

Supporting Information

Mechanistic insights into C-O Bond Cleavage in Erythritol During Hydrodeoxygenation on Ir-ReOx Catalyst

Ajin Rajan and Jithin John Varghese*

Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai
600036, India

* Email: jithinjv@iitm.ac.in (JJV)

S1. Catalyst model for DFT simulations

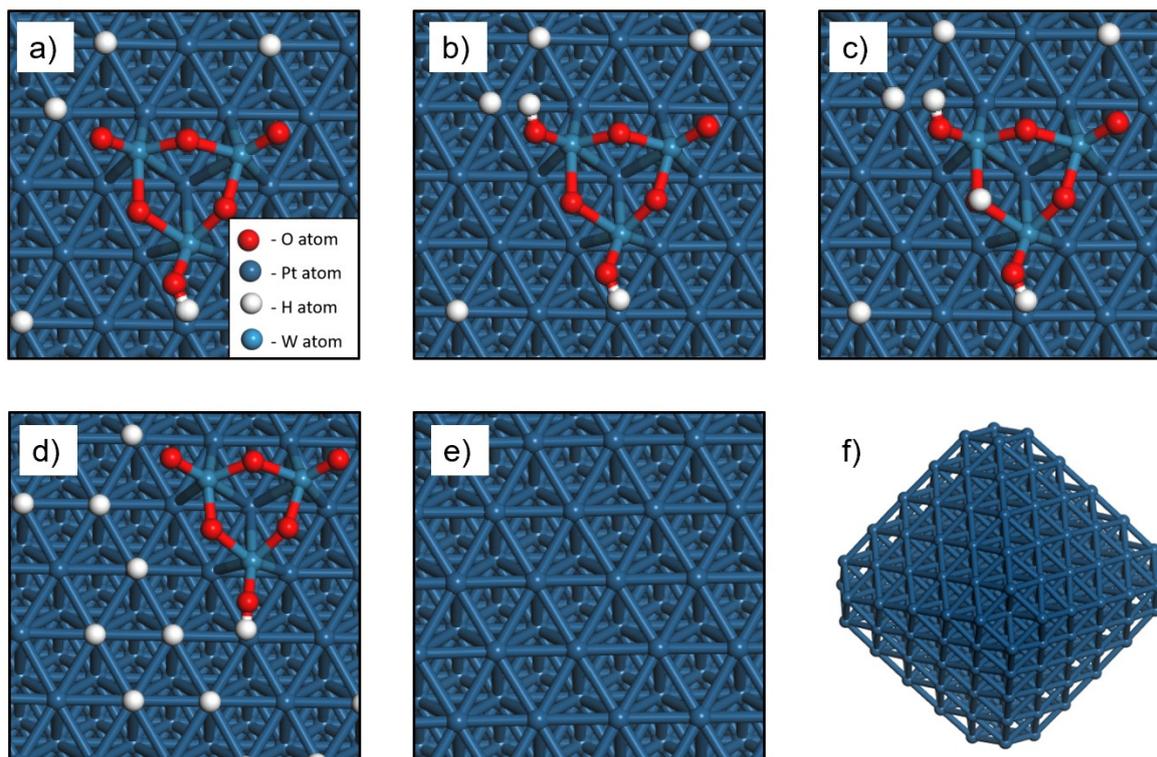


Fig.S1. Catalyst models used for DFT simulations a) $\text{Re}_3\text{O}_6\text{H}$ moiety representing the Brønsted acidic ReO_x cluster supported on a 4H^* covered $p(5\times 5)$ Ir(111) supercell with 4 Ir layers. b) To study the effect of Brønsted acid concentration, the ReO_x cluster on the above-mentioned catalyst model was replaced by $\text{Re}_3\text{O}_6\text{H}_2$ and c) $\text{Re}_3\text{O}_6\text{H}_3$ units. d) To study the H^* coverage, the 4H^* coverage in the model shown in Fig. S1a is updated with 10H^* . e) To compare the effect of undercoordinated sites, a well-coordinated $p(5\times 5)$ Ir(111) slab was modelled, and f) a Ir₂₂₅ nanoparticle in a 25.5Å cubic cell was modelled.

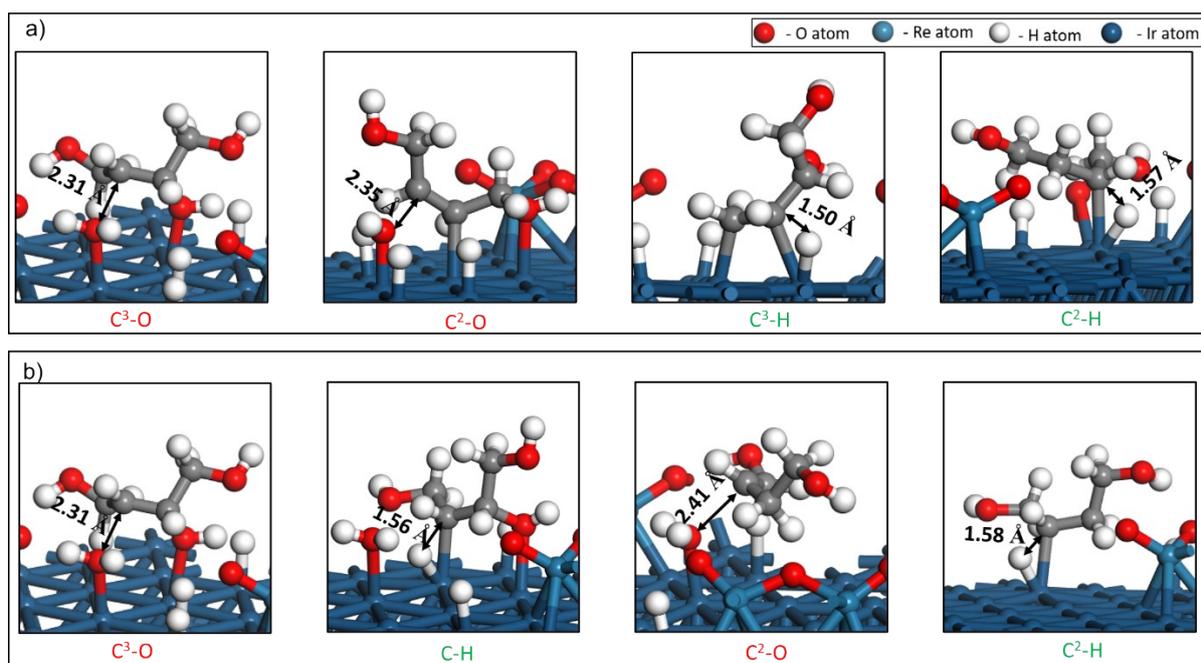


Fig.S2. Transition states identified for the hydrodeoxygenation of erythritol to 1,4-butanediol (1,4-BDO) via two pathways on Ir-ReO_x catalyst as represented in Figure 2a in the main manuscript. In (a), the protonation and dehydration of erythritol at the secondary OH is followed by another secondary C-O cleavage facilitated by the Ir. The two C-O cleavages are followed by sequential hydrogenation steps from the Ir to form 1,4-BDO without a butanetriol intermediate. In (b), the protonation and dehydration of erythritol from the ReO_x at the secondary OH is followed by hydrogenation from the Ir to form 1,2,4-butanetriol (1,2,4-BTO). 1,2,4-BTO undergoes another protonation and dehydration from the ReO_x at the secondary OH and a subsequent hydrogenation from Ir to form 1,4-BDO. In all the images, the relevant bond distances are also indicated.

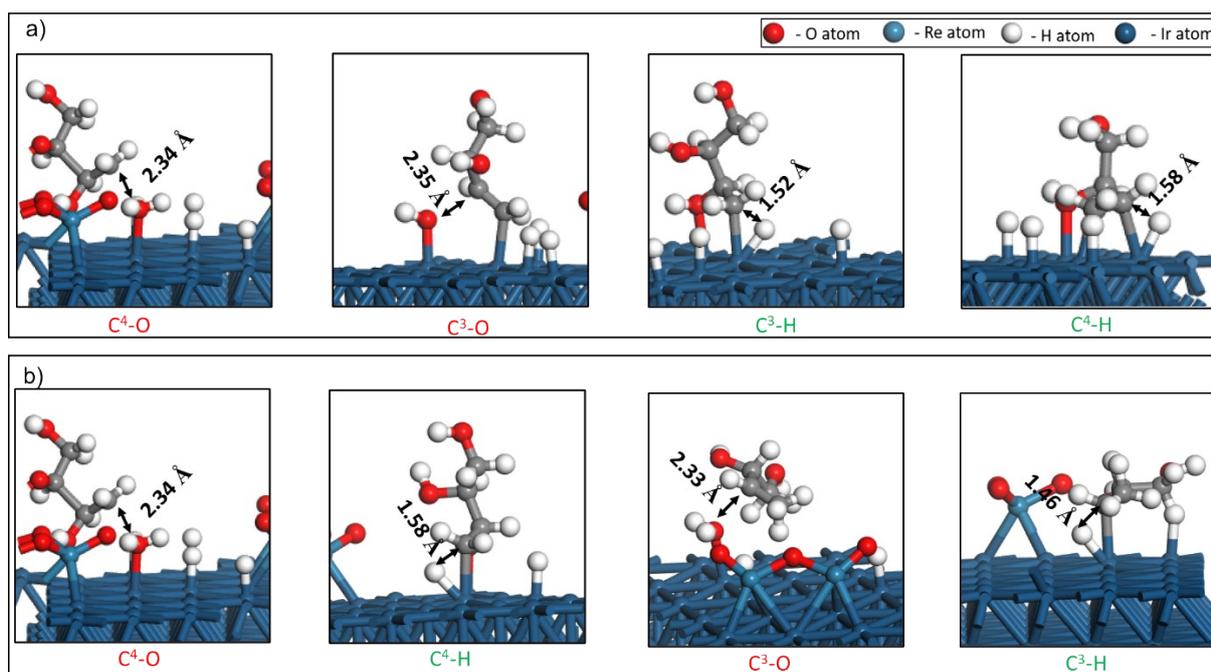


Fig.S3. Transition states identified for the hydrodeoxygenation of erythritol to 1,2-butanediol (1,2-BDO) via two pathways on Ir-ReO_x catalyst as represented in Figure 2b in the main manuscript. In (a), the protonation and dehydration of erythritol at the secondary OH is followed by another secondary C-O cleavage facilitated by the Ir. The two C-O cleavages are followed by sequential hydrogenation steps from the Ir to form 1,2-BDO without a butanetriol intermediate. In (b), the protonation and dehydration of erythritol from the ReO_x at the secondary OH is followed by hydrogenation from the Ir to form 1,2,3-butanetriol (1,2,3-BTO). 1,2,3-BTO undergoes another protonation and dehydration from the ReO_x at the secondary OH and a subsequent hydrogenation from Ir to form 1,2-BDO. In all the images, the relevant bond distances are also indicated.

Table S1: Comparison of the HDO of 20 wt.% aqueous erythritol, 1,2,3-butanetriol, and 1,2,4-butanetriol on Ir-ReO_x catalyst as reported by Gu et. al¹ at P_{H2} of 8 MPa and 100 °C.

Entry	Reactant	Duration (h)	Con	1,2,3-BTO	1,2,4-BTO	1,2-BDO	1,3-BDO	2,3-BDO	1,4-BDO	1-BO	2-BO	Others
1	Erythritol	4	23	27	37		10		13		1	1
2	1,2,3-BTO	4	7	-	-		61	13	-	8	13	6
3	1,2,4-BTO	4	45	-	-		8	-	80	10	1	1

Table S2: Comparison of the HDO of 20 wt.% aqueous 1,2-butanediol, 1,3-butanediol, and 1,4-butanediol on Ir-ReO_x catalyst as reported by Gu et al.¹ at P_{H2} of 8 MPa and 100 °C.

Entry	Duration (h)	Reactant	Conv	1-BO	2-BO	Others
1	2	1,2-BDO	48	86	10	5
2	2	1,3-BDO	14	47	45	6
3	4	1,4-BDO	16	92	-	6

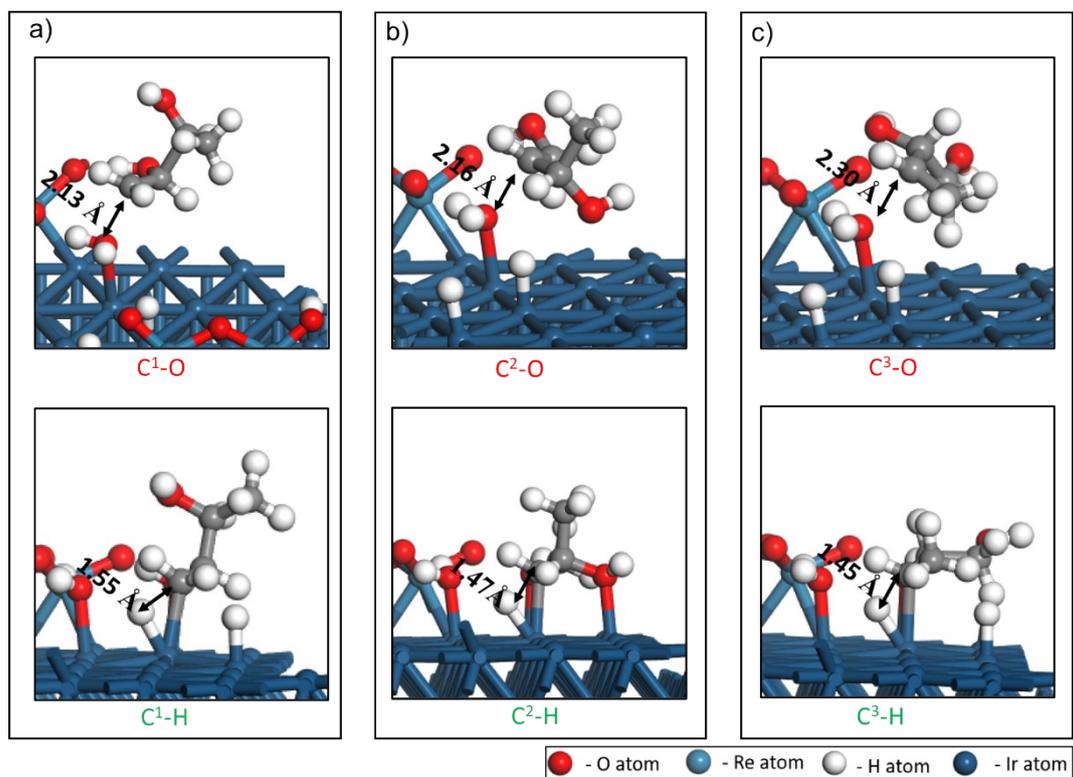


Fig.S4. Transition states identified for the hydrodeoxygenation of 1,2,3-BTO on Ir-ReO_x catalyst as represented in Figure 3a in the main manuscript to (a) 2,3-BDO, (b) 1,3-BDO, and (c) 1,2-BDO. In all the images, the figure on the top represents the C-O cleavage and the figure at the bottom represents the hydrogenation. The relevant bond distances are also indicated in each figure.

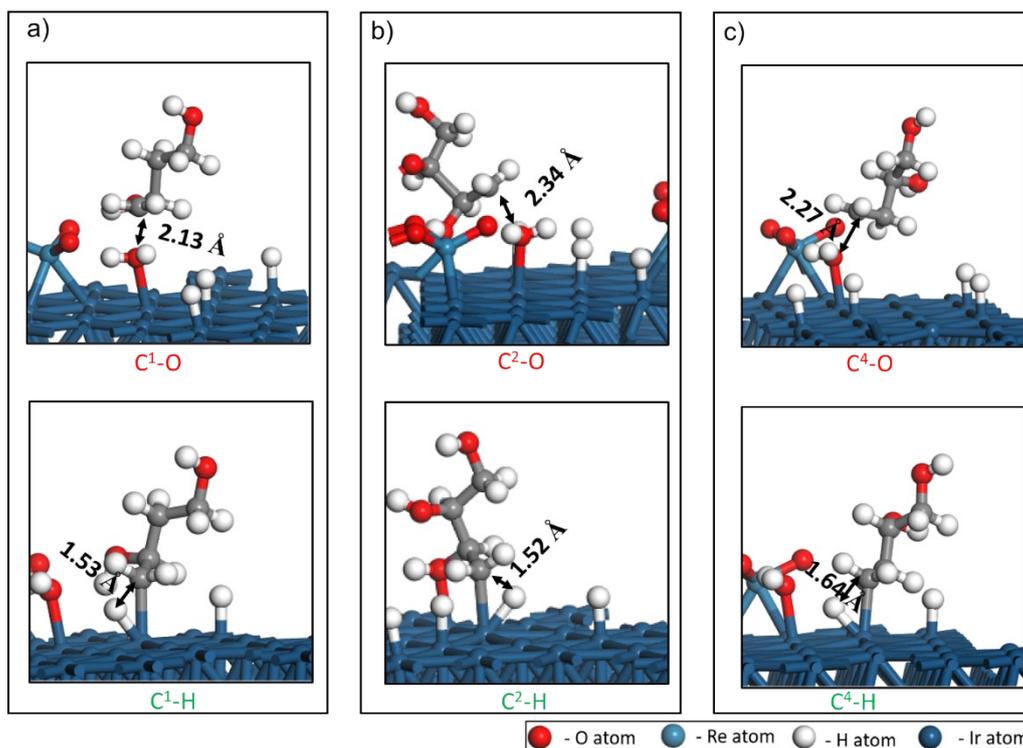


Fig.S5. Transition states identified for the hydrodeoxygenation of 1,2,4-BTO on Ir-ReO_x catalyst as represented in Figure 3b in the main manuscript to (a) 1,3-BDO, (b) 1,4-BDO, and (c) 1,2-BDO. In all the images, the figure on the top represents the C-O cleavage and the figure at the bottom represents the hydrogenation. In all the images, the relevant bond distances are also indicated.

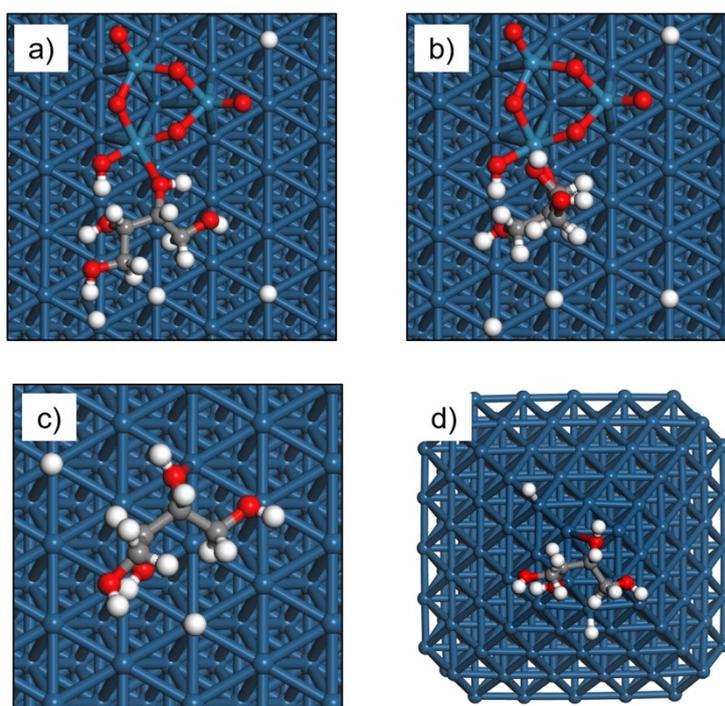


Fig.S6. Different erythritol adsorption configuration to initiate different reactions a) secondary C-O cleavage, b) primary C-O cleavage on Ir-ReO_x catalyst, c) secondary dihydroxylation on Ir[111] slab and d) Ir₂₂₅ nanoparticle

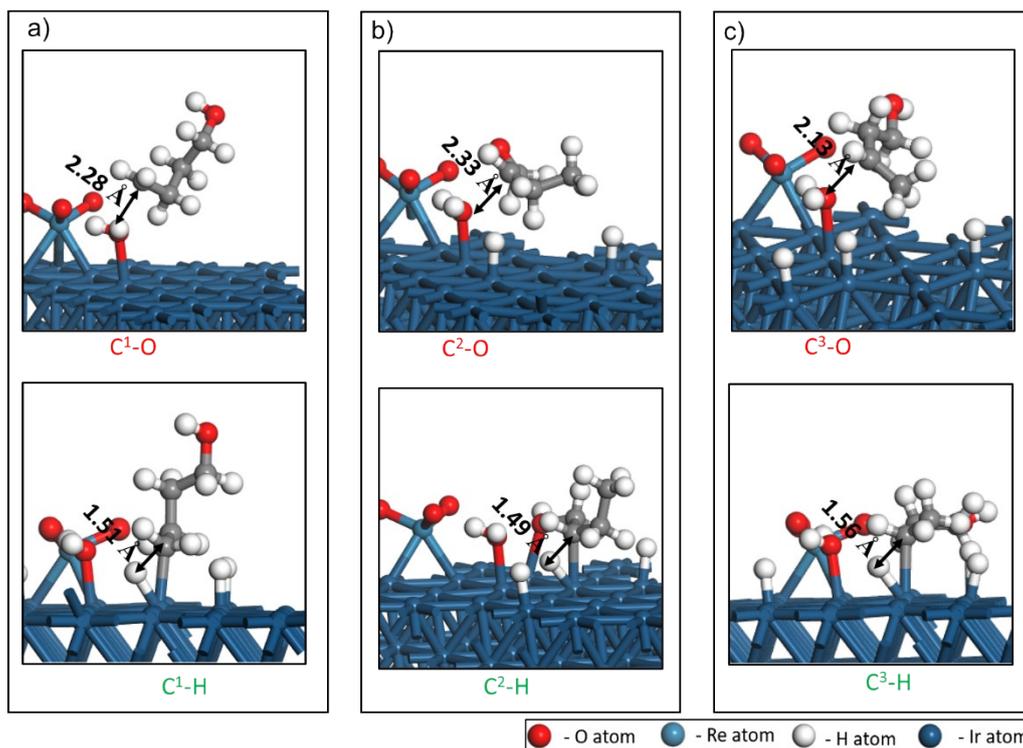


Fig.S7. Transition states identified for the formation of 1-BO on Ir-ReO_x catalyst as represented in Figure 4a in the main manuscript to from (a) 1,4-BDO, (b) 1,2-BDO, and c) 1,3-BDO. In all the images, the figure on the top represents the C-O cleavage and the figure at the bottom represents the hydrogenation. In all the images, the relevant bond distances are also indicated.

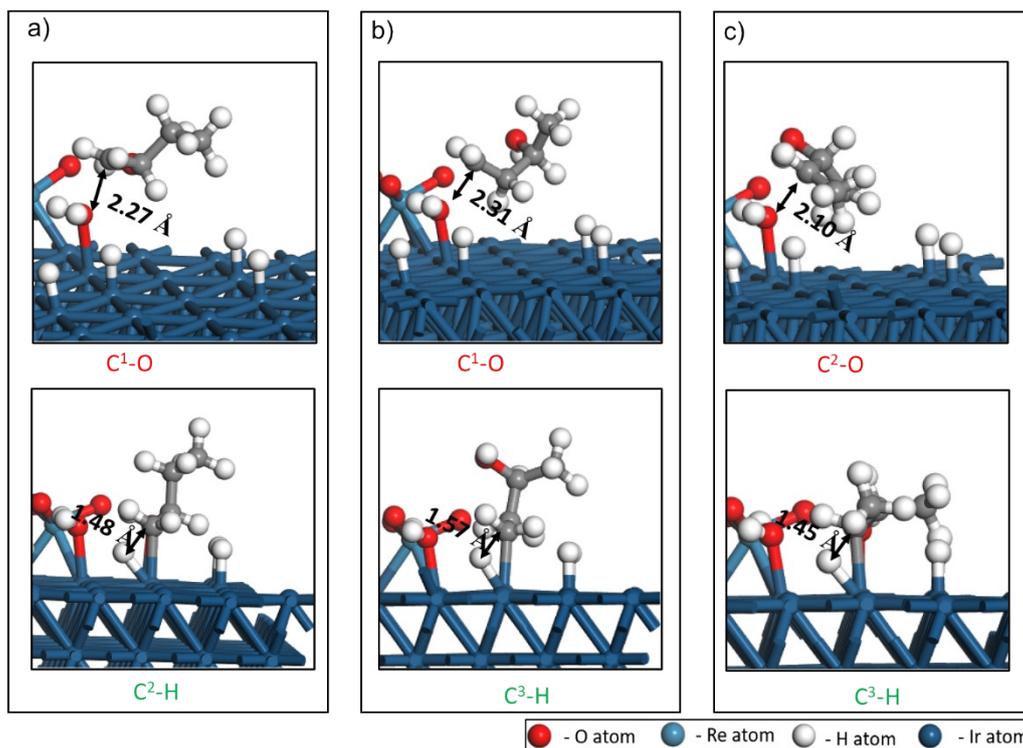


Fig.S8. Transition states identified for the formation of 2-BO on Ir-ReO_x catalyst as represented in Figure 4b in the main manuscript to from (a) 1,2-BDO, (b) 1,3-BDO, and c) 2,3-BDO. In all the images, the figure on the top represents the C-O cleavage and the figure at the bottom represents the hydrogenation. In all the images, the relevant bond distances are also indicated.

References

- 1 M. Gu, L. Liu, Y. Nakagawa, C. Li, M. Tamura, Z. Shen, X. Zhou, Y. Zhang and K. Tomishige, *ChemSusChem*, 2021, **14**, 642–654.