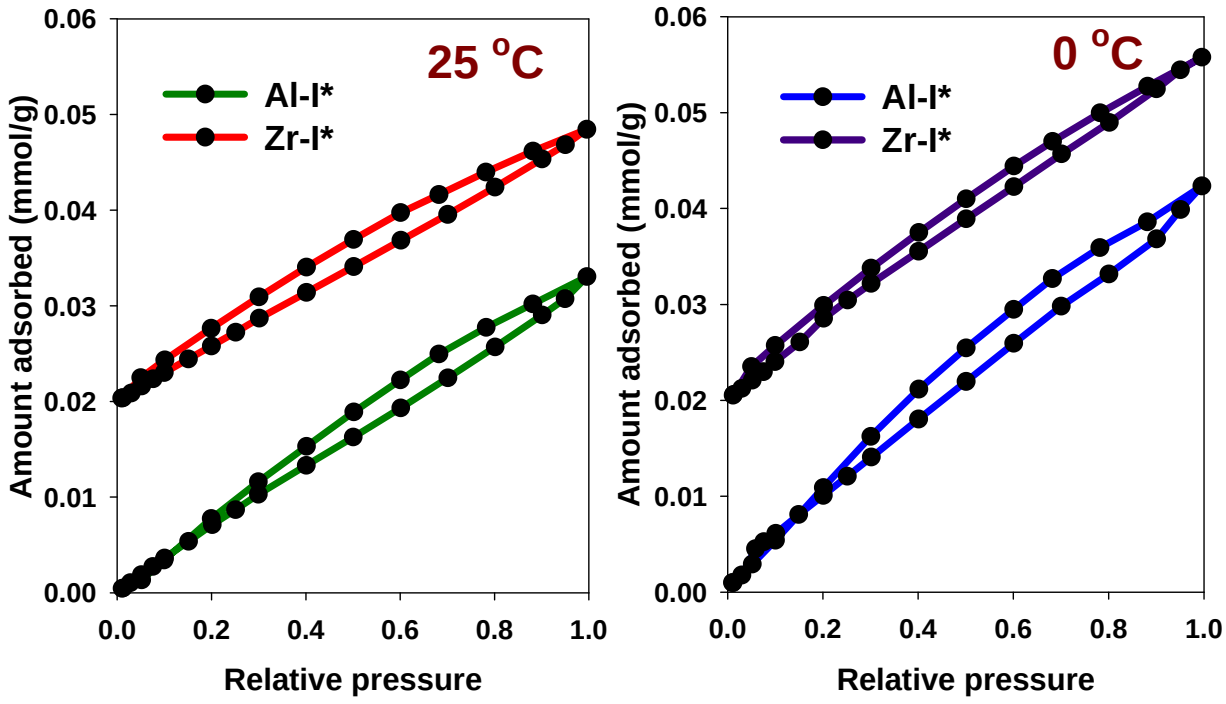

Figure S11. N_2 adsorption-desorption isotherms at 25 °C (left panel) and 0 °C (right panel) measured on the Al-I* and Zr-I * samples. The second isotherm curve on each panel is respectively shifted by 0.02 mmol/g in relation to the first isotherm curve.

Quantitative analysis of CO_2/N_2 selectivity

CO_2/N_2 selectivity was estimated by using the Henry's law constants for CO_2 and N_2 adsorption on Al-I* and Zr-I* samples. First, the adsorption isotherms measured for the aforementioned systems were fitted by the following form of virial equation.[1,2]

$$\ln\left[\frac{n}{p}\right] = A_0 + A_1 n + A_2 n^2 + A_3 n^3 \ldots$$

where n is the amount adsorbed (mol g^{-1}) at the equilibrium pressure p (bar). This fitting was perfomed by using the third-order polynomial (higher terms were neglected). The first virial coefficient A_0 is related to the Henry's constant $K_H = \exp(A_0)$. At the surface coverage tending to zero the above virial equation reduces to the Henry's law $n = K_H p$.

A_0 is related to the adsorbate-adsorbent interaction energy, while A_1 is related to adsorbate-adsorbate interactions. At a given temperature the CO_2/N_2 selectivity can be defined as the ratio of the corresponding Henry's constants, $K_H(CO_2)$ and $K_H(N_2)$:

$$S^T = K_H(CO_2)/K_H(N_2)$$

Adsorption isotherms measured for CO_2 and N_2 on the Al-I* and Zr-I* samples at 0 °C and 25 °C were used to evaluate the aforementioned selectivity. Figure S12 shows the experimental adsorption data (points) plotted as ln (n/p) *versus* n for the aforementioned systems together with the corresponding fitting curves (lines) represented by the third order polynomial as shown above. As can be seen in Figure S12 and Table S1, the fitting curves represent very well adsorption data (correlation coefficient values are in the range of 0.91-0.99).

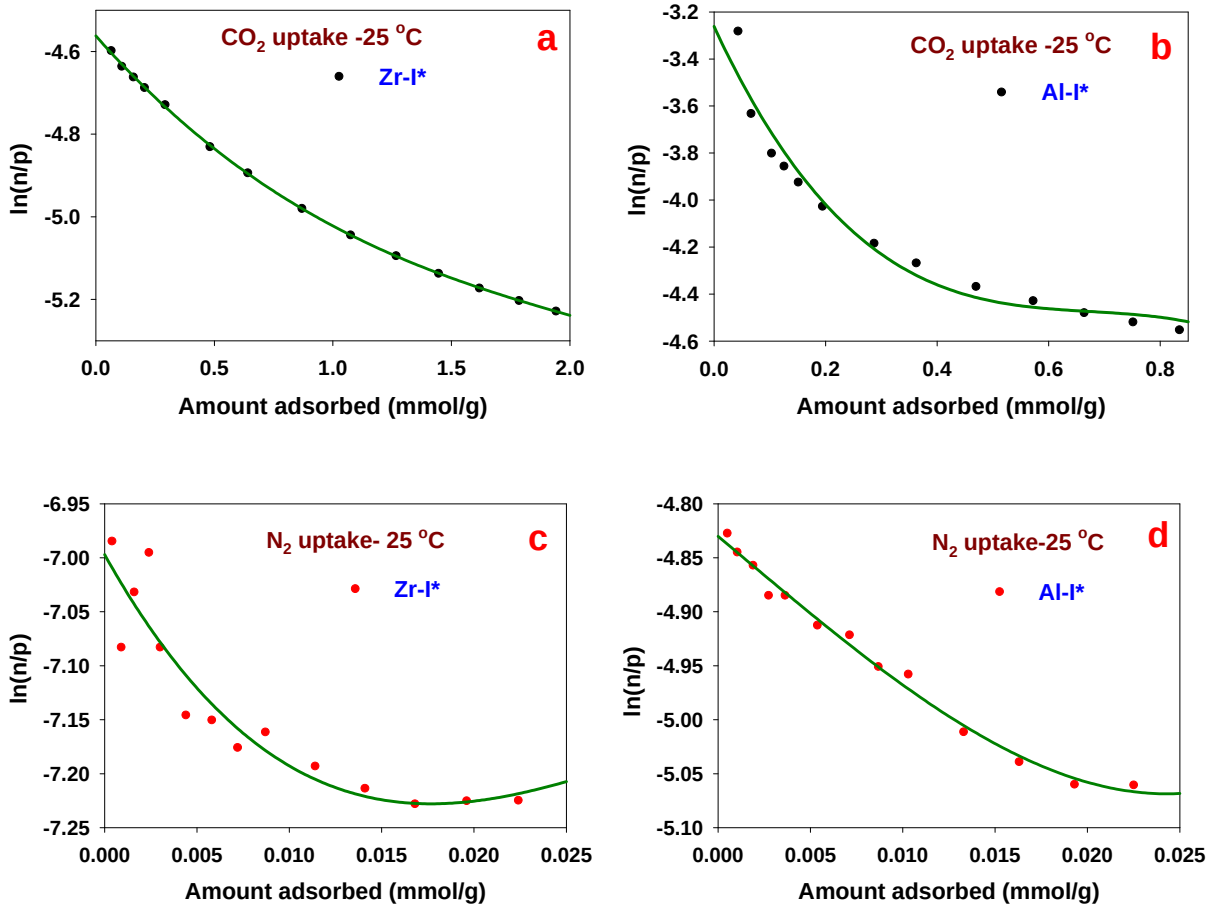

Figure S12. Experimental data (points) plotted as ln (n/p) *versus* n for CO_2 (panels a and b) and N_2 (panels c and d) adsorption on Zr-I* and Al-I* at 25 °C together with the corresponding fitting curves (lines) represented by the third order polynomial as shown above; amount adsorbed is expressed in mmol/g and pressure in bar.

Table S1. Comparison of the Henry's constants $K_H = \exp(A_0)$ obtained by using A_o coefficient of the thrid-order polynomial (see equation above) for CO_2 and N_2 adsorption on Zr-I* and Al-I* at 0 and 25 ^oC.

CO_2 uptake at 25 ^oC	1st virial coefficient A_0	Henry's constant K_H *	Correlation coefficient
Zr-I*	-4.562 ± 0.003	$10.4 \cdot 10^{-3}$	0.99
Al-I*	-3.261 ± 0.072	$38.4 \cdot 10^{-3}$	0.97

N_2 uptake at 25 ^oC			
Zr-I*	-6.997 ± 0.020	$0.91 \cdot 10^{-3}$	0.94
Al-I*	-4.830 ± 0.006	$7.98 \cdot 10^{-3}$	0.99

CO_2 uptake at 0 ^oC			
Zr-I*	-3.056 ± 0.009	$47.0 \cdot 10^{-3}$	0.99
Al-I*	-2.484 ± 0.073	$83.4 \cdot 10^{-3}$	0.91

N_2 uptake at 0 ^oC			
Zr-I*	-5.882 ± 0.009	$2.78 \cdot 10^{-3}$	0.99
Al-I*	-4.562 ± 0.031	$10.4 \cdot 10^{-3}$	0.99

* K_H values were calculated for adsorption expressed in µmol/g and pressure in bar.

Table S2. Selectivity data obtained on the basis of Henry's constants for adsorption of CO_2 and N_2 on Zr-I* and Al-I* at 0 and 25 ^oC .

Sample	S^{25}	S^{0}
Zr-I*	11.4	16.9
Al-I*	4.8	8.0

References

1. S. Yang, X. Lin,W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, . C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, *Nature Materials*, 2012, **11**,710–716.
2. J. G. Bell, X. Zhao, Y. Uygur and K. M. Thomas, *J. Phys. Chem. C*, 2011, **115**, 2776–2789.

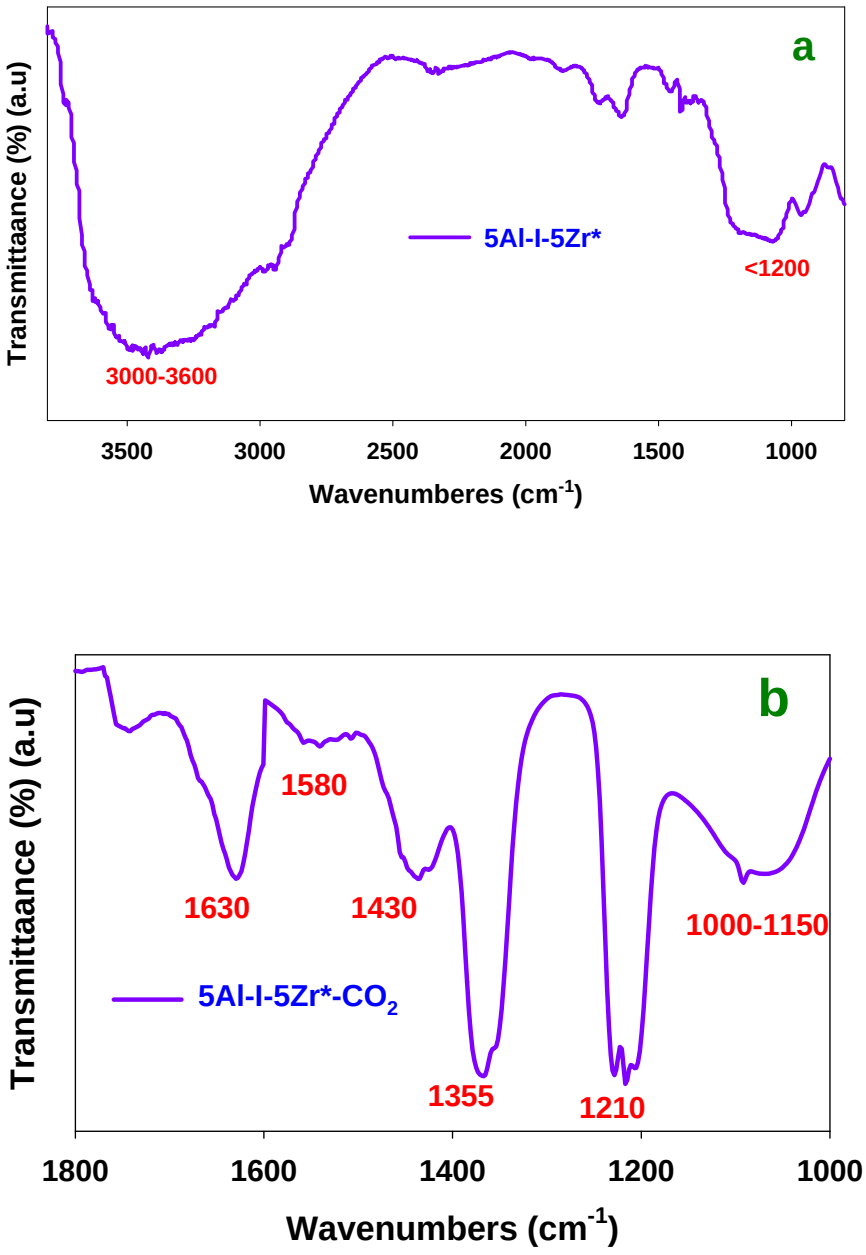

Figure S13. IR spectra of 5Al-I-5Zr* (a; top panel) and 5Al-I-5Zr*-CO_2 (b; bottom pannel).

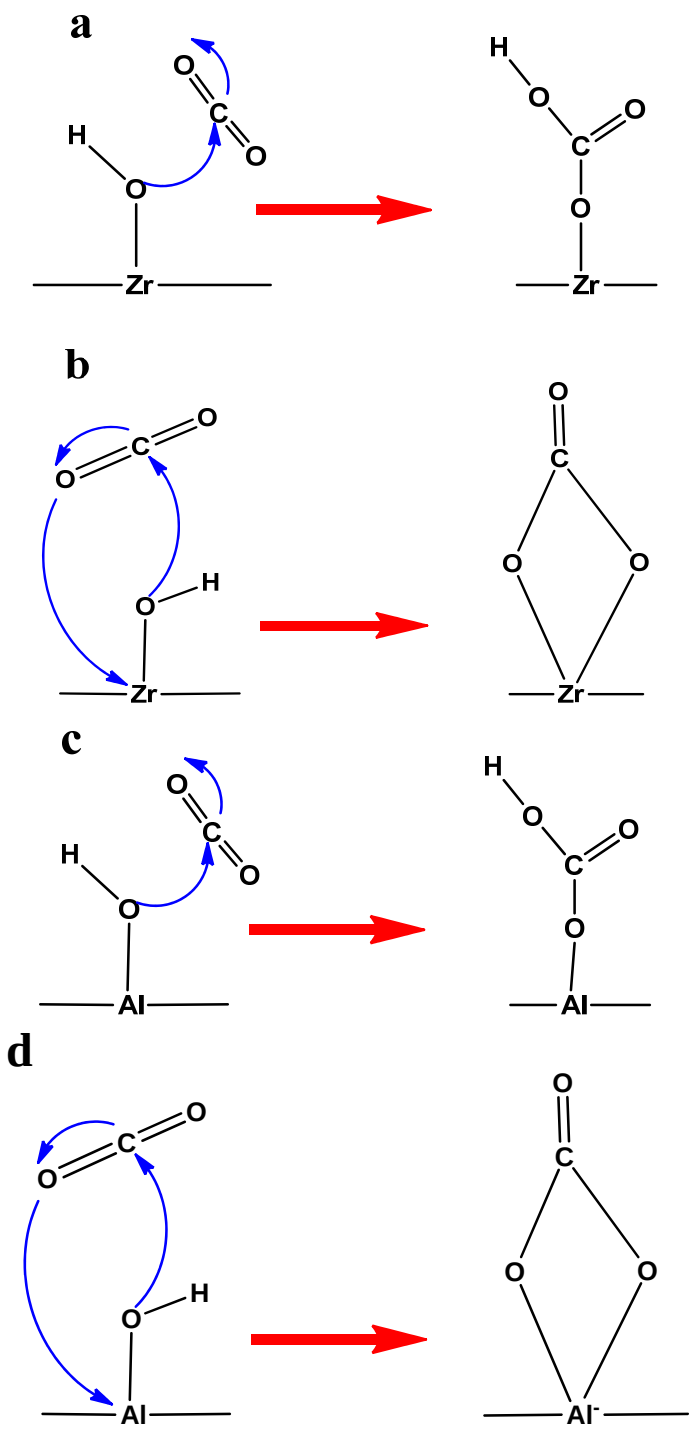

Figure S14. Schematic illustration of possible binding models for CO_2 on the surfaces of zirconia and alumina composite samples: (**a** and **c**) bicarbonate structures; (**b** and **d**) bi-dentate carbonate structures.