Supporting Information

One-Step Synthesis of Pentane Fuel from γ-Valerolactone with High Selectivity over Co/HZSM-5 Bifunctional Catalyst

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Experimental Section

Chemical

γ-Valerolactone (GVL, >98%, AR), Tetraethyl orthosilicate (TEOS, 98.6%, AR), Tetrapropylammonium hydroxide (TPAOH, 25%, AR), Aluminum isopropoxide (98%, AR), $Co(NO_3)_2 \cdot 6H_2O$ (99%, AR) were purchased from Xilong chemical co., LTD. All of the chemical reagents were directly used as received without further purification.

Catalyst characterization

Surface morphology of samples was measured by Scanning electron microscopy (SEM) using the Scanning Electron Microscope QUANTA F250 instrument made by American FEI company. Fine morphology of catalysts was detected by Transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (EDS) on a Titan G260-300 microscope at an extraction voltage of 3950 V. Phase compositions of the powder catalysts were determined by Powder X-ray diffraction (PXRD) with a Smartlab (Rigaku) X-ray diffractometer filtering Cu Kα radiation (λ = 1.5405 Å) and assisted by JADE software. Texture properties of catalysts were analyzed by N_2 adsorption-desorption isotherms using JWBK100B static specific surface analyzer. The specific surface area (S_{BET}) was based on Brunauer-Emmett-Teller (BET) equation, the internal surface area (S_{int}) and the external surface area (S_{ext}) were calculated using the t-plot method, the total pore volume (V_t) and the micropore volume (V_{mic}) were assessed according to Barrett-Joyner-Halenda (BJH) method and H-K method, respectively. The pore diameter (D_p) was the mean pore diameter of samples. The

density and strength of accessible acidic sites on catalysts were measured by NH_3-temperature programmed desorption (NH_3-TPD) using a DAS-7000 Instrument (Hunan HUASI) in the temperature range of 100 °C to 800 °C at a heating rate of 10 °C/min. Acid types of catalysts were determined by Pyridine adsorption infrared spectroscopy (Py-IR) using a Bruker VERTEX spectrometer. The reducibility of catalysts was analyzed by H_2-temperature programmed reduction (H_2-TPR) from 50 °C to 800 °C using the same machine and heating rate as that for NH_3-TPD. Cu valence states of catalysts were examined by X-ray photoelectron spectroscopy (XPS) on a Thermal XPS ESCALAB 250Xi Spectrometer. Thermogravimetric analysis (TG) was carried out on METTLER TGA/DSC in the temperature range of 50 to 900 °C at a heating rate of 10 °C/min.

Catalytic test

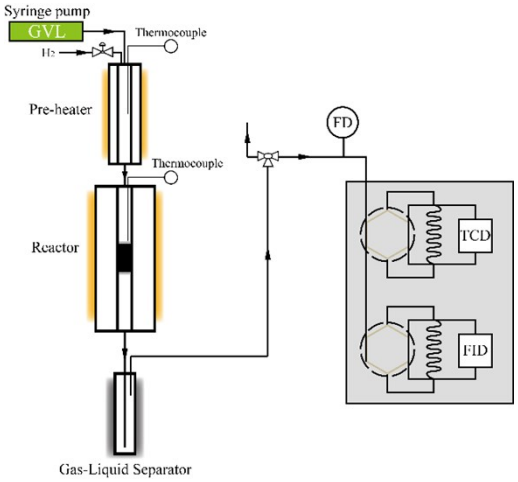

Fig. S1 The schematic diagram of continuous fixed-bed catalytic system.

The schematic diagram of the continuous fixed-bed catalytic system for the direct synthesis of pentane fuel from GVL was shown in Fig. S1. Typically, 0.5 g Co/HZSM-5 catalyst was loaded in the center of stainless steel tubular Reactor (300 mm length, 11

mm i.d.) between two end-plugs of quartz wool, which was pre-reduced by H_2 (60 mL/min) for 4 h at 400 °C, and then cooled down to the specified reaction temperature. After the reactor system was pressurized to the specified value and reached a stable state, GVL was continuously fed into Reactor through gasification process in Pre-heater. Liquid products were collected in Gas-Liquid Separator (0 °C) after condensation, which were identified by GC-MS (Agilent 5975C/7890A) and quantified by a gas chromatograph (FULI GC 97) with RB-5 capillary column. Gaseous products were detected online by a gas chromatograph (FULI GC 97) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Porapak Q and 5A MolSieve packed column were connected to TCD, while RB-PLOT Al_2O_3 capillary column was connected to FID. In addition, the contents of gaseous products were determined by the external standard method calibrated by the standard gas. The contents of liquid products were analyzed using calibration curves, with dichloromethane as internal standard. In general, the total carbon balance difference was within 5%.

GVL conversion, selectivity and yield of pentane were calculated using the equations as follow:

$$GVL\ conversion(C_{GVL}, mol\%) = \frac{mols\ of\ carbon_{GVL,in} - mols\ of\ carbon_{GVL,out}}{mols\ of\ carbon_{GVL,in}} \times 100\%$$

$$Pentane\ selectivity(S_{pentane}, mol\%) = \frac{mols\ of\ carbon\ of\ pentane}{mols\ of\ total\ carbon\ converted\ GVL\ feed} \times 100\%$$

$$Pentane\ yield(Y_{pentane}, mol\%) = \frac{mols\ of\ carbon\ of\ pentane}{mols\ of\ total\ carbon\ of\ GVL\ feed} \times 100\%$$

$$Pentane\ yield(Y_{pentane}, mol\%) = C_{GVL} \times S_{pentane}$$

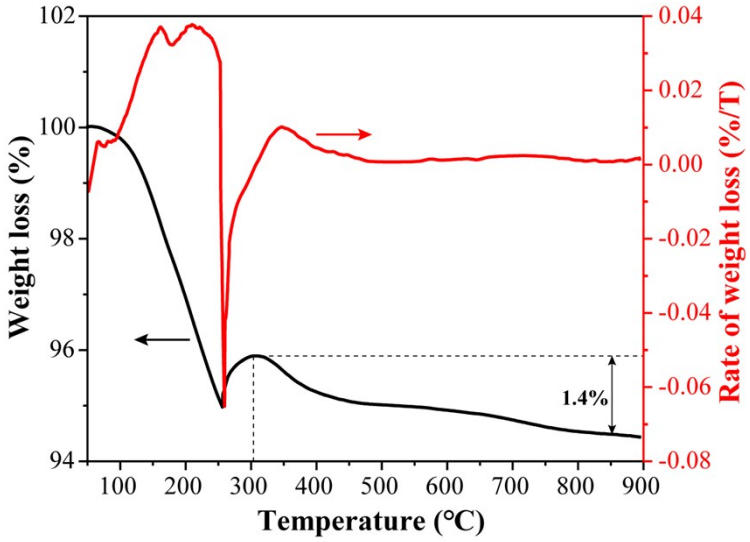

Fig. S2 TG-DTG analysis of the spent 20Co/HZ5 (80) catalyst after 100 h on stream.

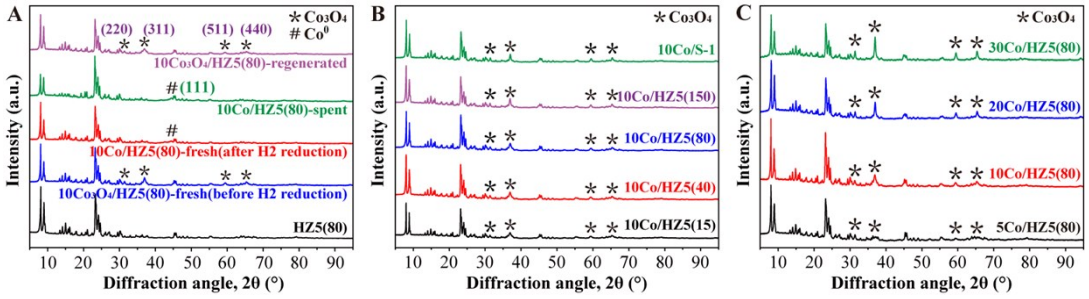

Fig. S3 PXRD patterns of Co/HZSM-5 catalysts with (A) samples before and after catalytic reaction, (B) different SAR and (C) different Co loading content.

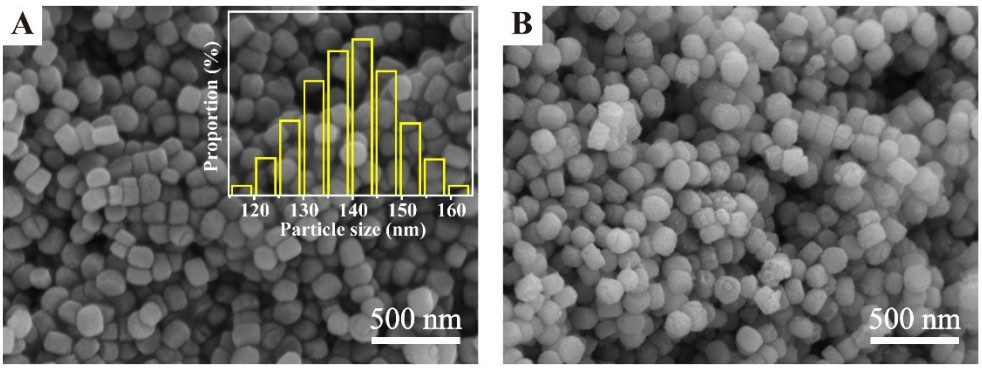

Fig. S4 (A) SEM image of HZ5 (80) zeolite. Inset is its particle sizes distribution. (B) SEM image of 20Co/HZ5 (80) sample.

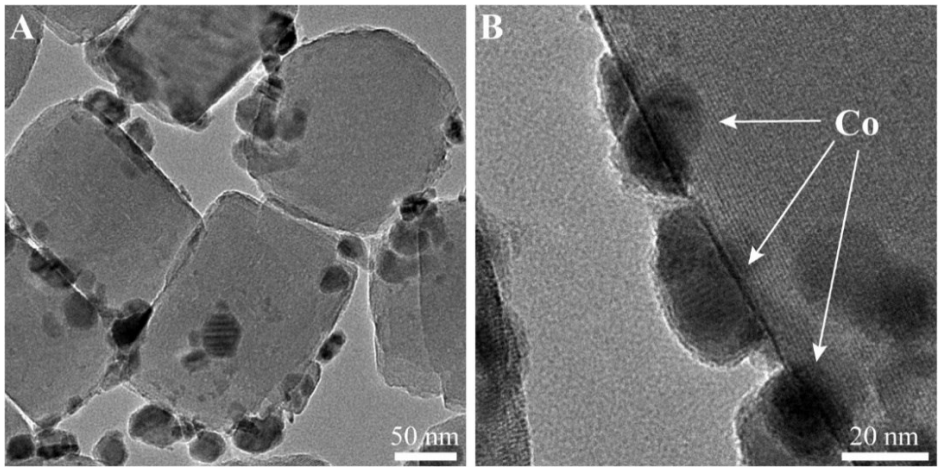

Fig. S5 TEM images of the spent 20Co/HZ5 (80) catalyst after 100 h on stream.

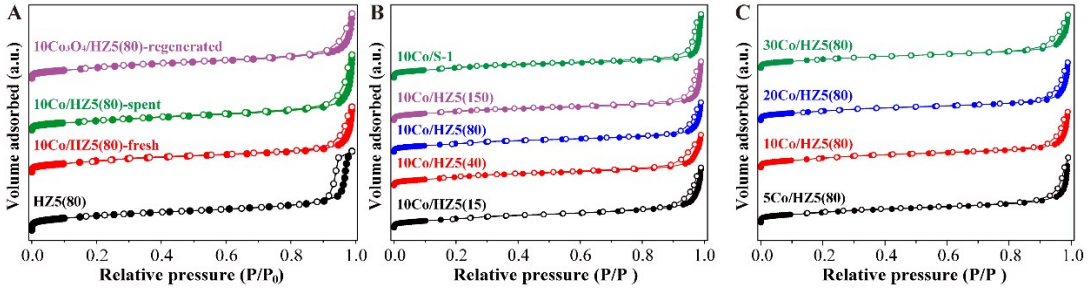

Fig. S6 N_2 adsorption-desorption isotherms of Co/HZSM-5 catalysts with (A) samples before and after catalytic reaction, (B) different SAR and (C) different Co loading content.

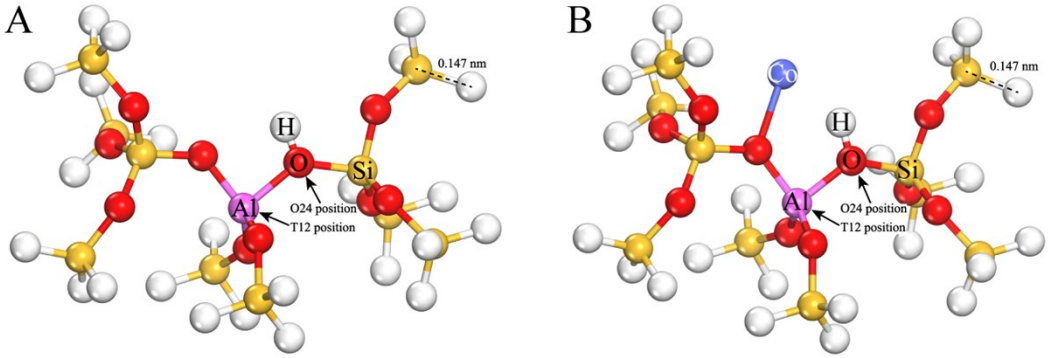

Fig. S7 (A) 11T cluster model of HZSM-5. (B) The model of Co/HZSM-5.

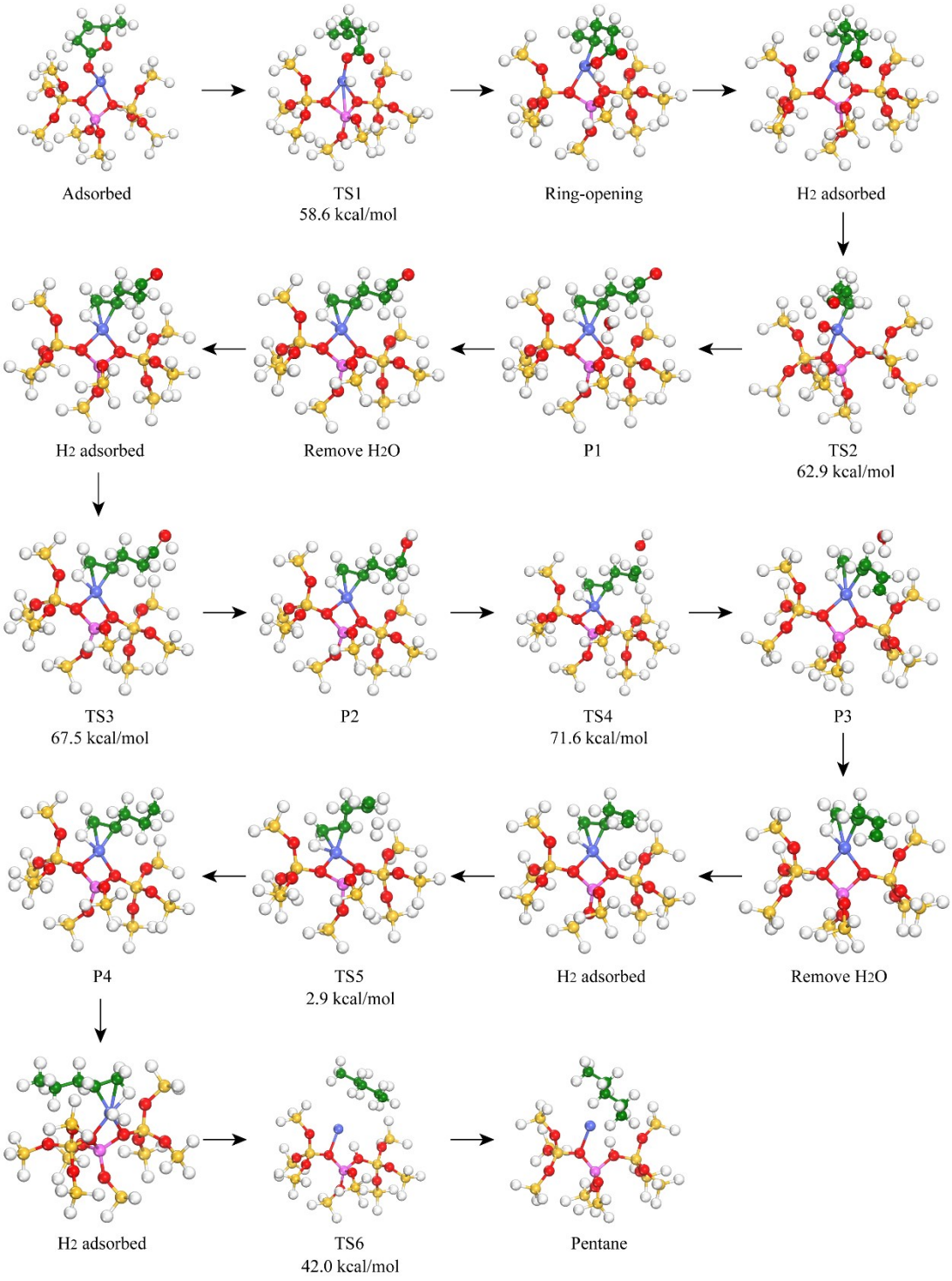

Fig. S8 Elementary reaction simulation for the formation of pentane from the cleavage of C4-O1 bond in GVL on Co/HZSM-5.

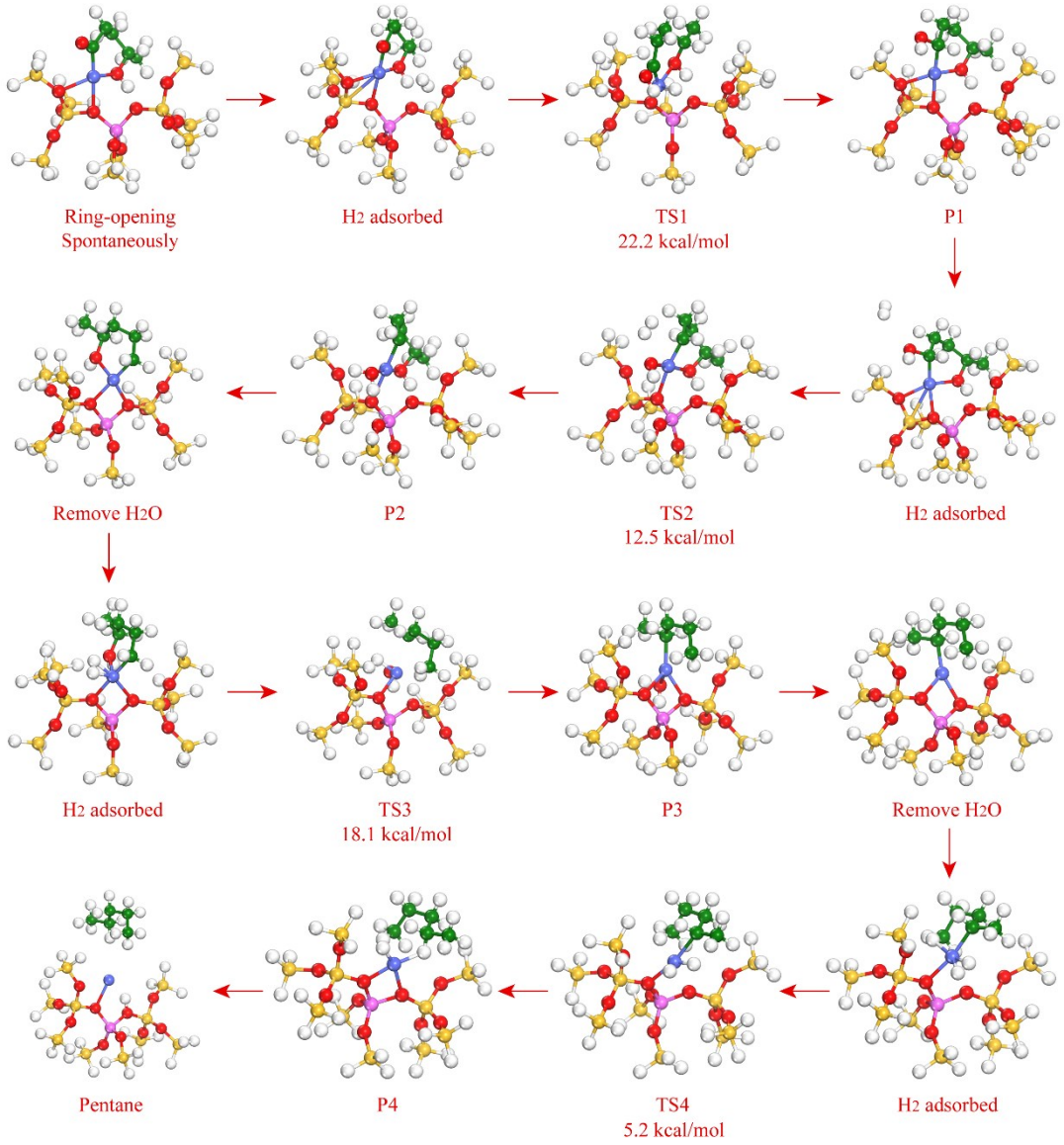

Fig. S9 Elementary reaction simulation for the formation of pentane from the cleavage of C1-O1 bond in GVL on Co/HZSM-5.

Table S1. Catalytic performance for GVL to pentane over 10Co/HZ5 (SAR) catalysts with different Si/Al molar ratios[a].

SAR	15	40	80	150	S-1
C_{GVL}	79.9	83.3	87.7	74.9	90.7
$S_{Pentane}$	73.4	79.1	83.6	67.7	1.8
$Y_{Pentane}$	58.6	65.9	73.3	50.7	1.6
Full components analysis (%)					
Non-hydrocarbon products					
butanol	0.0	0.0	0.0	0.0	7.5
2-methyltetrahydrofuran	0.2	0.5	1.1	7.7	63.1
pentanoic acid	14.9	10.6	7.0	13.1	0.0
pentanol	0.6[b]	0.5[b]	0.7[b]	0.8[b]	21.1[c]
pentyl valerate	4.9	3.6	2.4	4.6	0.0
Hydrocarbon products					
CH_4	0.3	0.2	0.3	0.2	3.6
$C_{2\text{-}4}^{0}$	0.6	1.0	1.2	0.6	2.9
$C_{2\text{-}4}^{=}$	0.0	0.0	0.0	0.1	0.0
C_5^{0}	73.4	79.1	83.6	67.7	1.8
$C_5^{=}$	5.1	4.5	3.7	5.2	0.0

[a] Reaction conditions: T = 200 °C, P = 1.0 MPa, WHSV = 0.6 h^{-1}, Flow of carrier gas H_2 = 60 $mL \cdot min^{-1}$, Time = 5 h. [b] Corresponding to 1-pentanol. [c] Corresponding to 2-pentanol.

Table S2. Catalytic performance of contrast experiments with 10Cu/S-1 to 10Co/S-1 catalysts at different temperature[a].

Sample/Temperature (℃)	10Cu/S-1			10Co/S-1		
	200	250	280	200	250	280
C_{GVL}	17.0	26.8	52.1	88.3	99.9	99.7
$S_{Pentane}$	0.0	0.1	0.1	5.7	4.2	2.0
$Y_{Pentane}$	0.0	0.0	0.1	5.0	4.2	2.0
Full components analysis (%)						
Non-hydrocarbon products						
ethanol	7.9	11.9	0.5	3.1	22.1	24.3
butanol	1.8	0.8	0.5	9.9	0.8	0.0
2-methyltetrahydrofuran	19.4	7.2	5.1	25.3	0.5	0.0
pentanoic acid	59.2	58.1	53.6	0.1	0.1	0.3
pentanol	10.4[b]	17.2[b]	27.7[b]	11.4[c]	0.4[c]	0.0[c]
pentyl valerate	0.4	1.9	8.2	0.0	0.1	0.0
others	0.1	1.0	3.0	3.3	0.1	0.1
Hydrocarbon products						
CH_4	0.0	0.0	0.0	26.9	53.5	60.4
$C_{2\text{-}4}^{0}$	0.0	0.1	0.0	13.7	18.2	12.9
$C_{2\text{-}4}^{=}$	0.2	0.4	0.3	0.3	0.0	0.0
C_5^{0}	0.0	0.1	0.1	5.7	4.2	2.0
$C_5^{=}$	0.6	1.3	1.0	0.3	0.0	0.0

[a] Reaction conditions: P = 0.1 MPa, WHSV = 0.6 h^{-1}, Flow of carrier gas H_2 = 60 $mL \cdot min^{-1}$, Time = 5 h. [b] Corresponding to 1-pentanol. [c] Corresponding to 2-pentanol.

Table S3. Catalytic performance for GVL to pentane over Co/HZ5 (80) catalysts with different Co loading content[a].

Loading content (wt.%)	0	5	10	20	30
C_{GVL}	38.5	58.7	87.7	99.5	99.8
$S_{Pentane}$	0.2	43.4	83.6	90.8	85.6
$Y_{Pentane}$	0.1	25.5	73.3	90.3	85.4
Full components analysis (%)					
Non-hydrocarbon products					
2-methyltetrahydrofuran	0.0	5.6	1.1	0.7	0.3
pentanoic acid	68.8	31.6	7.0	0.1	0.0
1-pentanol	0.1	1.3	0.7	0.4	0.4
pentyl valerate	0.0	9.7	2.4	0.1	0.0
Hydrocarbon products					
CH_4	0.1	0.2	0.3	2.3	4.1
C_{2-4}^0	0.7	0.6	1.2	5.5	9.6
$C_{2-4}^=$	17.5	0.1	0.0	0.0	0.0
C_5^0	0.2	43.4	83.6	90.8	85.6
$C_5^=$	6.1	7.5	3.7	0.1	0.0
C_{5+}	6.5	0.0	0.0	0.0	0.0

[a] Reaction conditions: T = 200 °C, P = 1.0 MPa, WHSV = 0.6 h^{-1}, Flow of carrier gas H_2 = 60 $mL \cdot min^{-1}$, Time = 5 h.

Table S4. Catalytic performance for GVL to pentane over 20Co/HZ5 (80) catalyst with different temperature[a].

Temperature (°C)	170	185	200	215	230
C_{GVL}	71.1	91.8	99.5	99.8	99.9
$S_{Pentane}$	31.8	59.0	90.8	81.4	66.6
$Y_{Pentane}$	22.6	54.2	90.3	81.2	66.5
Full components analysis (%)					
Non-hydrocarbon products					
2-methyltetrahydrofuran	55.2	33.1	0.7	0.1	0.0
pentanoic acid	0.7	0.5	0.1	0.0	0.1
1-pentanol	3.9	1.1	0.4	0.0	0.2
pentyl valerate	6.8	2.9	0.1	0.0	0.0
Hydrocarbon products					
CH_4	0.3	0.7	2.3	7.4	13.7
$C_{2\text{-}4}^{0}$	0.8	2.3	5.5	11.1	19.4
$C_{2\text{-}4}^{=}$	0.0	0.0	0.0	0.0	0.0
C_5^0	31.8	59.0	90.8	81.4	66.6
$C_5^=$	0.5	0.4	0.1	0.0	0.0

[a] Reaction conditions: P = 1.0 MPa, WHSV = 0.6 h^{-1}, Flow of carrier gas H_2 = 60 $mL \cdot min^{-1}$, Time = 5 h.

Table S5. Catalytic performance for GVL to pentane over 20Co/HZ5 (80) catalyst with different pressure[a].

Pressure (MPa)	0.1	0.5	1.0	1.5	2.0
C_{GVL}	94.4	97.9	99.5	99.6	99.7
$S_{Pentane}$	34.7	64.3	90.8	84.6	67.3
$Y_{Pentane}$	22.6	54.2	90.3	81.2	66.5
Full components analysis (%)					
Non-hydrocarbon products					
2-methyltetrahydrofuran	4.4	1.4	0.7	4.8	16.2
pentanoic acid	1.3	0.1	0.1	0.0	0.1
1-pentanol	2.1	1.1	0.4	5.4	11.9
pentyl valerate	0.3	0.1	0.1	0.0	0.8
Hydrocarbon products					
CH_4	26.1	13.5	2.3	1.2	0.8
$C_{2\text{-}4}^{0}$	29.7	19.4	5.5	4.0	2.9
$C_{2\text{-}4}^{=}$	0.5	0.0	0.0	0.0	0.0
C_5^0	34.7	64.3	90.8	84.6	67.3
$C_5^=$	0.9	0.1	0.1	0.0	0.0

[a] Reaction conditions: T = 200 °C, WHSV = 0.6 h^{-1}, Flow of carrier gas H_2 = 60 mL·min^{-1}, Time = 5 h.

Table S6. Catalytic performance for GVL to pentane over 20Co/HZ5 (80) catalyst with different WHSV of GVL[a].

WHSV (h^{-1})	0.08	0.15	0.3	0.6	1.0
C_{GVL}	99.9	99.9	99.9	99.5	90.6
$S_{Pentane}$	83.2	89.9	93.5	90.8	75.4
$Y_{Pentane}$	83.8	89.8	93.2	90.3	59.1
Full components analysis (%)					
Non-hydrocarbon products					
2-methyltetrahydrofuran	0.0	0.0	0.1	0.7	8.3
pentanoic acid	0.0	0.0	0.0	0.1	0.1
1-pentanol	0.0	0.0	0.1	0.4	3.7
pentyl valerate	0.0	0.0	0.0	0.1	0.1
Hydrocarbon products					
CH_4	6.1	3.1	1.4	2.3	4.3
$C_{2\text{-}4}^{0}$	10.7	6.9	4.9	5.5	8.0
$C_{2\text{-}4}^{=}$	0.0	0.0	0.0	0.0	0.0
C_5^0	83.2	89.9	93.5	90.8	75.4
$C_5^=$	0.0	0.0	0.0	0.1	0.1

[a] Reaction conditions: T = 200 °C, P = 1.0 MPa, Flow of carrier gas H_2 = 60 mL·min^{-1}, Time = 5 h.

Table S7. Comparison of fuels components selectivity and catalytic activity as well as reaction conditions with the previous reports.

Entry	Catalysts	Reactor	Reaction conditions and catalytic activity						Ref.[a]
			T (℃)	P (MPa)	WHSV (h^{-1})	GVL conv. (%)	Fuel components	Fuels sel. (%)	
1	SiO_2/Al_2O_3 (Ⅰ) + Amberlyst-70 (Ⅱ)	Dual-bed	375 (Ⅰ) 170 (Ⅱ)	3.6	0.22	99	C_8-C_{16} alkenes	60.0	Ref 16
2	Pd/Nb_2O_5 (Ⅰ) + $Ce_{0.5}Zr_{0.5}O_2$ (Ⅱ) + Ru/C (Ⅲ) + Amberlyst-70 (Ⅳ) + Ru/C (Ⅴ)	Multiple	325 (Ⅰ) 425 (Ⅱ) 150 (Ⅲ) 140 (Ⅳ) 160 (Ⅴ)	1.4 (Ⅰ) 1.4 (Ⅱ) 4.0 (Ⅲ) 0.1 (Ⅳ) 0.1 (Ⅴ)	0.72	96	C_{18}-C_{27} alkanes	~ 65	Ref 17
3	SiO_2/Al_2O_3 (Ⅰ) + $[CF_3CH_2OH_2][CF_3CH_2OBF_3]$ (Ⅱ)	Dual-batch	350 (Ⅰ) 10 (Ⅱ)	0.1 (Ⅰ) 0.1 (Ⅱ)	--	99	Gasoline	~ 80	Ref 18
4	100% H_3PO_4	Single-batch	240	0.1	--	99	Aromatics	33.5	Ref 12
5	HZSM-5	Single-bed	500	0.1	2.0	99	Aromatics	56.7	Ref 13
6	Pd/HY	Single-batch	260	8.0	--	99	Pentyl valerate	60.6	Ref 14
7	Pt/HZSM-5	Single-bed	250	1.0	2.0	60	Pentyl valerate	~ 80	Ref 15
8	Pd/HY	Single-batch	280	4.0	--	99	Pentane	23.1	Ref 14
9	Co/HZSM-5	Single-bed	200	1.0	0.3	99.9	Pentane	93.5	This work

[a] Corresponding to the References in the Manuscript.

Table S8. Textural properties of 10Co/HZ5 (80) catalysts before and after catalytic reaction with different Co species.

Samples	Surface area ($m^2 \cdot g^{-1}$)				Pore volume ($cm^3 \cdot g^{-1}$)		Pore diameter (nm)
	S_{BET}	S_{int}	S_{ext}	R_{ext}[a]	V_t	V_{mic}	D_p
HZ5(80)	474.8	367.1	107.7	0.227	0.49	0.19	4.14
10Co/HZ5(80)-fresh	407.2	311.2	96.0	0.236	0.42	0.16	4.10
10Co/HZ5(80)-spent	335.6	230.6	105.0	0.313	0.34	0.13	5.23
10Co/HZ5(80)-regenerated	390.5	291.6	98.9	0.253	0.41	0.16	4.20

[a] R_{ext}, external specific surface area (S_{ext}) / total specific surface area (S_{BET}).

Table S9. Textural properties of 10Co/HZ5 (SAR) catalysts with different SAR.

Samples	Surface area ($m^2 \cdot g^{-1}$)				Pore volume ($cm^3 \cdot g^{-1}$)		Pore diameter (nm)
	S_{BET}	S_{int}	S_{ext}	R_{ext}[a]	V_t	V_{mic}	D_p
10Co/HZ5(15)	402.1	290.8	111.3	0.277	0.47	0.16	4.72
10Co/HZ5(40)	400.3	291.3	108.9	0.272	0.42	0.16	4.22
10Co/HZ5(80)	407.2	311.2	96.0	0.236	0.42	0.16	4.10
10Co/HZ5(150)	418.6	324.6	94.0	0.225	0.47	0.17	4.53
10Co/S-1	423.2	320.6	102.5	0.242	0.50	0.17	4.72

[a] R_{ext}, external specific surface area (S_{ext}) / total specific surface area (S_{BET}).

Table S10. Textural properties of Co/HZ5 (80) catalysts with different Co content.

Samples	Surface area ($m \cdot g^{-1}$)				Pore volume ($cm^3 \cdot g^{-1}$)		Pore diameter (nm)
	S_{BET}	S_{int}	S_{ext}	R_{ext}[a]	V_t	V_{mic}	D_p
5Co/HZ5(80)	399.8	297.5	102.3	0.256	0.46	0.16	4.59
10Co/HZ5(80)	407.2	311.2	96.0	0.236	0.42	0.16	4.10
20Co/HZ5(80)	387.4	289.9	97.6	0.252	0.42	0.15	4.34
30Co/HZ5(80)	368.6	270.7	98.0	0.266	0.39	0.15	4.24

[a] R_{ext}, external specific surface area (S_{ext}) / total specific surface area (S_{BET}).

Table S11. Reduction and acidic properties of 10Co/HZ5 (SAR) catalysts with different Si/Al molar ratios.

Samples	H_2-TPR			NH_3-TPD	
	Top temp. (℃)	H_2 uptake (μmol/g)	Reducibility (%)[a]	Acid strength (μmol·g^{-1})	
	Peak Ⅰ/Ⅱ	Peak Ⅰ/Ⅱ	Total	Weak	Strong
10Co/HZ5(15)	330/530	511/550	34	37	47
10Co/HZ5(40)	295/515	558/1590	69	20	42
10Co/HZ5(80)	280/488	660/2036	87	12	40
10Co/HZ5(150)	265/354	525/1314	59	10	23
10Co/S-1	248/323	398/1612	65	1	4

[a] On the basis of total H_2 consumption for complete reduction of Co_3O_4 to Co^0.

Table S12. Reduction and acidic properties of Co/HZ5 (80) catalysts with different Co loading content.

Samples	H_2-TPR			NH_3-TPD	
	Top temp. (℃)	H_2 uptake (μmol/g)	Reducibility (%)[a]	Acid strength (μmol·g^{-1})	
	Peak Ⅰ/Ⅱ	Peak Ⅰ/Ⅱ	Total	Weak	Strong
5Co/HZ5(80)	255/420	160/790	61	61	68
10Co/HZ5(80)	280/488	660/2036	87	12	40
20Co/HZ5(80)	275/437	1302/4575	95	11	30
30Co/HZ5(80)	273/410	1590/6645	89	10	26

[a] On the basis of total H_2 consumption for complete reduction of Co_3O_4 to Co^0.

Table S13. Acidity properties of HZ5 (80) zeolite and 10Co/HZ5 (80) catalyst.

Samples	Acid strength (μmol·g^{-1})[a]		Acid type (μmol·g^{-1})[b]	
	Weak	Strong	Lewis	Brönsted
HZ5(80)	12	35	4	41
10Co/HZ5(80)	12	40	19	28

[a] Determined by NH3-TPD. [b] Determined by Py-IR.