Electronic Supplementary Material

Ex-LDH-Based Catalysts for CO_2 Conversion to Methanol and Dimethyl Ether

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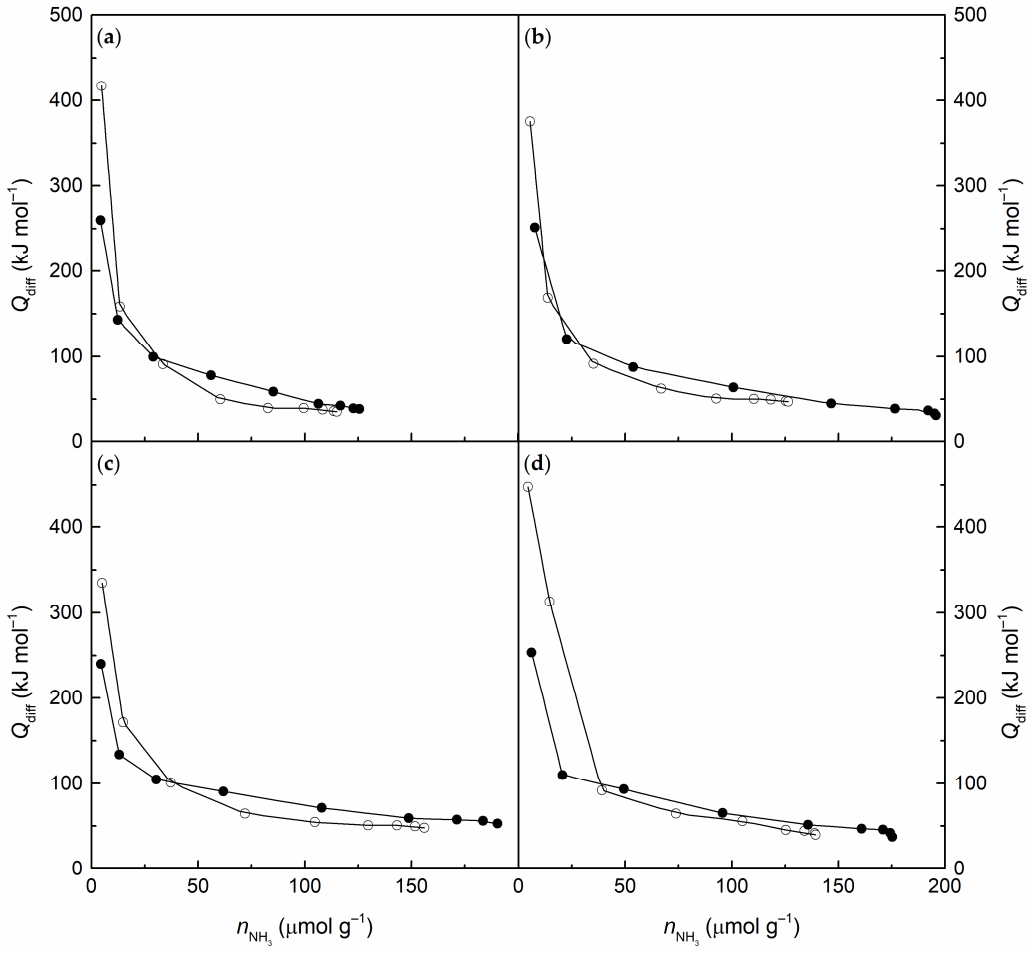

Figure S1. Differential heat of adsorption of NH_3 as a function of the amount of adsorbing sites for the ex-LDH samples as-prepared (○) and after H_2 treatment (●): (**a**) CuZnAl; (**b**) CuZnAlZr; (**c**) CuZnAlCe; (**d**) CuZnAlZrCe.

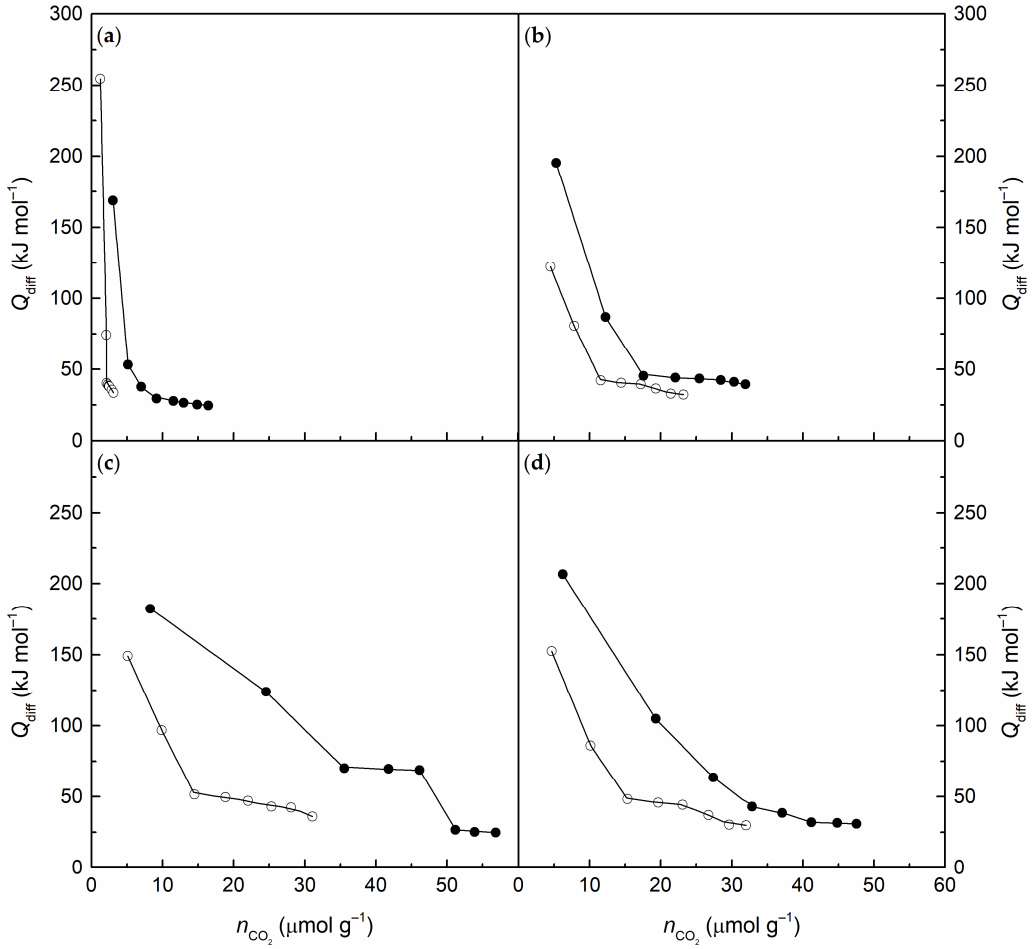

Figure S2. Differential heat of adsorption of CO_2 as a function of the amount of adsorbing sites for the ex-LDH samples as-prepared (○) and after H_2 treatment (●): (**a**) CuZnAl; (**b**) CuZnAlZr; (**c**) CuZnAlCe; (**d**) CuZnAlZrCe.

Table S1. Percentage of sites of different strength with respect to the total number and n_A/n_B ratios for the mixed oxides catalysts as-prepared and after H_2 treatment.

Sample		n_A distribution (%)		n_B distribution (%)		n_A/n_B ratio	
		$n_{A,w}/n_{A,tot}$	$n_{A,(m+s)}/n_{A,tot}$	$n_{B,w}/n_{B,tot}$	$n_{B,(m+s)}/n_{B,tot}$	$n_{A,tot}/n_{B,tot}$	$n_{A,(m+s)}/n_{B,(m+s)}$
CuZnAl	as-prep.	43	57	9	91	24.1	15.0
	H_2-treat.	65	35	43	57	11.7	7.3
CuZnAlZr	as-prep.	54	46	63	37	4.4	5.3
	H_2-treat.	62	38	62	38	3.8	3.8
CuZnAlCe	as-prep.	56	44	66	34	2.9	3.7
	H_2-treat.	71	29	41	59	2.9	1.4
CuZnAlZrCe	as-prep.	55	45	64	36	3.4	4.3
	H_2-treat.	66	34	41	59	3.2	1.9

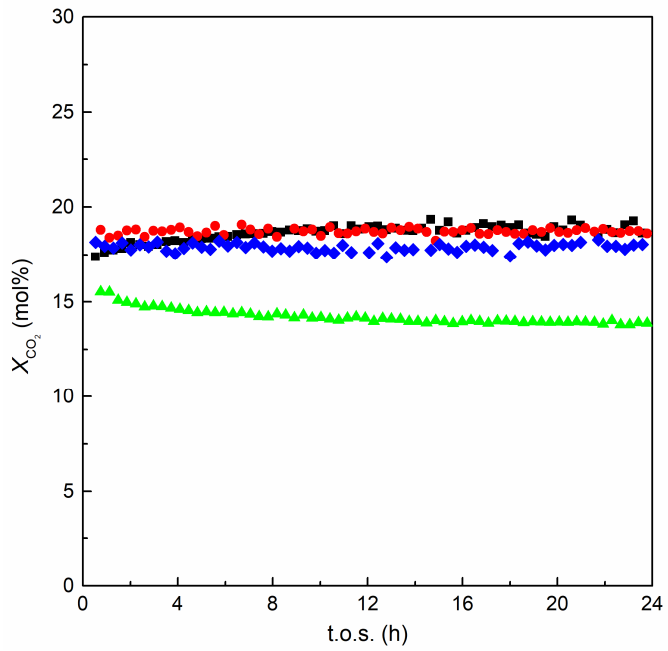

Figure S3. CO_2 conversion as a function of time on stream for the CO_2 hydrogenation to methanol on the ex-LDH catalysts: (■), CuZnAl; (●), CuZnAlZr; (▲), CuZnAlCe; (◆), CuZnAlZrCe. Reaction conditions: T = 250 °C; P = 3.0 MPa; H_2/CO_2 = 3 mol mol^{-1}; $GHSV$ = 12000 Ncm^3 g$_{cat}^{-1}$ h^{-1}.

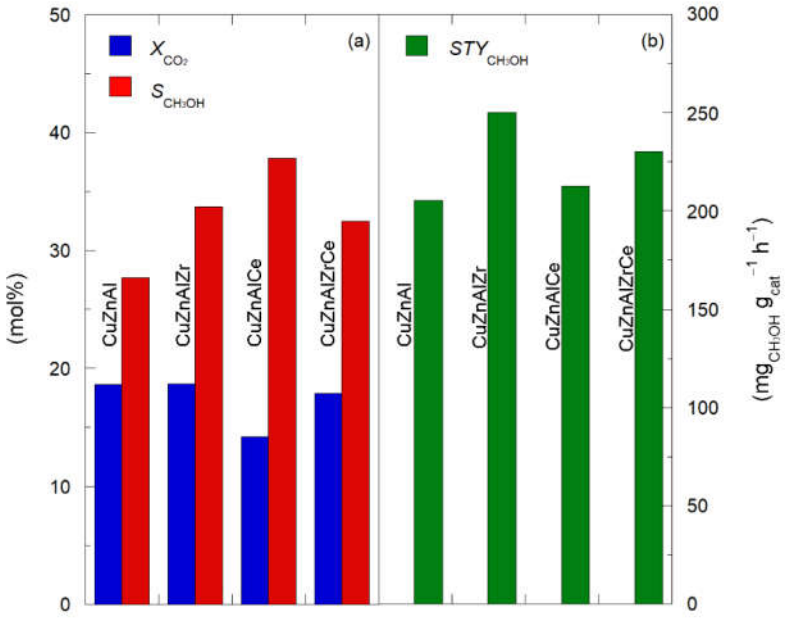

Figure S4. Catalytic results (average values over 24 hours on stream) for CO_2 hydrogenation to methanol on ex-LDH oxides. Reaction conditions: T = 250 °C; P = 3.0 MPa; H_2/CO_2 = 3 mol mol^{-1}; $GHSV$ = 12000 Ncm^3 g$_{cat}^{-1}$ h^{-1}.

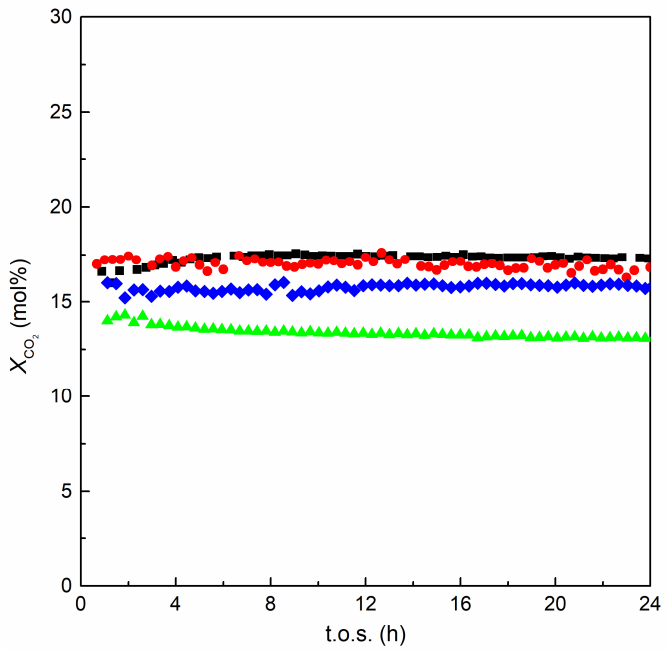

Figure S5. CO_2 conversion as a function of time on stream for the CO_2 conversion into DME on the ex-LDH/FER_20 bifunctional catalysts: (■), CuZnAl/FER_20; (●), CuZnAlZr/FER_20; (▲), CuZnAlCe/FER_20; (◆), CuZnAlZrCe/FER_20. Reaction conditions: T = 250 °C; P = 3.0 MPa; H_2/CO_2 = 3 mol mol^{-1}; $GHSV$ = 6000 Ncm^3 g$_{cat}^{-1}$ h^{-1}.

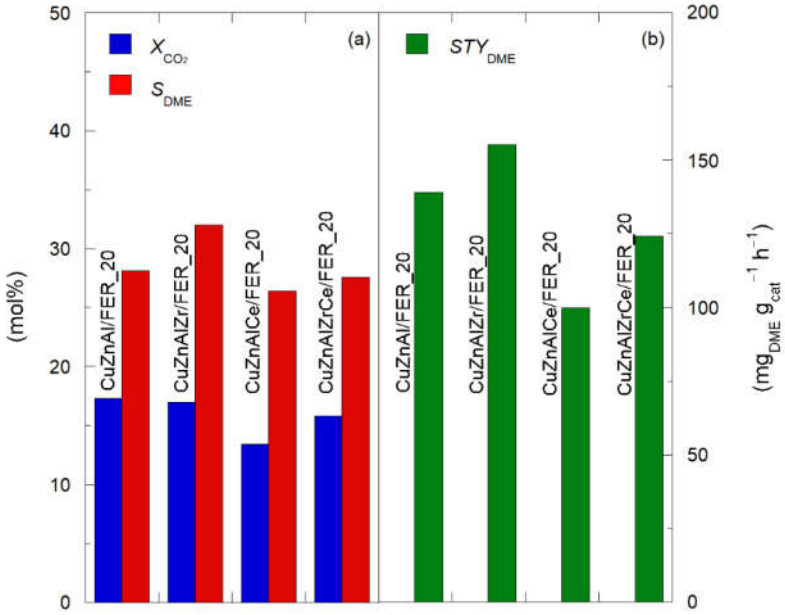

Figure S6. Catalytic results (average values over 24 hours on stream) for CO_2 hydrogenation to DME on ex-LDH/FER_20 bifunctional systems. Reaction conditions: T = 250 °C; P = 3.0 MPa; H_2/CO_2 = 3 mol mol^{-1}; $GHSV$ = 6000 Ncm^3 g$_{cat}^{-1}$ h^{-1}.

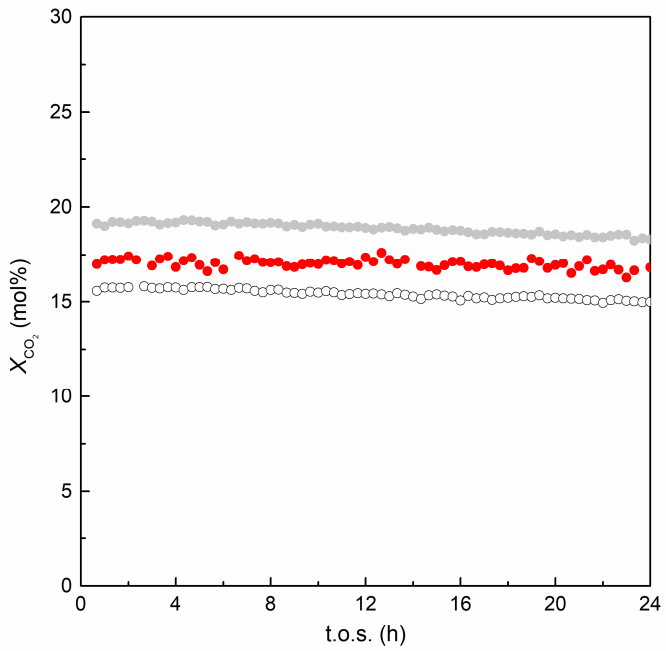

Figure S7. CO_2 conversion as a function of time on stream for the CO_2 conversion into DME on the CuZnAlZr/FER_20 and CuZnAlZr/ZSM5 bifunctional catalysts: (●), CuZnAlZr/FER_20; (○), CuZnAlZr/ZSM5_23; (●), CuZnAlZr/ZSM5_350. Reaction conditions: T = 250 °C; P = 3.0 MPa; H_2/CO_2 = 3 mol mol^{-1}; $GHSV$ = 6000 Ncm^3 g_{cat}^{-1} h^{-1}.

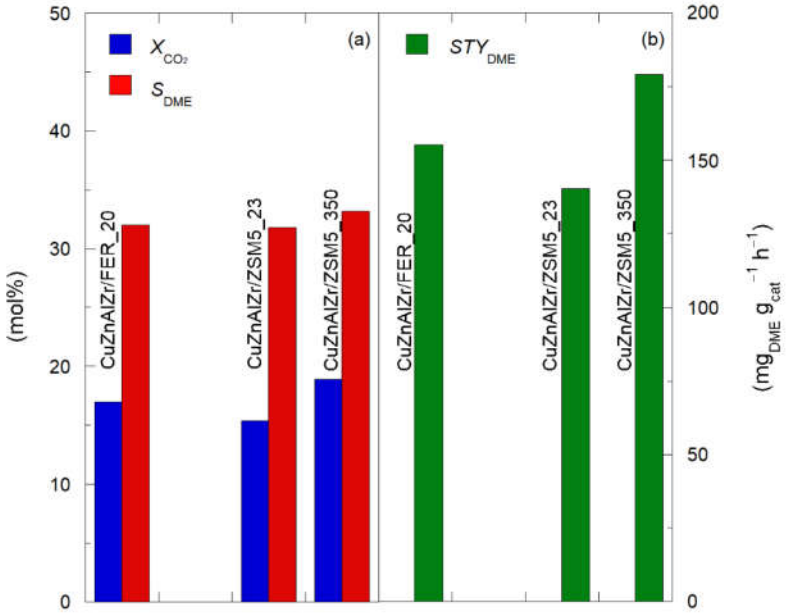

Figure S8. Catalytic results (average values over 24 hours on stream) for CO_2 hydrogenation to DME on the CuZnAlZr/FER_20 and CuZnAlZr/ZSM5 bifunctional catalysts. Reaction conditions: T = 250 °C; P = 3.0 MPa; H_2/CO_2 = 3 mol mol^{-1}; $GHSV$ = 6000 Ncm^3 g_{cat}^{-1} h^{-1}.