Influence of Solvent and the Metal on the Selective Hydrogenation of Oxygenate Intermediates

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Introduction

The catalytic hydrogenation of a wide range of fine chemical and pharmaceutical oxygenate intermediates as well as biorenewable platform chemical intermediates are carried out in solvents over supported metal particles.[1,2]. The metal as well as the solvent can cooperatively influence the kinetics and the governing reaction pathways. There have been very few efforts, however, focused on understanding the fundamental molecular transformations that occur between the metal and solvent and their influence on catalysis. The unique combination of the solvent and metal may offer the ability to tune the rate, selectivity and catalytic performance. Towards this end, we have carried out ab initio Density Functional Theoretical (DFT) calculations to elucidate the mechanisms that control the selective hydrogenation of methyl ethyl ketone and formaldehyde as probe intermediates of more complex ketones and aldehydes. The calculations are used to establish period trends in the transition metals as well as the solvents (neat, in water and in methanol) employed.

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 [5]. 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

We first examined the vapor phase hydrogenation of methyl ethyl ketone (MEK) and formaldehyde to 2-butanol on Group VIII and IB metals. Both follow classical Horiuti-Polanyi mechanisms which involve the adsorption of MEK (or formaldehyde) and hydrogen, and subsequently follow the successive addition of hydrogen atoms to form 2-butanol. MEK was found to adsorb in di-σ mode on all of the closed packed transition metals with the exception of Ru, Pt, Ag, Au and Cu where it binds in atop mode with oxygen on the metal atom [6]. The adsorption of MEK does not follow the oxygen binding energy trend on the ideal single crystal substrates. This is attributed to large distortion MEK molecule undergoes during adsorption. The hydrogenation of the RC=O bond can proceed in two different ways. The first involves the addition of the first hydrogen atom to the oxygen atom to form the hydroxyalkl intermediates followed by the addition of the second hydrogen to the carbon end to form the alcohol. In the second, atomic hydrogen is thought to react first at the adsorbed carbon to form the alkoxy intermediate which subsequently hydrogenates to the alcohol. The results indicate that the calculated reaction energy for the first hydrogenation step follows the C-binding energy on these surfaces i.e. increases from right to left in a period (except Rh group) and down a group. Reaction energy for the second step follows the inverse of C-binding energy. This behavior is attributed to the strong adsorption energy of C-bound hyroxyalkyl intermediate that forms on these surfaces. The calculated activation barriers scale with the overall reaction energies thus following an Evans-Polanyi relationship. The adsorption of MEK in solution is thought to proceed in a similar manner but requires the desorption or displacement of at least one water molecule on the surface. The calculated displacement energies appear to follow the calculated vapor phase desorption energies.

As observed in the vapor phase, the reaction energy for the first step follows the C-binding energy and the second step follows the inverse of C-binding energy trend. The hydroxyalkyl intermediate is stabilized via hydrogen bonding thus making the first step more exothermic than the second step.

We observed that presence of water as well as other protic solvents can provide an alternate reaction pathway which has a significantly lower activation barrier. This solvent mediated mechanism involves formation of a 3-center transition state and the proton is transferred to the O-site via a solution phase water molecule with an activation barrier 0.11 eV lower than the metal mediated mechanism for Ru(0001). Similar behavior has been observed by Desai et al [3].

To extend our understanding of the solvent effects, we studied the reaction in presence of explicit methanol molecules as the solvent. The structure of "liquid" methanol on Ru(0001) was obtained by carrying out ab initio simulated annealing studies. As expected, the displacement energy of MEK in this case was lower than that in water by 0.6 eV as water binds more strongly than methanol to Ru. The calculated reaction energies and the activation barriers for the two hydrogenation steps are shown in Table 1 for the three medium analyzed. We found that the activation barriers in presence of methanol is lower than that in vapor phase but is higher than that in water. This behavior can be attributed to greater hydrogen bonding capability of water over methanol which helps in stabilizing the reaction intermediate.

Table 1. Energetics for MEK hydrogenation

	Step I		Step II	
	ΔE_{rxn}	E_a	ΔE_{rxn}	E_a
Vapor	+0.15	0.38	-0.03	0.62
MeOH	-0.61	0.33	+0.05	0.60
H_2O	-0.57	0.21	+0.19	0.42

Significance

The results presented herein establish the reaction pathways, energetics and kinetics involved in the hydrogenation of model aldehydes and ketones over different metal substrates which will be useful in understanding the selective hydrogenation of more complex oxygenates used in fine chemical and pharmaceutical syntheses. The periodic trends can be rationalized in terms of the reaction and the electronic properties of the metal. The findings suggest that the solvent can help to stabilize polar transition states and in addition provide new low energy pathways by which protons may transfer.

References
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