

STEPS IN METHANOL ABSORPTION AND DECOMPOSITION REACTION ON SUB- NANOMETER SIZED Pd_N (N = 4, 8) CLUSTERS

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INTRODUCTION

Experimental findings indicate that supported Pd catalysts are quite active for generation of hydrogen from methanol. It is well-established that nanometer-sized particles show high relative activity for most reactions compared to much larger particles. However, the activity of sub-nanometer sized particles < 1nm (or n < 50) is not very well known, primarily because it is technically challenging to prepare and stabilize such particles.

METHOD

To explore this problem computationally, we have carried out density functional theory (DFT) based calculations for the methanol decomposition reaction on a Pd₄ cluster. We have considered reaction pathways proceeding through C–O, C–H and O–H bond scissions. We present detailed potential energy surfaces (PES) for methanol decomposition, incorporating most reaction pathways. We also report activation energy barriers calculated with the climbing image nudged elastic band method (CI-NEB) for all possible reaction paths in the PES. Comparisons with earlier studies on single crystal surfaces and on large Pd particles show a significant decrease in activation energy barriers on Pd₄ that could be mainly due to the smaller size.

CONCLUSION

To further understand that how particle size affects the elementary reaction steps, we also present an analysis of methanol decomposition on Pd₈ clusters.