Electronic Supplementary Information (ESI)

Zr-Al-Beta zeolite with open Zr(IV) sites: an efficient bifunctional Lewis-Brønsted acidic catalyst of cascade reaction

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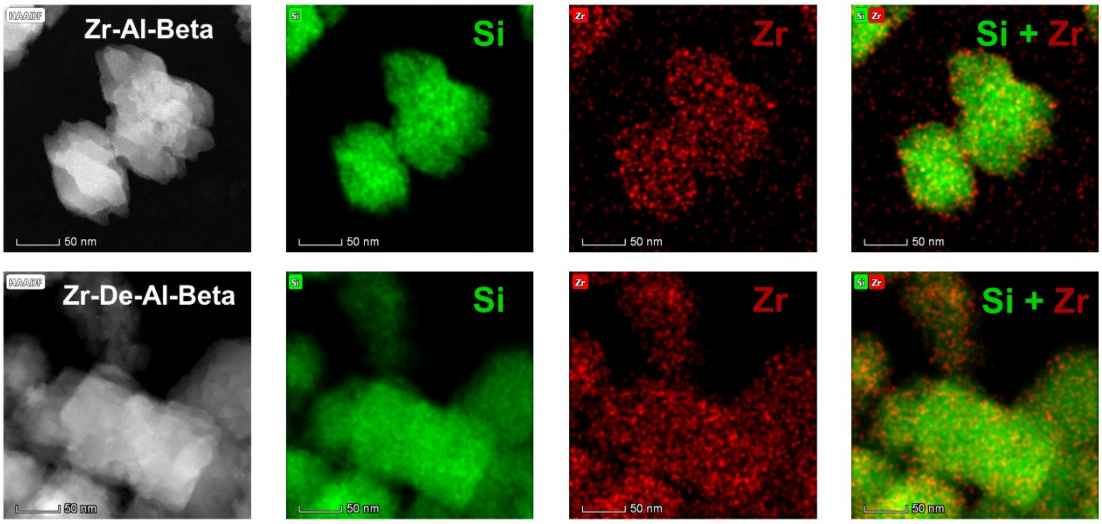
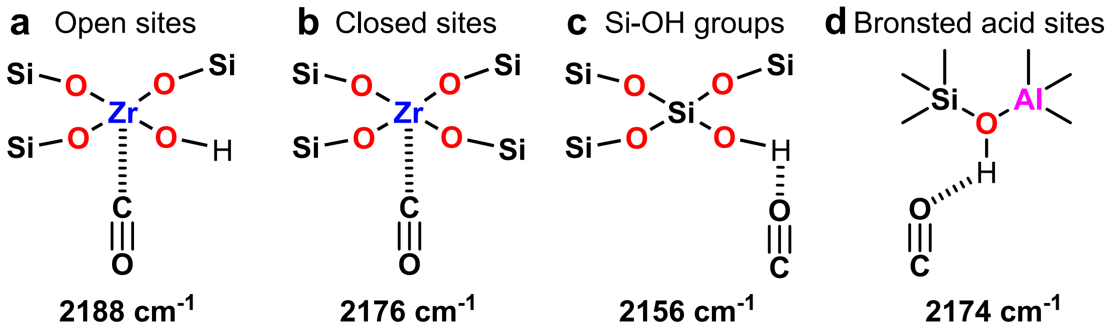


Figure S1. HAADF-STEM images and super-X-EDS mapping images of Zr-Al-Beta (up) and Zr-De-Al-Beta (down).



Scheme S1. The representative structure configurations of CO adsorbed over different sites.

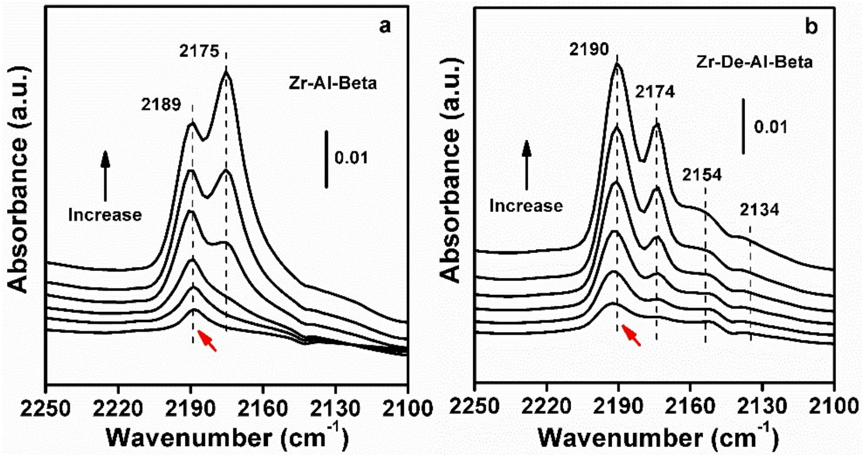


Figure S2. FT-IR spectra adsorbed CO over Zr-Al-Beta (a) and Zr-De-Al-Beta (b) with the increase in CO coverage.

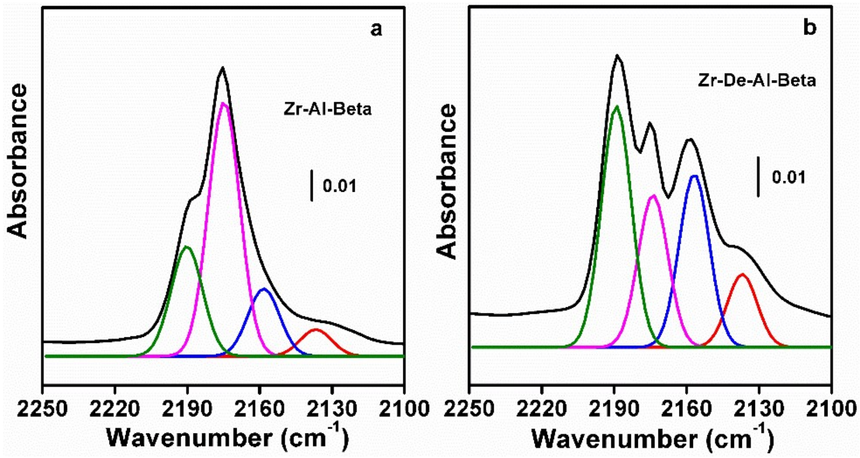


Figure S3. Deconvolution of FT-IR spectra after CO adsorption over Zr-Al-Beta (a) and Zr-De-Al-Beta (b).

Table S1. Relative peak area of the open sites in Zr-Al-Beta and Zr-De-Al-Beta.

Catalyst	Open sites (2189 cm^{-1})
Zr-Al-Beta	0.2968
Zr-De-Al-Beta	0.0811
Ratio	3.4[a]

[a]Normalized by Zr contents from Table 1.

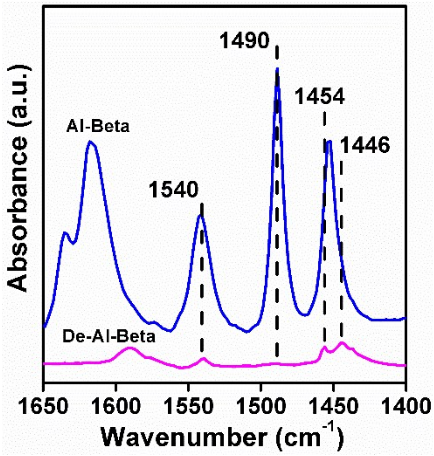


Figure S4. Pyridine-FT-IR spectra desorption at 573 K of Al-Beta and De-Al-Beta.

Table S2. Catalytic performance of reported catalysts for the MPV reduction of CAL.

Entry	catalyst	CAL Conv. (%)	CPE yield (%)	Reference
1	Zr-Al-Beta	97.3[a]	93.9	This work
2	Zr-Al-Beta-F	80.0[b]	60.0	*J. Catal.* 2006, 241, 25.
3	SiO_2-Al_2O_3	21.6[c]	14.5	*Catal. Sci. Technol.* 2017, 7, 4511.
4	Zr-UiO-66	17.0[d]	2.0	*J. Catal.* 2016, 340, 136.

a: 2 mmol of cinnamaldehyde, 100 mmol of isopropanol, 100 mg of catalyst, 82 ^{o}C, reflux, 5 h.

b: 1.3 mmol of cinnamaldehyde, 83 mmol of isopropanol, 100 mg of catalyst, 82 ^{o}C, reflux, 5 h.

c: 0.5 mL of cinnamaldehyde, 10 mL of isopropanol, 200 mg of catalyst, 150 ^{o}C, 4 h.

d: 1.15 mmol of cinnamaldehyde, 3.3 mL of isopropanol, 7.8% mol of Zr, 82 ^{o}C, reflux, 24 h.

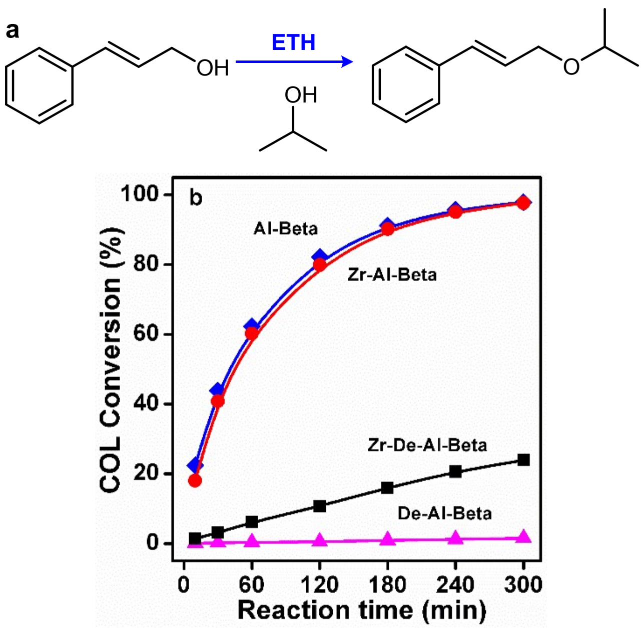


Figure S5. Scheme of the etherification of COL with IPA (a), catalytic performance of Al-Beta, Zr-Al-Beta, Zr-De-Al-Beta and De-Al-Beta for the etherification of COL with IPA (b).

Reaction conditions: 2 mmol of cinnamyl alcohol, 100 mmol of isopropanol, 100 mg of catalyst, 82 ^{o}C, reflux.

Table S3. Catalytic results of Al-Beta, Zr-Al-Beta and Zr-De-Al-Beta for the cascade reaction with or without the addition of DBT-Py.

Sample	10 min	30 min	1 h	2 h	3 h	4 h	5 h
Al-Beta[a]							
CAL Conv. (%)	7.4	12.2	18.8	27.4	34.5	41.2	47.1
COL Yield (%)	1.9	1.9	1.3	0.6	0.4	0.3	0.3
CPE Yield (%)	5.5	10.3	17.5	26.8	34.1	40.9	46.8
Al-Beta (DTB-Py)[b]							
CAL Conv. (%)	0.5	0.9	1.2	1.8	2.5	2.7	2.9
COL Yield (%)	0.5	0.9	1.2	1.8	2.5	2.7	2.9
CPE Yield (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zr-Al-Beta[a]							
CAL Conv. (%)	18.6	42.3	65.1	87.7	94.6	96.7	97.3
COL Yield (%)	10.9	17.4	20.7	18.9	12.5	7.2	3.4
CPE Yield (%)	7.7	24.9	44.4	68.8	82.1	89.5	93.9
Zr-Al-Beta (DTB-Py)[b]							
CAL Conv. (%)	4.9	11.2	20.9	35.2	47.9	57.9	65.5
COL Yield (%)	4.5	10.4	19.0	32.3	44.0	53.0	60.3
CPE Yield (%)	0.4	0.8	2.0	2.8	3.9	4.9	5.2
Zr-De-Al-Beta[a]							
CAL Conv. (%)	1.2	3.4	7.4	15.6	23.9	32.8	41.0
COL Yield (%)	1.2	2.8	5.6	8.7	11.3	13.6	14.1
CPE Yield (%)	0.0	0.6	1.8	6.9	12.6	19.2	26.9
Zr-De-Al-Beta (DTB-Py)[b]							
CAL Conv. (%)	0.5	1.3	2.8	5.5	8.6	11.7	14.3
COL Yield (%)	0.5	1.3	2.8	5.5	8.6	11.7	14.3
CPE Yield (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a]Reaction conditions: 2 mmol of cinnamaldehyde, 100 mmol of isopropanol, 100 mg of catalyst, 82 ^{o}C, reflux. [b] Reaction conditions: 2 mmol of cinnamaldehyde, 100 mmol of isopropanol, 100 mg of catalyst, 1.0 equals of total acids of DTB-Py, 82 ^{o}C, reflux.

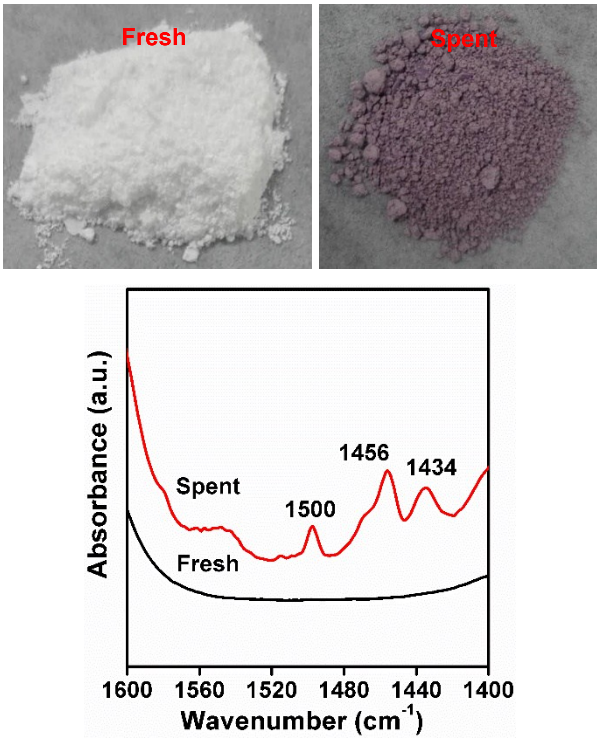


Figure S6. Photos and FT-IR spectra of fresh and spent Zr-Al-Beta.

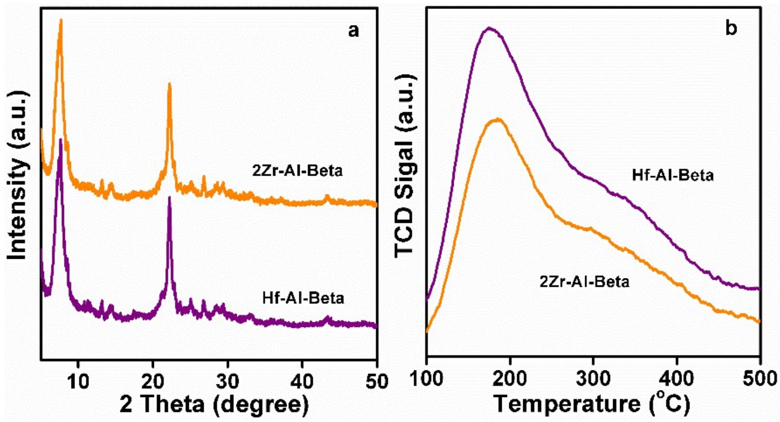


Figure S7. XRD patterns and NH_3-TPD profiles of 2Zr-Al-Beta and Hf-Al-Beta.