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Electronic Supplementary Information (ESI)

Synthesis of isoalkanes over core (Fe-Zn-Zr)-shell (zeolite) catalyst from CO_2 hydrogenation

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Experimental section

Catalyst preparation

Fe-Zn-Zr core preparation

The Fe-Zn-Zr core was prepared according to the reference by a co-precipitation method.[1] The typical prepared steps were as follows: 10.1 g $Fe(NO_3)_3 \cdot 9H_2O$, 7.5 g $Zn(NO_3) \cdot 6H_2O$, and 6.7 g $ZrO(NO_3) \cdot 2H_2O$ were dissolved in 75 g H_2O. The mixed solution was concurrently added with 0.4 M NaOH solution to a beaker and stirred continuously at 65 °C. The pH value was kept at about 7.0. The precipitate was aged for 2 h, then filtered and washed with distilled water. The obtained gels were dried at 100 °C for 12 h, and then calcined at 400 °C for 4 h. The Fe-Zn-Zr catalyst was pelletized and crushed to obtain 30–40 mesh sizes.

Fe-Zn-Zr@zeolite core-shell catalysts preparation

The core-shell catalysts with Fe-Zn-Zr as core and zeolite (one or two types of HZSM-5, Hbeta and HY zeolites) as shell were prepared by a simple cladding method according to the reference.[2] HZSM-5(SiO_2/Al_2O_3=38) and Hbeta(SiO_2/Al_2O_3=26) were purchased from NanKai University Catalyst Co. Ltd. (Tianjin, China). HY(SiO_2/Al_2O_3=5) was purchased from JGC Catalysts and Chemicals Ltd. (Japan). The detailed preparation procedures were as follows: A certain amount of silica sol (30 wt.%) was diluted with 1.5 times deionized water in weight. The diluted silica sol, as binder, was used to moisten the Fe-Zn-Zr catalyst. And then an half of zeolite powder (one or two types of HZSM-5, Hbeta and HY zeolites) was mixed with the soaked Fe-Zn-Zr core in a round bottomed flask by simple manual stirring, and this step was repeated twice until forming one uniform, compact zeolite shell coating on the surface of Fe-Zn-Zr core. The obtained sample was finally treated by calcination at 500 °C for 2 h. The zeolite encapsulating Fe-Zn-Zr core was noted as Fe-Zn-Zr@zeolite(x:y)(x:y=2:1~16:1, stands for the weight ratio of Fe-Zn-Zr and zeolite). The mechanical mixture catalyst was obtained by physically mixing the Fe-Zn-Zr catalyst and an equal granular size zeolite, which was labeled as Fe-Zn-Zr/zeolite(x':y')(x':y'=2:1). Otherwise, Fe-Zn-Zr@zeolite catalysts with double-zeolites shell were also synthesized by the above processes, and Fe-Zn-Zr:zeolite=2:1 or 4:1(weight ratio).

Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded on a D8 advance diffractometer using Cu Ka radiation run at 40 kV and 100 mA. NH_3-temperature programmed desorption (NH_3-TPD) profiles were obtained using a TP-5080 chemisorption instrument. Typically, the pure zeolite (100 mg) or the Fe-Zn-Zr@zeolite (300 mg) was pretreated at 600 °C under N_2 flow (30 ml min^{-1}) for 0.5 h and then cooled to 100 °C to adsorb NH_3. The TPD profiles were recorded from 100 to 600 °C at a heating rate of 10 °C/min. SiO_2/Al_2O_3 ratios and Fe, Zn, Zr contents of as-prepared samples were determined on a Thermo ICAP 6300 inductive coupled plasma emission spectrometer (ICP). The textural characteristics were measured using Micromerities company Tristar 3000 physical adsorption apparatus at 77 K. Scanning electron microscopy (SEM) images were obtained on JSM-7001F scanning electron microscopy.

Catalytic tests

The CO_2 hydrogenation was performed in a fixed bed reactor. In a typical experiment, the 6 g catalyst was packed in the reactor. The prereduction was conducted using a stream of diluted hydrogen (10% H_2 in N_2) at 340 °C for 12 h. After prereduction, the reactant gas ($H_2/CO_2/N_2$=69/23/8) was introduced into the reactor under 5.0 MPa. The pipeline from the catalyst bed to the gas chromatography was heated at 120 °C so as to prevent the possible condensation of the products. During the reaction, all effluent gases were analyzed by on-line gas chromatographs using carbon molecular sieve column for hydrogen, carbon monoxide and methane, GDX-403 column for hydrocarbons, methanol and dimethyl ether. N_2 was used as the internal standard for chromatographic analysis. The analytical results from different gas chromatographs were connected by methane concentration. The carbon balance is calculated by the following formula. C_{out}(mol/h/g) stands for the carbon moles of all products on per gram catalyst per hour, and C_{in}(mol/h/g) means the carbon moles of CO_2 in feed gas on per gram catalyst per hour.

$$\text{Carbon balance}(\%) = \frac{C_{out}(\text{mol/h/g})}{C_{in}(\text{mol/h/g})} \times 100\%$$

Supplementary Figures and Tables

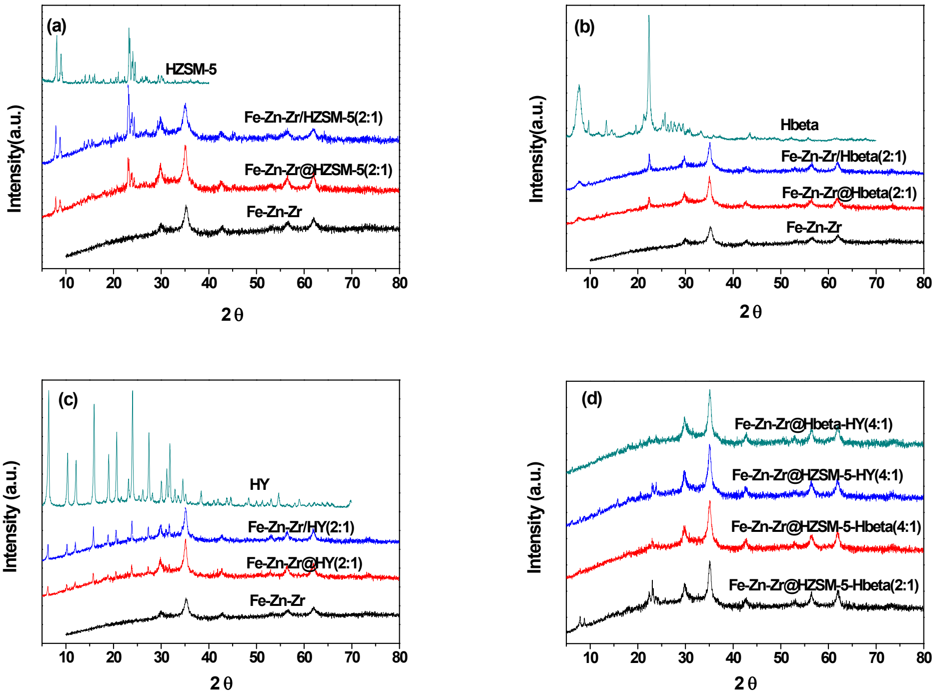

Fig. S1 XRD patterns of Fe-Zn-Zr@zeolite with (a) HZSM-5, (b) Hbeta, (c) HY single-zeolite shell, and with (d) double-zeolites shell catalysts.

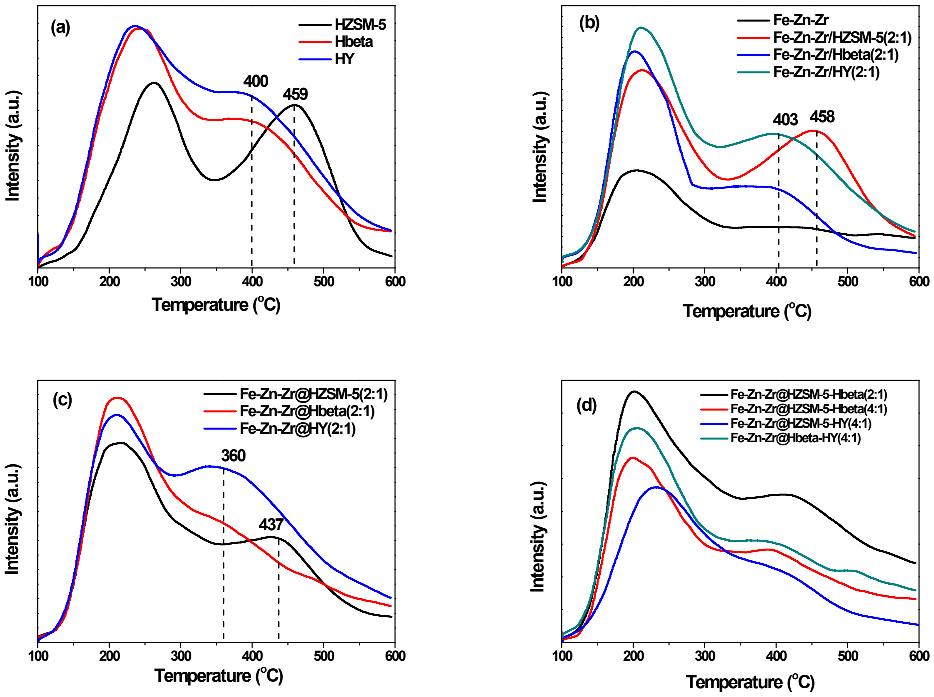

Fig. S2 NH_3-TPD profiles of (a) different zeolites, (b) Fe-Zn-Zr/zeolite mixture, (c) Fe-Zn-Zr@zeolite with single-zeolite shell, and (d) Fe-Zn-Zr@zeolite with double-zeolites shell catalysts.

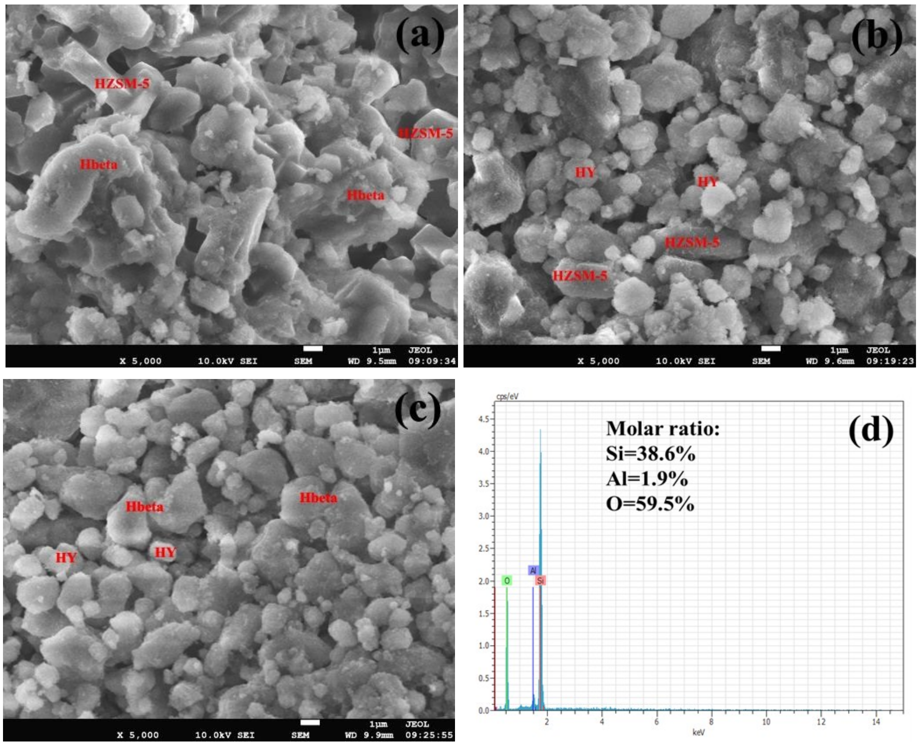

Fig. S3 Surface SEM images of (a) Fe-Zn-Zr@HZSM-5-Hbeta(4:1), (b) Fe-Zn-Zr@HZSM-5-HY(4:1), (c) Fe-Zn-Zr@Hbeta-HY(4:1) and EDS analysis of (d) Fe-Zn-Zr@HZSM-5-Hbeta(4:1) catalysts.

(a) $CO_2+3H_2 \xrightarrow{\text{Fe-Zn-Zr}} CH_3OH+H_2O$

(b) $CO_2+H_2 \xrightarrow{\text{Fe-Zn-Zr}} CO+H_2O$

(c)

$$\begin{tikzcd}
CO_2+3H_2 \arrow[r, "\text{Fe-Zn-Zr}"] & CH_3OH \arrow[r, "\text{Zeolite}"] & CH_3OCH_3 \arrow[r, "\text{Zeolite}"] \arrow[d, "\text{Zeolite}"'] & C_{2=}+C_{3=} \arrow[r, "\text{Zeolite}"] \arrow[d, "\text{Zeolite}"', "CH_3OH"] & \text{i-}C_5 \\
& \text{i-}C_5 & \text{i-}C_{4=} \arrow[l, "\text{Zeolite}"', "CH_3OH"] \arrow[r] & \text{i-}C_4 &
\end{tikzcd}$$

Fig. S4 The possible reaction routes of CO_2 hydrogenation to isoalkanes over (a,b) Fe-Zn-Zr and (c) Fe-Zn-Zr@zeolite catalysts.

Table S1 Reaction performances of Fe-Zn-Zr@HZSM-5 catalysts with different core and shell weight ratio on CO_2 hydrogenation.

Catalysts	C-CO_2 (%)	C balance (%)	Selectivity (C-mol%)			Distribution of hydrocarbons (C-mol%)							i-HC /t-HC (%)
			CO	Oxy	HC	C_1	C_2	C_3	i-C_4	C_4	i-C_{5+}	C_{5+}	
Fe-Zn-Zr@HZSM-5 (16:1)	11.9	100.7	71.1	27.2	1.7	78.1	6.3	7.9	4.5	3.2	0.0	0.0	4.5
Fe-Zn-Zr@HZSM-5 (8:1)	17.7	96.6	52.2	1.2	46.5	2.6	12.4	14.6	31.7	4.4	33.0	1.3	64.7
Fe-Zn-Zr@HZSM-5 (4:1)	16.0	99.4	44.5	0.0	55.5	1.9	4.6	19.0	35.1	5.7	32.6	1.0	67.8
Fe-Zn-Zr@HZSM-5 (2:1)	15.8	99.6	50.3	0.0	49.7	2.3	4.1	22.4	36.8	7.1	25.9	1.3	62.7

Reaction conditions: 5.0 MPa; 340 ^oC; 2 h; 3000 ml/g/h; $H_2/CO_2/N_2$=69/23/8.

Fe-Zn-Zr=1:1:1(atomic ratio); Fe-Zn-Zr:HZSM-5= 16:1~2:1(weight ratio).

HC=hydrocarbons; Oxy=oxygen compounds(MeOH+Me_2O); i-HC(i-C_4+i-C_{5+})=isoalkanes; t-HC=total hydrocarbons.

Table S2 Reaction performances of core-shell catalysts with different zeolites weight ratio on CO_2 hydrogenation.

Catalysts	$C\text{-}CO_2$ (%)	C balance (%)	Selectivity (C-mol%)			Distribution of hydrocarbons (C-mol%)							i-HC /t-HC (%)
			CO	Oxy	HC	C_1	C_2	C_3	$i\text{-}C_4$	C_4	$i\text{-}C_{5+}$	C_{5+}	
Fe-Zn-Zr@HZSM-5 (4:1)	16.0	99.4	44.5	0.0	55.5	1.9	4.6	19.0	35.1	5.7	32.6	1.0	67.8
Fe-Zn-Zr@HZSM-5 -Hbeta(4:1)(2:1)	15.6	99.3	49.7	0.4	49.9	2.2	4.9	9.9	43.7	3.2	35.5	0.6	79.2
Fe-Zn-Zr@HZSM-5 -Hbeta(4:1)(1:1)	14.9	102.8	38.6	0.6	60.8	1.5	4.3	9.0	55.1	3.3	26.2	0.6	81.3
Fe-Zn-Zr@HZSM-5 -Hbeta(4:1)(1:2)	16.1	101.2	41.6	0.4	57.9	1.6	4.1	9.8	53.8	3.6	26.5	0.7	80.3
Fe-Zn-Zr@Hbeta (4:1)	15.1	103.6	37.7	0.3	62.0	1.3	3.6	12.0	58.3	4.3	19.7	0.8	78.0

Reaction conditions: 5.0 MPa; 340 ^oC; 2 h; 3000 ml/g/h; $H_2/CO_2/N_2$=69/23/8.

Fe-Zn-Zr=1:1:1(atomic ratio); Fe-Zn-Zr:zeolite= 4:1(weight ratio); HZSM-5:Hbeta=2:1~1:2(weight ratio).

HC=hydrocarbons; Oxy=oxygen compounds(MeOH+Me_2O); i-HC($i\text{-}C_4$+$i\text{-}C_{5+}$)=isoalkanes; t-HC=total hydrocarbons.

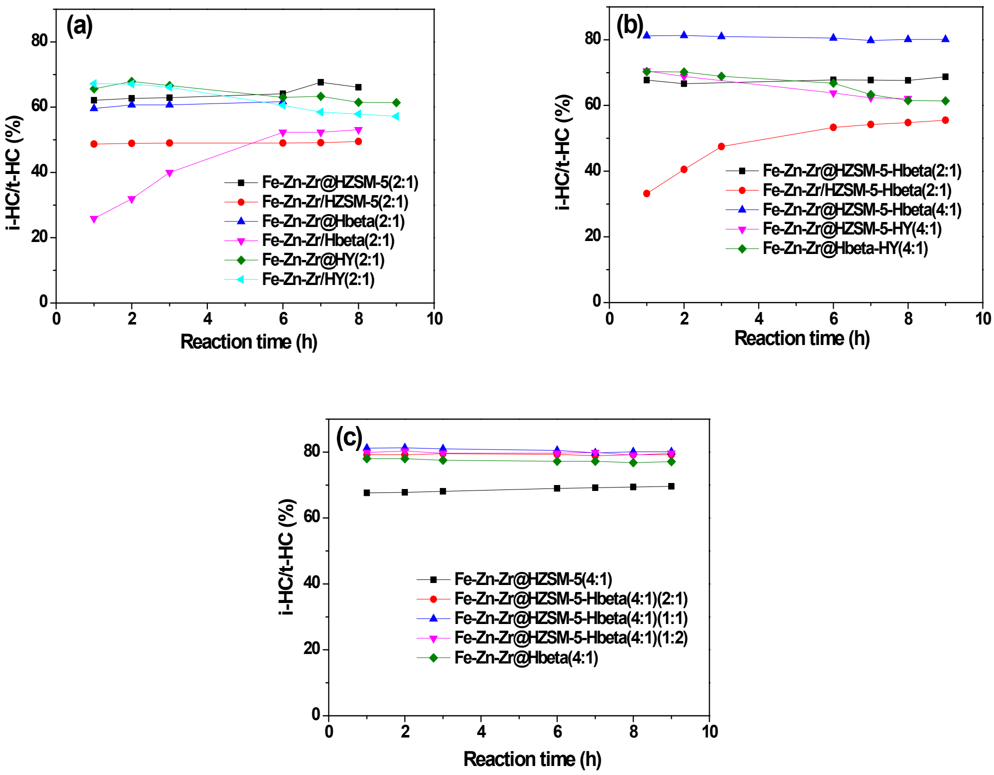

Fig. S5 I-HC/t-HC ratio versus time on stream over (a) Fe-Zn-Zr@zeolite with single-zeolite shell, (b) Fe-Zn-Zr@zeolite with double-zeolites shell and (c) Fe-Zn-Zr@HZSM-5-Hbeta with different zeolite ratio catalysts.

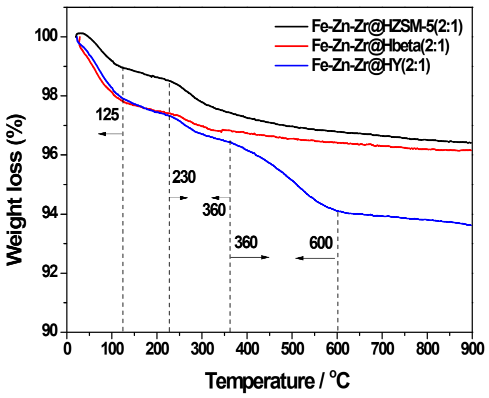

Fig. S6 TG profiles of Fe-Zn-Zr@zeolite(2:1) catalysts with different single-zeolite shell after 9 h time on stream.

References

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2 G. Yang, C. Xing, W. Hirohama, Y. Jin, C. Zeng, Y. Suehiro, T. Wang, Y. Yoneyama and N. Tsubaki, *Catal. Today*, 2013, **215**, 29.