

Supporting information for:

A Combined Theoretical and Experimental

Approach for Platinum Catalyzed

1,2-Propanediol Aqueous Phase Reforming

Roberto Schimmenti,[†] Remedios Cortese,[†] Lidia Godina,[‡] Antonio Prestianni,[†]
Francesco Ferrante,[†] Dario Duca,^{*,†} and Dmitry Yu. Murzin^{*,‡}

[†]*Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze
Ed. 17, I-90128 Palermo, Italy*

[‡]*Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre,
Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo/Turku, Finland*

E-mail: dario.duca@unipa.it; dmitry.murzin@abo.fi

Phone: +39 09123897975;

Other intermediates

The optimized geometries of INT1r and INTer, briefly discussed in the manuscript for their implications with edge coordination effects, are reported in Figure S1 and S2, respectively.

Extended model

In order to account for the effect of the size of the model chosen, INT1, INT2, INT3 and INT4 were optimized on an extended model catalyst, a Pt₆₃ cluster. This was developed starting

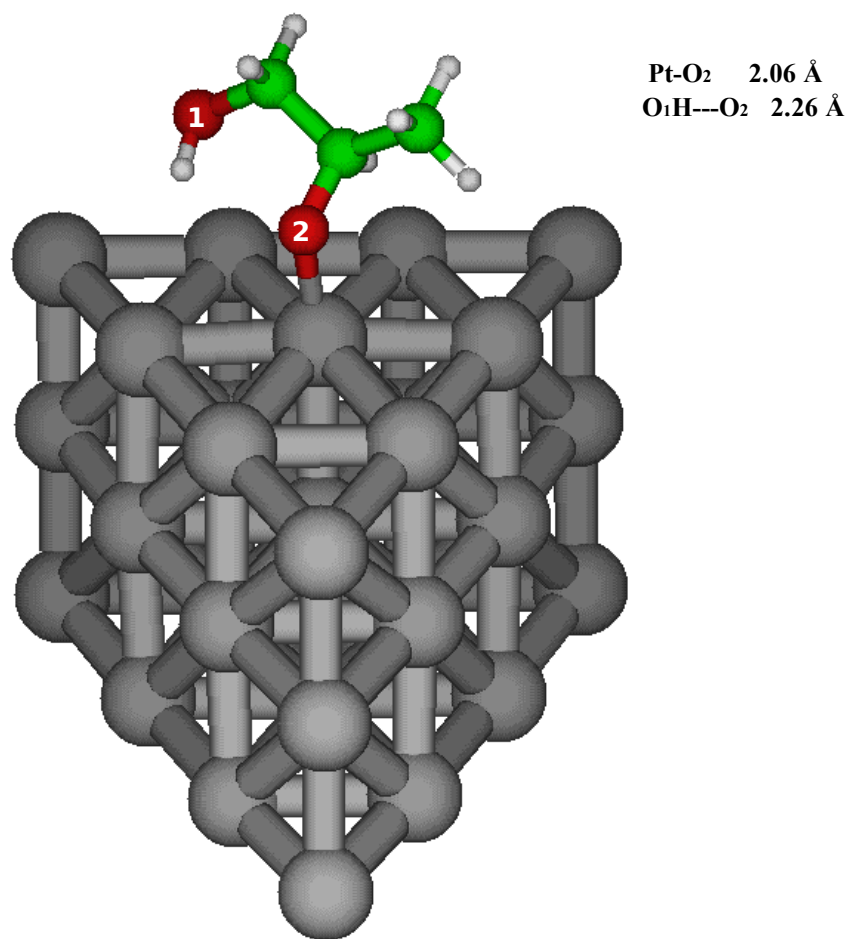


Figure S1: Optimized structure of INT1r. Relevant geometric descriptors are reported in the inset.

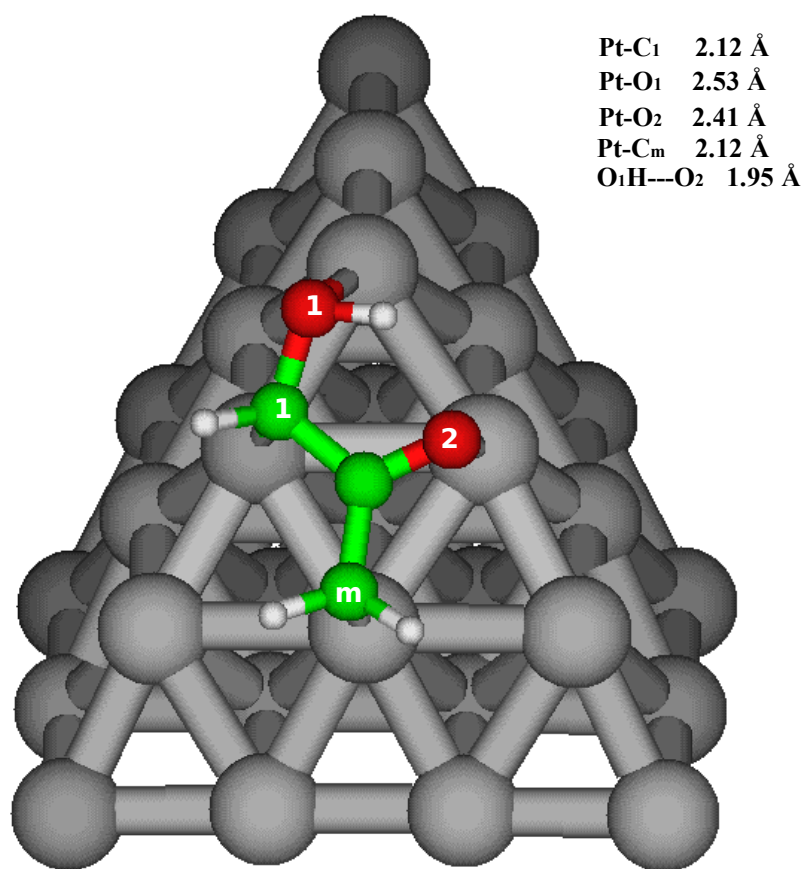


Figure S2: Optimized structure of INTER. Relevant geometric descriptors are reported in the inset.

from the already used Pt_{30} cluster, adding rows of atoms in order to provide neighbouring Pt atoms to the edges of Pt_{30} , possibly interacting with the reaction intermediates. Due to the increased computational cost of these calculations, with respect to those provided in the manuscript, the optimizations were carried out through the SIESTA code,^{S1} using the computational settings proposed by Vlachos and co-workers.^{S2} The optimized geometry of Pt_{63} is reported in Figure S3.

The optimized geometries of INT1, INT2, INT3 and INT4 on the Pt_{63} cluster are reported in Figure S4, S5, S6 and S7, respectively. The energetic ordering (taking INT3 as reference) among these reaction intermediates is reported in Table S1. For the sake of comparison, results obtained with the Pt_{30} cluster model used in the manuscript and the periodic DFT calculations of Vlachos and co-workers^{S2} and Liu and Greeley^{S3} are reported. For these latter studies, dealing with glycerol, INT1, INT2, INT3 and INT4 indicates reaction intermediates originating from the primary hydroxyl, primary carbon, secondary carbon and secondary hydroxyl dehydrogenation, respectively. All the models predict a preferential stabilization of INT3, hence, in general, of the species arising from a C–H bond cleavage over those formed by a O–H one. The energetic ordering of these reaction intermediates is substantially reproduced by all the models presented.

Table S1: Energetic ordering of INT1, INT2 and INT4 on different catalyst models. The energy of INT3 (or the intermediate originating from the secondary carbon atom dehydrogenation) was taken as reference. Energy differences are expressed in kJ mol^{-1} .

Model/Computational Method	ΔE_{INT2}	ΔE_{INT4}	ΔE_{INT1}
$\text{Pt}_{30}/\text{M06-L}$	28.5	64.3	78.3 ^a
$\text{Pt}_{63}/\text{PBE}$	$\simeq 0$	57.0	69.0
$\text{Pt}(111)/\text{PBE}^{\text{S2}}$	13.5	93.6	99.4
$\text{Pt}(111)/\text{PW91}^{\text{S3}}$	7	65.6	63.7

^a INT1r is considered

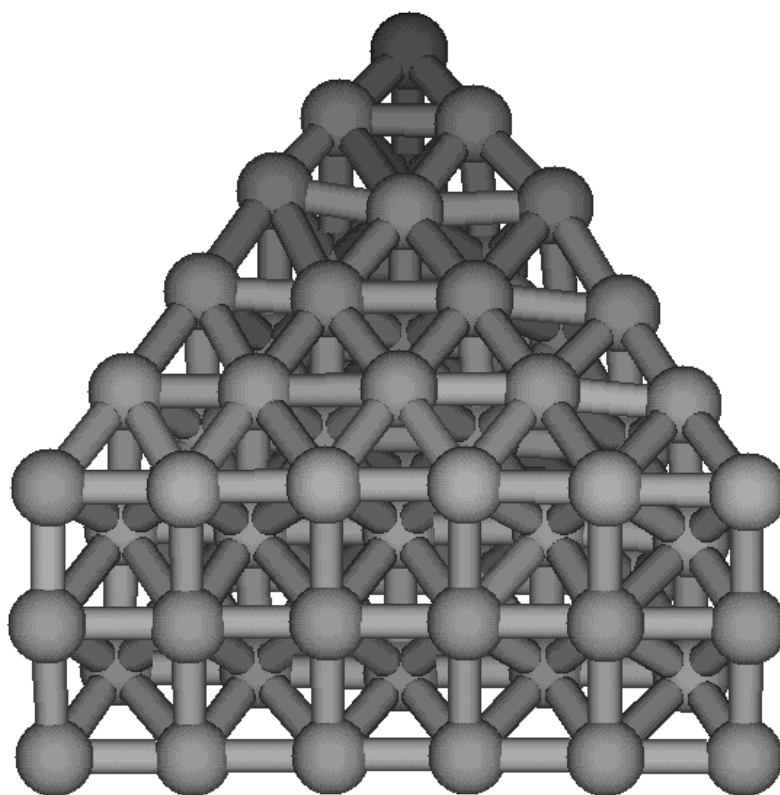


Figure S3: Optimized structure of the Pt₆₃ cluster.

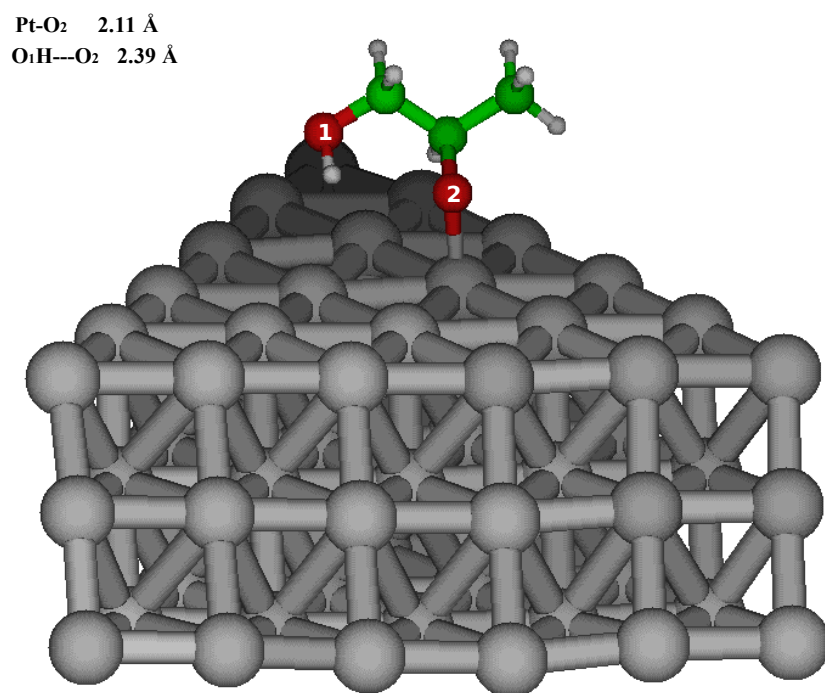


Figure S4: Optimized structure of INT1 on the Pt₆₃ cluster. Relevant geometric descriptors are reported in the inset.

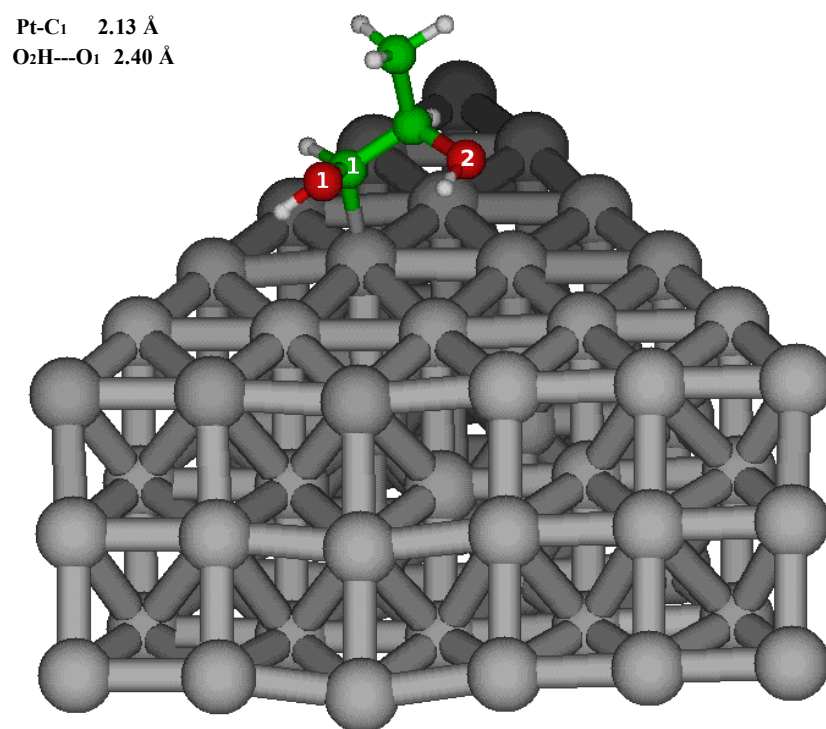


Figure S5: Optimized structure of INT2 on the Pt₆₃ cluster. Relevant geometric descriptors are reported in the inset.

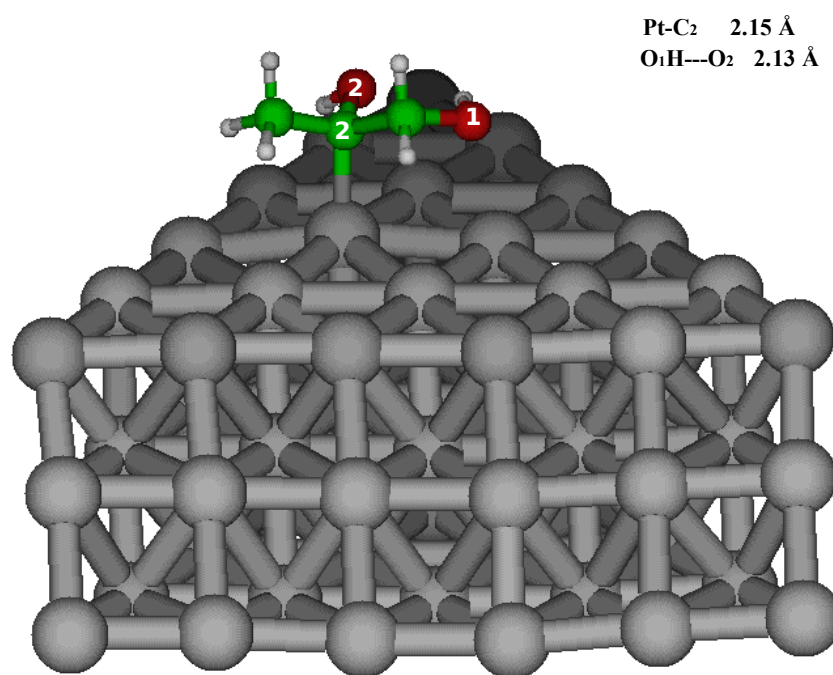


Figure S6: Optimized structure of INT3 on the Pt₆₃ cluster. Relevant geometric descriptors are reported in the inset.

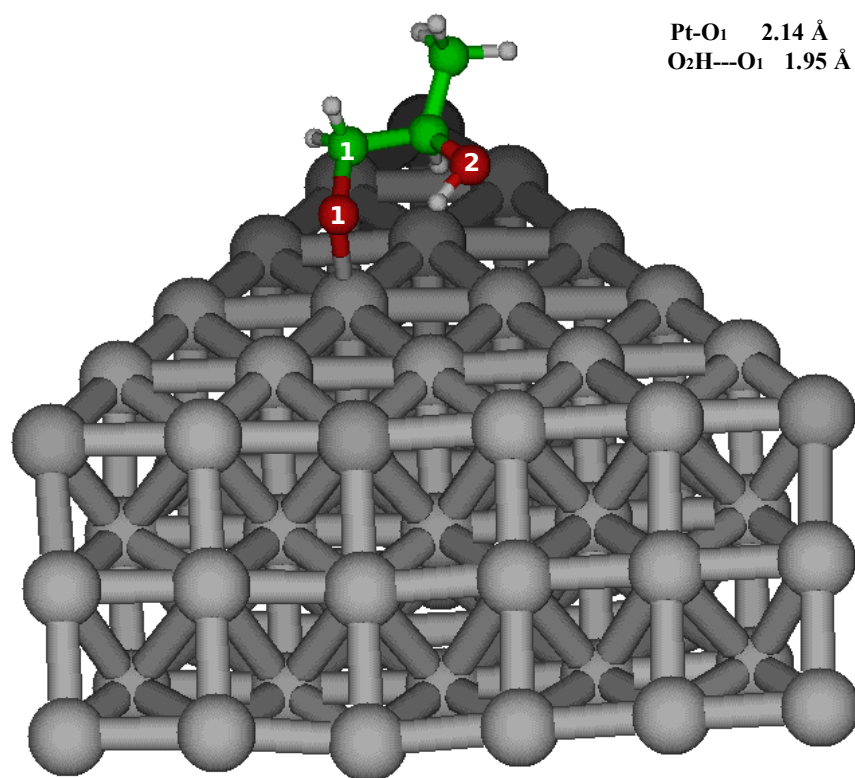


Figure S7: Optimized structure of INT4 on the Pt₆₃ cluster. Relevant geometric descriptors are reported in the inset.

References

- (S1) Soler, J. M.; Artacho, E.; Gale, J. D.; Garcia, A.; Junquera, J.; Ordejon, P.; Sanchez-Portal, D. The SIESTA Method for Ab Initio Order-N Materials Simulation. *J. Phys.: Condens. Matter* **2002**, *14*, 2745–2779.
- (S2) Chen, Y.; Saliccioli, M.; Vlachos, D. G. An Efficient Reaction Pathway Search Method Applied to the Decomposition of Glycerol on Platinum. *J. Phys. Chem. C* **2011**, *115*, 18707–18720.
- (S3) Liu, B.; Greeley, J. Decomposition Pathways of Glycerol via C–H, O–H, and C–C Bond Scission on Pt(111): A Density Functional Theory Study. *J. Phys. Chem. C* **2011**, *115*, 19702–19709.