

A First Principles Analysis of the Solution Phase Hydrogenolysis of Glycerol over Ru

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Introduction

In 2004, only 2-3% of the 140 billion kilograms of industrial chemicals produced in US were derived from biorenewable resources[1]. The U.S Department of Energy has set goals to produce 10% of the chemicals from renewable resources by the year 2020 with this percentage increasing to 50% by 2050[1]. Thus, there has been an increased emphasis on efficiently and economically converting biorenewable feedstock to value-added chemicals. While the availability of raw materials is not an issue, thermal instability and high oxygen content in biorenewable feedstock makes its conversion to useful chemicals a challenge. To counter the volatile nature of raw materials and the high oxygen content, these reactions are typically carried out in aqueous phase[2]. Hydrogenolysis of a C₆ sugar alcohol like Sorbitol gives a broad product distribution of products due to very large number of isomerization, dissociation, C-C and C-O bond cleavage reactions. Thus, the analysis of role of metal and the solvent on these reactions is very difficult. In order to simplify the reaction mechanism, we have looked at the hydrogenolysis of a C₃ polyol, Glycerol, on Ru(0001) in presence of the solution (water) using *ab initio* theoretical calculations.

Methods

Periodic gradient-corrected density functional theoretical calculations as implemented in the Vienna *ab initio* Simulation program (VASP) were used herein to follow the catalytic reaction pathways and calculate the corresponding energies[3]. The Kohn Sham equations are solved using a plane-wave basis set with a cutoff energy of 400 eV. The PW91 functional was used to describe the exchange correlation term. The core electrons and the nuclei of the atoms were described by the Vanderbilt ultrasoft pseudopotential. A 3 x 3 x 1 *k*-point grid was used. Transition states were isolated using the nudged elastic band approach.

Results and Discussion

Glycerol hydrogenolysis is thought to follow a complex mechanism comprised of both metal-catalyzed reactions as well as solution phase reactions which involve dehydration, hydrogenation reactions and carbon-carbon bond breaking reactions either through surface hydrogenolysis or through the solution phase retro-aldol condensation[4]. While there have been a number of different studies the controlling pathways and the active catalytic materials are still unresolved. Maris and Davis[5] suggested the mechanism highlighted in figure 1 which is loosely based on Montassier's mechanism[4]. We have calculated the binding modes and reaction pathways of all the intermediates involved in the reaction network in vapor phase as well as in solution. Glycerol prefers to undergo oxidation of primary OH in glycerol is the preferred pathway with an activation barrier of 0.40 eV (in vapor phase). Formation of glyceraldehyde is consistent with experimental results[5]. Table 1 compares the reaction energies for the most important reaction steps in vapor and solvent phase reactions. A comparison of reaction energies for route 1, 2 and 3 in figure 1 suggests that retro-aldol condensation (1) is the favored route, as proposed by experiments.

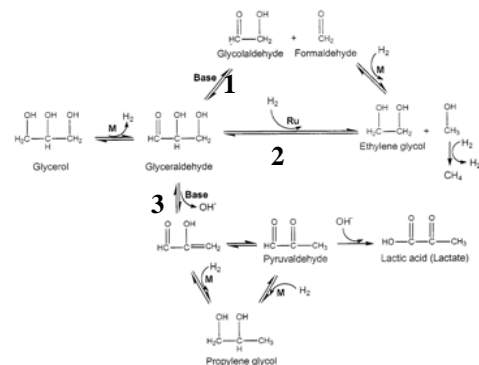


Figure 1. Modified mechanism for glycerol hydrogenolysis on Ru(0001) by Maris and Davis[5]

Table 1. Reaction energies for important steps in vapor and solvent phase reactions

Reaction		ΔE_{rxn} - Vapor Phase (eV)	ΔE_{rxn} - Solvent Phase (eV)
Hydrogenation: Formaldehyde	C-H	0.28	0.26
	O-H	0.09	-0.28
Hydrogenation: Glycolaldehyde	C-H	0.10	-0.56
	O-H	0.21	-0.13
Hydrogenolysis: Glyceraldehyde	C-C	0.05	-0.19
	C-O	-0.46	-1.15

Our results reveal that the solution plays an important role in solvating charged reaction intermediates and can also create novel reaction pathways. Hydrogenolysis steps were found to be more favorable (more exothermic reaction) in solution. The influence of solvent can be described in terms of relative stabilization of reactant, product and transition state via hydrogen bonding.

Significance

Ethylene glycol, propylene glycol and lactic acid produced from the hydrogenolysis of glycerol are industrially important chemicals[2]. A mechanistic study of solvent phase hydrogenolysis of glycerol, using theoretical methods like DFT, is expected to improve our understanding of the exact role of the metal, solvent and the base in the reaction, and hence a tool to better control the reaction for desired activity and selectivity.

References

1. Miller, D.J., *NSF Workshop Report on Catalysis for Biorenewables*. 2004.
2. Pagliaro, M. and M. Rossi, *The future of glycerol*. 1 Ed, Springer Verlag, New York, 2008.
3. Kresse, G. and J. Hafner, *Physical Review B* 47, 558 (1993).
4. Montassier, C., et al., *Journal of Molecular Catalysis* 70, 99 (1991).
5. Maris, E.P. and Davis, R.J., *Journal of Catalysis* 249, 328 (2007).