

## Selectivity in Olefin Isomerization: From Studies on Model Systems and Theory to Real Catalysts

Ilkeun Lee,<sup>1</sup> Françoise Delbecq,<sup>2</sup> and Francisco Zaera<sup>1,\*</sup>

<sup>1</sup> Department of Chemistry, University of California, Riverside, CA 92521 (USA)

<sup>2</sup> Université de Lyon, Laboratoire de Chimie - UMR CNRS 5182, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07 (France)

\*zaera@ucr.edu

### Introduction

The effect of structural factors in heterogeneous catalysis has been long recognized, and studies using model systems have shown that different surface planes can display widely different chemistries. Those differences could potentially provide a way to improve catalytic selectivity by controlling surface structure. However, because of the difficulty in preparing supported catalysts with well-defined particle shapes, that promise has yet to be fully realized. Here we report on a case where reaction selectivity in a real catalytic system was successfully tuned via the specific control of particle shape. Our example involves the selective isomerization of trans olefins to their less thermodynamically favorable cis conformation.

### Materials and Methods

Temperature programmed desorption (TPD) experiments were carried out in a standard ultrahigh vacuum (UHV) setup.<sup>1-3</sup> Density Functional theory (DFT) calculations were performed using the VASP package at the GGA level (Perdew-Wang 91) with the PAW method (plane-wave cut-off of 400 eV).<sup>4</sup> The supported catalysts were prepared by a colloidal synthetic method and dispersed on a high-surface-area silica xerogel support.<sup>5</sup>

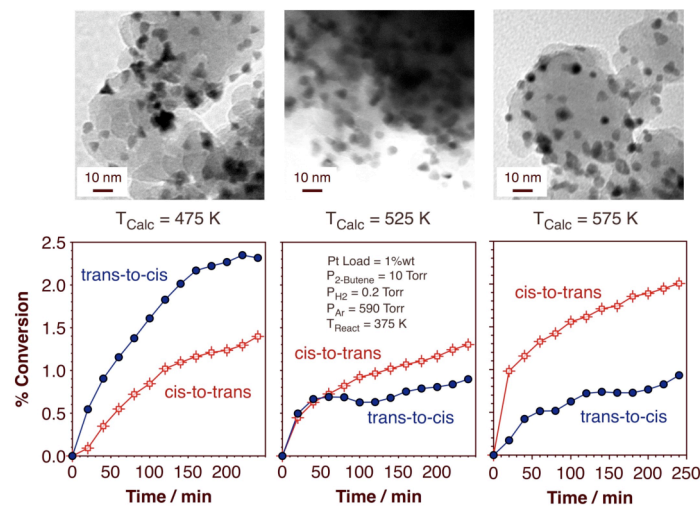
### Results and Discussion

TPD data on single crystals showed that the isomerization of trans olefins to their cis counterparts is promoted by (111) facets of platinum, and that such selectivity is reversed on more open surfaces. DFT calculations suggested that the extra stability of cis olefins seen on hydrogen-saturated Pt(111) surfaces may be due to the fact that their bonding requires less surface reconstruction, the dominant factor in the adsorption on close-packed platinum surfaces. Kinetic data using catalysts made out of dispersed tetrahedral Pt nanoparticles corroborated the selective promotion of the trans-to-cis isomerization on the (111) facets of the metal. The key results are shown in Fig. 1, where preferred trans-to-cis isomerization is seen on catalyst calcined at 475 K, a treatment that preserves most of the (111) facets intact. Cis-to-trans conversion dominates on the catalyst calcined at 575 K, after the initial tetrahedral structure of the platinum dispersed particles is lost.

Several unique aspects of this work are worth highlighting up front: (1) the effects originating from particle shape in dispersed catalysts were decoupled from those of particle size (the parameter often considered in practical catalysis); (2) a switch in reaction selectivity was observed as the particle shape, and therefore the structure of the exposed surfaces, was modified; (3) the reported reaction selectivity change is for a reaction traditionally considered mild, and therefore assumed to be structure insensitive; (4) the identification of the key

structural factors that define selectivity in supported catalysts was possible thanks to information obtained from experimental results using single-crystal models and quantum mechanics calculations; and (5) shape control in supported catalysts was accomplished by using novel self-assembly chemistry.

### 2-Butene Cis-Trans Isomerization on Pt<sub>Tetrahedral</sub>/SiO<sub>2</sub>



**Figure 1.** Kinetic data for the isomerization of cis- and trans-2-butene promoted by tetrahedral Pt/xerogel SiO<sub>2</sub> catalysts. The bottom panels show kinetic data from experiments with catalysts calcined to T<sub>Calc</sub> = 475, 525, and 575 K, treatments that, according to the TEM pictures shown at the top, lead to an increasing loss of tetrahedral particle shape.

### Significance

Controlling selectivity in olefin isomerizations is important in the food industry, in the manufacturing of certain vitamins, and in other synthetic processes. For instance, the selective production of cis olefins during partial hydrogenation of edible oils would prevent the formation of health-adverse trans fats. The ability to control reaction selectivities via the preparation of catalysts with well-defined shapes may also be extended to other processes.

### References

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