Oxidative Dehydrogenation of Propane on Small Pt Clusters. A Density Functional Study

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Introduction

Small metal clusters have been shown to possess reactivity properties not observed in their bulk analogs, which can make them attractive for catalysis.[1] Recently, Vajda et al[2] reported the first investigation of size-preselected clusters under realistic high temperature catalytic conditions. The clusters containing 8-10 Pt atoms were supported on an amorphous alumina surface. The study revealed a very high activity of the subnanometer Pt-clusters for the oxidative dehydrogenation (ODH) of propane to propylene. The subnanometer clusters are more active than platinum and vanadia catalysts for propane ODH, while at the same time maintaining selectivity towards formation of propylene over carbon oxide species and cracked by-products.

We have carried out density functional calculations of reaction pathways for oxidative dehydrogenation to investigate the activity and selectivity of the supported Pt clusters compared to an extended Pt surface. We have also investigated the interaction of the clusters with an alumina surface and effects of the surface-cluster interaction on the catalytic properties of the cluster. The calculations indicate that the under-coordination of the Pt atoms in the clusters is responsible for the surprisingly high reactivity compared to extended surfaces and that the alumina surface serves to stabilize the clusters, but has very little effect on the catalytic activity.

Computational Methods

Reaction pathway calculations were initially carried on gas phase Pt_4 and Pt_8 clusters using the B3LYP density functional method with a general basis set consisting of 6-31G* on C, H and O and LANL2DZ on Pt. Transition states were located with QST2 and QST3 Synchronous Transit-Guided Quasi-Newton (STQN) methods. Periodic calculations on Pt(111) were carried out with transition states for C-H bond cleavage in propane on the (111) surface located by the Climbing Image Nudged Elastic Band algorithm.[3] We also carried out calculations with the Pt clusters on an alumina support included using periodic calculations and the PW91 functional.

Results and Discussion

The calculated transition state for breaking the first C-H bond in propane is shown in Figure 1. The "apparent" barrier for this reaction step is 0.18 eV. The remainder of the pathway is thermodynamically downhill to formation of propylene. Our calculations also indicate that dissociated oxygen atoms adsorbed on the cluster do not significantly affect the calculated C-H bond reactions in the pathway to formation of propylene. In the overall reaction scheme, oxygen serves as a means for removal of hydrogen as water based on these calculations. The experimental barrier for propylene formation from propane on the subnanometer Pt clusters is estimated to be 0.2 eV, which is consistent with the barrier found
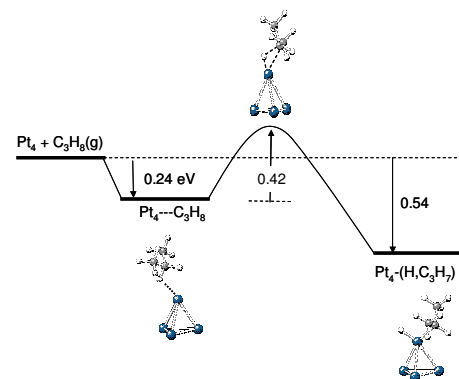
Figure 1. Calculated reaction pathway for breaking the C-H bond in propane on a Pt_4 cluster.

in our DFT investigation. The barrier for breaking the first C-H bond in propane was also calculated for an eight-atom cluster and found to be in agreement with the four-atom cluster. Similarly good agreement with experiment is found when we include a model for the Al_2O_3 support in our calculations. The apparent barrier for C-H breaking is 0.19 eV, a small change from the result for the gas phase Pt_8 cluster. While more detailed studies are needed to fully elucidate the effect of the substrate, these results indicate that the support has little effect on the reaction barrier in this case.

In contrast to the low C-H bond scission barrier found on Pt clusters, DFT calculations for C-H bond scission in propane on a Pt(111) surface give an apparent activation barrier 1 eV, which is much larger than the corresponding barrier on the small Pt clusters. Thus, both theory and experiment lead to the conclusion that under-coordinated Pt sites in small Pt clusters are much more active than a Pt surface for propane ODH. This can be explained by the favorable interaction between the under-coordinated Pt in the cluster and the C-H bond in propane. In addition, we find that the calculated activation barriers for breaking C-C bonds in propane and the C=C bond in propylene are much larger (1-2 eV) than that for the C-H bond due to less favorable overlap interaction with the Pt cluster.[4] These larger barriers are consistent with the selectivity towards propylene formation observed in the experiment.

References
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