281c Ab Initio Reaction Path Analysis of Catalytic Reactions: Benzene Hydrogenation and Cyclohexane Dehydrogenation

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Introduction

Kinetic modeling of complex catalytic reactions is a major challenge in the chemical and petrochemical industry. Realistic models, consistent with the elementary reaction steps that occur on the catalyst, allow optimization of the selectivity and reactor performance over much wider process conditions. In addition, a molecular level understanding of the reaction steps allows to further optimize the catalyst selectivity towards the desired product.

For multistep catalytic reactions such as benzene hydrogenation and cyclohexane dehydrogenation, a large number of possible reaction paths can be envisioned. Hence, it is difficult to put forward a most likely reaction path and establish the presence and location of a rate determining step based on chemical intuition. Hence, a large number of possible kinetic models, each containing a significant number of parameters, can be postulated. This makes model discrimination based on experimental data very difficult. Recently, surface science studies in combination with first principles modeling have provided detailed molecular level insight into the mechanisms of relatively simple reactions such as ethene hydrogenation and ethene epoxidation. In the present study, we have used density functional theory calculations, in combination with experimental surface science data, to elucidate the reaction path of the more complex benzene hydrogenation and cyclohexane dehydrogenation mechanisms (Figure 1). Taking into account the reduced symmetry of the adsorbed molecules, 180 possible reaction paths connecting benzene and cyclohexane can be drawn. In this study, we have analyzed the possible reaction paths using fundamental concepts introduced by Boudart[1]. In particular the following questions were addressed:

1. From the 180 possible reactions paths, is there a dominant path along which activation energies are lower than along any other possible path branching from this dominant path, or does the hydrogenation / dehydrogenation occur randomly.
2. Is there a rate determining step along the reaction path

Method

Adsorption energies and hydrogenation activation energies were calculated using relativistic density functional theory with the Becke Perdew functional and a double zeta quality Slater type basis set. The reaction was studied on the Pt(111) surface and the surface was modeled by a Pt(14,8) cluster model, with the Pt-Pt distance constrained at the bulk value of 277 pm. All calculation were performed using the Amsterdam Density Functional (ADF) program[2]. To improve the accuracy of the cluster DFT energies, accurate gas phase standard enthalpies of formation were determined for all reaction intermediates, either from experimental data or from high level CBS-QB3 calculations. These values provided reference points at the different steps of the hydrogenation reaction. This approach greatly improved the overall accuracy of the method, mostly through the inclusion of zero point energy and enthalpy corrections to the reaction enthalpies[3]. The accuracy of this approach was validated against periodic slab calculations or against experimental data where available. In general, the agreement was found to be better than 10-20 kJ/mol for adsorption energies and activation energies. Dehydrogenation activation energies were obtained from the thermodynamic relationship,

E_a(dehydro) = E_a(hydro;DFT) – DH_r (surface).

Results

Benzene hydrogenation*[4]*. The reaction path was analyzed step by step (Figure 1). The adsorption of benzene was studied first. Benzene was found to adsorb at the hollow site with an adsorption energy of –71 kJ/mol and at the bridge site with an adsorption energy of –102 kJ/mol. Both values compare reasonably well with reported experimental values of –85 and –120 kJ/mol respectively. Two mechanisms were distinguished for the hydrogenation of bridge bound benzene, with activation energies of 100 and 106 kJ/mol. Only one hydrogenation pathway was found for the more weakly bound hollow site benzene, with a lower activation energy of 74 kJ/mol. Hence, the dominant reaction path is the hydrogenation of the hollow site species. This is consistent with the hydrogenation of ethene, where hydrogenation of p-bound ethene was postulated to be the kinetically dominant mechanism.

Since the activation energy for the hydrogenation of hollow site benzene is 26 kJ/mol lower than the activation energies for alternative paths, it can be considered the dominant reaction path. At 500 K, assuming similar values for the pre-exponential factors and similar coverages, such a difference in activation energies corresponds to a 500-fold difference in reaction rates. Hence, for the second hydrogenation step only the hydrobenzene formed via hydrogenation of hollow site benzene was considered. Five different reaction path could be distinguished for the second hydrogenation step; 2 leading to 1,3-dihydrobenzene, 2 to 1,3-cyclohexadiene, and 1 to 1,4-cyclohexadiene. The lowest barrier was calculated for the mechanism forming 1,3-dihydrobenzene. The difference with the activation energies for the competing pathways is again larger than 20 kJ/mol, so the dominant reaction path leads to 1,3-dihydrobenzene. 1,3-cyclohexadiene and 1,4-cyclohexadiene are at best minor byproducts during the hydrogenation of benzene. For the hydrogenation of 1,3-dihydrobenzene, 3 pathways were distinguished. Again, hydrogenation in meta-position dominated with an activation energy of 77 kJ/mol, 18 kJ/mol lower than the activation energy for hydrogenation in ortho position. Only a single reaction path is possible for the next three hydrogenation steps, with activation energies significantly higher than for the first three steps. The dominant reaction path is indicated in Figure 1. The values for the fourth and sixth hydrogenation steps are consistent with barriers for hydrogenation in ortho position, i.e. about 88 kJ/mol. The dominant reaction path does not pass via cyclohexene and cyclohexene is at best a minor byproduct during benzene hydrogenation. The highest activation energy, 104 kJ/mol, was calculated for the hydrogenation of 1,2,3,5-tetrahydrobenzene, the fifth step, and this step is likely the rate determining step in benzene hydrogenation. The high value can be related to a rather strong adsorption of the reactant.

Cyclohexane dehydrogenation. Our ab initio reaction path analysis revealed the presence of a dominant reaction path for cyclohexane dehydrogenation as well (Figure 1), though the difference with the activation energies along competing reaction paths is smaller than for benzene hydrogenation. Interestingly, the dominant reaction path for cyclohexane dehydrogenation is very different from reaction path for benzene hydrogenation and goes via cyclohexene, cyclohexenyl and 1,3-dihydrobenzene. Cyclohexene and cyclohexenyl have indeed been identified experimentally during surface science studies of cyclohexane dehydrogenation. A small fraction of the dehydrogenation paths might go via 1,3-cyclohexadiene, since the difference with the activation energy along the dominant path is only 11 kJ/mol. The highest activation energy along the dominant path was calculated for the first step, consistent with experimental data indicating alkane activation is a difficult step. Also for cyclohexenyl dehydrogenation a significant barrier was calculated.

Conclusions

Ab initio reaction path analysis was used to study benzene hydrogenation and cyclohexane dehydrogenation on Pt(111). In both cases, a dominant reaction path was identified out of the 180 competing pathways. Along the dominant path, the activation energies for every step are lower than for any of the alternative paths branching away from it. Cyclohexene and cyclohexadiene are not on the dominant reaction path and are at best minor byproducts during benzene hydrogenation. In contrast, the dominant reaction path for cyclohexane dehydrogenation passes through cyclohexene and cyclohexenyl. Cyclohexadiene might be a minor byproduct of cyclohexane dehydrogenation, but is not formed along the dominant path. For benzene hydrogenation, the fifth hydrogenation step has the highest activation energy and may be rate determining. Along the cyclohexane dehydrogenation path cyclohexane activation has the highest activation energy.

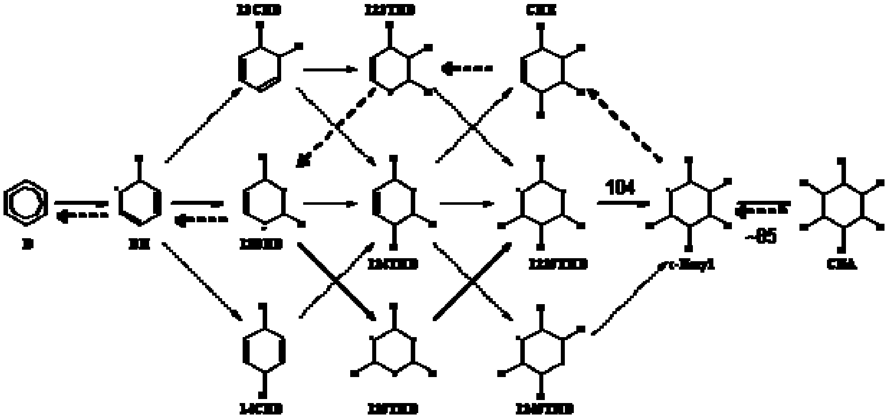

Figure 1. Reaction paths for benzene hydrogenation and cyclohexane dehydrogenation. The dominant reaction paths for benzene hydrogenation (___) and cyclohexane dehydrogenation (...) are indicated, as well as the activation energies for the possible rate determining steps.

References

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