

Supplementary Information

Iridium Catalysts for C–C and C–O Hydrogenolysis: Catalytic Consequences of Iridium Sites

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Table S1. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/Al₂O₃ catalyst. Reaction conditions: T = 250 °C; P_{H₂} = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Acids			
Lactic acid	90	C ₃ H ₆ O ₃	0.03
Propanoic acid	74	C ₃ H ₆ O ₂	0.72
Methyltartronic acid	134	C ₄ H ₆ O ₅	0.03
Propanoic acid, 2-hydroxy-2-methyl-	104	C ₄ H ₈ O ₃	0.46
Alcohols C ₁ -C ₃			
Methanol	32	CH ₄ O	0.46
Ethyl alcohol	46	C ₂ H ₆ O	1.56
Ethylene glycol	62	C ₂ H ₆ O ₂	1.77
Isopropyl alcohol	60	C ₃ H ₈ O	0.27
1-Propanol	60	C ₃ H ₈ O	30.88
Propylene glycol	76	C ₃ H ₈ O ₂	8.46
1,3-Propanediol	76	C ₃ H ₈ O ₂	2.72
Alcohols C ₄ +			
1-Butanol	74	C ₄ H ₁₀ O	0.19
1,2-Butanediol	90	C ₄ H ₁₀ O ₂	0.90
1,2,3-Butanetriol	106	C ₄ H ₁₀ O ₃	0.12
3-Buten-2-ol	72	C ₄ H ₈ O	0.22
1,2,3-Propanetriol, monoacetate	134	C ₅ H ₁₀ O ₄	2.24
1-Butanol, 2-methyl	88	C ₅ H ₁₂ O	0.10
1-Pentanol	88	C ₅ H ₁₂ O	0.10
3-Pentanol	88	C ₅ H ₁₂ O	0.10
3-Ethoxy-1,2-propanediol	120	C ₅ H ₁₂ O ₃	0.88
4-Penten-2-ol, 3-methyl-	100	C ₆ H ₁₂ O	1.49
1-Hexanol	102	C ₆ H ₁₄ O	0.18
meso-3,4-Hexanediol	118	C ₆ H ₁₄ O ₂	0.16
1,2-Hexanediol	118	C ₆ H ₁₄ O ₂	0.56
3-Hexanol, 2-methyl-	116	C ₇ H ₁₆ O	0.13
4-Heptanol	116	C ₇ H ₁₆ O	1.65
DL-4,5-Octanediol	146	C ₈ H ₁₈ O ₂	0.75
5-Nonanol, 5-methyl-	158	C ₁₀ H ₂₂ O	0.17
Aldehydes			
Acetaldehyde	44	C ₂ H ₄ O	0.04
Propanal	58	C ₃ H ₆ O	0.85
Hexanal, 2-methyl-	114	C ₇ H ₁₄ O	0.08

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Table S1. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/Al₂O₃ catalyst. Reaction conditions: T = 250 °C; PH₂ = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h (cont.)

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Ketones			
Acetone	58	C ₃ H ₆ O	0.48
1,2-Propadiene-1,3-dione	68	C ₃ O ₂	0.20
Acetol	74	C ₃ H ₆ O ₂	4.21
2-Butanone	72	C ₄ H ₈ O	0.02
1-Hydroxy-2-butanone	88	C ₄ H ₈ O ₂	0.78
2-Propanone, 1-methoxy-	88	C ₄ H ₈ O ₂	1.65
2-Butanone, 3-hydroxy-	88	C ₄ H ₈ O ₂	0.12
2-Butanone, 3-methyl-	86	C ₅ H ₁₀ O	0.64
4-Penten-2-one	84	C ₅ H ₈ O	0.42
Cyclopentanone, 2-methyl-	98	C ₆ H ₁₀ O	0.16
Cyclopentanone, 3-methyl-	98	C ₆ H ₁₀ O	0.11
2,5-Hexanedione	114	C ₆ H ₁₀ O ₂	1.47
2,3-Hexanedione	114	C ₆ H ₁₀ O ₂	5.98
3-Pentanone, 2-methyl-	100	C ₆ H ₁₂ O	0.58
2-Pentanone, 3-methyl-	100	C ₆ H ₁₂ O	0.03
2-Hexanone	100	C ₆ H ₁₂ O	0.27
1-Isopropoxyacetone	116	C ₆ H ₁₂ O ₂	0.30
4-Hydroxy-3-hexanone	116	C ₆ H ₁₂ O ₂	0.71
2-Furanone, 2,5-dihydro-3,5-dimethyl	112	C ₆ H ₈ O ₂	0.09
4-Hepten-2-one,	112	C ₇ H ₁₂ O	0.39
2,3-Heptanedione	128	C ₇ H ₁₂ O ₂	0.05
4,5-Octanedione	142	C ₈ H ₁₄ O ₂	0.05
3-Heptanone, 2,4-dimethyl-	142	C ₉ H ₁₈ O	0.20
Esters			
Formic acid, 2-propenyl ester	86	C ₄ H ₆ O ₂	0.04
Propanoic acid, 2-hydroxy-, ethyl ester	118	C ₅ H ₁₀ O ₃	0.41
2-Propyn-1-ol, acetate	98	C ₅ H ₆ O ₂	0.90
Methyl 2-oxohexanoate	144	C ₇ H ₁₂ O ₃	0.58
Pentyl glycolate	146	C ₇ H ₁₄ O ₃	0.34
Ethane-1,1-diol dipropanoate	174	C ₈ H ₁₄ O ₄	3.25
Oxalic acid, dicyclobutyl ester	198	C ₁₀ H ₁₄ O ₄	0.11
Oxalic acid, cyclohexyl butyl ester	228	C ₁₂ H ₂₀ O ₄	0.47
Orthoformic acid, triisobutyl ester	232	C ₁₃ H ₂₈ O ₃	1.34
Ethers			
Dimethyl ether	46	C ₂ H ₆ O	0.29
Methane, dimethoxy-	76	C ₃ H ₈ O ₂	1.41
Methyl propyl ether	74	C ₄ H ₁₀ O	0.02
1,2-Propanediol. 3-methoxy-	106	C ₄ H ₁₀ O ₃	1.75
Acetic anhydride	102	C ₄ H ₆ O ₃	0.14
Oxirane, 2,3-dimethyl-	72	C ₄ H ₈ O	0.20
Oxirane, 3-hydroxypropyl-	102	C ₅ H ₁₀ O ₂	0.07
Methane, diethoxy-	104	C ₅ H ₁₂ O ₂	1.68
Propanoic acid, anhydride	130	C ₆ H ₁₀ O ₃	0.06
1,3-Dioxolane, 2-ethyl-4-methyl-	116	C ₆ H ₁₂ O ₂	0.09
1,3-Dioxolane-4-methanol, 2-ethyl-	132	C ₆ H ₁₂ O ₃	2.55
1,4-Dioxane-2,6-dimethanol	148	C ₆ H ₁₂ O ₄	1.61
Di- <i>n</i> -propyl ether	102	C ₆ H ₁₄ O	0.36
Diisopropyl ether	102	C ₆ H ₁₄ O	0.88
2-Propanol, 1-(1-methylethoxy)-	118	C ₆ H ₁₄ O ₂	0.31
2-Acetyl-2-methyltetrahydrofuran	128	C ₇ H ₁₂ O ₂	0.02
Propanoic acid, 2-methyl-, anhydride	158	C ₈ H ₁₄ O ₃	0.11
1,3-Dioxolane-2-propanoic acid, 2,4-dimethyl-, ethyl ester	202	C ₁₀ H ₁₈ O ₄	0.13

Table S2. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/ZrO₂ catalyst. Reaction conditions: T = 250 °C; PH₂ = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Acids			
Lactic acid	90	C ₃ H ₆ O ₃	0.01
Acetic acid	60	C ₂ H ₄ O ₂	0.29
Propanoic acid	74	C ₃ H ₆ O ₂	1.66
Methyltartronic acid	134	C ₄ H ₆ O ₅	0.01
Propanoic acid, 2-hydroxy-2-methyl-	104	C ₄ H ₈ O ₃	0.39
Alcohols C ₁ -C ₃			
Metanol	32	CH ₄ O	0.12
Ethyl alcohol	46	C ₂ H ₆ O	0.50
Ethylene glycol	62	C ₂ H ₆ O ₂	0.98
Isopropyl alcohol	60	C ₃ H ₈ O	0.28
1-Propanol	60	C ₃ H ₈ O	29.58
Propylene Glycol	76	C ₃ H ₈ O ₂	2.83
1,3-Propanediol	76	C ₃ H ₈ O ₂	1.80
Alcohols C ₄₊			
1-Propanol, 2-methyl-	74	C ₄ H ₁₀ O	0.04
1-Butanol	74	C ₄ H ₁₀ O	0.17
2-Propanol, 2-methyl-	74	C ₄ H ₁₀ O	0.04
DL-2,3-Butanediol	90	C ₄ H ₁₀ O ₂	0.10
1,2-Butanediol	90	C ₄ H ₁₀ O ₂	0.54
1,2,3-Butanetriol	106	C ₄ H ₁₀ O ₃	0.27
3-Buten-2-ol	72	C ₄ H ₈ O	0.42
1-Penten-3-ol	86	C ₅ H ₁₀ O	0.02
1,2,3-Propanetriol, monoacetate	134	C ₅ H ₁₀ O ₄	3.79
1-Butanol, 2-methyl-	88	C ₅ H ₁₂ O	0.11
1-Pentanol	88	C ₅ H ₁₂ O	0.16
3-Pentanol	88	C ₅ H ₁₂ O	0.36
3-Ethoxy-1,2-propanediol	120	C ₅ H ₁₂ O ₃	0.56
2-Butanol, 2,3-dimethyl-	102	C ₆ H ₁₄ O	0.02
3-Hexanol	102	C ₆ H ₁₄ O	0.02
2-Hexanol	102	C ₆ H ₁₄ O	0.05
1-Hexanol	102	C ₆ H ₁₄ O	0.32
meso-3,4-Hexanediol	118	C ₆ H ₁₄ O ₂	0.36
Triethylene glycol	150	C ₆ H ₁₄ O ₄	1.65
1-Isopropyl-3,3-bis(trifluoromethyl)diaziridine	222	C ₆ H ₈ F ₆ N ₂	0.73
4-Heptanol	116	C ₇ H ₁₆ O	1.57
meso-4,5-Octanediol	146	C ₈ H ₁₈ O ₂	0.82
Aldehydes			
Propanal	58	C ₃ H ₆ O	0.39
Butanedial	86	C ₄ H ₆ O ₂	0.33
Pentanal, 2-methyl-	100	C ₆ H ₁₂ O	0.09
2-Butenal, 2-ethyl-	98	C ₆ H ₁₀ O	0.05
3-Pentenal, 4-methyl-	98	C ₆ H ₁₀ O	0.05
Acetaldehyde, dipropyl acetal	146	C ₈ H ₁₈ O ₂	0.02
Ketones			
Acetone	58	C ₃ H ₆ O	0.22
2,3-Butanedione	86	C ₄ H ₆ O ₂	0.27
Acetol	74	C ₃ H ₆ O ₂	2.20
2-Butanone	72	C ₄ H ₈ O	0.22
1-Hydroxy-2-butanone	88	C ₄ H ₈ O ₂	0.46
2-Butanone, 3-hydroxy-	88	C ₄ H ₈ O ₂	1.63
2-Pentanone	86	C ₅ H ₁₀ O	0.02
2-Butanone, 3-methyl-	86	C ₅ H ₁₀ O	0.87

Table S2. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/ZrO₂ catalyst. Reaction conditions: T = 250 °C; PH₂ = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h (cont.)

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Ketones			
Cyclopentanone, 2-methyl-	98	C ₆ H ₁₀ O	0.10
Cyclopentanone, 3-methyl-	98	C ₆ H ₁₀ O	0.02
(R)-(+)-3-Methylcyclopentanone	98	C ₆ H ₁₀ O	0.05
Cyclohexanone	98	C ₆ H ₁₀ O	0.02
4-Penten-2-one, 4-methyl-	98	C ₆ H ₁₀ O	0.63
2,5-Hexanedione	114	C ₆ H ₁₀ O ₂	0.77
2,3-Hexanedione	114	C ₆ H ₁₀ O ₂	5.69
3-Pentanone, 2-methyl-	100	C ₆ H ₁₂ O	0.19
3-Hexanone	100	C ₆ H ₁₂ O	0.94
2-Hexanone	100	C ₆ H ₁₂ O	0.31
1-Isopropoxyacetone	116	C ₆ H ₁₂ O ₂	0.18
4-Hydroxy-3-hexanone	116	C ₆ H ₁₂ O ₂	0.94
4-Hepten-2-one,	112	C ₇ H ₁₂ O	0.66
Cyclopropane, [(1-propenyloxy)methyl]-	112	C ₇ H ₁₂ O	0.79
2-Pentanone, 3-ethyl-	114	C ₇ H ₁₄ O	0.02
4,5-Octanedione	142	C ₈ H ₁₄ O ₂	0.22
2,2,4-Trimethyl-3-pentanone	128	C ₈ H ₁₆ O	0.15
4-Hydroxy-3-methylacetophenone	150	C ₉ H ₁₀ O ₂	0.33
<i>t</i> -Butyl isobutyl ketone	142	C ₉ H ₁₈ O	0.87
2,4-Dimethyl-3-heptanone	142	C ₉ H ₁₈ O	0.20
2-Propanone, 1,1-dipropoxy-	174	C ₉ H ₁₈ O ₃	0.28
Esters			
1-Propen-2-ol, formate	86	C ₄ H ₆ O ₂	0.09
Acetic acid ethenyl ester	86	C ₄ H ₆ O ₂	0.18
Propanoic acid, 2-hydroxy-, ethyl ester	118	C ₅ H ₁₀ O ₃	5.93
Acetic acid, hydroxy-, propyl ester	118	C ₅ H ₁₀ O ₃	0.50
2-Propyn-1-ol, acetate	98	C ₅ H ₆ O ₂	0.42
Butanoic acid, 2-oxo-, methyl ester	116	C ₅ H ₈ O ₃	0.20
Butanedioic acid, hydroxy-, dimethyl ester	162	C ₆ H ₁₀ O ₅	0.76
Propanoic acid, propyl ester	116	C ₆ H ₁₂ O ₂	0.14
Propanoic acid, 1-methylethyl ester	116	C ₆ H ₁₂ O ₂	2.16
(S)-Isopropyl lactate	132	C ₆ H ₁₂ O ₃	0.45
Hydroxymethyl 2-hydroxy-2-methylpropionate	148	C ₆ H ₁₂ O ₄	0.08
Propanoic acid, 2-methylpropyl ester	130	C ₇ H ₁₄ O ₂	2.63
Pentyl glycolate	146	C ₇ H ₁₄ O ₃	0.32
Ethane-1,1-diol dipropionate	174	C ₈ H ₁₄ O ₄	0.18
Butanoic acid, (tetrahydro-2-furanyl)methyl ester	172	C ₉ H ₁₆ O ₃	0.37
1,3-Dioxolane-2-propanoic acid, 2,4-dimethyl-, ethyl ester	202	C ₁₀ H ₁₈ O ₄	0.23
Oxalic acid, cyclohexyl butyl ester	228	C ₁₂ H ₂₀ O ₄	0.13
Orthoformic acid, tri- <i>sec</i> -butyl ester	232	C ₁₃ H ₂₈ O ₃	0.19
Orthoformic acid, triisobutyl ester	232	C ₁₃ H ₂₈ O ₃	0.52
Ethers			
Dimethyl ether	46	C ₂ H ₆ O	0.38
Ethyl methyl ether	60	C ₃ H ₈ O	0.49
Methyl propyl ether	74	C ₄ H ₁₀ O	0.02
Ethyl ether	74	C ₄ H ₁₀ O	0.02
1,2-Propanediol, 3-methoxy-	106	C ₄ H ₁₀ O ₃	0.99
Acetic anhydride	102	C ₄ H ₆ O ₃	0.26
1,3-Dioxane	88	C ₄ H ₈ O ₂	0.02
Oxetane, 2,4-dimethyl-, <i>trans</i> -	86	C ₅ H ₁₀ O	0.11
1,3-Dioxane, 2-methyl-	102	C ₅ H ₁₀ O ₂	0.04
Ethyl propyl ether	88	C ₅ H ₁₂ O	0.65

Table S2. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/ZrO₂ catalyst. Reaction conditions: T = 250 °C; PH₂ = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h (cont.)

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Ethers			
Butane, 1-methoxy-	88	C ₅ H ₁₂ O	0.02
Methane, diethoxy-	104	C ₅ H ₁₂ O ₂	1.06
Propanoic acid, anhydride	130	C ₆ H ₁₀ O ₃	0.02
1,3-Dioxolane, 2-ethyl-4-methyl-	116	C ₆ H ₁₂ O ₂	0.02
1,3-Dioxolane-4-methanol, 2-ethyl-	132	C ₆ H ₁₂ O ₃	3.81
1,4-Dioxane-2,6-dimethanol	148	C ₆ H ₁₂ O ₄	0.96
Propane, 1-(1-methylethoxy)-	102	C ₆ H ₁₄ O	0.02
Di- <i>n</i> -propyl ether	102	C ₆ H ₁₄ O	0.19
2-Propanol, 1-propoxy-	118	C ₆ H ₁₄ O ₂	0.10
2-Propanol, 1-(1-methylethoxy)-	118	C ₆ H ₁₄ O ₂	0.08
3-Butenyl propyl ether	114	C ₇ H ₁₄ O	0.19
Ether, <i>sec</i> -butyl isopropyl	116	C ₇ H ₁₆ O	0.02
Butanoic acid, anhydride	158	C ₈ H ₁₄ O ₃	0.04
Propanoic acid, 2-methyl-, anhydride	158	C ₈ H ₁₄ O ₃	0.90
1-Heptene, 3-methoxy-	128	C ₈ H ₁₆ O	0.07
1,3-Dioxolane, 2-methyl-2-(4-methyl-3-methylenepentyl)-	184	C ₁₁ H ₂₀ O ₂	0.05

Table S3. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/SiO₂ catalyst. Reaction conditions: T = 250 °C; PH₂ = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Acids			
Propanoic acid, 2-hydroxy-2-methyl-	104	C ₄ H ₈ O ₃	0.16
Alcohols C ₁ -C ₃			
Methyl alcohol	32	CH ₄ O	0.66
Isopropyl alcohol	60	C ₃ H ₈ O	0.11
Ethyl alcohol	46	C ₂ H ₆ O	1.02
1-Propanol	60	C ₃ H ₈ O	46.67
Propylene glycol	76	C ₃ H ₈ O ₂	24.43
Ethylene glycol	62	C ₂ H ₆ O ₂	1.24
1,3-Propanediol	76	C ₃ H ₈ O ₂	0.55
Alcohols C ₄ +			
1-Propanol, 2-methyl-	74	C ₄ H ₁₀ O	0.07
1-Butanol	74	C ₄ H ₁₀ O	0.15
1-Butanol, 2-methyl-	88	C ₅ H ₁₂ O	0.08
1-Pentanol	88	C ₅ H ₁₂ O	0.08
1-Hexanol	102	C ₆ H ₁₄ O	0.08
4-Heptanol	116	C ₇ H ₁₆ O	0.33
3-Hexanol, 2-methyl-	116	C ₇ H ₁₆ O	0.33
4-Heptanol, 3-methyl-	130	C ₈ H ₁₈ O	0.42
Aldehydes			
Propanal	58	C ₃ H ₆ O	0.40
Ketones			
Acetone	58	C ₃ H ₆ O	0.61
Acetol	74	C ₃ H ₆ O ₂	4.88
3-Pentanone	86	C ₅ H ₁₀ O	0.11
3-Pentanone, 2-methyl-	100	C ₆ H ₁₂ O	0.16
3-Hexanone	100	C ₆ H ₁₂ O	0.60
2-Hexanone	100	C ₆ H ₁₂ O	0.16
Cyclopentanone, 2-methyl-	98	C ₆ H ₁₀ O	0.17
Cyclopentanone, 3-methyl-	98	C ₆ H ₁₀ O	0.11
Propane, 2-ethoxy-	88	C ₅ H ₁₂ O	0.26

Table S3. List of products obtained in the study of the effect of support on conversion and selectivity of glycerol hydrogenolysis for Ir/SiO₂ catalyst. Reaction conditions: T = 250 °C; P_{H₂} = 550 psi; m_{catalyst} = 1 g; 150 mL of 50% glycerol solution; t_{reaction} = 12 h (cont.)

Product	Molecular weight / (g mol ⁻¹)	Molecular formula	Selectivity / %
Ketones			
1-Hydroxy-2-butanone	88	C ₄ H ₈ O ₂	0.06
4-Hydroxy-3-hexanone	116	C ₆ H ₁₂ O ₂	0.14
2-Butanone, 3-hydroxy-	88	C ₄ H ₈ O ₂	0.27
2,5-Hexanedione	114	C ₆ H ₁₀ O ₂	0.43
2-Propanone, 1,1-dipropoxy-	174	C ₉ H ₁₈ O ₃	0.14
Esters			
Propanoic acid, 2-hydroxy-, 2-methylpropyl ester	146	C ₇ H ₁₄ O ₃	0.07
Acetic acid, 2-propenyl ester	100	C ₅ H ₈ O ₂	0.48
Isopropenyl acetate	100	C ₅ H ₈ O ₂	0.23
Propanoic acid, 2-methylpropyl ester	130	C ₇ H ₁₄ O ₂	6.44
Ethers			
2-Propanol, 1-(1-methylethoxy)-	118	C ₆ H ₁₄ O ₂	0.02
Ethanol, 2-tert-butoxy-	118	C ₆ H ₁₄ O ₂	3.68
Ethanol, 2-propoxy-	104	C ₅ H ₁₂ O ₂	0.78
1,2-Dibutoxyethane	174	C ₁₀ H ₂₂ O ₂	3.43