Electronic Supplementary Information (ESI)

Hydrodeoxygenation of Biomass-derived Furans into Liquid Alkanes over Ru/WO_3-ZrO_2 Catalyst

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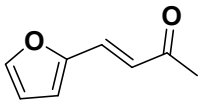
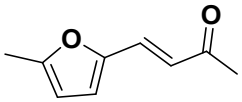
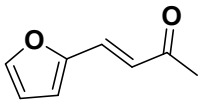
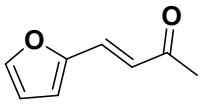
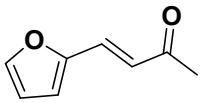
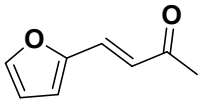
Materials and Instrumentation.

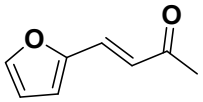
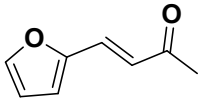
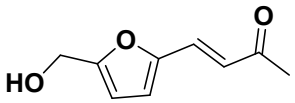
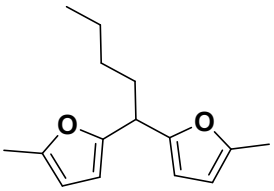
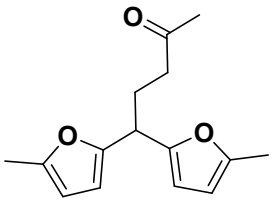
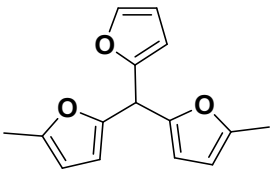
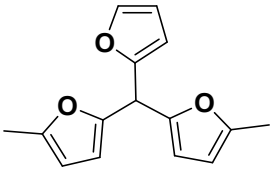
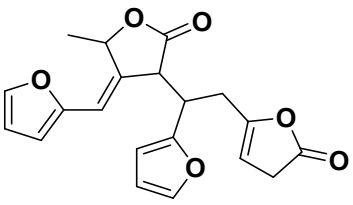
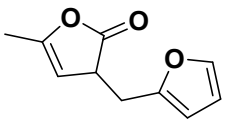
All the chemical reagents and metal salts were available commercially and were used as such without any further purification. $RuCl_3.xH_2O$, ammonium metatungstate, sodium borohydride, furfural, 5-methyl furfural, and acetone were purchased from Sigma Aldrich, India and TCI analytics, India. High-purity hydrogen gas was procured from Sigma Gases, India.

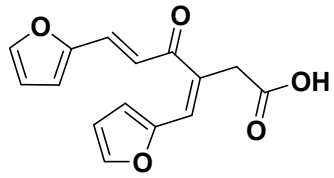
Powder X-ray Diffraction (P-XRD) measurements were performed using Rigaku Smart Lab, an Automated Multipurpose X-ray diffractometer at 40 kV and 30 mA (Cu_α λ=1.5418 Å) over a 2θ range of 15° to 80°. Field emission scanning electron microscopic (FE-SEM) images were collected with a JOEL-7610 F Plus. X-ray photoelectron spectroscopy (XPS) was performed using Omricon ESCA (Electron Spectroscope for Chemical Analysis), Oxford Instrument, Germany. Aluminium (Al) anode was used as a monochromatic X-ray source (1486.7 eV) for XPS measurements. Transmission electron microscopic (TEM) imaging and energy dispersive X-ray spectroscopy (EDS) mapping were performed on the FEI Titan Themis with an operating voltage of 300 kV. For TEM analysis, the catalyst was suspended in ethanol, and a few drops of the suspension were deposited over the amorphous carbon-coated 400 mesh Cu grid and dried at room temperature. The NH_3 TPD measurements were performed using BELCAT II. Prior to the TPD analyses, the sample was outgassed under a He flow of 20 mL/min with a heating ramp of 10°C/min up to 150 °C. The NH_3 TPD experiments were started by cooling the temperature to 50 °C followed by treating it with an ammonia stream (10 vol%

in He) of 20 mL/min for 30 min. After this, the physically adsorbed NH_3 was removed by flowing He (20 mL/min) for 30 min. Finally, temperature-programmed desorption was performed by subjecting the sample to a heating rate of 10 °C/min up to 700 °C. N_2 adsorption-desorption was performed using a Quantachrome Autosorb iQ2 TPX automated gas sorption system at 77 K. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface areas of the adsorption data for the relative pressure (P/P_0) range of 0.05-0.30. GC-MS analysis was performed using Shimadzu GC-MS, QP2010 Mass Spectrometer and RTX-5MS tubular 5% diphenyl/95% dimethyl polysiloxane capillary column, 30 m long, 0.25 mm inner diameter with a df value of 1.0 μm. The oven temperature was varied from 30 to 200 °C at a heating rate of 20 °C min^{-1}, and the detector temperature was set at 350 °C.

Table S1 Literature reported catalytic systems for HDO of biomass-derived furans to alkanes.

Entry	Substrate	Catalyst	Solvent	Conditions	Product (yield%)	Ref.
1		**$Ru/5WO_3$-ZrO_2**	**Cyclo-hexane**	**150 °C, 2 MPa H_2, 3 h**	**Octane (78)**	**This work**
2		**$Ru/5WO_3$-ZrO_2**	**Cyclo-hexane**	**150 °C, 2 MPa H_2, 6 h**	**Nonane (96)**	**This work**
3		Pt/Co_2AlO_4, $Pt/NbOPO_4$	Ethanol	(i)130-150 °C, 2.0 MPa H_2; (ii) 175 °C, 2.5 MPa H_2	Octane (76)	S1
4		$Pd/NbOPO_4$	Cyclo-hexane	170 °C, 2 MPa H_2, 24 h	Octane (94)	S2
5		Pd/Nb_2O_5	Cyclo-hexane	170 °C, 2 MPa H_2, 24 h	Octane (96)	S2
6		$Pd/10Nb_2O_5/SiO_2$	Cyclo-hexane	170 °C, 2.5 MPa H_2, 24 h	Octane (95.3)	S3

7		$NiCu/Nb_2O_5$	Cyclo-hexane	250 °C, 4 MPa H_2, 12 h	Octane (86.5)	S4
8		Pd/C HPW	Cyclo-hexane	130 °C, 1 MPa H_2, 4 h	Octane (96.6)	S5
9		(i) Pd/C, glacial acetic acid; (ii) Pd/C-$La(OTf)_3$	Acetic acid	(i) 65 °C, 0.37 MPa H_2, 2 h; (ii)100 °C, 2.07 MPa H_2, 200 °C, 16 h	Nonane (87)	S6
10		$Pd/2.5FeO_x/SiO_2$	Neat	200 °C, 0.1 MPa H_2 (flow rate:110 mL min^{-1} at STP), 5 h	C9-C14 alkanes (87-94)	S7
11		Ir-MoO_x/SiO_2	Cyclo-hexane	180 °C, 5 MPa H_2, 24 h	C15 alkane (85)	S8
12		Ir-MoO_x/SiO_2	Cyclo-hexane	180 °C, 5 MPa H_2, 24 h	C15 alkane (43)	S8
13		Ir-ReO_x/SiO_2	Cyclo-hexane	180 °C, 5 MPa H_2, 20 h	C15 alkane (60.6)	S9
14		Pd/C + H_3PO_4	Water	240 °C, 4 MPa H_2, 12 h	C12, C14 and C18 alkanes (57.1)	S10
15		Ru/HAP + HZSM-5	Cyclo-hexane	180 °C, 4 MPa H_2, 10 h	C8-C10 alkanes (91.9)	S11

16		Pd-Ru/HAP + ZrP	Cyclo-hexane	200 °C, 4 MPa H_2, 10 h	C8-C15 alkanes (81.56)	S12

HPW – phospho tungstic acid, ZrP – zirconium phosphate, HAP - hydroxyapatite

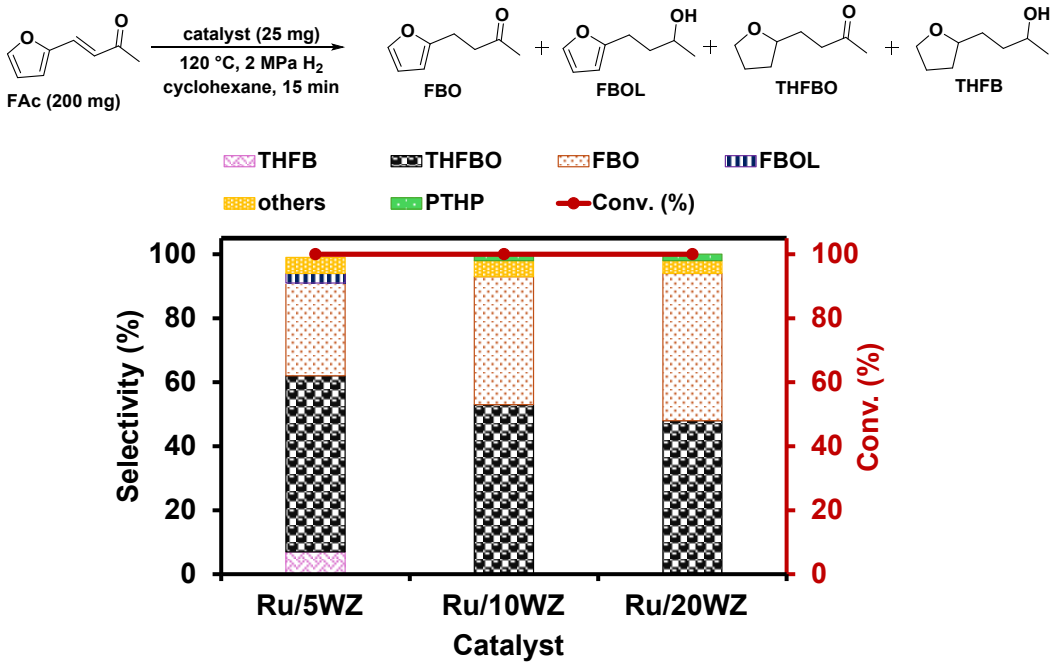


Fig. S1 Control experiment to evaluate the effect of higher WO_3 loading on HDO of FAc over Ru/5WZ, Ru/10WZ and Ru/20WZ catalysts. Reaction conditions: FAc (200 mg), Ru/xWZ (25 mg), 120 °C, 2 MPa H_2, cyclohexane (10 mL), 15 min.

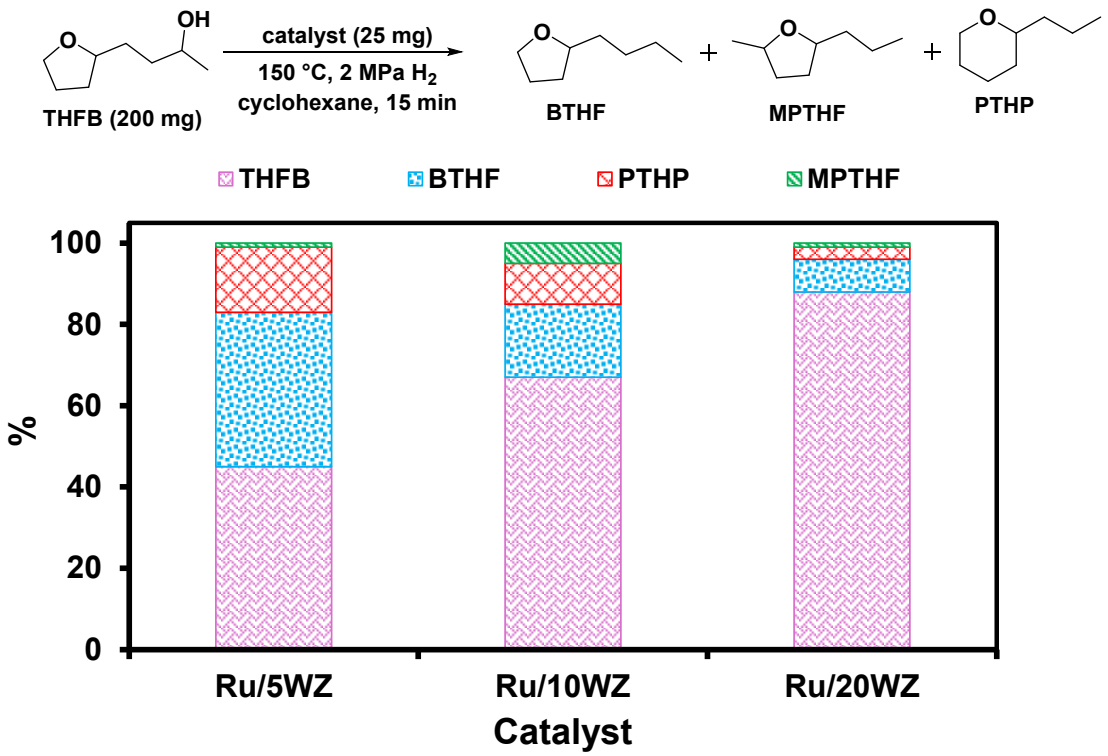


Fig. S2 Control experiment to evaluate the effect of higher WO_3 loading on HDO of THFB over various Ru/xWZ catalysts. Reaction conditions: THFB (200 mg), Ru/xWZ (25 mg), 150 °C, 2 MPa H_2, cyclohexane (10 mL), 15 min.

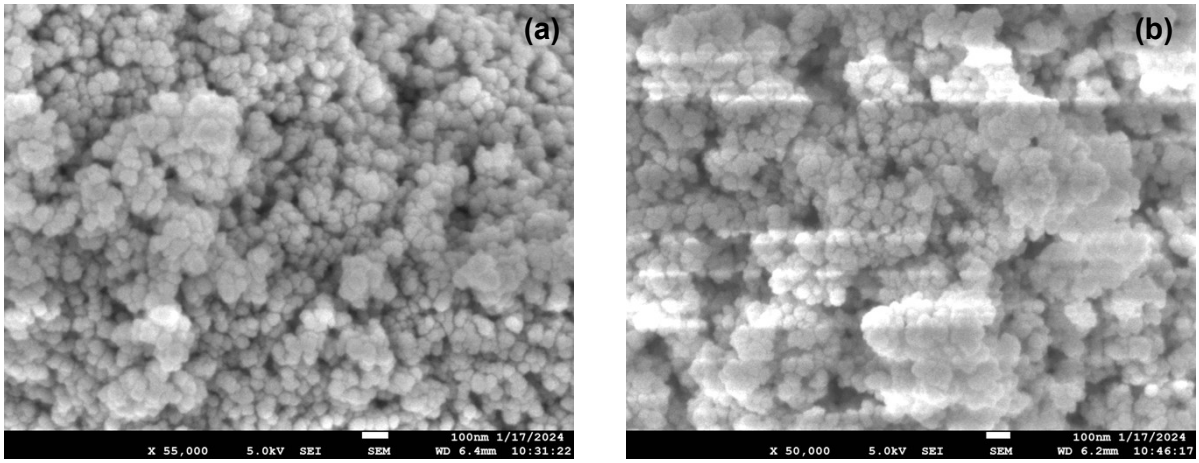


Fig. S3 FESEM images of **(a)** 5WZ, and **(b)** Ru/5WZ catalyst.

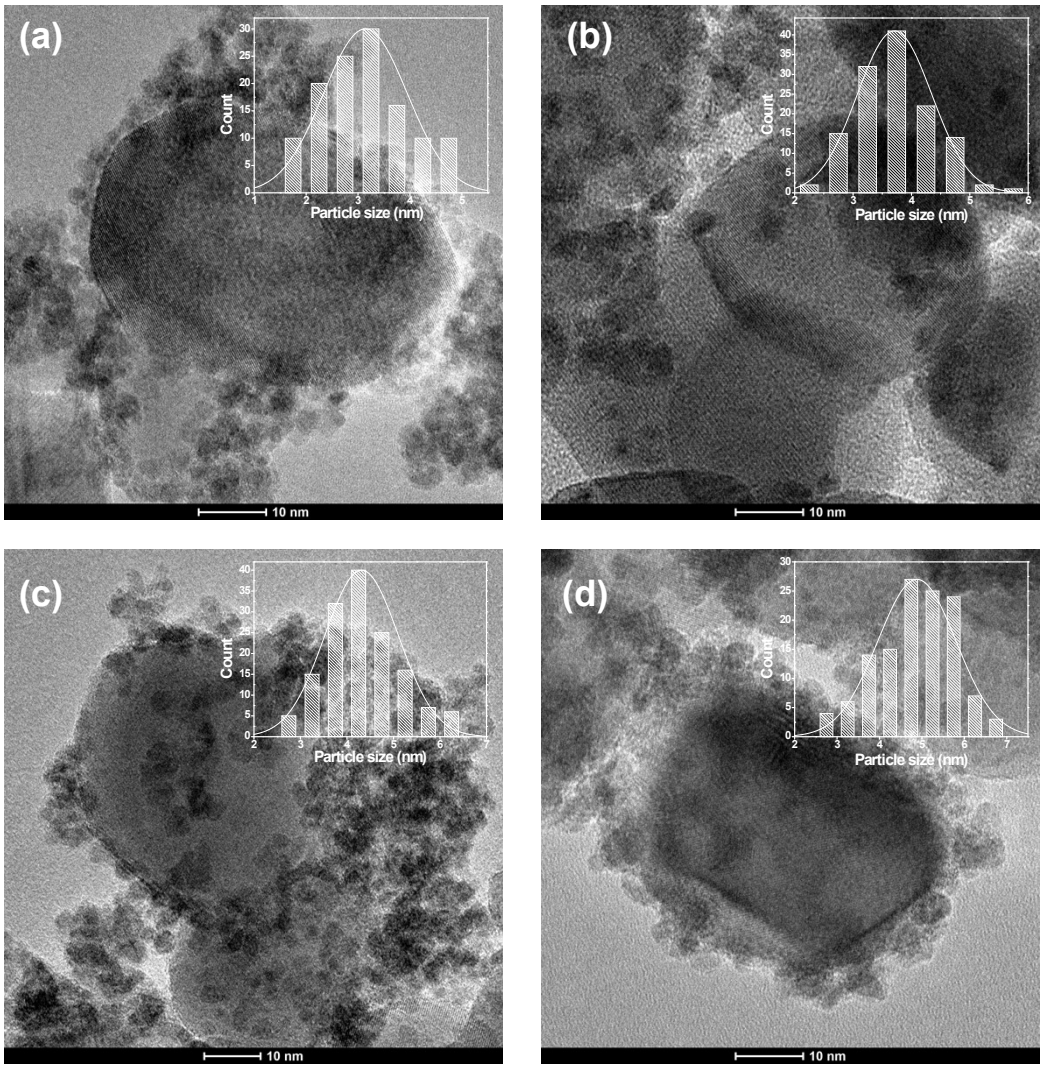


Fig. S4 HR-TEM images for **(a)** Ru/2.5WZ, **(b)** Ru/5WZ, **(c)** Ru/10WZ, and **(d)** Ru/20WZ with particle size distribution curves (inset).

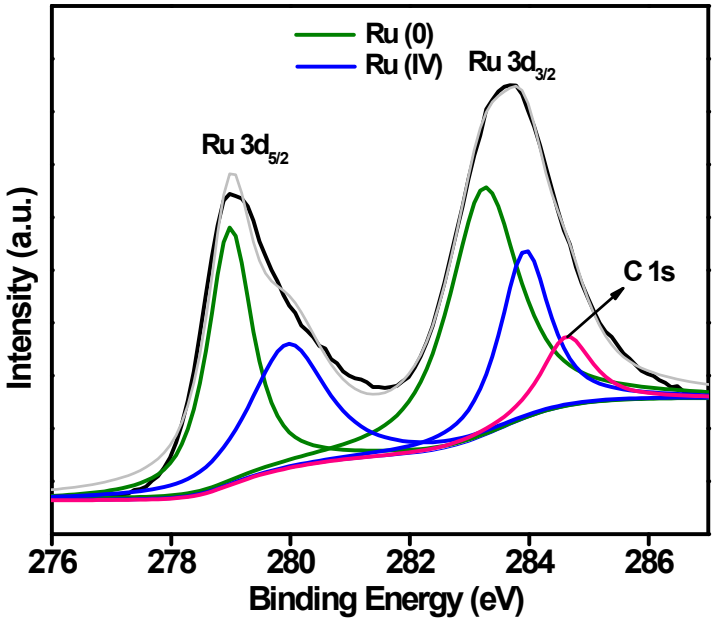


Fig. S5 XPS of Ru 3d core levels of Ru/5WZ catalyst.

Table S2 HDO of FAc over various catalysts.

Catalyst	Product Selectivity (%)				
	BTHF	**PTHP**	**MPTHF**	**Octanols**	**Alkanes**
Ru/Z	15	73	7	-	5
Ru/1WZ					23
Ru/2.5WZ	12	6	5	-	77
Ru/5WZ	-	-	-	-	100
Ru/7.5WZ	-	7	6	-	87
Ru/10WZ	6	12	3	4	75
Ru/20WZ	43	32	5	-	20
Ru/W	55	36	7	2	-

Reaction Conditions: FAc (200 mg), catalyst (50 mg), 150 °C, 2 MPa H_2, cyclohexane (10 mL), 3 h. Conversion was >99% in all the cases.

Table S3 Textural properties of different supported Ru catalysts.

Catalyst	S_{BET} (m^2/g)[a]	Pore size (nm)[b]	Pore volume (g/cm^3)[b]	Acidic sites (mmol/g)[c]	Average particle size (nm)[d]
Ru/Z	25.7	3.08	0.015	0.533	n.d.
Ru/1WZ	22.4	3.07	0.013	n.d.	n.d.
Ru/2.5WZ	24.1	3.07	0.015	n.d.	3.1
Ru/5WZ	25.2	3.07	0.015	0.708	3.7
Ru/7.5WZ	25.4	3.43	0.014	n.d.	n.d.
Ru/10WZ	21.5	3.07	0.013	0.790	4.3
Ru/20WZ	18.4	3.43	0.012	0.910	4.8
Ru/W	11.5	3.08	0.006	n.d.	n.d.

[a]Surface area was calculated using N_2 adsorption-desorption at 77 K.

[b]Pore size and pore volume were calculated using the BJH method.

[c]Acidic sites were measured by NH_3-TPD analysis.

[d]Particle size was calculated from HR-TEM images.

n.d. – not determined

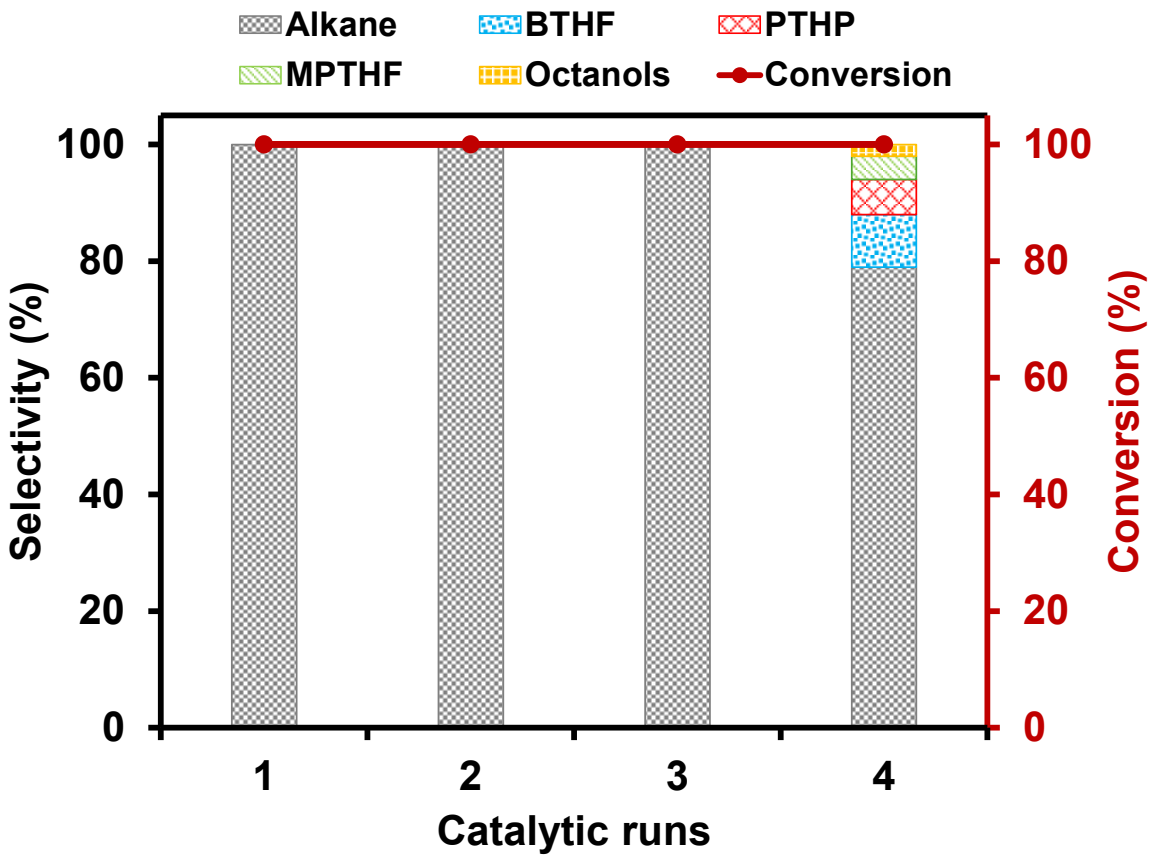


Fig. S6 Recyclability experiment of Ru/5WZ catalyst for HDO of FAc to alkanes. Reaction Conditions: FAc (200 mg), Ru/5WZ (50 mg), 150 °C, 2 MPa H_2, cyclohexane (10 mL), 3 h.

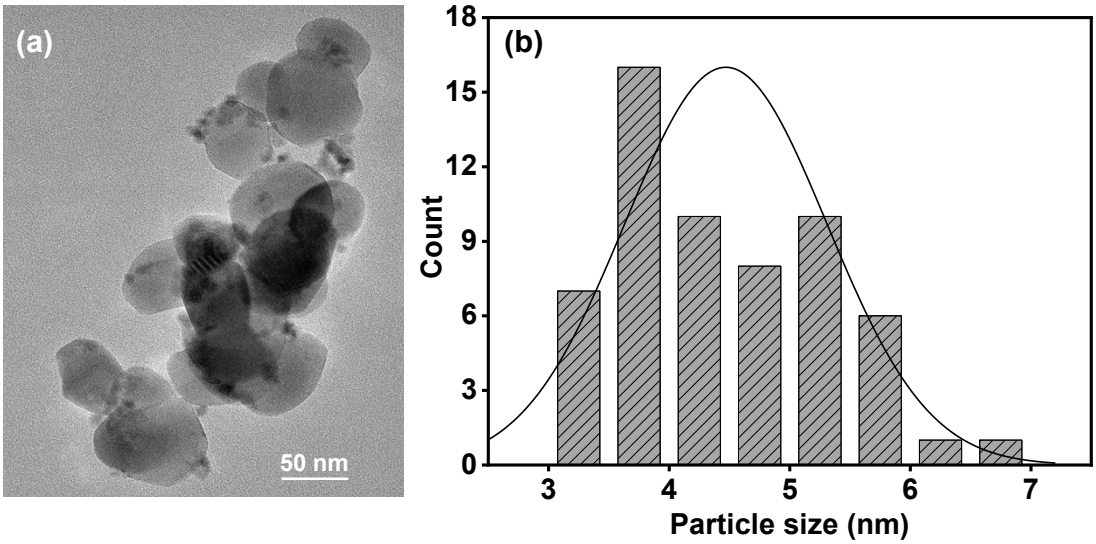


Fig. S7 (a) TEM image and **(b)** particle size distribution curve for spent Ru/5WZ catalyst.

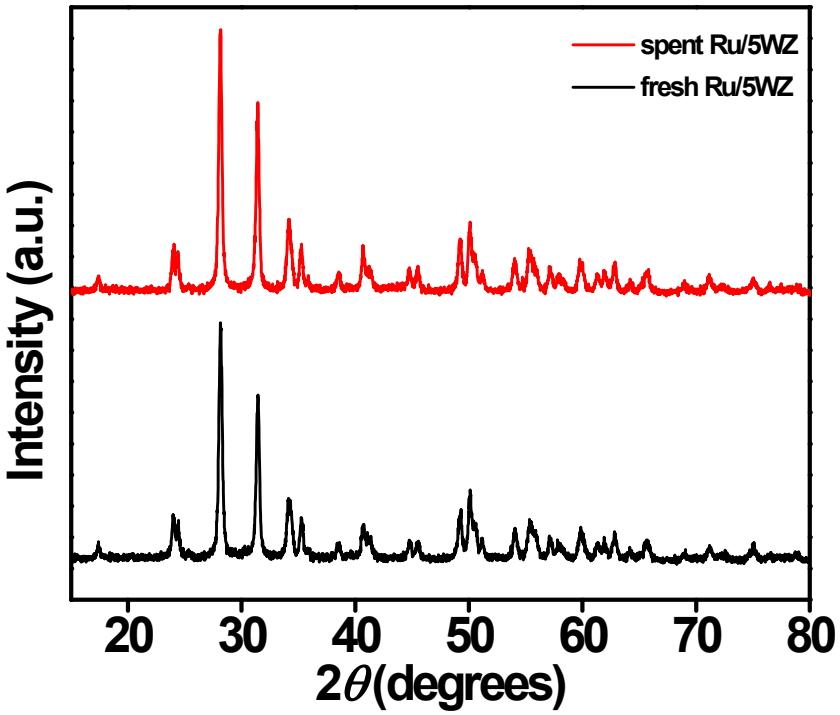
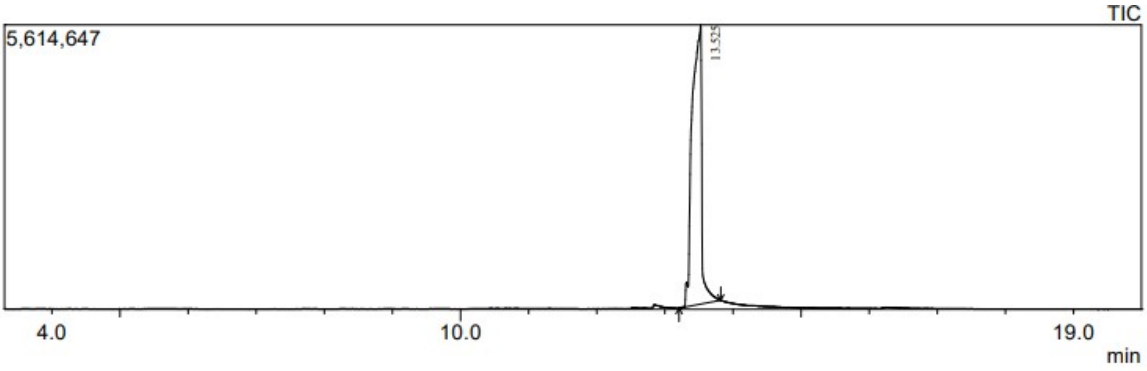


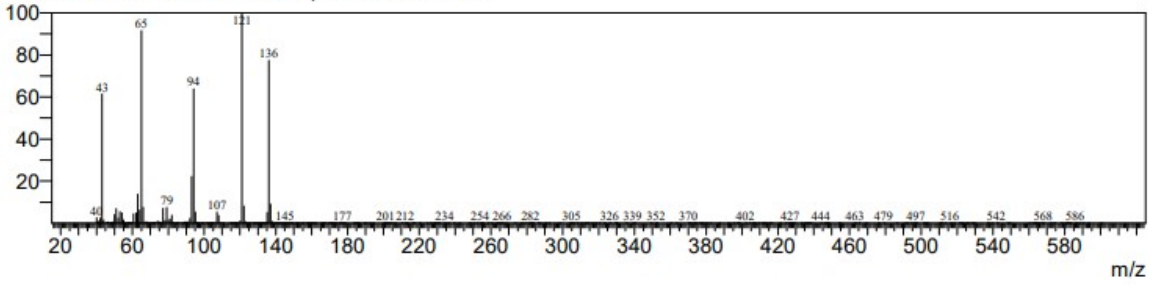
Fig. S8 PXRD of fresh (below) and spent (above) Ru/5WZ catalyst.



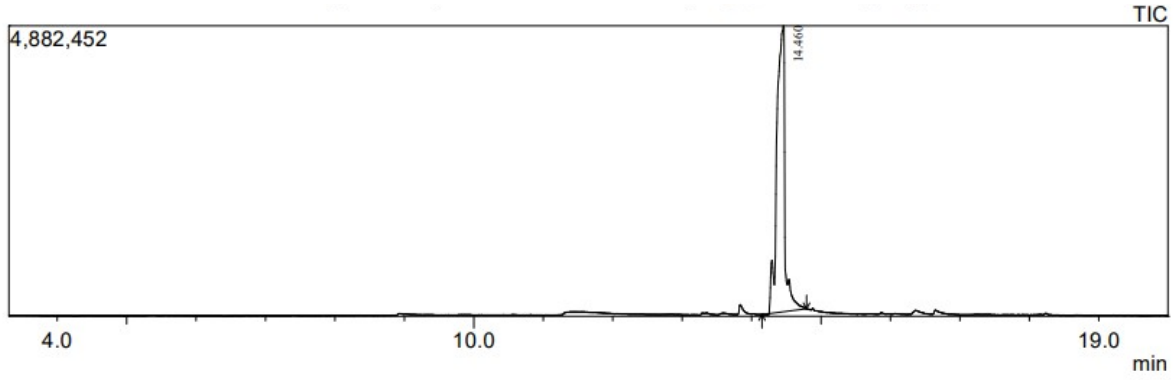
Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	13.525	4133208	100.00	5511214	100.00	9.82	Furfurylideneacetone
		4133208	100.00	5511214	100.00		

Line#:1 R.Time:13.525(Scan#:2046)
MassPeaks:292
RawMode:Averaged 13.520-13.530(2045-2047) BasePeak:121(978033)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



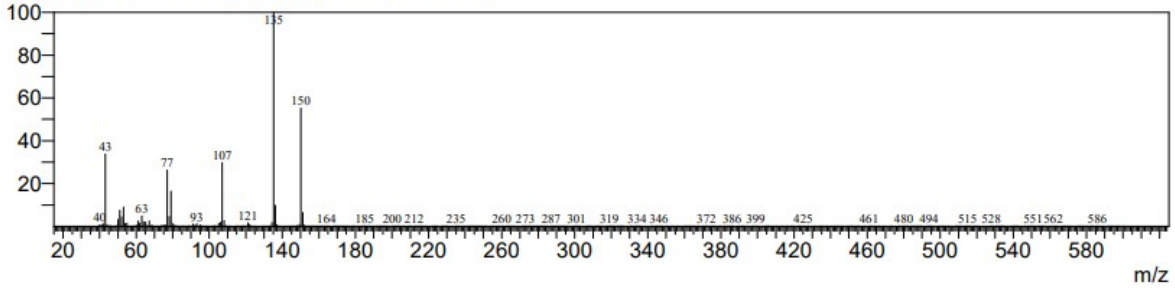
GC-MS data for FAc



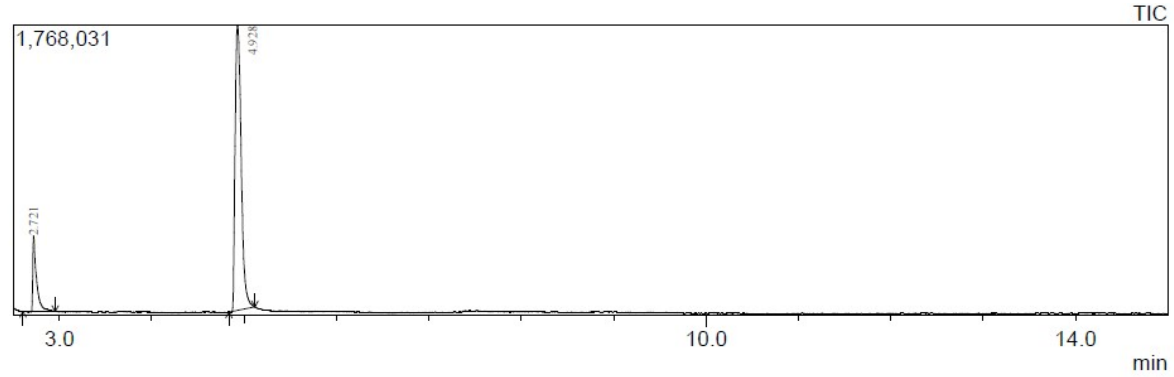
Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	14.460	8970026	100.00	4804357	100.00	8.11	4-methyl furfurylidene acetone
		8970026	100.00	4804357	100.00		

Line#:1 R.Time:14.460(Scan#:2233)
MassPeaks:370
RawMode:Averaged 14.455-14.465(2232-2234) BasePeak:135(1353095)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



GC-MS data for MeFAc



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	2.721	1262644	13.66	459734	20.93	2.75	Heptane
2	4.928	7979542	86.34	1737054	79.07	4.59	Octane
		9242186	100.00	2196788	100.00		

Spectrum

Line#:1 R.Time:2.720(Scan#:45)
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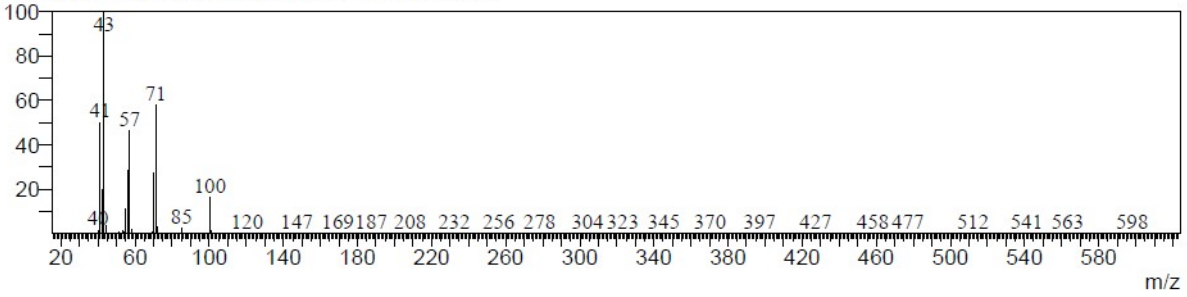
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



Line#:2 R.Time:4.930(Scan#:487)
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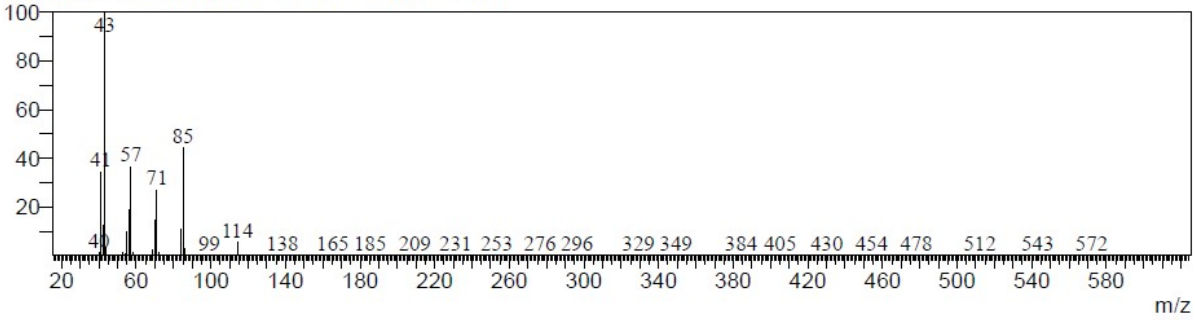
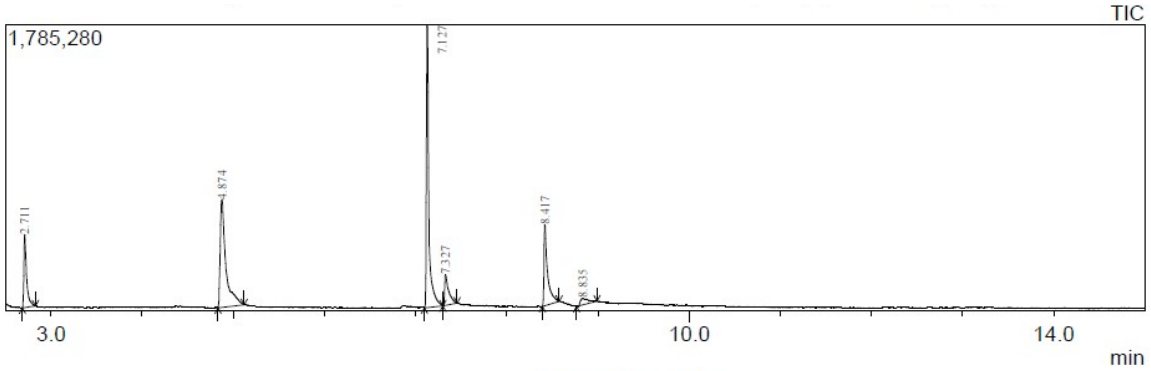


GC-MS data for HDO of FAc over Ru/5WZ catalyst.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	2.711	944655	10.09	454613	12.53	2.08	Heptane
2	4.874	2907176	31.04	673337	18.56	4.32	Octane
3	7.127	3337505	35.63	1764057	48.64	1.89	2-Propyltetrahydropyran
4	7.327	587983	6.28	189283	5.22	3.11	5-Methyl, 2-propyltetrahydrofuran
5	8.417	1357330	14.49	505915	13.95	2.68	Furan, 2-butyltetrahydro-
6	8.835	231660	2.47	39840	1.10	5.81	1-Octanol
		9366309	100.00	3627045	100.00		

Spectrum

Line#:1 R.Time:2.710(Scan#:43)
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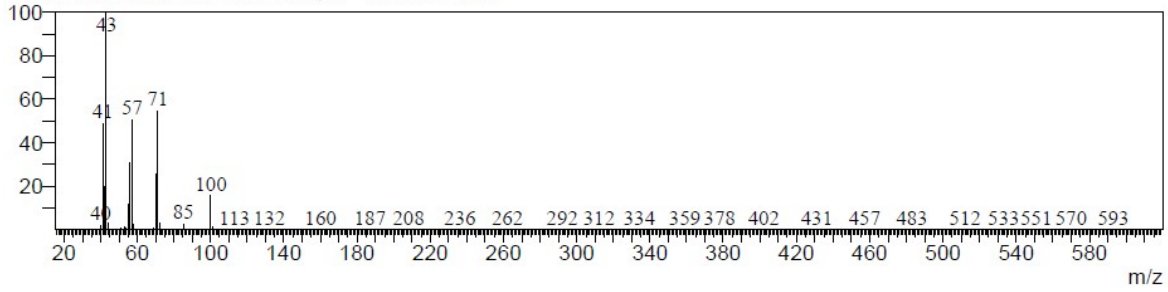
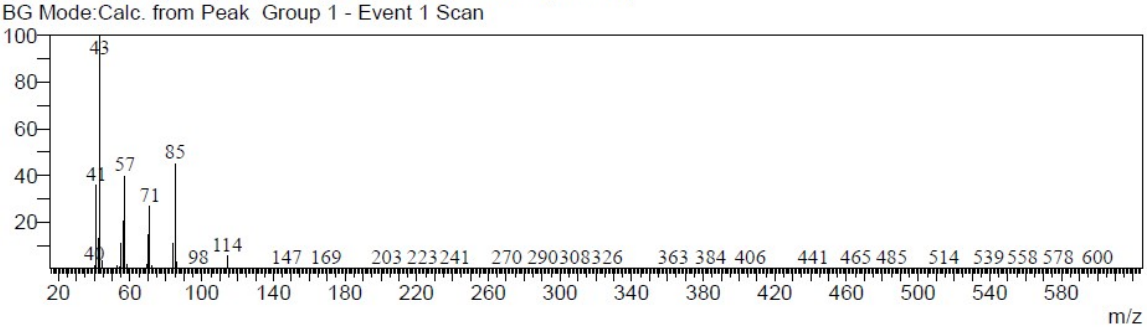
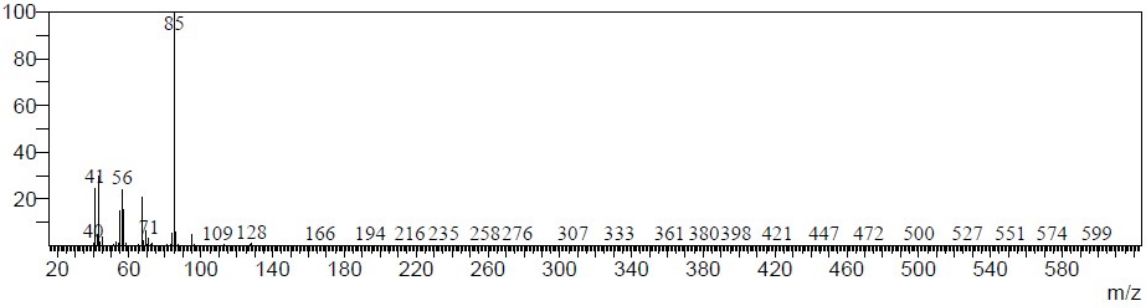
RawMode:Averaged 2.705-2.715(42-44) BasePeak:43(110390)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



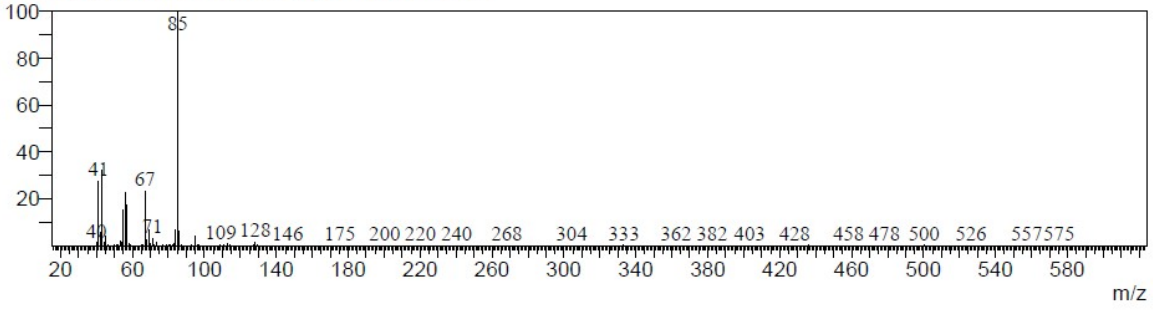
Line#:2 R.Time:4.875(Scan#:476)
MassPeaks:277
RawMode:Averaged 4.870-4.880(475-477) BasePeak:43(194419)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

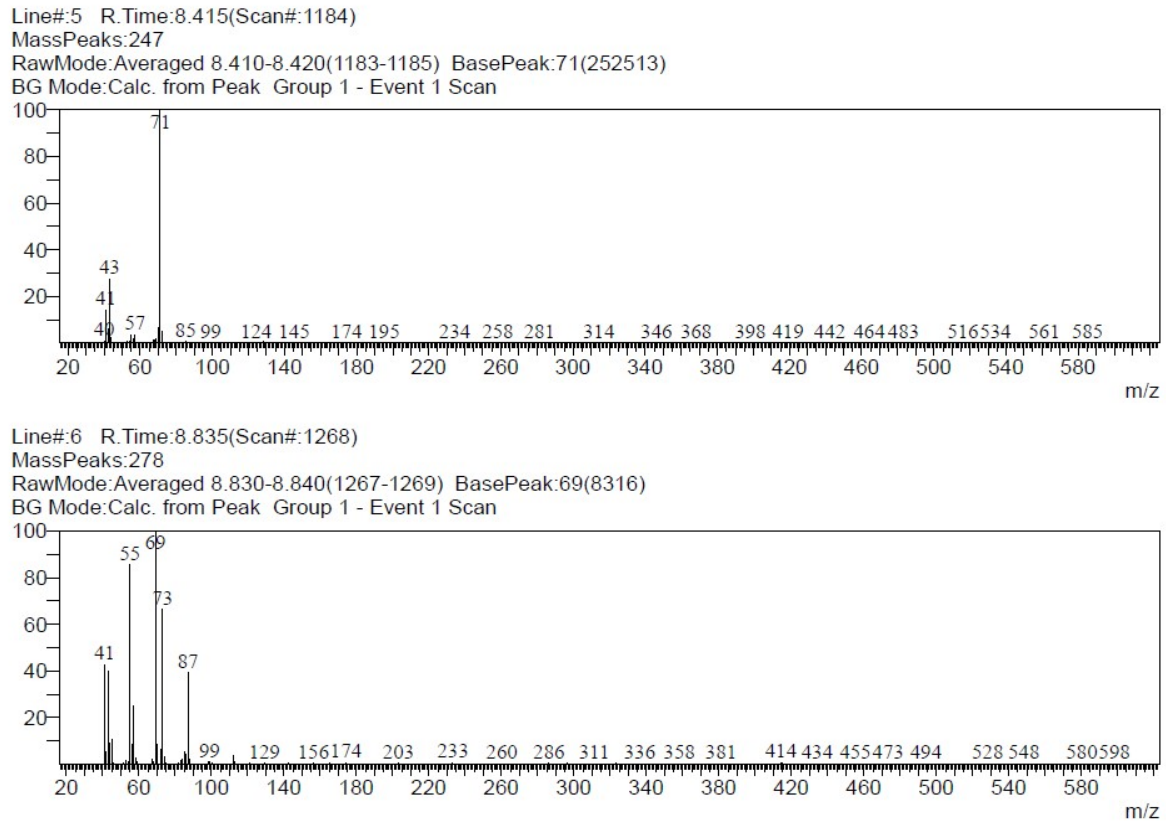


Line#:3 R.Time:7.125(Scan#:926)
MassPeaks:310
RawMode:Averaged 7.120-7.130(925-927) BasePeak:85(571516)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



Line#:4 R.Time:7.325(Scan#:966)
MassPeaks:329
RawMode:Averaged 7.320-7.330(965-967) BasePeak:85(59450)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan





GC-MS data for HDO of FAc over Ru/5WZ catalyst showing the presence of all the intermediates.

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