Communication

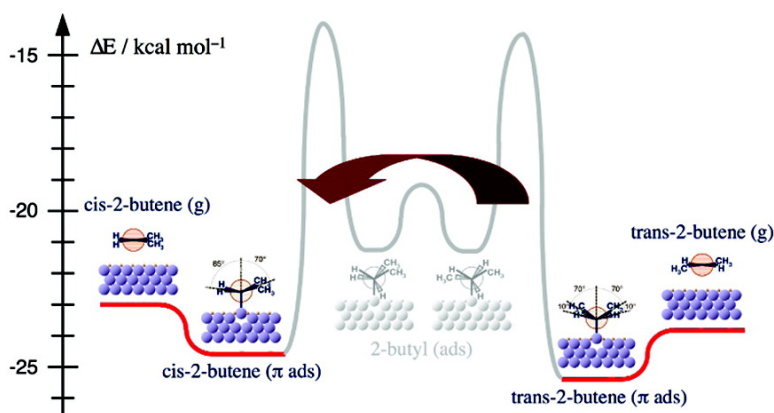# Origin of the Selectivity for Trans-to-Cis Isomerization in 2-Butene on Pt(111) Single Crystal Surfaces

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Origin of the Selectivity for Trans-to-Cis Isomerization in 2-Butene on Pt(111) Single Crystal Surfaces

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A preference was identified in previous surface-science studies for the promotion of the conversion of trans-2-butene to its cis isomer on Pt(111) single-crystal surfaces.[1−3] This is a surprising result that runs counter to thermodynamic expectations, and not what is usually observed in alkene catalytic conversions.[4,5] It was hypothesized that the cis−trans isomerization reversal may be associated with structural details of the surface, which could therefore be used to tune selectivity in catalysis.[1] The quantum-mechanical calculations reported here provide a molecular-level picture of the factors that control selectivity in these reactions. Two observations stand out from the data reported below: (1) selectivity is heavily influenced by the coverage of the coadsorbed hydrogen atoms present on the surface, and (2) the relative stability of the cis vs trans olefins on surfaces depends not only on the energies of molecular deformations and alkene−surface interactions but also on those associated with surface restructuring. Our results point to the central role that atomic rearrangements may play in defining selectivity in catalytic reactions.

All DFT calculations were performed using the VASP package[6,7] at the GGA level (Perdew−Wang 91)[8] with the PAW method (plane-wave cutoff of 400 eV),[9] as described in more detail elsewhere.[10,11] A 3×3 Pt(111) unit cell with one butene molecule ($\Theta_{C4} = 0.11$) and 0, 7, 8, or 9 H atoms ($\Theta_H = 0.00$, 0.78, 0.89, or 1.00 ML, respectively) was used. The Brillouin zone integration was performed mostly on a $3 \times 3 \times 1$ k-point mesh (5 K points), but some calculations were performed with a $5 \times 5 \times 1$ k-point mesh (13 K points) to check the accuracy of the results (see Supporting Information). Adsorption was allowed on one side of either four- or six-layer thick metallic slabs separated by five vacuum layers. Dipole corrections along the direction of the surface normal were performed to account for spurious interactions between the repeating slabs. The two uppermost metal layers and the adsorbate were relaxed during the geometry optimizations.

The adsorption of cis- versus trans-2-butene was contrasted in their two possible bonding modes: via a π interaction of the double bond with one platinum atom on the surface, and by di-σ bonding to two adjacent Pt surface atoms. Both modes are well-known in organometallic complexes and on metal surfaces,[12−14] and are believed to play different roles in the catalytic conversion of alkenes.[5,15,16] Binding energies determined as a function of hydrogen coverage using a four-layer slab are reported, referenced to the energy of the hydrogen-covered surface, in Figure 1 (and in Table S1, Supporting Information). A few trends are apparent from these results: (1) the binding of both butenes in both binding modes becomes weaker with increasing hydrogen coverage, as seen experimentally;[17,18] (2) di-σ bonding leads to stronger adsorption on the clean surface, but π bonding becomes more favorable on hydrogen-saturated substrates (again, in accordance with experi-
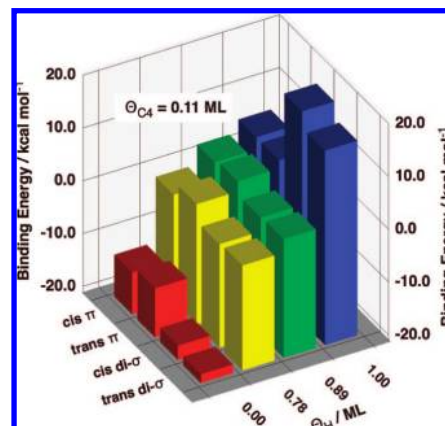

Figure 1. Binding energies for cis- and trans-2-butene on Pt(111) surfaces as a function of coadsorbed atomic hydrogen coverage. Data are reported for 1/9 of a monolayer of the di-σ- and π-bonded butenes on a four-layer thick slab. The alkene binding energies increase with hydrogen coverage in all cases, but less so with the π-bonded species: whereas the most stable species on the clean surface is the di-σ trans butene, on the H-saturated case it is the π-bonded cis isomer.

mental observations);[18,19] (3) in the di-σ bonding mode the trans is the most stable of the two isomers in all cases; and (4) in the π state the opposite appears to be the case, that is, the cis isomer is slightly more stable than the trans. The latter is perhaps the most important conclusion from the data in Figure 1.

A more detailed analysis of the results for the hydrogen-saturated Pt(111) surface was performed by using a six-layer slab and 5 K points and by decomposing the binding energy into three components (as described in more detail in the Supporting Information): (1) the deformation energy of the molecule, (2) the deformation energy of the surface, and (3) the interaction energy between the two, that is, the stabilizing two-electron interaction (which is negative). The results from those calculations are summarized in Figure 2 (and in Table S2, Supporting Information). In the case of di-σ bonding, both isomers undergo significant rehybridization and sit relatively close to the surface (see below), and therefore demand little rearrangement of the Pt atoms, approximately the same in both cases. Interestingly, adsorption of the trans isomer requires a significantly larger molecular deformation energy, but also displays a higher interaction energy. The two approximately cancel out, hence the close values of the binding energies for the cis and trans isomers seen in Figure 1. The adsorbed trans-2-butene is nevertheless 3−4 kcal/mol more stable than the cis counterpart.

The situation with the π-bonded species is quite different. Molecular deformation is minimal, even if it requires a bit more energy in the case of the trans isomer compared to the cis butene, and it is the surface deformation energies that dominate. Those are certainly larger here than in the di-σ cases, and also larger than the molecular deformation energies in these π-bonding states. Perhaps
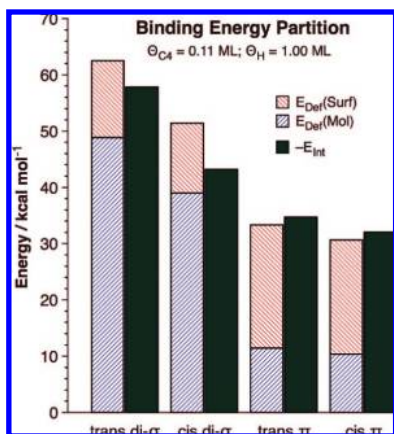
Figure 2. Partition of the binding energy for 2-butene on H-saturated Pt(111) (six-layer thick slab) into the deformation energies of the molecule and the surface (E_{Def}(Mol) and E_{Def}(Surf), respectively) and the interaction energy between the two (E_{Int}). In the case of di-σ bonding, the higher molecular deformation energy required by the trans isomer is compensated by a larger interaction energy, so the trans isomer ends up being slightly more stable than the cis counterpart. In the case of π adsorption, the trans isomer requires slightly higher energies for both molecular and surface deformations.
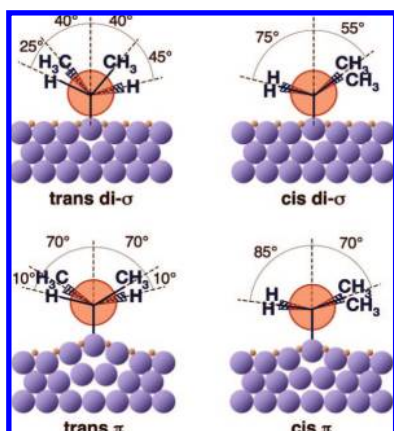

Figure 3. Structural details of the alkenes adsorbed on H-saturated Pt(111) surfaces. In the case of di-σ adsorption, the cis isomer undergoes some tilting to minimize steric hindrance from the methyl groups, but still retains its σ_v plane of symmetry. In contrast, the di-σ trans moiety displays significant twisting along the central C−C bond. In reference to the π species, they both display only minimal distortion from their original planar configuration and bind fairly far away from the surface, but do pull the coordinating Pt atom out of the surface plane.

more relevant to our discussion, they are slightly larger for the trans isomer compared to the cis. The combination of larger energies for molecular restructuring and surface reconstruction in the case of π-bonded trans butene explains the slightly higher stability of the π-bonded cis isomer on the hydrogen-saturated surface.

Figure 3 (and Table S3, Supporting Information) summarizes the resulting structures obtained from these DFT calculations. Extensive rehybridization from sp^2 to sp^3 is observed in both di-σ bonded species, perhaps a little more in the trans case. This is manifested mainly by a reduction in the CH$_3$−C=C angles and an increase in the CH$_3$−C=C−Pt dihedral angles. In addition, the cis isomer is slightly tilted, quite possibly to minimize any repulsive

interactions between its methyl groups and the underlying platinum atoms. In the case of trans-2-butene, significant twisting is seen around the central C−C bond, leading to a dihedral angle between the two methyl groups of less than 100° and a slight asymmetry between the two central hydrogen atoms. It is this molecular twisting that makes the molecular deformation energy for di-σ trans-2-butene so much larger compared to that for the cis isomer.

Molecular deformations in the π-bonded species are much more subtle, with only marginal deviations from their original molecular planarity. Nevertheless, some twisting is still seen for the trans isomer, perhaps the reason for the slightly higher deformation energy estimated in the calculations. In addition, important changes are also seen in the restructuring of the surface, again to a slightly larger extent with the trans isomer. Overall, the cis isomer appears to be somewhat more stable than the trans in the π state. Π-bonded olefins are the species that participate directly in hydrogenation and isomerization catalytic reactions,[5,15] so the stabilization of the cis isomer in that bonding mode is what leads to the preferential isomerization of trans-to-cis 2-butene on Pt(111) surfaces.[2] The role of surface restructuring in defining catalytic selectivity is particularly noteworthy here. Given that rougher surfaces would presumably require less restructuring energy to accommodate adsorbates, it is reasonable to expect that selectivity may be tuned by choosing the appropriate surface topography.[1,20]

Supporting Information Available: Additional details on the calculation methods and tables with energies and geometrical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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