

# Role of special sites on the selective activation of C-H and C-C bonds by nanoparticles: Ru<sub>13</sub> as a test-case

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## ABSTRACT

Can DFT play a role in the rational design of nanocatalysts? Owing to the size of these chemical species and to the chemical complexity and diversity of the events that occur on their surface, theoretical chemists must remain humble, although some recent studies show that DFT studies start to improve the perspective that chemists have on the surface chemistry of nanoparticles (NPs). The question addressed in this paper deals with nanoparticles' selectivity regarding C-H versus C-C activation in ethane. This catalytically important model reaction has been investigated on a small Ru<sub>13</sub> cluster able to nicely reproduce a defect-free island at the surface of ruthenium nanoparticles as well as a hinge-like defect that may be present at the surface of such NPs. Such defect favors C-C bond breaking and the formation of methyls, whereas C-H activation occurs on the defect-free cluster. In connection with the easy deformability of this cluster, these computational experiments open speculative discussions on the possible relationship between plasticity and catalytic activity on NPs' surfaces.

**Keywords:** DFT, C-H activation, C-C activation, nanocatalysis, plasticity

## 1 CONTEXT

The question addressed in this paper deals with nanoparticles' selectivity regarding C-H versus C-C activation on such substrate. Is it possible to design special sites able to favor one reaction against the other? Using kinetically inert  $\sigma$ -C-H bonds as latent functional groups is considered as a powerful tool in organic synthesis. Yet, most C-H bond activation by homogeneous catalysts are achieved under harsh reaction conditions, so that there is still a need to develop new catalysts able to favor mild reactions [1]. From a mechanistic point of view, oxidative addition is the most common mechanism by which a C-H bond cleaves, resulting in the formation of M-C and M-H bonds [2]. On the other hand, one of the most important industrial processes, the refining of petroleum to chemicals and fuels, is grounded on the cleavage of the weaker carbon-carbon bonds by transition-metal-containing heterogeneous catalysts.  $\sigma$  C-H or C-C bonds cleavage preferentially occur along

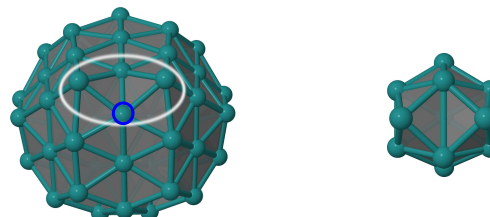


Figure 1: Ru<sub>55</sub> (a) Marks decahedron-like Ru<sub>55</sub> nanocluster, inspired from a Gupta cluster published in ref. 7 (see also [8]). A butterfly-like site is highlighted in white, together with the atom with maximal adsorption property (blue circle); (b) Ru<sub>13</sub> model cluster (later called IC<sup>?</sup>).

the step or edges of metal surfaces [3]. Since defects are inherent to a given  $hkl$  crystallographic plane, tuning the selectivity of a given metal is roughly obtained by selecting a given surface. More efficient catalysts need to be developed, yet the task of discovering novel alternatives has proven to be extremely challenging. It is in this context that nanocatalysis has recently emerged as a major new field. It is now well known that size and shape of nanocatalysts affect their catalytic properties. By mastering the art of synthesis of colloidal NPs, experimentalists are now on the edge to rationally design improved catalysts [4]. We will show in this paper that despite the complexity of such chemical processes, theoretical chemists may contribute to this task [5]. We have recently provided a relevant atomic theoretical descriptor for adsorption strength, derived from the so-called  $d$ -band center model [6]. Such model is in close relation with frontier molecular orbital theory, one cornerstone of rational chemical synthesis. Owing to this model, we have identified on the surface of an hcp Ru<sub>55</sub> nanocluster a site with an enhanced trend to strongly adsorb chemical species (figure 1a), this local property being also related to the deformability of this area.

An isomer of a scale model, namely Ru<sub>13</sub> (figure 1b), has been shaped in order to exhibit approximately the same surface defect and a significant plasticity around it. The adsorption of ethane and subsequent  $\sigma$ -C-H and  $\sigma$ -C-C cleavages have been investigated by DFT-based explorations of reaction pathways. Comparison with a defect-free cluster will also be done.

The trapping-mediated dissociative chemisorption stu-

dy of ethane on Ru(0001) yielded activation energies for the C-H bond cleavages of 9.3 kcal/mol [9]. Cycloalkanes were also investigated by the same experimental technique [10], showing that C-C bond cleavage occurs over the entire temperature range studied for cyclopentane, whereas dissociative chemisorption of both cyclohexane and cyclooctane occurs via initial C-H bond cleavage. The transition states of the elementary reactions for the dissociation of methane on the Ru(0001) surface were also investigated by Ciobică *et al.* with DFT periodic calculations and the nudged elastic band method (NEB) for 25% coverages [11]. The first C-H activation energy was found to be 20.3 kcal/mol, whereas it is thermodynamically favored by a small amount only (-2.1 kcal/mol). According to the so-called bond-order conservation-Morse potential (BOC-MP) method, the  $\text{H}_3\text{C}-\text{CH}_3$  scission energy on Ru(0001) should lie at 11 kcal/mol. More recently, a microcanonical unimolecular rate theory (MURT) was used to characterize methane dissociative chemisorption on Ru(0001) [12]. It indicated that the threshold activation energy for  $\text{CH}_4$  dissociative chemisorption on Ru(0001) is 14.1 kcal/mol.

## 2 COMPUTATIONAL DETAILS

All computations were performed within the framework of the density functional theory (DFT) considering the spin unpolarized or polarized constraint, depending of the system under study. The exchange-correlation potential was approximated by the generalized gradient approach proposed by Perdew, Burke, and Ernzerhof (PBE) [13]. Calculation of the energetic parameters as well as the geometry optimizations were carried out using the projector augmented waves (PAW) full-potential reconstruction [14, 15] implemented in the Vienna ab initio simulation package, VASP [16, 17]. As already proposed in a previous paper [18], after careful analysis of the  $k$ -points sampling, we found that a kinetic energy cutoff of 500 eV was sufficient to achieve a total energy convergence within several millielectronvolts for  $\text{CH}_n$  species. A  $\Gamma$ -centered [19] calculation was used, with a Gaussian smearing of 0.02 eV width for the partial occupancies. For geometry optimizations of reactants and products, atoms were free to move until the residual forces on any direction were less than 0.02 eV/Å. The supercell size was set to  $25 \times 25 \times 26$  Å for  $\text{Ru}_{55}$  and to  $18 \times 19 \times 20$  Å for  $\text{Ru}_{13}$ , which ensures a vacuum space of *ca.* 16 Å between the periodic images of these clusters. These parameters were tested and proven to be sufficient to model accurately the ruthenium clusters dressed by ligands for a reasonable computational cost. Reaction barriers were estimated by the climbing image nudge elastic band (CINEB) method [20–22] with a spring force between images of 5 eV and a force tolerance of 0.02 eV/Å. Nature of the TS was confirmed by an harmonic frequency calculation with the dynamical

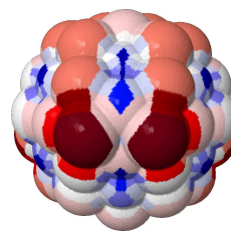


Figure 2: Density of states-derived map for adsorption strength. The darker the red, the higher the expected adsorption energies, whereas blue zones designate sites with low adsorption energies [23].

cal matrix code implemented in VASP. When necessary, the DIMER method was used to refine the localization of the saddle point.

## 3 RESULTS

**$\text{Ru}_{55}$  cluster.** Using H atoms as a probe of the adsorption strength at the surface of the  $\text{Ru}_{55}$  cluster shown in Figure 1, we have found that the special site highlighted in white adsorbs very strongly. To study the relative stability of different sites, one can compare adsorption energies of  $n$  hydrogen atoms on the metallic surface. This energy corresponds to the dissociative adsorption of  $\text{H}_2$  molecule at the surface, and can be calculated using the following definition:

$$E_{\text{ads}} = \frac{1}{n} \left( E_{n\text{H}^*} - E_{\text{cluster}} - \frac{n}{2} E_{\text{H}_2} \right)$$

where  $E_{n\text{H}^*}$ ,  $E_{\text{cluster}}$ , and  $E_{\text{H}_2}$  stand for the total energies of the surface of a  $\text{Ru}_m$  cluster dressed with adsorbed hydrogens, the bare cluster, and the  $\text{H}_2$  molecule, respectively.

Several sites have been probed individually, *i.e.* by adsorbing a single H atom. For the purpose of comparison, one shall have in mind that adsorption on the fcc 3-fold site of the compact hcp Ru(0001) surface is exothermic by *ca.* -13.6 kcal/mol. The same adsorption energy is found on the opposite side of the  $\text{Ru}_{55}$  cluster shown in figure 1, which exhibits the same atomic close-packing of a Ru(0001) plane. The defect highlighted in white on figure 1 can be seen as a tetrahedron deformed into a butterfly-like structure. This site also exhibits a subsurface vacancy, which increases the undercoordination of surface atoms. Adsorption of H on top of one of these four atoms (highlighted in blue) is particularly strong, since it is stabilized by twice the adsorption energy on Ru(0001) (-27.3 kcal/mol). But according to our electronic descriptor (not explained in details here, see figure 2 for a brief overview) the stronger adsorption should occur on the atoms on the wings of the butterfly, not on the small diagonal. A careful similarity/structure analysis has shown that, upon adsorption, this atom moves away by  $\sim 1.1$  Å from its initial po-

sition - a somewhat large value. The mobility of this atom upon adsorption thus involves an electronic reorganization and the transfer of the enhanced adsorption property in the neighborhood of the site identified by our descriptor. Overall, this gives a status of special site to this butterfly-like feature on the surface, both in terms of electronic structure and rigidity. This intriguing site motivated an exhaustive exploration of its selectivity with respect to test reactions, namely C-H and C-C activation. However, performing intensive transition states search on this average size cluster is not so easily affordable, so that a small model was built as a first step.

**Ru<sub>13</sub> model.** Actually, the Ru<sub>13</sub> cluster shown in figure 1b is a deformed icosahedron (**IC'**), less stable than the perfect icosahedron by 2 kcal/mol. This cluster can easily isomerize from one structure to the other by a hinge-like deformation. The barrier height from the closed form, *i.e.* the icosahedron (**IC**), to the open form (**IC'**) is 9.6 kcal/mol only (figure 3). This small model may thus easily undergo an adaptive isomerization between **IC** and **IC'** according to the nature of adsorbed species.

**C-H vs. C-C activation.** All the results are gathered in figure 3. We shall first focus on the reactions that occur on the underformed icosahedron. While according to thermodynamics, the C-C bond breaking is slightly favored (-9.9 kcal/mol for C-C *vs.* -9.5 kcal/mol for C-H), the kinetic product would correspond to the C-H bond cleavage (9.1 kcal/mol for C-H *vs.* 27.0 kcal/mol for C-C). Incidentally, the 9.1 kcal/mol activation barrier for the C-H activation is very close to the experimental value of Jachimowski and Weinberg measured for ethane on Ru(0001) [9]. Cleavage reactions that occur on **IC** and **IC'** are both exothermic. However, on **IC'** the formation of the bis-alkyl product by the C-C bond breaking is more stable by 11.5 kcal/mol than the C-H bond cleavage (**2'b** *vs.* **3'b**). Both cleavage reactions first take place on a bridge of the butterfly-like defect (**2'a** and **3'a**). The C-H bond activation (**2'a**) leads to the formation of an ethyl-Ru bond in one wing of the butterfly-like defect and a 2-fold H atom on the bottom. The C-C bond cleavage (**3'a**) leads to the formation of a methyl-Ru bond in one wing of butterfly-like defect and a second methyl-Ru bond on the small diagonal. The final products are obtained by the migration of the hydrogen atom (**2'b**) and of the second methyl group (**3'b**) to the ruthenium atom located on the second wing of the butterfly.

**Discussion.** We will now briefly show that M-C and M-H bond strengths provide key information on the thermodynamics of these reactions. M-H bonds are ex-

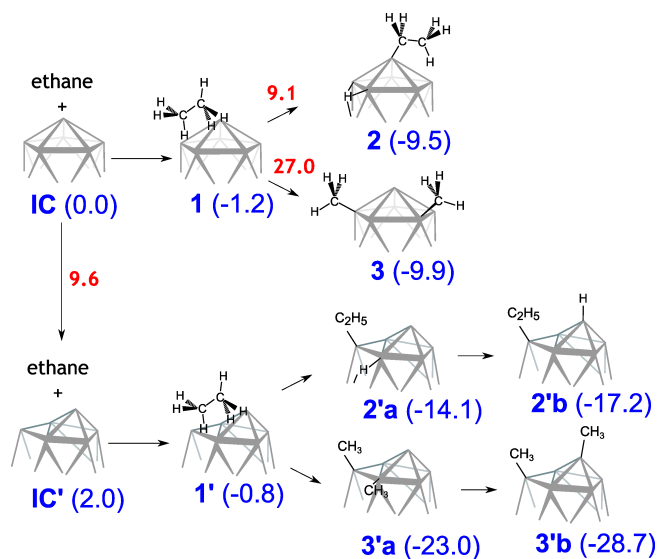


Figure 3: C-H vs. C-C activation pathways for ethane. The reference energy is the sum of the Ru<sub>13</sub> icosahedron and of the gas-phase ethane energies. Thermodynamic and kinetic parameters are printed in blue and red color respectively.

pected to be stronger than M-C bonds, as a result of exchange repulsions between occupied metal orbitals and the fully occupied  $\sigma$ -orbital on CH<sub>3</sub> [24]. Ru<sub>13</sub>-H, Ru<sub>13</sub>-CH<sub>3</sub> and Ru<sub>13</sub>-C<sub>2</sub>H<sub>5</sub> bond dissociation energies calculated for compounds **2**, **3**, **2'a** and **3'a** confirm this bonding property (see table 1). It is remarkable that the methyl and ethyl groups adsorb stronger on the defect than on the icosahedron (by  $\sim 13$  kcal/mol and 10 kcal/mol respectively), whereas it is not the case for H atoms. These individual adsorption energies nicely explain that the favorable thermodynamics observed in **3'a** compared to **3** originate from the stronger bonds made by the *two* methyl groups with the surface. Since **2'a** takes advantage of the enhanced adsorption of *one* alkyl group only, the thermodynamics for C-H cleavage is less favorable. Ziegler and co-workers [24] underlined that the strength of the M-CH<sub>3</sub> bond in M-CH<sub>3</sub><sup>+</sup> is enhanced as a result of electron charge transfer. We thus performed a Bader charge analysis for the two Ru<sub>13</sub> isomers. But it did not show any significant positive charge on the atoms of the butterfly-like defect. This suggests a better availability of *d* orbitals in **IC'** than in **IC** - *i.e.* an orbital-control - rather than a charge-control. Besides, a careful analysis of the molecular orbitals (MOs) of Ru<sub>13</sub>-CH<sub>3</sub> shows a strong interaction between a pending orbital of the defect and the 2 $\sigma$  MO of the methyl group.

## 4 SUMMARY AND OUTLOOK

Thermodynamic and kinetic parameters of the C-H *vs.* C-C activation by a Ru<sub>13</sub> cluster have been shown,

Table 1: M-X bond dissociation energies (BDEs, in kcal/mol)

compound	X	BDE	X	BDE
<b>2</b>	H	-65.4	C <sub>2</sub> H <sub>5</sub>	-47.3
<b>2'a</b>	H	-66.3	C <sub>2</sub> H <sub>5</sub>	-57.7
<b>3</b>	CH <sub>3</sub>	-50.9		
<b>3'a</b>	CH <sub>3</sub>	-63.6		

in close connection with the matter of selectivity at the surface of these species. Such cluster can be seen as a model for easily deformable zones at the surface of ruthenium NPs. We have shown the role played by a butterfly-like special site which formation is favored by the plasticity of Ru<sub>13</sub>. This theoretical study establishes a link between surface topology, adsorption strength, ease of deformation and electronic properties. Even if such defect is not present at the surface of NPs, it may appear upon adsorption and thermodynamically favor some reactions with respect to the defect-free surface. In the present case, this process enhances by a rather large amount ( $\sim 13$  kcal/mol) the M-C bond strength whereas M-H is insensitive to this deformation. It must now be checked that kinetics follow these trends. Such work is under progress. Catalyst's design is of course more easy to achieve *in silico* than experimentally. So far, no experiments support these conclusions. Such theoretical reflection no doubt would be stimulated by any concrete experimental outcome around the role of special sites on these reactions of utmost importance.

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