Dehydrogenation, Hydrogenolysis and Oxidation of Ethane on Pt: Density Functional Theory Study and Microkinetic Analysis

Ying Chen[1] and Dionisios (Dion) G. Vlachos*
*Department of Chemical Engineering
and Center for Catalytic Science and Technology (CCST)
University of Delaware, Newark, DE 19716, USA*
*vlachos@udel.edu, tel. 302-831-2830

Introduction

Partial oxidation of fuels on noble metals is key to producing (1) syngas and hydrogen for a potential hydrogen economy from fossil fuels and biomass derivatives and (2) alkenes, such as ethylene which is the basic unit for polyethylene. The former process requires C-C bond cleavage, whereas the latter (oxidative) dehydrogenation. The best catalyst for the latter process is platinum[1]. The degree of syngas or alkene forming depends critically on the fraction of oxygen fed in a reactor. Preliminary calculations we conducted using the bond-order conservation method indicate that C-C bond scission cannot explain the speed of the reaction observed experimentally. The mechanisms for dehydrogenation, hydrogenolysis and oxidation of ethane on Pt surface are still under debate.

We carefully studied all the elementary steps for hydrogenolysis, dehydrogenation, and oxidation of ethane on Pt(111) and Pt(211). We then developed a microkinetic model of these proposes and compared to data. Analysis indicates several unexpected results.

Methodology

In this work, the SIESTA code[2] was used with Troullier-Martins norm-conserving scalar relativistic pseudopotentials[3]. A double zeta plus polarization (DZP) basis set was utilised. The localization radii of the basis functions were determined from an energy shift of 0.01 eV. A standard DFT supercell approach with the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) functional[4] was implemented with a mesh cutoff of 200 Ry. We have used the nonspin polarized version to describe this system. The calculated equilibrium lattice constant was 4.02 Å. All reactions were simulated on the flat Pt(111) and the stepped Pt(211). In studying reactions on terraces, the surface was modelled with four layers of metals and the vacuum region between slabs was around 10 Å. A p(2×2) unit cell was utilized and surface Monkhorst Pack meshes of 5×5×1 k-point sampling in the surface Brillouin zone were used. The bottom two layers of metal atoms were fixed and the top two layers and the adsorbates were relaxed. In studying reactions at steps, a repeated slab of twelve Pt(211) layers and p(2×1) unit cell are utilised. The surface Monkhorst Pack meshes of 3×4×1 k-point sampling in the surface Brillouin zone was used on the stepped surface. The top six layers and the adsorbates were relaxed.

Results and Discussion

Using DFT, we calculated all the activation barriers of dehydrogenation and hydrogenation of C_2 species, and all the C-C bond cleavage reactions and isomerization reactions on Pt(111) and Pt(211). It has been found that: (i) CCH_3 is the most stable C_2 species on Pt(111) and Pt(211); (ii) On Pt(211), ethane dissociation to CH_2CH_2 and $CHCH_3$ is a rapid process at low surface temperatures; (iii) Isomerization reactions appear to be energetically

unfavored on Pt; (iv) On Pt(111), the lowest barrier of C-C cleavage is 0.9 eV in CHC, whereas on Pt(211), the lowest barrier of C-C cleavage is 1.11 eV in CH_2CH_3. From our microkinetic analysis, we find that the reaction pathway for C-C cleavage mainly takes place via $CHCH_3$ and the dominant species on the surface is adsorbed H. The reaction pathway for hydrogenolysis of ethane is shown in Fig.1. More than 90% of CH_2CH_3 is dehydrogenated to $CHCH_3$ and $CHCH_3$ can be further dehydrogenated to form CCH_3 and cracked to form CH and CH_3. The agreement of the hydrogenolysis part of the model with experimental data is very good. On the other hand, we have found that first-principle results do not describe ethylene hydrogenation to ethane well. Using an iterative approach, we have identified the most abundant reactive intermediate and then repeated select DFT simulations to account for the effect of adsorbate-adsorbate interactions. Our results are in good agreement with data and indicate the importance of adsorbate-adsorbate interactions.

Under O-rich conditions, some other reactions like oxidative coupling reactions, oxidative dehydrogenation, and decomposition of C_2H_xO and C_2H_xOH have been studied via DFT. We find that (i) CCH_3 and CCH_2 are important links between C_2H_x and C_2H_xO; (ii) On Pt(211), the lowest barrier of the C-C bond cleavage in C_2H_xO is only 0.22 eV in CH_2CHO; (iii) On Pt(111), it is easy to form C_2H_xOH species by C_2H_x +OH with low barriers, but the barriers of C-C bond cleavage in C_2H_xOH are > 1 eV; (iv) the barriers of oxidative dehydrogenation of C_2H_x species are very high. The corresponding microkinetic model is compared with data from our lab. The full model is then used to describe partial oxidation of ethane to ethylene.
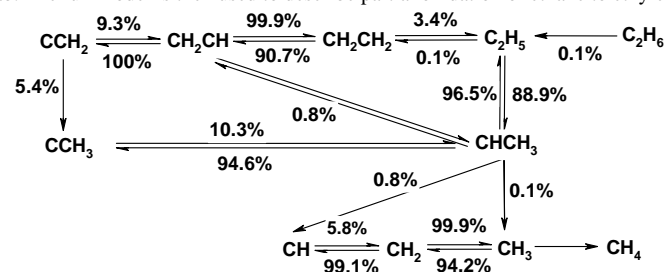

Figure 1. Mechanistic pathway for hydrogenolysis of ethane using reaction path analysis

Significance

Partial oxidation of ethane is a promising process to produce ethylene. Reducing undesired side reactions of C-C cleavage is important to increase the ethylene selectivity. Our work is the first full first-principles microkinetic model that is capable to describe the ethane chemistry on Pt for all relevant processes and provide insights into control of conversion and selectivity.

References

1. A.S. Bodke, D.A. Olschki, L.D. Schmidt, E. Ranzi, *Science*, 285, 712 (1999).
2. Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J. ; Ordejón, P.; Sánchez-Portal, D. *J. Phys.: Condens. Matter* 14, 2745 (2002).
3. Troullier, N.; Martins, J. L. *Phys. Rev. B*. 43, 1993 (1991).
4. Perdew, J. P.; Burke, K.; Ernezerhof, M. *Phys. Rev. Lett.*, 77, 3865 (1996).