Supplementary information

Macroscopic assembly style of catalysts significantly determining their efficiency for converting CO_2 to gasoline

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Table S1. Reaction performances of Fe–Zn–Zr@HZSM-5 core–shell catalysts with different SiO_2/Al_2O_3 molar ratios of HZSM-5 on CO_2 hydrogenation.

Catalysts	CO_2 conv. (%)	Selectivity (C-mol%)			Hydrocarbon distribution (C-mol %)			I-C_{5+} /C_{5+}(%)	Aromatics /C_{5+}(%)
		CO	Oxy	HC	C_1	C_{2-4}	C_{5+}		
Fe–Zn–Zr@HZSM-5(38)	22.5	42.0	0.0	58.0	1.3	53.3	45.4	75.4	19.7
Fe–Zn–Zr@HZSM-5(50)	21.2	42.8	0.1	57.1	1.5	42.3	56.2	90.6	6.4
Fe–Zn–Zr@HZSM-5(100)	22.5	83.0	14.7	2.3	69.2	20.3	10.5	87.6	0.0
Fe–Zn–Zr/HZSM-5(50)	19.7	45.1	0.0	54.9	1.4	55.0	43.6	74.4	19.9

5.0 MPa; 340 ^oC; 6 h; 3000 ml/g/h; $H_2/CO_2/N_2$=72/24/4; Fe–Zn–Zr:HZSM-5=4:1 (weight ratio).

Oxy=oxygen compounds ($MeOH+Me_2O$); HC=hydrocarbon.

I-C_{5+}=C_{5+} isoalkanes; C_{5+}=C_{5+} hydrocarbons.

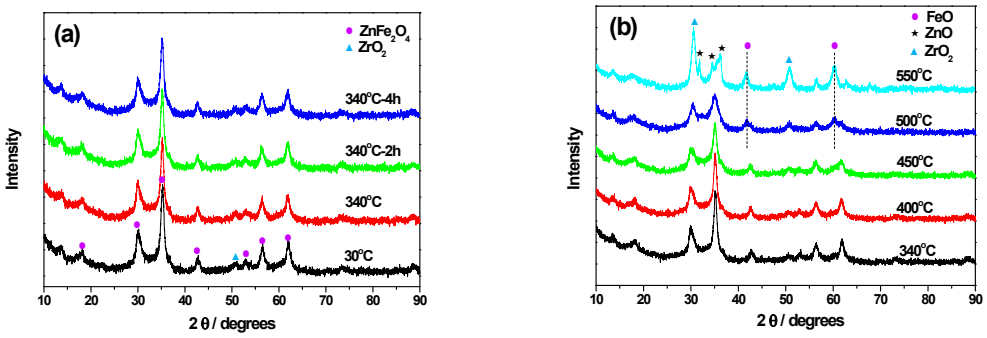

Fig. S1. In situ XRD patterns of Fe–Zn–Zr core. (a) Reduced at 340 °C with different time, (b) Reduced at different temperature and keep 0.5 h.

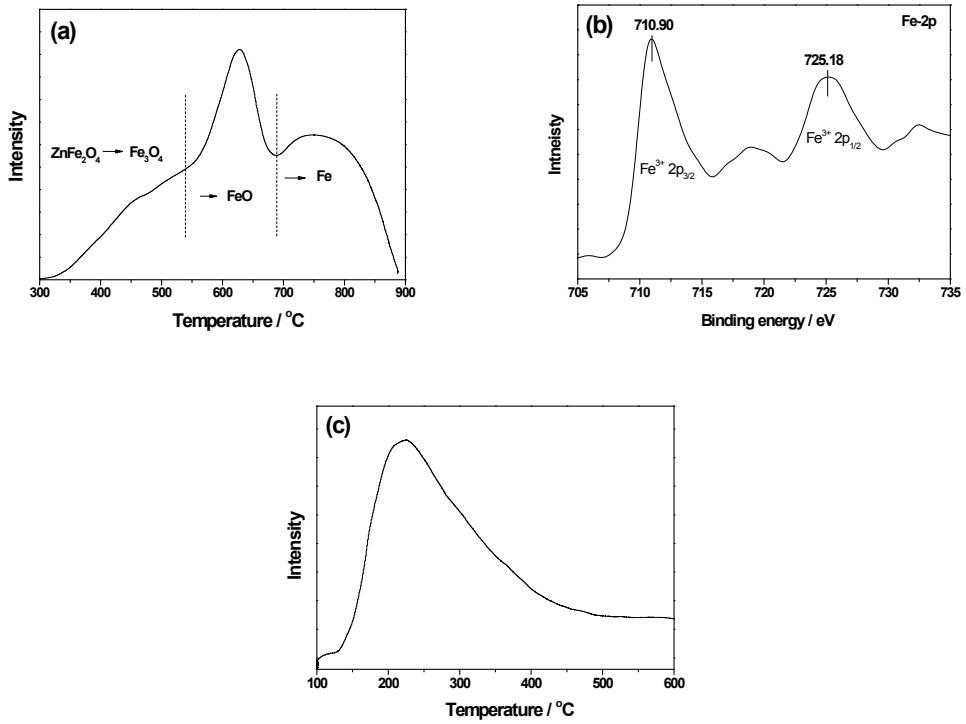

Fig. S2. (a) H_2-TPR (b) XPS, and (c) NH_3-TPD profiles of Fe–Zn–Zr core.

Table S2. Peak areas integrated from NH_3-TPD profiles of the different samples.

Samples	Total acid sites[a] (μmol/g)	Weak acid sites[b] (μmol/g)	Mediate acid sites[b] (μmol/g)	Strong acid sites[b] (μmol/g)
Fe–Zn–Zr	93.5	28.4	65.1	0.0
HZSM-5(100)	69.7	36.1	0.0	33.6
HZSM-5(50)	280.9	152.5	0.0	128.4
HZSM-5(38)	440.0	237.4	0.0	202.6
Fe–Zn–Zr@HZSM-5(100)[c]	55.3	12.7	28.4	14.2
Fe–Zn–Zr@HZSM-5(50)[c]	86.8	29.7	30.1	27.0
Fe–Zn–Zr@HZSM-5(38)[c]	92.0	35.6	24.1	32.3
Fe–Zn–Zr/HZSM-5(50)[c]	107.7	45.0	24.7	38.0

[a] Determined by NH_3-TPD.

[b] Quantified by deconvolution of the NH_3-TPD profiles with Gaussian peaks (R^2> 0.99).

[c] Fe–Zn–Zr:HZSM-5=4:1(weight ratio)

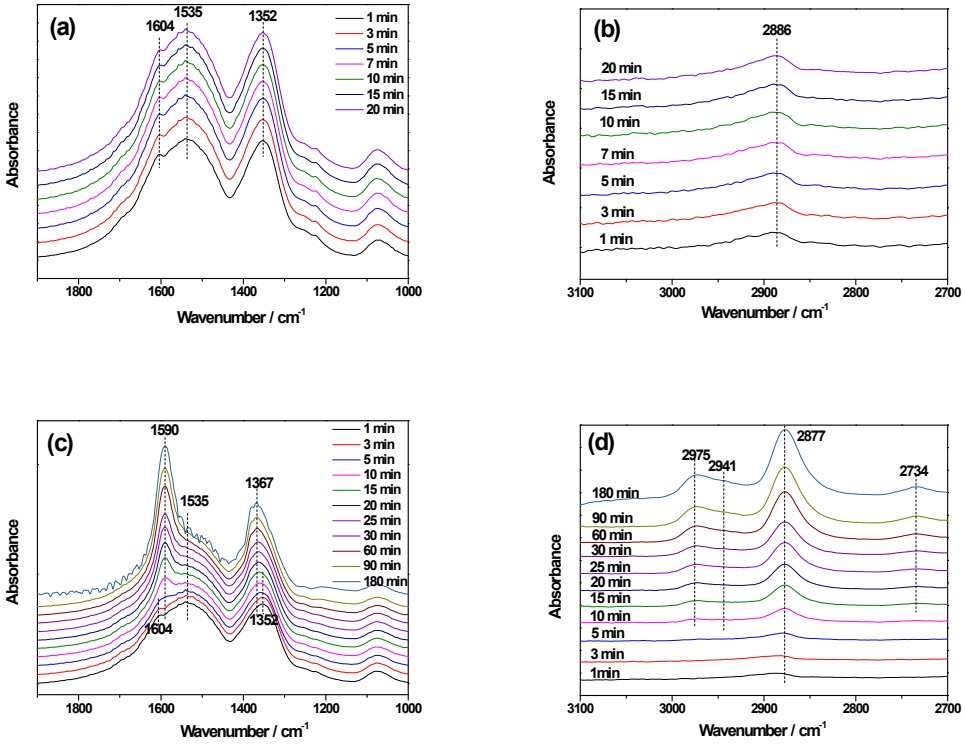

Fig. S3. In situ DRIFT spectra of (a,b) CO_2 adsorption and (c,d) CO_2 hydrogenation on Fe–Zn–Zr core.

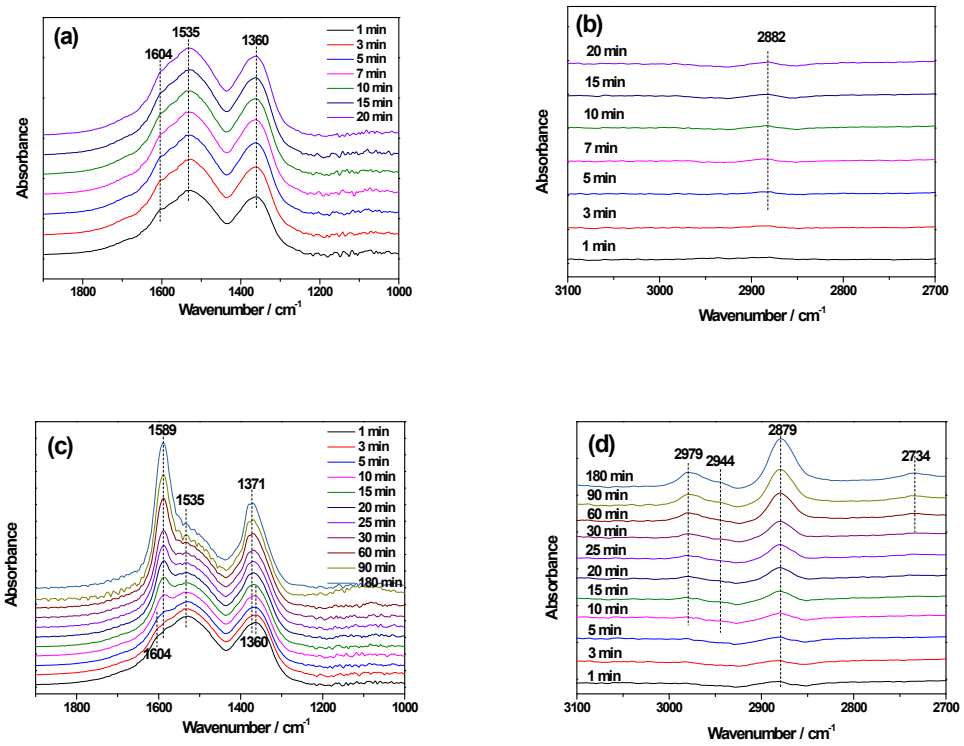

Fig. S4. In situ DRIFT spectra of (a,b) CO_2 adsorption and (c,d) CO_2 hydrogenation on Fe–Zn–Zr@HZSM-5(50) core–shell catalyst with Fe–Zn–Zr and HZSM-5 weight ratio of 6:1.

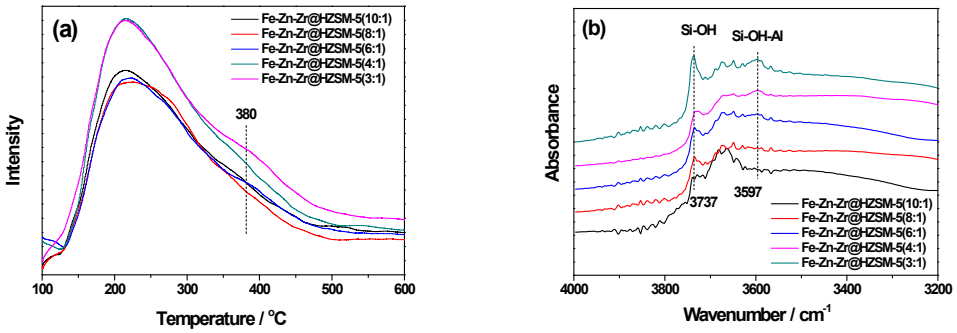

Fig. S5. NH_3-TPD profiles (a) and DRIFT spectra in the OH stretching region (b) of Fe–Zn–Zr@HZSM-5(50) core–shell catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios.

Table S3. Bulk contents and peak areas integrated from NH_3-TPD profiles of Fe–Zn–Zr@HZSM-5(50) core–shell catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios.

Samples	Fe–Zn–Zr:HZSM-5 (weight ratio)[a]	Total acid Sites[b] (μmol/g)	Weak acid Sites[c] (μmol/g)	Mediate acid Sites[c] (μmol/g)	Strong acid Sites[c] (μmol/g)
Fe–Zn–Zr@HZSM-5(10:1)	17.3:1	73.0	19.8	33.9	19.3
Fe–Zn–Zr@HZSM-5(8:1)	14.7:1	72.0	19.6	32.1	20.3
Fe–Zn–Zr@HZSM-5(6:1)	13.3:1	64.1	21.9	20.7	21.5
Fe–Zn–Zr@HZSM-5(4:1)	7.9:1	86.8	29.7	30.1	27.0
Fe–Zn–Zr@HZSM-5(3:1)	6.3:1	95.7	34.2	24.2	37.3

[a] Determined by ICP.

[b] Determined by NH_3-TPD.

[c] Quantified by deconvolution of the NH_3-TPD profiles with Gaussian peaks (R^2> 0.99).

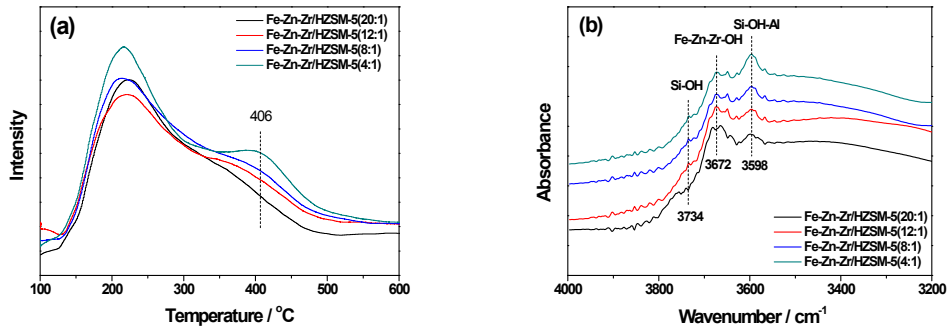

Fig. S6. NH_3-TPD profiles (a) and DRIFT spectra in the OH stretching region (b) of Fe–Zn–Zr/HZSM-5(50) granular–mixing catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios.

Table S4. Peak areas integrated from NH_3-TPD profiles of Fe–Zn–Zr/HZSM-5(50) granular-mixing catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios.

Samples	Total acid sites[a] (μmol/g)	Weak acid sites[b] (μmol/g)	Mediate acid sites[b] (μmol/g)	Strong acid sites[b] (μmol/g)
Fe–Zn–Zr/HZSM-5(20:1)	90.5	29.1	34.8	26.6
Fe–Zn–Zr/HZSM-5(12:1)	77.6	28.2	18.8	30.6
Fe–Zn–Zr/HZSM-5(8:1)	91.8	29.7	27.7	34.4
Fe–Zn–Zr/HZSM-5(4:1)	107.7	45.0	24.7	38.0

[a] Determined by NH_3-TPD.

[b] Quantified by deconvolution of the NH_3-TPD profiles with Gaussian peaks (R^2> 0.99).

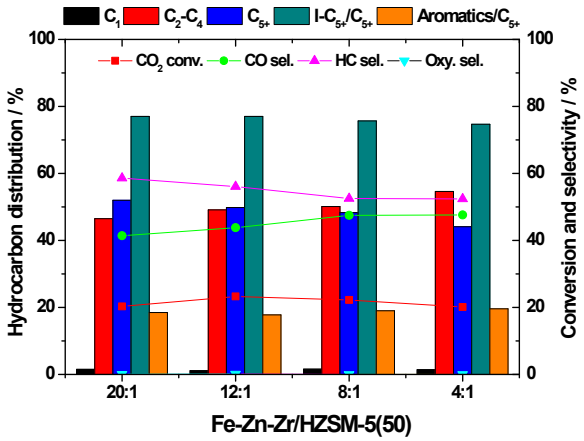

Fig. S7. CO_2 conversion and hydrocarbon distribution of CO_2 hydrogenation to gasoline over Fe–Zn–Zr/HZSM-5(50) granular–mixing catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios. (Reaction conditions: 5.0 MPa; 340 ^{o}C; 2 h; 3000 ml/g/h; $H_2/CO_2/N_2$=72/24/4.)

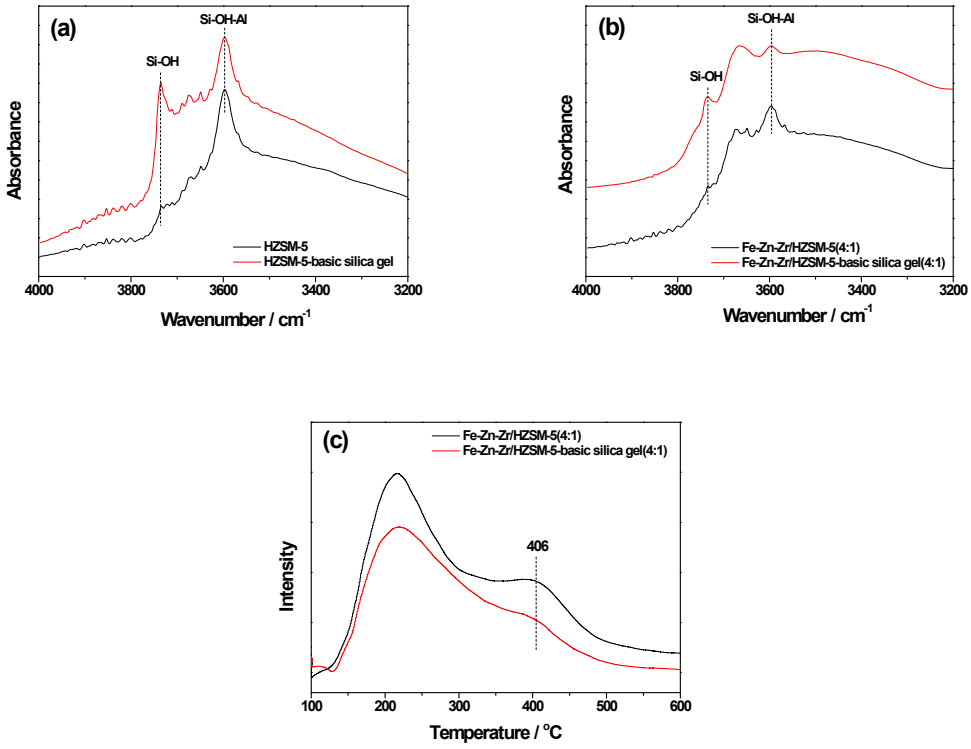

Fig. S8. Characterizations of HZSM-5(50) zeolite and Fe–Zn–Zr/HZSM-5(4:1) granular–mixing catalysts with SiO_2/Al_2O_3 of 50 before and after soaking by basic silica gel: (a, b) DRIFT spectra in the OH stretching region, (c) NH_3-TPD profiles.

Table S5. Peak areas integrated from NH_3-TPD profiles of Fe–Zn–Zr/HZSM-5(50) granular–mixing catalysts before and after soaking by basic silica gel.

Samples	Total acid sites[a] (μmol/g)	Weak acid sites[b] (μmol/g)	Mediate acid sites[b] (μmol/g)	Strong acid sites[b] (μmol/g)
Fe–Zn–Zr/HZSM-5(4:1)	107.7	45.0	24.7	38.0
Fe–Zn–Zr/HZSM-5-basic silica gel(4:1)	77.6	28.5	19.2	29.9

[a] Determined by NH_3-TPD.

[b] Quantified by deconvolution of the NH_3-TPD profiles with Gaussian peaks (R^2> 0.99).

Table S6. Reaction performances of Fe–Zn–Zr@HZSM-5(50) core–shell catalyst (Fe–Zn–Zr:HZSM-5=6:1) on CO_2 hydrogenation.

Space velocity (mL/g/h)	CO_2 conv.(%)	Selectivity (C-mol%)			Hydrocarbon distribution (C-mol %)			I-C_{5+}/ C_{5+}(%)	Aromatics/ C_{5+}(%)
		CO	Oxy	HC	C_1	C_2-C_4	C_{5+}		
3000	22.8	39.1	0.1	60.9	2.2	39.8	58.0	91.5	6.0
20000	12.3	34.3	5.0	60.7	2.4	44.0	53.7	89.6	7.1

5.0 MPa; 340 °C; 2 h; $H_2/CO_2/N_2$=72/24/4.

Oxy=oxygen compounds (MeOH+Me_2O); HC=hydrocarbon.

I-C_{5+}=C_{5+} isoalkanes; C_{5+}=C_{5+} hydrocarbons.

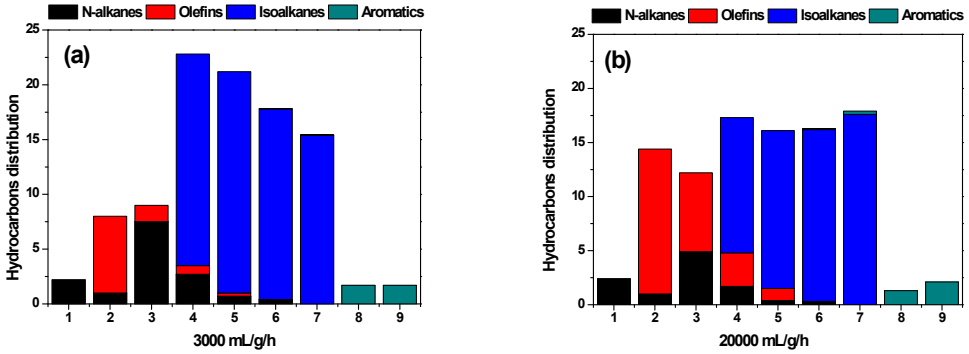

Fig. S9. Hydrocarbon distribution of Fe–Zn–Zr@HZSM-5(50) core–shell catalyst (Fe–Zn–Zr:HZSM-5=6:1) on CO_2 hydrogenation with different space velocity. (a) 3000 mL/g/h, (b) 20000 mL/g/h.

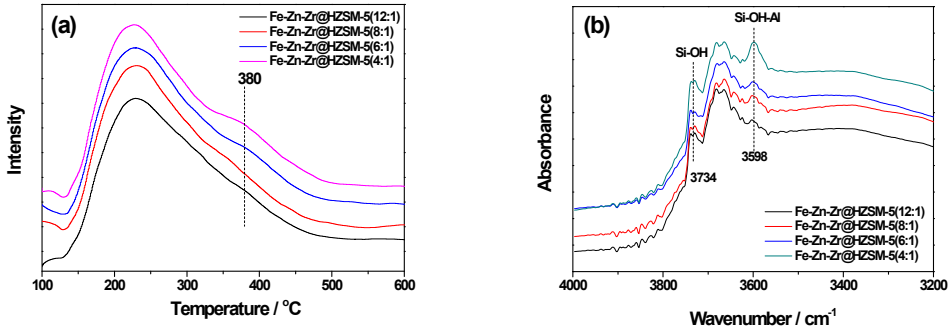

Fig. S10. NH_3-TPD profiles (a) and DRIFT spectra in the OH stretching region (b) of Fe–Zn–Zr@HZSM-5(38) core–shell catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios.

Table S7. Peak areas integrated from NH_3-TPD profiles of Fe–Zn–Zr@HZSM-5(38) core–shell catalysts with different Fe–Zn–Zr and HZSM-5 weight ratios.

Samples	Total acid sites[a] (μmol/g)	Weak acid sites[b] (μmol/g)	Mediate acid sites[b] (μmol/g)	Strong acid sites[b] (μmol/g)
Fe–Zn–Zr@HZSM-5(12:1)	89.1	34.2	32.8	22.1
Fe–Zn–Zr@HZSM-5(8:1)	83.5	29.1	31.5	22.9
Fe–Zn–Zr@HZSM-5(6:1)	88.5	27.2	33.3	28.0
Fe–Zn–Zr@HZSM-5(4:1)	92.0	35.6	24.1	32.3

[a] Determined by NH_3-TPD.

[b] Quantified by deconvolution of the NH_3-TPD profiles with Gaussian peaks (R^2> 0.99).