Single Pot Selective Hydrogenation of Furfural to 2-Methylfuran Over Carbon Supported Iridium Catalysts

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Supporting Information

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Table S1: Specific BET surface area 1 to 6% Ir/C

Sr. no	Catalyst	Surface area, m^2/g
1	Act. charcoal	108
2	1% Ir/C	117
3	2% Ir/C	129
4	4% Ir/C	169
5	5% Ir/C	189
6	6% Ir/C	215

Table S2: NH_3 TPD Table: Acidity values

Sr No	Catalyst	Distribution of acidic sites, mmol gm-1			Total NH_3 desorbed ,mmol gm-1
		<200 ^oC	200-400 ^oC	>400 ^oC	
1	Fresh 5% Ir/C	0.0471	0.0071	0.1092	0.1633
2	Spent 5% Ir/C	0.0492	0.0092	0.1085	0.1669

Table S3: Calculation Table of TON and TOF calculation

Sr. No.	Metal loading, %	Conv, % {Time, min}	Moles of FFR converted	Moles of metal in catalyst	TON	TOF h^{-1}
1	1%	14{30}	0.00364	1.30×10^{-5}	280	560
2	2%	21{30}	0.00514	2.60×10^{-5}	208	416
3	4%	26{30}	0.0067	5.20×10^{-5}	128	256
4	5%	39{30}	0.01015	6.50×10^{-5}	158	316
5	6%	40{30}	0.01030	7.80×10^{-5}	130	264

Reaction conditions: Furfural, 2.5 g; Catalyst loading, 0.25g; Temperature, 220 ^{o}C; H_2 pressure, 100 psig.

Figure S4: Controlled experiment

Sr No	Catalyst	Press., psig	Conv., %	Selectivity, %				
				FAL	THFAL	2-MF	2-MeTHF	Other
1	**5% Ir/C**	**500**	**>99**	**-**	**1**	**92**	**7**	**-**
2	**5% Ir/C**	**500**	**>99**	**SM**	**5**	**85**	**10**	**-**
3	**5% Ir/C**	**500**	**>99**	**-**	**-**	**SM**	**100**	**-**
4	**5% Ir/C**	**100**	**>99**	**-**	**1**	**95**	**4**	**-**
5	**5% Ir/C**	**100**	**>99**	**-**	**-**	**SM**	**100**	**-**
5	**5% Ir/C unreduced**	**100**	**60**	**SM**	**-**	**94**	**1**	**5**
6	**5% Ir/C (H_2 reduced#)**	**100**	**>99**	**-**	**29**	**25**	**38**	**8**

Reaction conditions: Substrate, 2.5g; solvent (IPA), 95ml; catalyst, 0.25g; temperature, 220^{o}C; Agitation speed, 1000, time, 5h. {SM- Starting Material/Substrate}; #= Furfural and THF (4%)

Reduction protocol:

$$\text{RT} \xrightarrow[\text{20 min, } N_2 \text{ atm}]{10^oC/min} 100^oC \xrightarrow[\text{10 min, } H_2 \text{ atm}]{5^oC/min} 200^oC \xrightarrow[\text{150 min, } H_2 \text{ atm}]{5^oC/min} 250^oC \xrightarrow[\text{Cooling, } N_2]{10^oC/min} \text{RT}$$

Table S5: Solvent reuse table

Sr No	Catalyst	Conv., %	Selectivity, %				
			FAL	THFAL	2-MF	2-MeTHF	Other
1	Fresh	>99	-	1	95	4	-
2	R1	>99	-	1	94	4	-
3	R2	98	1	1	93	5	-

Reaction conditions: Substrate, 2.5g; solvent (IPA), 95ml; catalyst, 0.25g; temperature, 220^{o}C; H_2 pressure, 100 psig; Agitation speed,1000, Reaction time, 5h.

Table S6: XPS table

Sr. No	Catalyst	Binding energy, e.V.(%)				Satelllite peaks e.V.
		Metallic Iridium		Oxides of Iridium		
		4f $_{7/2}$	4f $_{5/2}$	4f $_{7/2}$	4f $_{5/2}$	
1	5% Ir/C Fresh	60.9 **(27)**	63.94 **(12)**	61.5 **(11)** 62.21 (21)	64.41 **(20)** 64.53 **(9)**	66.31 69.21
2	5% Ir/C Used	60.95 **(4)** 59.85 **(1)**	63.92 **(25)**	61.11 **(20)** 61.32 (21) 62.68 **(10)**	64.75 **(19)**	66.11 68.15
3	5% Ir/ C w/o reduction	--	--	61.29 **(72)** 63.62 **(22)**	64.59 **(6)**	59.08

Figure S1: XPS of 5% Ir/C Fresh catalyst: Carbon

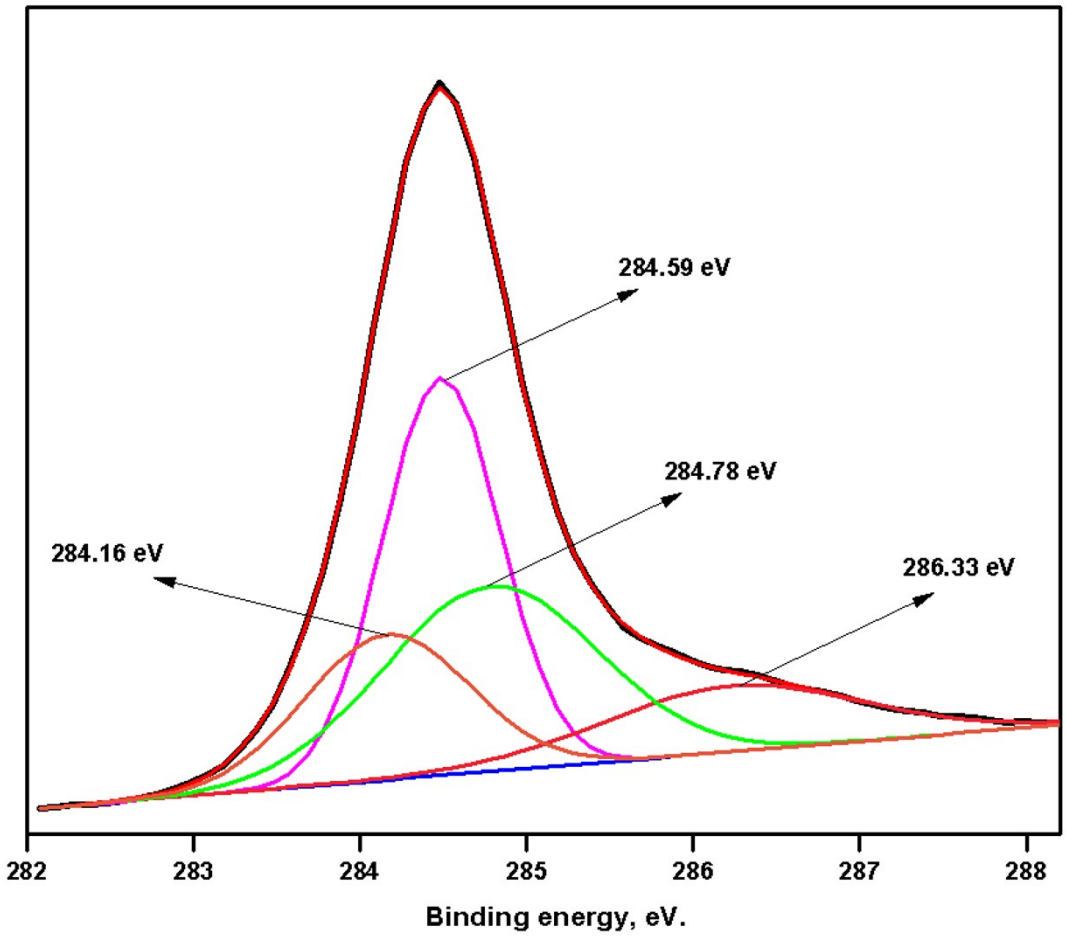


Figure S2: NH_3-TPD of 5% r/C catalyst

A] Fresh B] Used

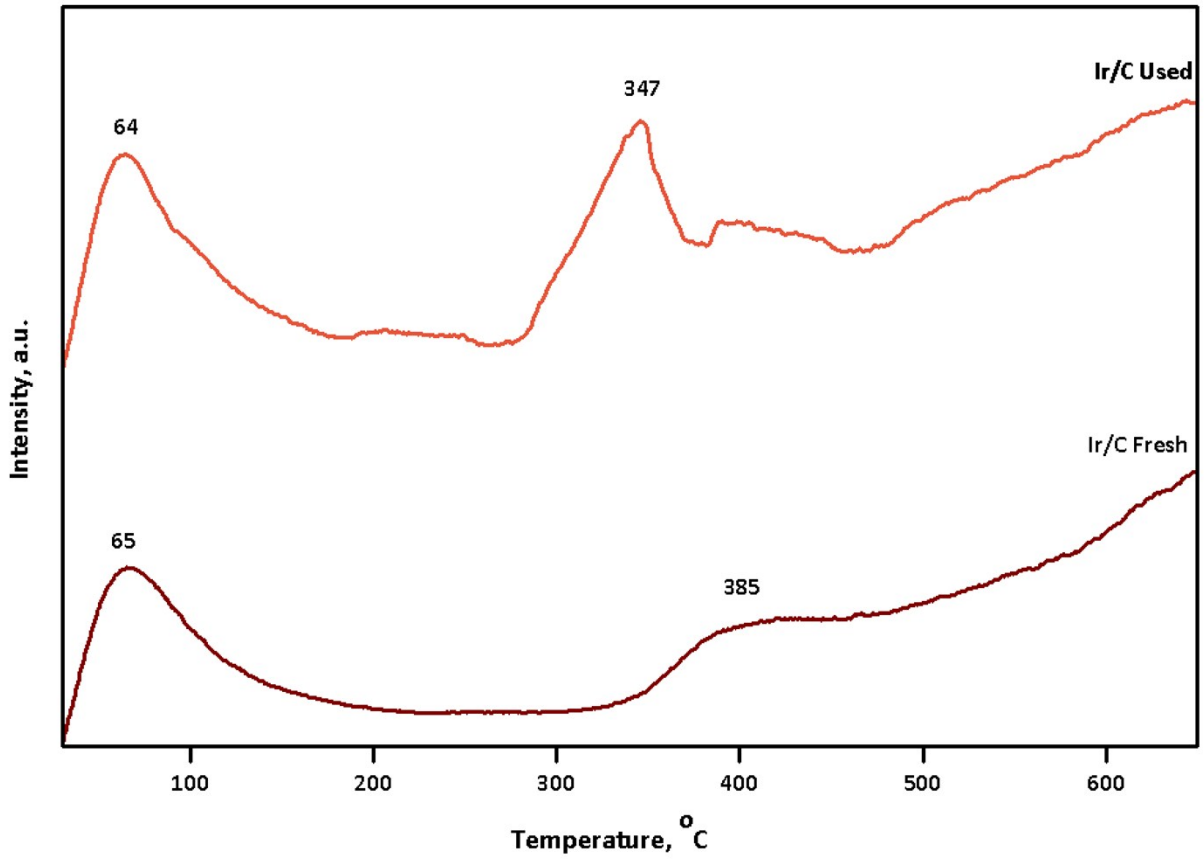


Figure S3: Py-IR of 5% Ir/C catalyst

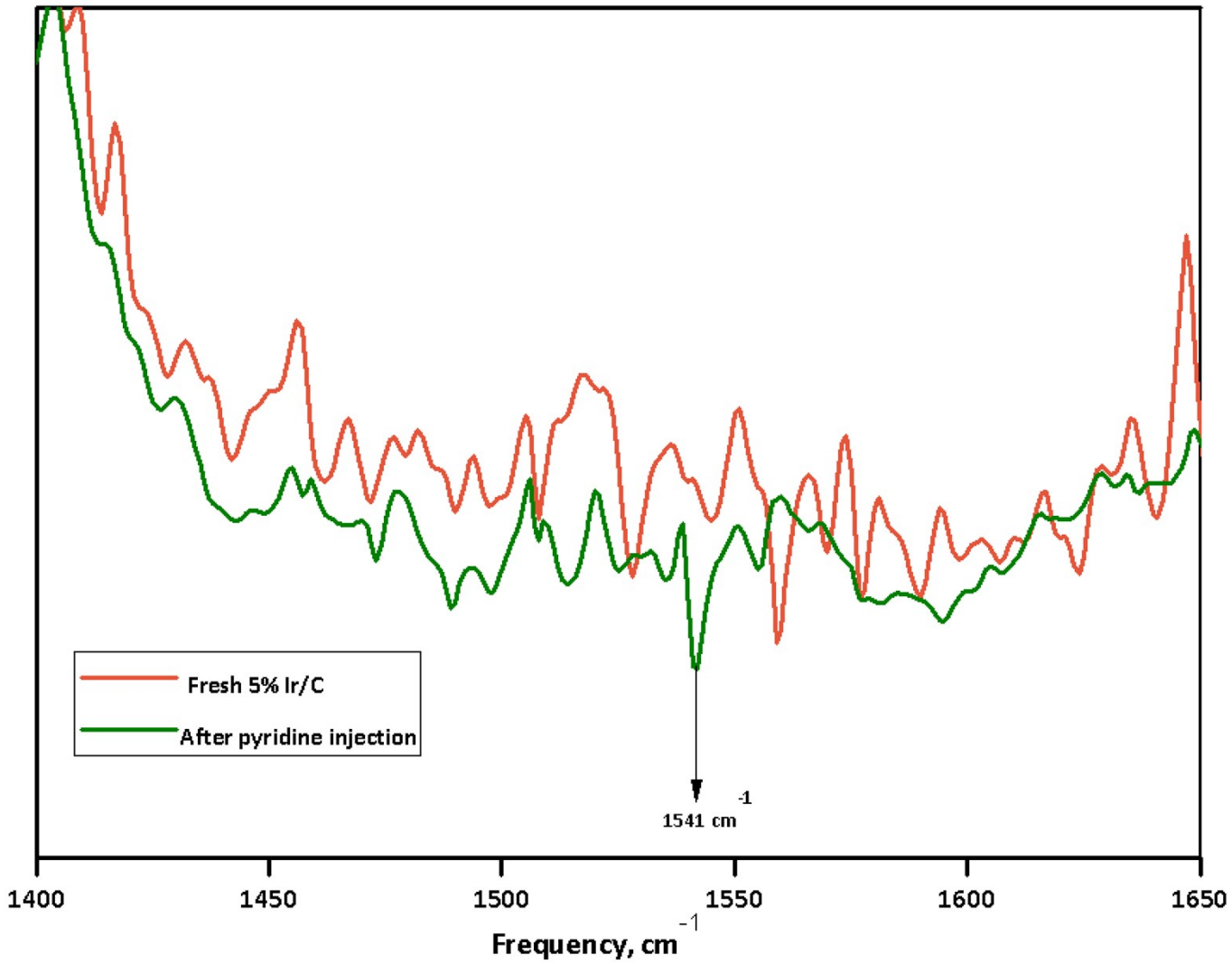
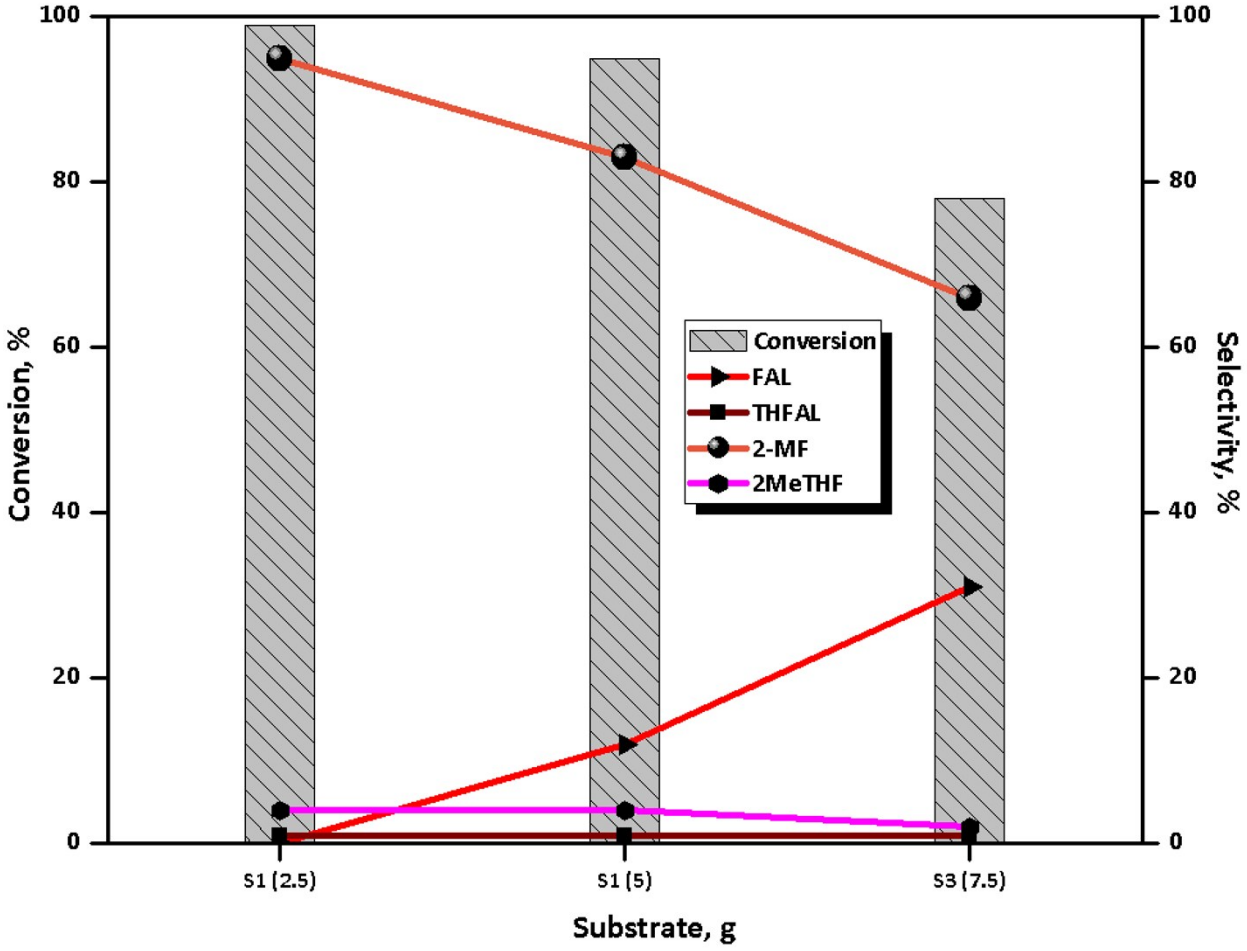
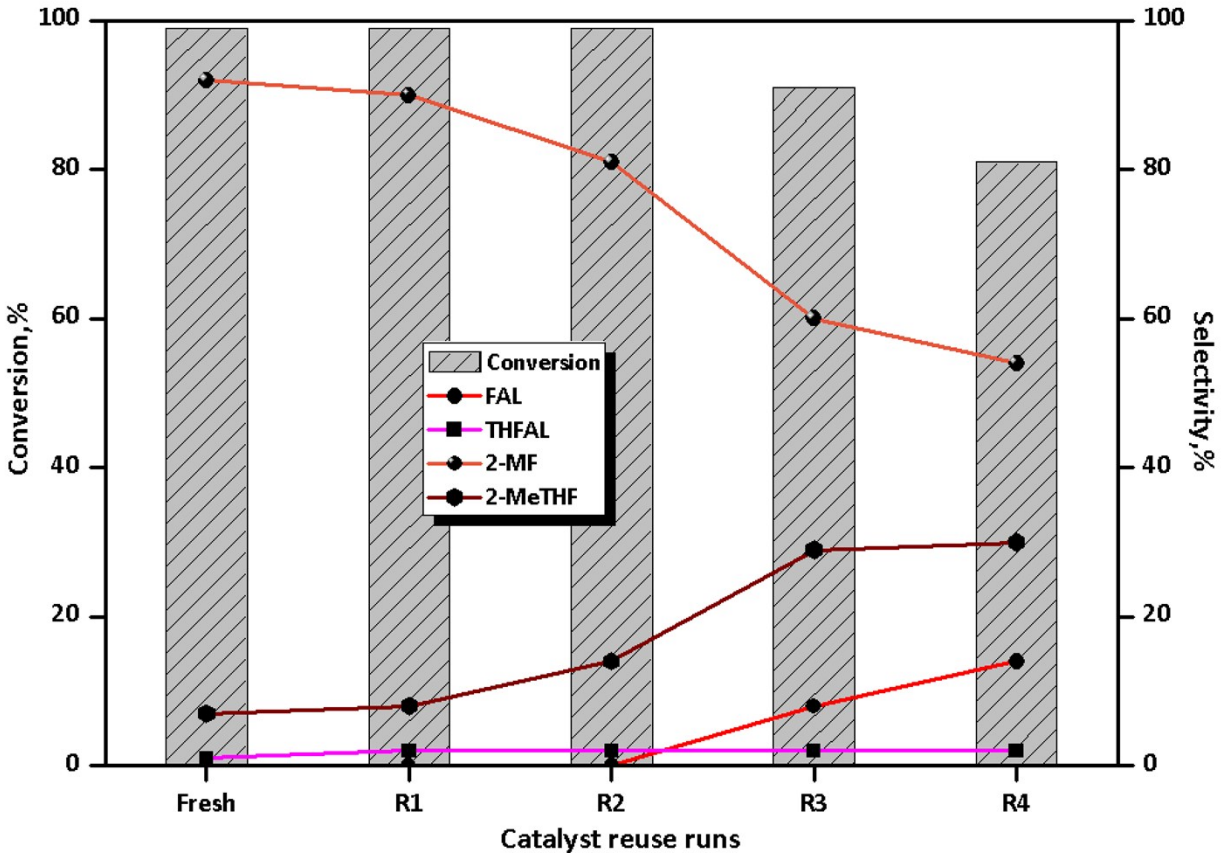


Figure S4: Effect of substrate loading



Reaction conditions: furfural, 2.5g; solvent (IPA), 95ml; catalyst, 0.25g, temp., 220 ^{o}C; pressure, 100 psig; Agitation speed, 1000 rpm, time, 5h.

Figure S5: Catalyst recycle at high pressure: 500 psig



Reaction conditions: furfural, 2.5g; solvent (IPA), 95ml; catalyst, 0.25g, temp., 220 ^{o}C; pressure, 500 psig; Agitation speed, 1000 rpm, time, 5h.

Figure S6: XRD of used 5% Ir/C)

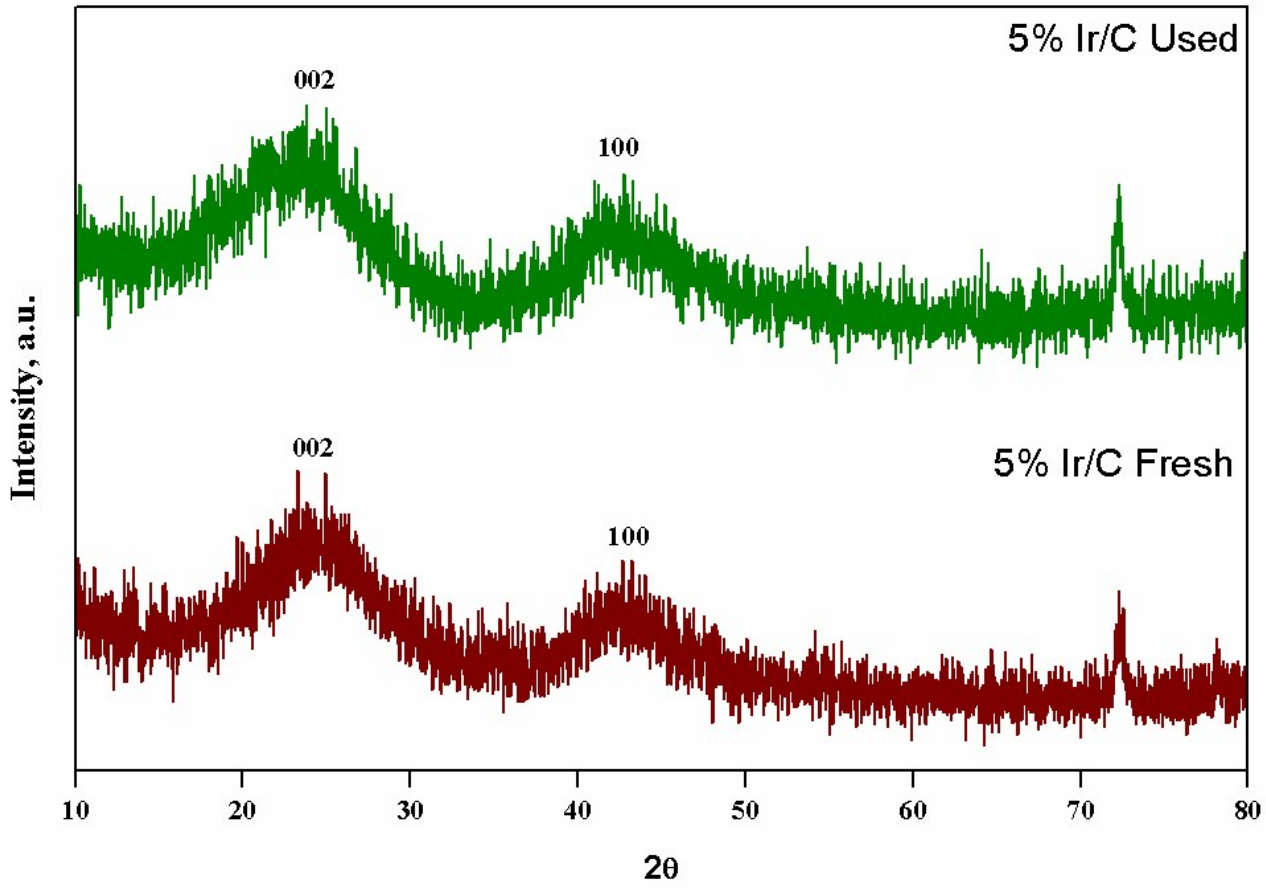


Figure S7: XPS of 5% Ir/C used catalyst: Oxygen

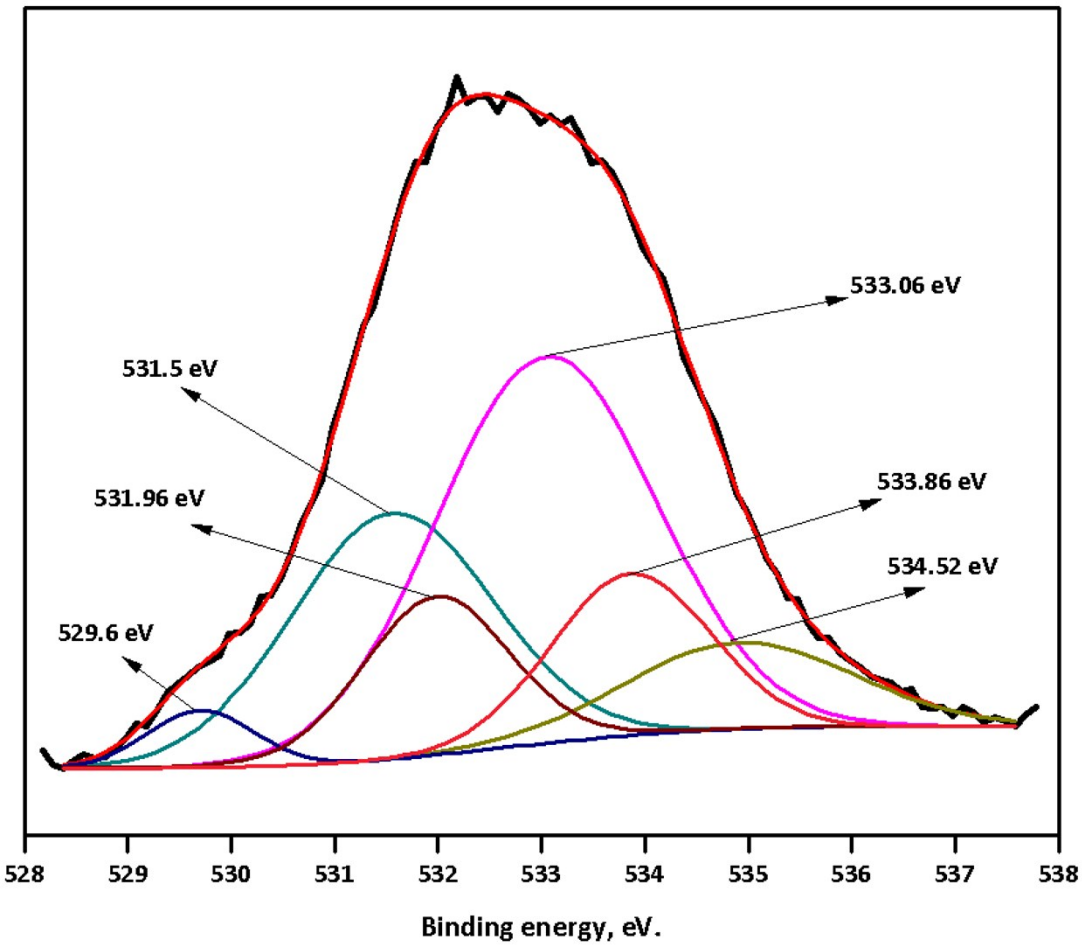
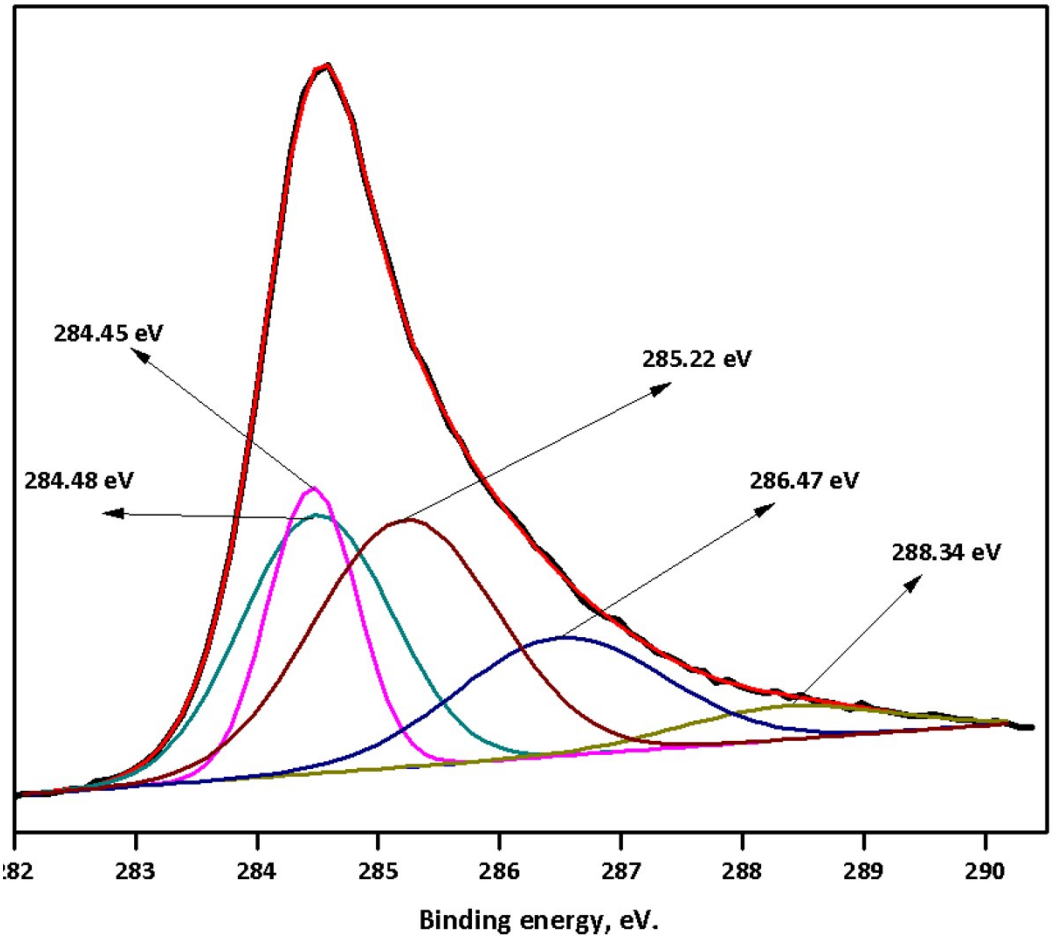
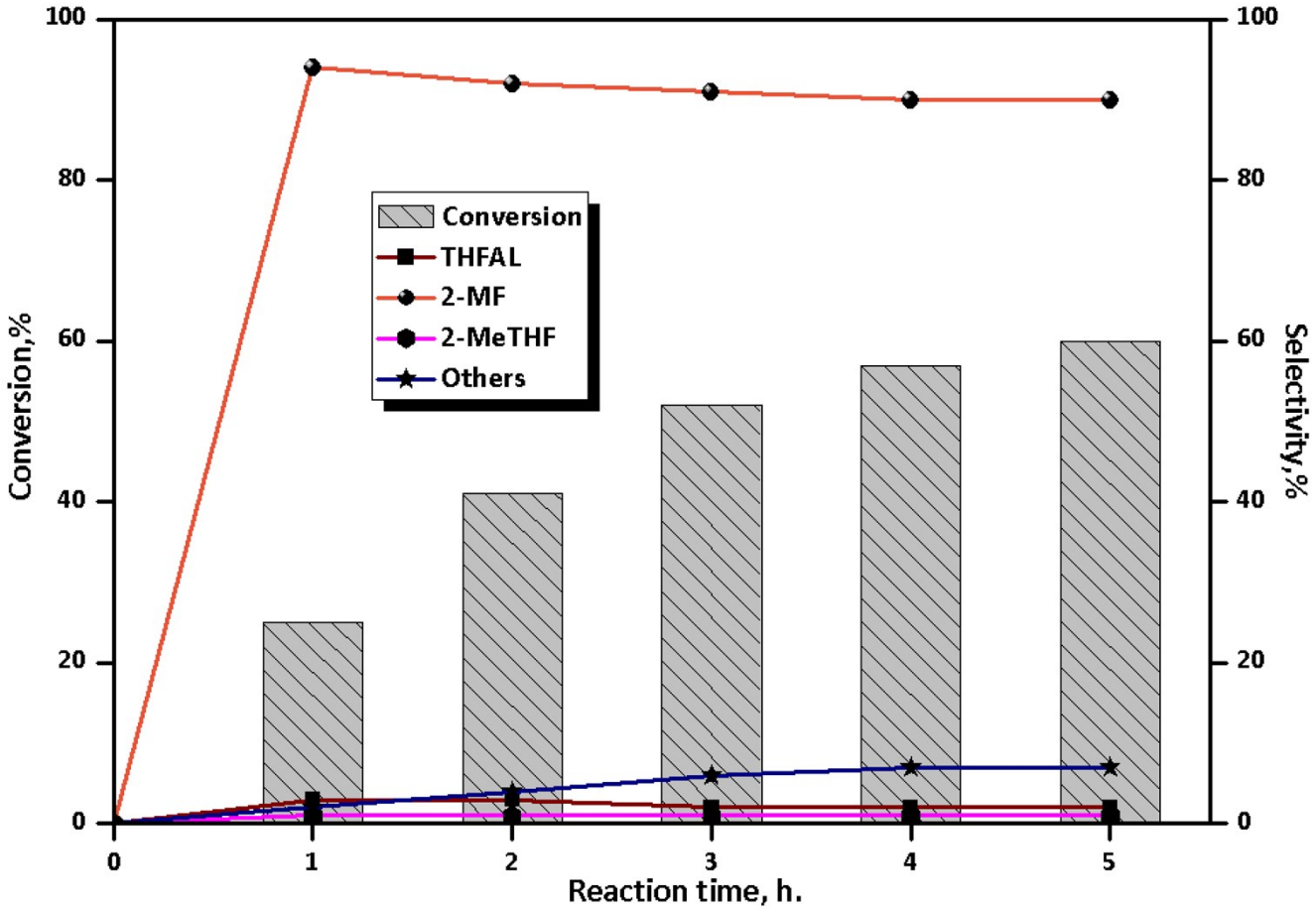


Figure S8: XPS of 5% Ir/C used catalyst Carbon



S9: CT profile over IrO_2/IrO_3/C catalyst: 5% Ir/C unreduced



Reaction conditions: Furfuryl alcohol, 2.5g; solvent (IPA), 95ml; catalyst, 0.25g; temperature, 220 ^{O}C; H_2 pressure, 100 psig; Agitation speed, 1000 rpm, time, 5h.

Figure S10: XPS of 5% Ir/C unreduced.

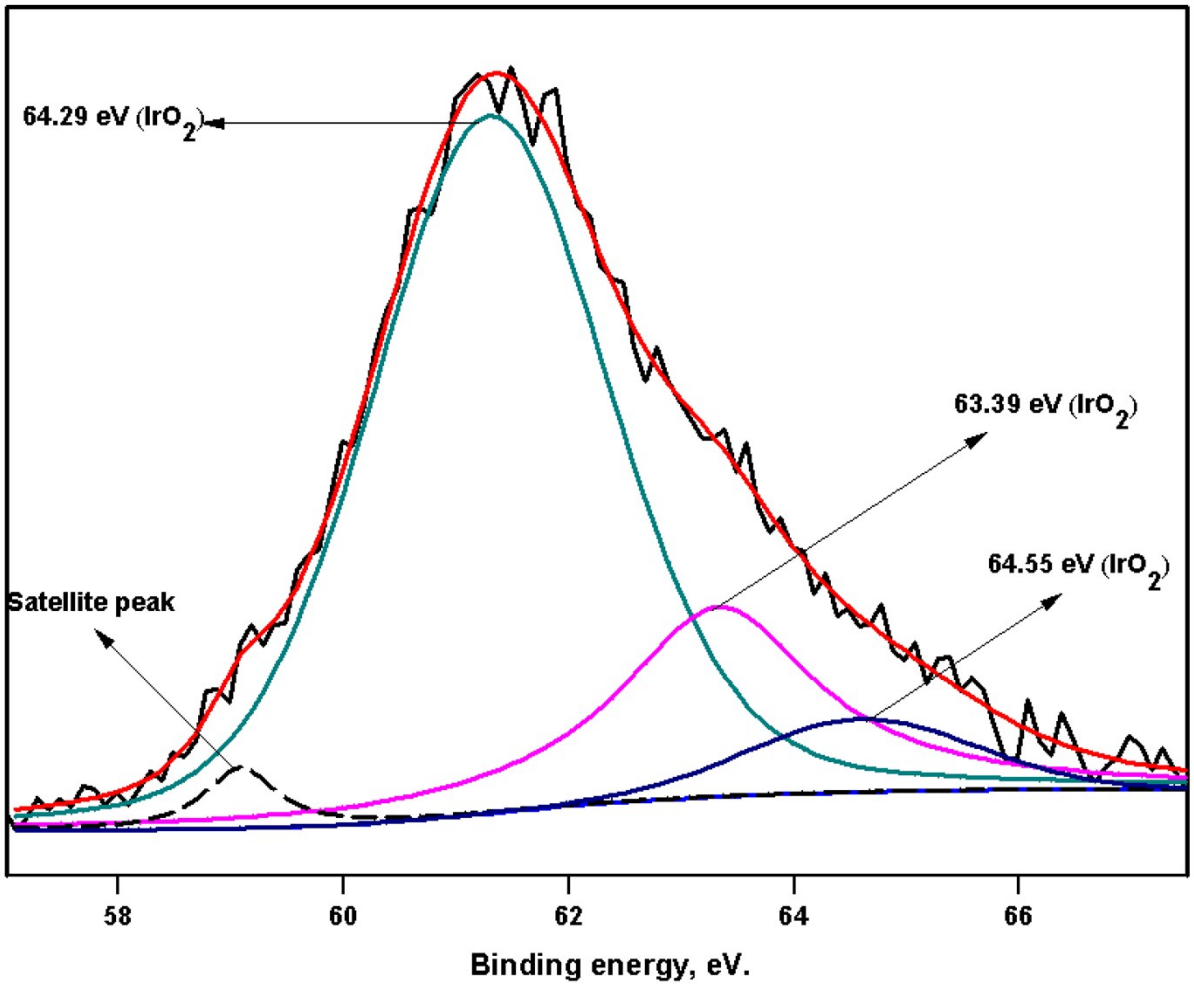
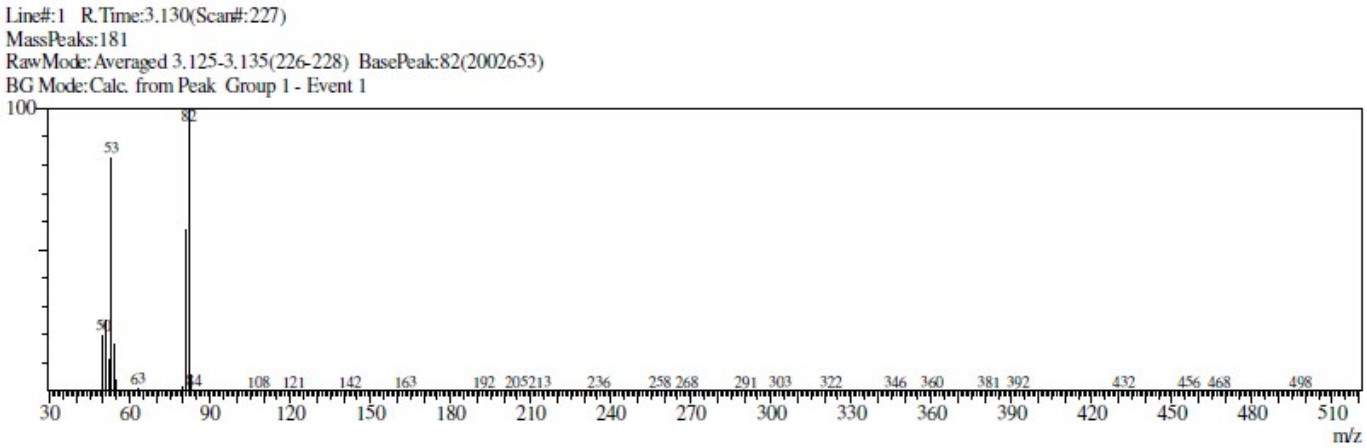
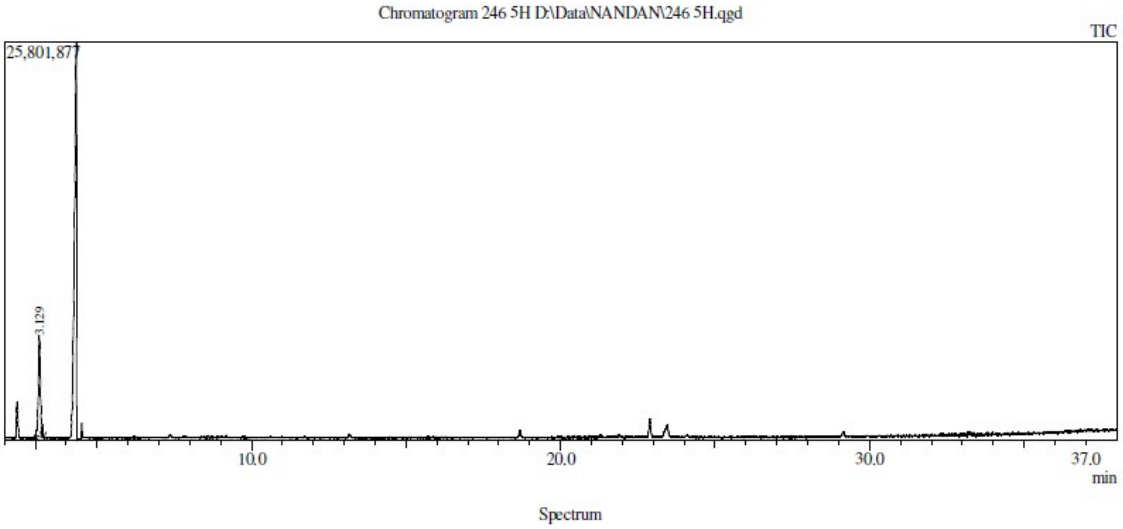


Figure S11: Mass spectrum of 2-Methyl furan along with GC mass.





Peaks originates between 22 and 23, are mainly due to traces of FAL and FFR. Arises due to high sensitivity of mass spectrum.