Supporting Information

Hydrodeoxygenation Reactivity of Carbonyl Group and Carboxyl Group and Their Interaction: Taking 2-Pentanone, Valeric Acid, and Levulinic Acid as Examples

Xi Xi[a], Ye Yang[a], Hualiang An*[a], Xinqiang Zhao*[a] and Yanji Wang[a]

[a]Hebei Provincial Key Lab of Green Chemical Technology and Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China.

*Corresponding author: Dr Hualiang An: anhl@hebut.edu.cn;

Prof Xinqiang Zhao: zhaoxq@hebut.edu.cn

List of supporting information

13. Py-IR analysis results of Ru/HZSM-5 catalysts with different Si/Al ratios

（Figure SI-6）

1. Experimental

1.1 Preparation of Ru/HZSM-5 catalyst

Ru/HZSM-5 was prepared by an impregnation process. HZSM-5 (industrial grade, Nankai University Catalyst Plant) was calcined at 550 ℃ for 3 h before use. An aqueous solution of $RuCl_3$ was prepared by dissolving 0.164 g of $RuCl_3 \cdot xH_2O$ (AR, Sinopharm Group Chemical Reagent Co., Ltd.) in 50 mL distilled water. 4 g of the calcinated HZSM-5 and the aqueous solution of $RuCl_3$ were put into a rotary flask and ultrasonically stirred for 60 min and evaporated at 70 ℃ for 1.5 h to remove water. The resulting solid was dried at 110 ℃ for 12 h, calcinated at 550 ℃ for 4 h, and reduced at 450 ℃ for 4 h in a H_2:N_2=40:60 atmosphere to obtain Ru/HZSM-5 catalyst.

1.2 HDO reaction of model compounds

Liquid-phase HDO reactions and kinetic experiments of 2-pentanone (99%, J&K Scientific Co., Ltd.), valeric acid (>99%, Innochem Technology Co., Ltd.), a mixture of 2-pentanone and valeric acid, and levulinic acid (98%, J&K Scientific Co., Ltd.) were carried out in a 300 mL Parr autoclave. Taking 2-pentanone as an example, the specific operation steps were as follows: 12 g of Ru/HZSM-5 catalyst and 120 g of 2-pentanone were placed in the autoclave, sealed and replaced with hydrogen for 3 times, and then heated under stirring. When the reaction temperature was reached, the hydrogen flow was introduced for HDO reaction. After the completion of reaction, the autoclave was cooled down to room temperature. The residual gas was collected by a gas collection bag and analyzed by gas chromatography. The liquid product was separated from the catalyst by filtration and then the compositions of filtrate were analyzed by gas chromatography.

1.3 HDO reaction product analysis

1.3.1 Qualitative analysis of liquid products

The qualitative analysis of HDO products was performed on a Shimadzu QP2010 gas chromatography-mass spectrometry (GC-MS) equipped with a RTx-WAX column (30 m×0.25 mm×0.25 μm). The temperature of column was controlled by programmed temperature as follows. For the HDO reaction products of a mixture of 2-pentanone and valeric acid: an initial temperature of 50 ℃ and maintained for 2 min, elevated to 53 ℃ at a rate of 1 ℃/min, increased to 85 ℃ at 15 ℃/min, and finally raised to 250 ℃ at 3 ℃/min and

maintained for 5 min. For the LA HDO reaction products: an initial temperature of 50 ℃ and maintained for 2 min, raised to 53 ℃ at 1 ℃/min, increased to 85 ℃ at 15 ℃/min, and finally elevated to 250 ℃ at 3 ℃/min and maintained for 5 min. The mass spectrometry conditions are as follows: EI source temperature of 250 ℃, quadrupole detector temperature of 200 ℃, mass range: 20-550 m/z.

1.3.2 Quantitative analysis of liquid products

(1) The composition of 2-pentanone HDO reaction solution was determined on a Shimadzu GC-2018 gas chromatograph equipped with a flame ionization detector (FID). The components were separated on a KB-1 capillary column whose temperature was controlled as following program: an initial temperature of 50 ℃ and maintained for 2 min, raised to 53 ℃ at a ramp of 1 ℃/min, elevated to 85 ℃ at a rate of 15 ℃/min, increased to 200 ℃ at a ramp of 3 ℃/min and maintained for 5 min. The internal standard method was used for quantitative calculation and cyclohexanol was used as the internal standard.

(2) The composition of HDO reaction liquid of valeric acid, a mixture of 2-pentanone and valeric acid, and LA was separately analyzed by a Shimadzu GC-2030A gas chromatograph equipped with an FID. The internal standard method was also used for quantitative calculation. The components were separated on an SH-RTx-WAX capillary column whose temperature was controlled by the program as follows.

For valeric acid HDO reaction liquid: ethyl hexanoate was used as internal standard. The column temperature control program was as follows: an initial temperature of 50 ℃ and maintained for 2 min, raised to 53 ℃ at a rate of 1 ℃/min, then increased to 200 ℃ at a ramp of 3 ℃/min and maintained for 5 min.

For HDO reaction liquid of a mixture of 2-pentanone and valeric acid: ethyl hexanoate was used as internal standard. The column temperature control program was the same as that in GC-MS analysis.

For LA HDO reaction liquid: ethyl hexanoate as the internal standard. The column temperature control program was the same as that in GC-MS analysis.

$$\text{Conversion} = (\text{amount of model compound charged} - \text{amount of model compound left}) / \text{amount of model compound charged} \times 100\%$$

$$\text{Yield} = (\text{amount of target product } n\text{-pentane formed/amount of model compound charged}) \times 100\%$$

1.3.3 Analysis of gaseous products

(1) The composition of the gas products was determined using a Shimadzu GC-2018 gas chromatograph equipped with a thermal conductivity detector (TCD). The gaseous products

such as CO, CO_2 and H_2 were separated on a TDX-01 packed column. The content of each gas component in the gas phase was determined by an external standard method.

(2) To quantitatively analyze C_1~C_4 components, a Shimadzu GC-2030A gas chromatograph equipped with an FID was used. The gaseous products were separated on a KB-Al_2O_3/Na_2SO_4 capillary column whose temperature was controlled according to the following program: started at 60 ℃ and maintained for 2 min, then raised to 200 ℃ at a rate of 10 ℃/min and maintained for 10 min. The internal standard method was used for quantitative calculation and isobutane was used as the internal standard.

2. Effect of reaction conditions on 2-pentanone HDO

Table SI-1 Influence of reaction conditions on 2-pentanone HDO

Entry	Reaction conditions				X_{MPK}/%	Yield/%		Selectivity/%	
	Catalyst amount/wt.%	temp/℃	$P_{(H2)}$/MPa	time/h		Pentane	MPA	Pentane	MPA
1	4	190	3	6	81.6	27.9	28.2	34.2	34.6
2	6	190	3	6	82.3	52.7	2.1	64.0	2.6
3	8	190	3	6	79.6	50.7	0.6	63.7	0.8
4	10	190	3	6	80.2	50.6	0.8	63.1	1.0
5	6	150	3	6	99.5	20.9	51.0	21.0	51.3
6	6	170	3	6	98.9	27.2	44.1	27.5	44.6
7	6	210	3	6	44.8	18.1	0.4	40.4	0.9
8	6	230	3	6	40.9	11.3	0.2	27.6	0.5
9	6	190	1	6	23.8	3.1	0.1	13.0	0.4
10	6	190	2	6	45.0	16.3	0.2	36.2	0.4
11	6	190	4	6	86.1	59.3	1.9	68.9	2.2
12	6	190	5	6	91.8	71.3	2.3	77.7	2.5
13	6	190	6	6	99.4	72.3	0.4	72.7	0.4
14	6	190	5	2	91.4	68.1	5.8	74.5	6.3
15	6	190	5	4	91.9	67.9	4.7	73.9	5.1
16	6	190	5	8	90.3	54.4	5.2	60.2	5.8

MPK: 2-pentanone; MPA: 2-pentanol; X: conversion

3. Effect of reaction conditions on valeric acid HDO

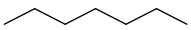
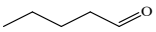
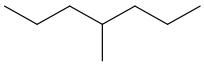
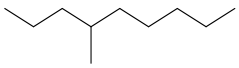
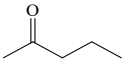
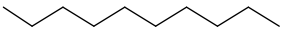
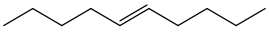
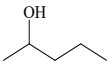
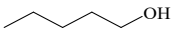
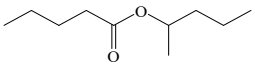
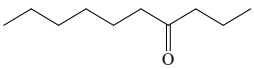
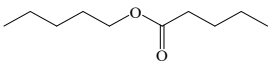
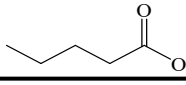
Table SI-2 Influence of reaction conditions on valeric acid HDO

Entry	Reaction conditions				X_{VA}/%	S_{C5}/%	Amount of gas products ($\times10^{-2}$ mmol)						
	catalyst amount/wt.%	temp/℃	$P_{(H2)}$/MPa	time/h			CO	$H_2\times10^2$	CO_2	C_1	C_2	C_3	C_4
1	5	250	5	4	14.9	13.2	563.6	37.5	0	30.8	111.6	2.8	35.0
2	10	250	5	4	27.7	8.0	586.0	36.0	0	156.0	124.0	8.0	80.0
3	15	250	5	4	30.1	7.8	601.0	34.1	737.4	200.9	135.2	9.7	49.2
4	10	230	5	4	20.0	7.3	735.1	42.1	0	53.8	81.3	3.5	13.1
5	10	240	5	4	33.1	7.6	765.6	42.0	0	87.2	13.8	7.4	96.3
6	10	260	5	4	27.2	7.3	576.7	30.2	760.0	176.3	30.0	159.6	64.7
7	10	240	3	4	21.7	2.2	440.3	33.0	0	68.4	75.0	4.7	48.4
8	10	240	4	4	32.4	5.0	643.9	32.3	0	66.6	11.0	3.8	46.1
9	10	240	6	4	31.6	9.2	989.1	72.7	915.0	83.8	13.9	4.9	69.3
10	10	240	5	2	28.3	4.4	704.2	41.3	0	130.0	12.4	6.7	58.1
11	10	240	5	6	30.6	12.8	456.4	26.2	539.8	93.6	80.5	10.6	93.3

VA: valeric acid, C_1: CH_4, C_2: C_2H_4+C_2H_6, C_3: C_3H_8, C_4: C_4H_{10}+C_4H_8, C_5: C_5H_{12}, X: conversion, S: selectivity.

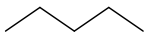
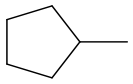
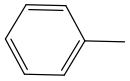
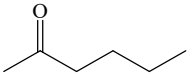
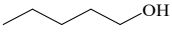
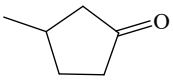
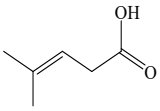
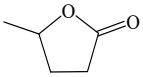
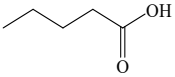
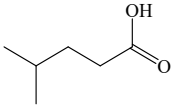
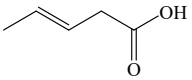
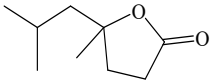
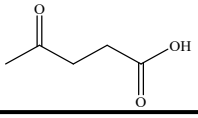
4. GC-MS analysis results of HDO reaction of the mixture of 2-pentanone and valeric acid

Table SI-3 Identification of components in Ru/HZSM-5 catalyzed HDO reaction of a mixture of 2-pentanone and valeric acid

Symbol	Retention time /min	Chemical name	Chemical formula	Constitutional formula	Similarity /%
A	1.733	*n*-Pentane	C_5H_{12}		93
B	1.883	*n*-Heptane	C_7H_{16}		97
C	1.997	*n*-Valeraldehyde	$C_5H_{10}O$		96
D	2.173	4-Methylheptane	C_8H_{18}		95
E	2.392	*n*-Nonane	C_9H_{20}		95
F	2.556	4-Methylnonane	$C_{10}H_{22}$		93
G	2.662	2-Pentanone	$C_5H_{10}O$		97
H	2.864	*n*-Decane	$C_{10}H_{22}$		96
I	2.932	5-Decene	$C_{10}H_{20}$		90
J	3.553	2-Pentanol	$C_5H_{12}O$		97
K	4.877	*n*-Pentanol	$C_5H_{12}O$		95
L	5.712	Butyl 2-Methylvalerate	$C_{10}H_{20}O_2$		92
M	6.200	4-Decanone	$C_{10}H_{20}O$		94
N	7.119	Pentyl pentanoate	$C_{10}H_{20}O_2$		95
O	10.739	Valeric acid	$C_5H_{10}O_2$		94

5. GC-MS analysis results of levulinic acid HDO reaction

Table SI-4 Identification of reaction components in levulinic acid HDO catalyzed by Ru/HZSM-5

Symbol	Retention time /min	Chemical name	Chemical formula	Constitutional formula	Similarity /%
A	1.817	*n*-Pentane	C_5H_{12}		87
B	1.858	*n*-Valeraldehyde	$C_5H_{10}O$		87
C	1.917	Methyl cyclopentane	C_6H_{12}		98
D	2.108	Acetone	C_3H_6O		96
E	3.058	Toluene	C_7H_8		98
F	3.358	2-Hexanone	$C_6H_{12}O$		96
G	4.832	*n*-Pentanol	$C_5H_{12}O$		95
H	5.712	3-Methylcyclopentanone	$C_6H_{10}O$		92
I	7.225	Acetic acid	$C_2H_4O_2$		97
J	9.142	4-Methyl-3-pentenoic acid	$C_6H_{10}O_2$		95
K	9.358	γ-Valerolactone	$C_5H_8O_2$		96
L	10.675	Valeric acid	$C_5H_{10}O_2$		90
M	11.442	4-Methylpentanoic acid	$C_6H_{12}O_2$		96
N	12.008	3-Pentenoic acid	$C_5H_8O_2$		93
O	12.600	5-isobutyl-5-Methyldihydrofuran-2(3H)-one	$C_9H_{16}O_2$		92
P	16.567	Levulinic acid	$C_5H_8O_3$		96

6. Calculation of carbon balance in HDO reactions

Table SI-5 Carbon balance of HDO reactions

	Reaction substrate			
	2-pentanone	valeric acid	2-pentanone & valeric acid	levulinic acid
carbon balance/%	94.1	71.3	76.9	92.7

7. 2-Pentanone HDO reaction kinetics

7.1 Effect of internal and external diffusion at different reaction temperatures

2-Pentanone HDO catalyzed by Ru/HZSM-5 is a gas-liquid-solid three-phase reaction system and the mass transfer resistance will have a certain effect on the reaction rate. In order to calculate the reaction rate constant and activation energy, the effects of internal and external diffusion should be excluded firstly. The Weisz-Prater criterion and Mears criterion were calculated. The specific calculation process is as follows:

(1) Weisz-Prater criterion is utilized to evaluate the effect of internal diffusion:

$$\Phi_A = \frac{-r_{A,obs}\rho_P R_P^2}{D_{A,e}C_{A,s}} < 1$$

(2) Mears criterion is applied to evaluate the effect of external diffusion:

$$\frac{-r_{A,obs}\rho_P R_P n}{k_A C_{A,s}} < 0.15$$

Where $r_{A,obs}$ represents the observed reaction rate of component A, $mol/kg \cdot s$; ρ_P indicates the catalyst particle density, kg/m^3; R_P stands for catalyst particle radius, m; n represents reaction order; C_A indicates liquid concentration of 2-pentanone, mol/m^3; $D_A\ stands\ for\ effective\ diffusion\ coefficient$, m^2/s; k_A represents mass transfer coefficient, m/s.

Since D_A and k_A cannot be directly measured, they were obtained by calculation. The specific calculation process is as follows:

Calculation of D_A: Since the average free path of liquid molecule is much less than the pore size of catalyst [S1] in the heterogeneous system, Knudsen diffusion (D_k) can be ignored [S2]. Total diffusion can be simplified to molecular diffusion only, i.e., the total diffusion coefficient $D = D_{AB}$. The above diffusion coefficient was calculated according to the Wilke-

Chang equation:

$$D_{AB} = 7.4 \times 10^{-10} \frac{T(XM_A)^{1/2}}{\mu V_b^{0.6}} (cm^2/s)$$

The structure of 2-pentanone includes ketone carbonyl group, methylene group and methyl group. According to the group contribution method[S1], V_b=22.7+27.4×2+21.3×2=120.1. Similarly, according to the Van Velzen group contribution method [S3], the calculation formula for μ can be derived as $\log \mu = 738.50 \times [(T)^{-1} - (245.38)^{-1}]$.

Calculation of k_A: according to Frossling relation[S1],

$$Sh = 2 + 0.6Re^{1/2}Sc^{1/3} = 2 + 0.6 \times \left(\frac{Ndd_P}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

$$Sh = \frac{k_A d_P}{D_{AB}}$$

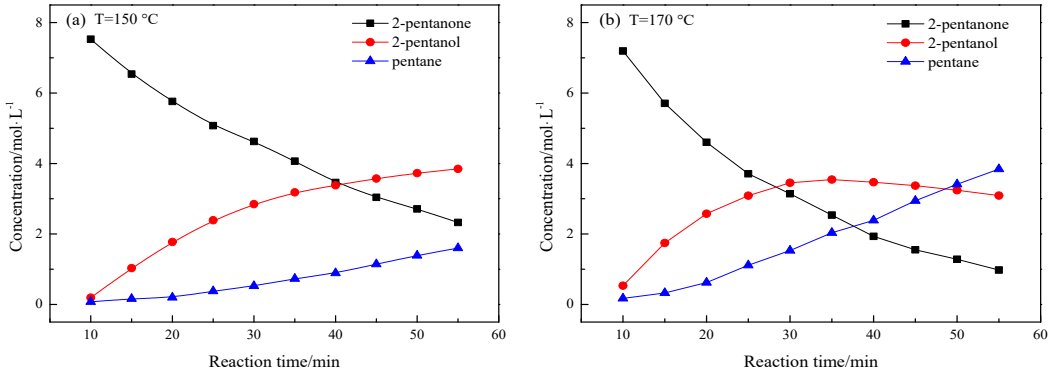
Where N represents stirring rate, 500 rpm; d indicates impeller diameter, 0.033 m; d_P stands for particle size, mm; ν represents the dynamic viscosity, m^2/s.

The effects of internal and external diffusion at 150 ℃, 170 ℃ and 190 ℃ were calculated using the above criteria and the results are shown in Table SI-6. It can be seen that the Weisz-Prater criterion value is less than 1 and the Mears criterion value is less than 0.15, indicating that there is no mass transfer effect under the experimental conditions.

Table SI-6 Effect of internal and external diffusion at different reaction temperatures

T/℃	$r_{A,obs}$/ mol/kg/s	k_A/ m/s	$D_{A,e}$/ cm²/s	$C_{A,S}$/ mol/m³	$\frac{-r_{A,obs}\rho_P R_P n}{k_A C_{A,s}}$	$\Phi_A = \frac{-r_{A,obs}\rho_P R_P^2}{D_{A,e}C_{A,s}}$
150	6.20×10^{-4}	1.25×10^{-7}	3.02×10^{-8}	1.39×10^{6}	0.000193	0.000999
170	6.16×10^{-4}	1.20×10^{-7}	3.80×10^{-8}	1.39×10^{6}	0.000199	0.000791
190	5.13×10^{-4}	1.16×10^{-7}	4.68×10^{-8}	1.39×10^{6}	0.000172	0.000534

7.2 Kinetic experiment data



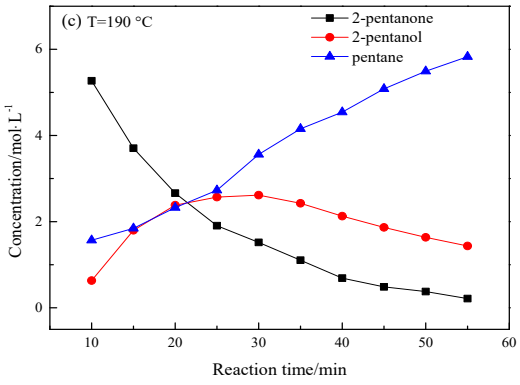


Figure SI-1 Concentration of each component vs reaction time at different temperatures (a):150 ℃, (b): 170 ℃, (c):190 ℃

7.3 Comparison of experimentally measured concentrations with those predicted by Langmuir-Hinshelwood models

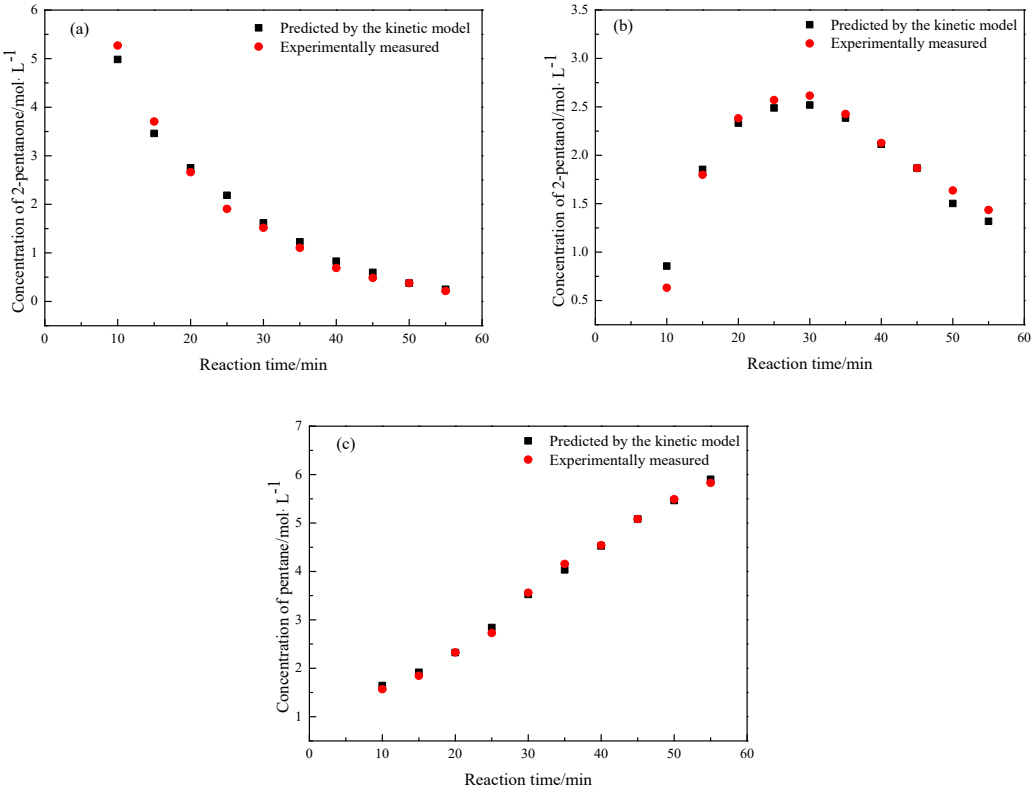


Figure SI-2 Comparison of experimentally measured concentrations with those predicted by Langmuir-Hinshelwood models (a): 2- pentanone, (b): 2- pentanol, (c): *n*-pentane

8. Valeric acid HDO reaction kinetics

8.1 Effect of internal and external diffusion at different reaction temperatures

The Weisz-Prater criterion and the Mears criterion were also used to calculate the effects of internal and external diffusion at 220 ℃, 230 ℃, and 240 ℃, respectively. The results are

shown in Table SI-7. The Weisz-Prater criterion value is less than 1 and the Mears criterion value is less than 0.15, indicating that there is no mass transfer effect under the experimental conditions.

Table SI-7 Effect of internal and external diffusion at different reaction temperatures

T/℃	$r_{A,obs}$/ mol/kg/s	k_A/ m/s	$D_{A,e}$/ m^2/s	$C_{A,S}$/ mol/m^3	$\frac{-r_{A,obs}\rho_P R_P n}{k_A C_{A,s}}$	$\Phi_A = \frac{-r_{A,obs}\rho_P R_P^2}{D_{A,e}C_{A,s}}$
220	1.13×10^{-4}	4.54×10^{-8}	0.99×10^{-8}	1.12×10^{5}	0.000102	6.91×10^{-6}
230	1.50×10^{-4}	4.49×10^{-8}	1.09×10^{-8}	1.12×10^{5}	0.000137	8.39×10^{-6}
240	1.87×10^{-4}	4.44×10^{-8}	1.18×10^{-8}	1.12×10^{5}	0.000173	9.62×10^{-6}

8.2 Kinetic experiment data

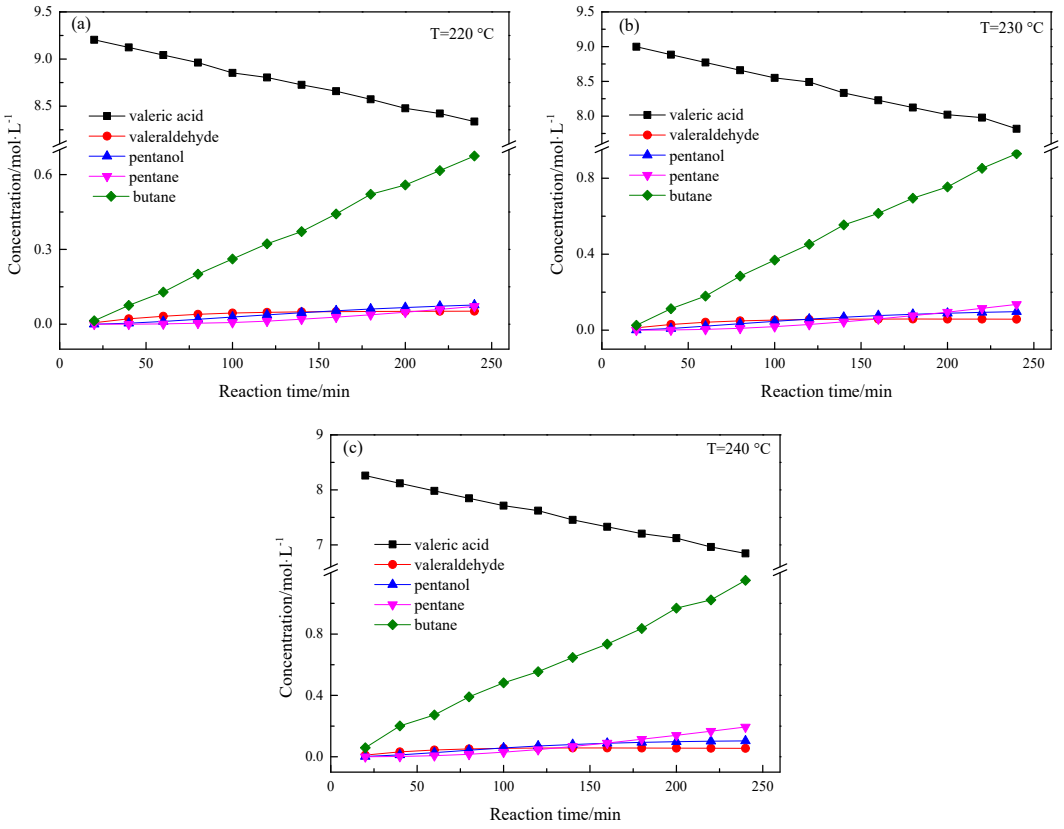


Figure SI-3 Concentration of each component vs reaction time at different temperatures (a):220 ℃, (b): 230 ℃, (c):240 ℃

9. HDO reaction kinetics of the mixture of 2-pentanone and valeric acid

9.1 Effect of internal and external diffusion at different reaction temperatures

The Weisz-Prater criterion and the Mears criterion were used to calculate the effects of internal and external diffusion at 190 ℃, 215 ℃, and 240 ℃, respectively. The results are shown in Table SI-8. It can be seen that the Weisz-Prater criterion value is less than 1 and the

Mears criterion value is less than 0.15, indicating that there is no mass transfer effect under this experimental condition.

Table SI-8 Effect of internal and external diffusion at different reaction temperatures

T/℃	$r_{A,obs}$/ mol/kg/s	k_A/ m/s	$D_{A,e}$/ cm^2/s	$C_{A,S}$/ mol/m^3	$\frac{-r_{A,obs}\rho_P R_P n}{k_A C_{A,S}}$	$\Phi_A = \frac{-r_{obs}\rho_P R_P^2}{D_{A,e}C_{A,S}}$
190	2.37×10^{-4}	4.96×10^{-8}	7.71×10^{-7}	1.02×10^{6}	0.000256	2.05×10^{-5}
215	3.13×10^{-4}	4.76×10^{-8}	1.05×10^{-6}	1.02×10^{6}	0.000351	1.99×10^{-5}
240	3.53×10^{-4}	4.59×10^{-8}	1.39×10^{-6}	1.02×10^{6}	0.000411	1.69×10^{-5}

9.2 Kinetic experiment data

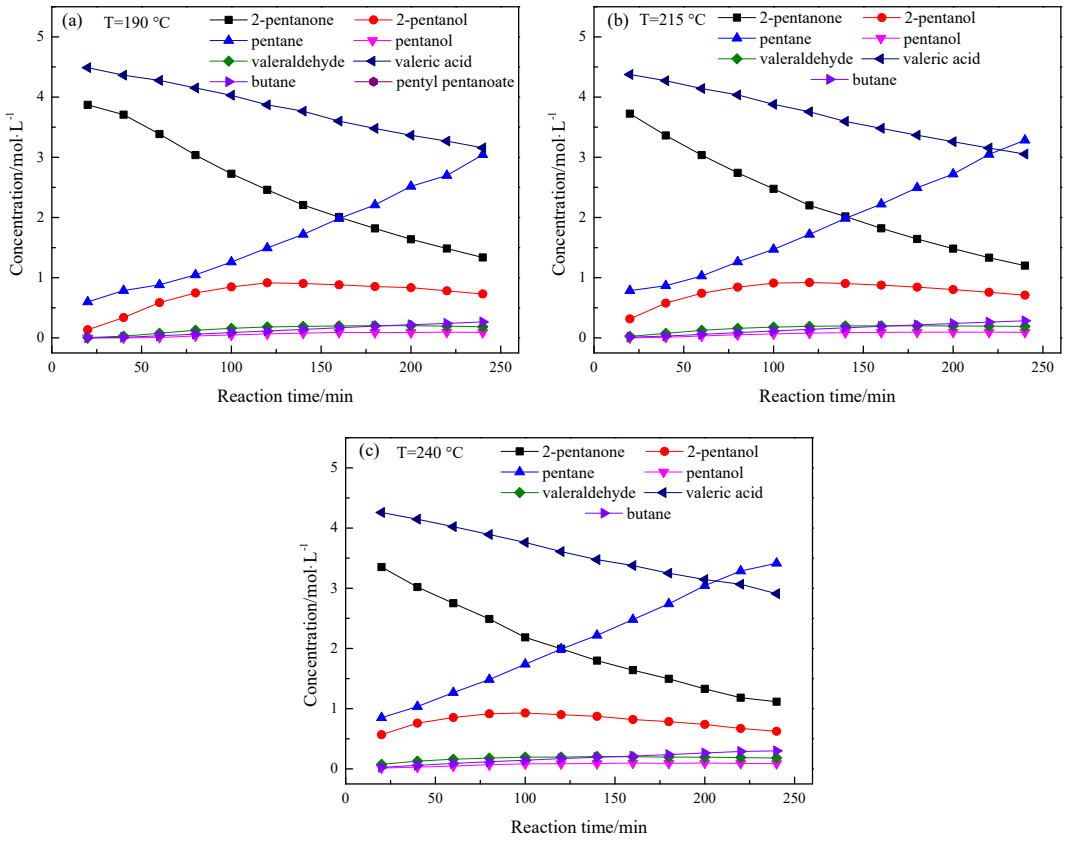


Figure SI-4 Concentration of each component vs reaction time at different temperatures (a):190 ℃, (b): 215, (c):240 ℃

10. Levulinic acid HDO reaction kinetics

10.1 Effect of internal and external diffusion at different reaction temperatures

The Weisz-Prater criterion and the Mears criterion were used to calculate the effects of internal and external diffusion at 190 ℃, 215 ℃, and 240 ℃, respectively. The results are

shown in Table SI-9. It can be seen that the Weisz-Prater criterion value is less than 1 and the Mears criterion value is less than 0.15, indicating that there is no mass transfer effect under the experimental condition.

Table SI-9 Effect of internal and external diffusion at different reaction temperatures

T/℃	$r_{A,obs}$/ mol/kg/s	k_A/ m/s	$D_{A,e}$/ cm^2/s	$C_{A,S}$/ mol/m^3	$\frac{-r_{A,obs}\rho_P R_P n}{k_A C_{A,S}}$	$\Phi_A = \frac{-r_{obs}\rho_P R_P^2}{D_{A,e}C_{A,S}}$
190	2.37×10^{-4}	4.96×10^{-8}	7.71×10^{-7}	1.02×10^{6}	0.000256	2.05×10^{-5}
215	3.13×10^{-4}	4.76×10^{-8}	1.05×10^{-6}	1.02×10^{6}	0.000351	1.99×10^{-5}
240	3.53×10^{-4}	4.59×10^{-8}	1.39×10^{-6}	1.02×10^{6}	0.000411	1.69×10^{-5}

10.2 Kinetic experiment data

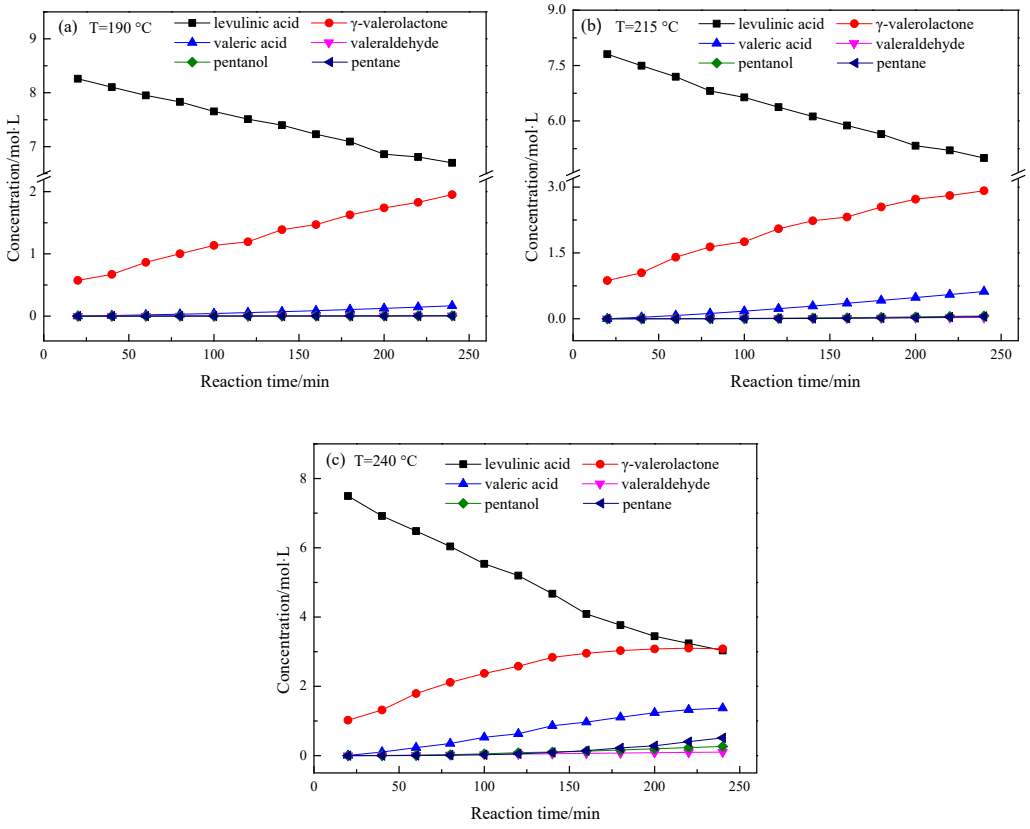


Figure SI-5 Concentration of each component vs reaction time at different temperatures (a):190 ℃, (b): 215, (c):240 ℃

11. HDO reaction kinetic model statistics

Table SI-10 Model Statistics

Model	Reaction temperature /℃	Experiment No.	Free variation No.	Regression square sum	Residual squares sum	Correlation index	F
2-Pentanone	150	10	3	27.13	0.0506	0.9992	1199
	170	10		13.46	0.0162	0.9996	
	190	10		2.55	0.0146	0.9993	
	150	10	3	23.77	0.0518	0.9985	955
	170	10		13.18	0.0251	0.9991	
	190	10		2.58	0.0106	0.9983	
	150	10	3	22.75	0.0513	0.9986	849
	170	10		9.62	0.0169	0.9985	
	190	10		1.74	0.0223	0.9741	
Valeric acid	220	12	3	12.02	0.0341	0.9983	1753
	230	12		11.11	0.0262	0.9972	
	240	12		9.69	0.0099	0.9943	
	220	12	3	10.17	0.0082	0.9957	1910
	230	12		15.00	0.0547	0.9790	
	240	12		11.78	0.0302	0.9854	
	220	12	3	11.38	0.0270	0.9865	1126
	230	12		12.16	0.0325	0.9843	
	240	12		16.67	0.0505	0.9824	
	220	12	3	17.41	0.0749	0.9747	679
	230	12		19.69	0.0695	0.9792	
	240	12		23.13	0.1413	0.9651	
	220	12	3	15.28	0.0316	0.9986	1199
	230	12		12.91	0.0763	0.9998	
	240	12		11.89	0.0217	0.9969	
Mixture of 2-pentanone and valeric acid	190	12	3	12.72	0.0104	0.9907	2466
	215	12		11.89	0.0135	0.9912	
	240	12		10.88	0.0299	0.9880	
	190	12	3	10.32	0.0694	0.9847	519
	215	12		2.87	0.0090	0.9965	
	240	12		1.63	0.0325	0.9967	
	190	12	3	3.34	0.0143	0.9978	719
	215	12		4.69	0.0113	0.9988	
	240	12		0.84	0.0120	0.9835	
	190	12	3	3.17	0.0036	0.9967	2488
	215	12		2.51	0.0041	0.9899	

	240	12		2.46	0.0025	0.9996	
	190	12		13.75	0.0226	0.9965	
	215	12	3	14.57	0.0357	0.9979	1355
	240	12		10.89	0.0322	0.9986	
	190	12		11.15	0.0198	0.9993	
	215	12	3	8.34	0.0159	0.9989	2212
	240	12		12.43	0.0111	0.9992	
	190	12		9.99	0.0322	0.9991	
	215	12	3	2.26	0.0175	0.9968	1017
	240	12		2.04	0.0035	0.9985	

1

2 **Table SI-10** Model Statistics (Continuation)

Model	Reaction temperature /℃	Experiment No.	Free variation No.	Regression square sum	Residual squares sum	Correlation index	F
	190	12		12.79	0.0402	0.9852	
	215	12	3	12.38	0.0298	0.9877	1017
	240	12		16.35	0.0575	0.9832	
	190	12		19.14	0.1031	0.9731	
	215	12	3	11.10	0.0412	0.9808	912
	240	12		9.88	0.0216	0.9893	
	190	12		10.55	0.0312	0.9852	
	215	12	3	18.73	0.0786	0.9793	1427
Levulinic acid	240	12		11.23	0.0132	0.9998	
	190	12		8.94	0.0015	0.9987	
	215	12	3	12.11	0.0112	0.9984	7332
	240	12		13.91	0.0478	0.9896	
	190	12		5.68	0.0064	0.9968	
	215	12	3	13.09	0.0190	0.9987	1760
	240	12		10.78	0.0604	0.9979	
	190	12		11.12	0.0263	0.9991	
	215	12	3	10.83	0.0491	0.9924	948
	240	12		7.70	0.0253	0.9962	

3 ## 12. NH_3-TPD analysis results of Ru/HZSM-5 catalysts with different Si/Al ratios

4 **Table SI-11** Acid properties of Ru/HZSM-5 catalysts with different Si/Al ratio

Catalyst	NH_3 desorption peak at lower temperature		NH_3 desorption peak at medium temperature		NH_3 desorption peak at higher temperature		Total acid amount/ μmol·g^{-1}
	Peak top temperature/ ℃	Weak acid amount/ μmol·g^{-1}	Peak top temperature/ ℃	Strong acid amount/ μmol·g^{-1}	Peak top temperature/ ℃	Strong acid amount/ μmol·g^{-1}	
Ru/HZSM-5(21)	190.9	319.2	263.9	231.6	347.1	143.8	694.6
Ru/HZSM-5(61)	184.6	130.4	——	——	303.4	194.3	324.7
Ru/HZSM-5(130)	180.7	101.0	——	——	283.3	191.9	292.9
Ru/HZSM-5(360)	162.1	26.5	——	——	260.0	75.3	101.8

5 ## 13. Py-IR analysis results of Ru/HZSM-5 catalysts with different Si/Al ratios

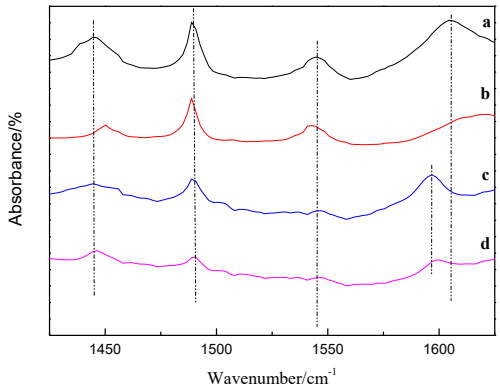


Fig. SI-6 Py-IR spectra of Ru/HZSM-5 with different Si/Al ratios
a: HZSM-5(21); b: HZSM-5(60); c: HZSM-5(130); d: HZSM-5(360)

Reference

[S1] L.L. Zhao, H.L. An, X.Q. Zhao, Y.J. Wang, TiO_2-catalyzed n-valeraldehyde self-condensation reaction mechanism and kinetics. ACS Catal. 7 (2017) 4451-4461. https://doi.org/10.1021/acscatal.7b00432.

[S2] P.F. Zito, A. Caravella, A. Brunetti, E. Drioli, G. Barbieri, Discrimination among gas translation, surface and Knudsen diffusion in permeation through zeolite membranes. J Membrane Sci. 564 (2018) 166-173. https://doi.org/10.1016/j.memsci.2018.07.023

[S3] Y. Nannoolal, J. Rarey, D. Ramjugernath, Estimation of pure component properties. Part 4: Estimation of the saturated liquid viscosity of non-electrolyte organic compounds via group contributions and group interactions. Fluid Phase Equilibr, 281 (2009) 97-119. https://doi.org/10.1016/j.fluid.2009.02.016.