

Site-selective Desorption of CO from Pt under Low-Temperature Plasma Exposure

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Abstract: We investigate the effect of plasma exposure on the binding energy of CO to Pt catalyst nanoparticles. Temperature-programmed desorption measurements show that the binding of CO is more strongly reduced in the case of under-coordinated sites (steps and edges) compared to well-coordinated sites (terraces). Both plasma-induced charging and electric fields contribute to this effect, as confirmed by DFT calculations

1. Introduction

Low-temperature, non-thermal plasmas are well-known for activating heterogeneous chemistry when in contact with catalysts. This has been shown for a broad range of chemistries, from ammonia synthesis to CO₂ hydrogenation reactions, to name a few.[1, 2] Unfortunately, the complexity of the plasma-material interface makes it difficult to identify the dominant activation mechanism, hampering further advancements such as the optimization of catalysts for plasma activation.

Here we address this issue by investigating the effect of plasma exposure on the desorption kinetics of CO from Pt clusters. We use a combination of in-situ characterization and atomistic computations to elucidate how different surface sites respond to the low-temperature plasma.

2. Methods

1 nm Pt clusters, supported on 20 nm alumina particles, are first baked in H₂ to reduce the surface, then saturated with CO. The system is evacuated and refilled with argon at a pressure of 3 Torr. An RF-driven plasma is formed to generate a spatially uniform, stable plasma impinging onto the CO-terminated catalyst. The whole system fits within the sample compartment of a commercial FTIR. Temperature-programmed desorption measurements are performed with and without plasma exposure. The Redhead analysis is used to extract the CO binding energy. This is done in a site-selective manner by deconvoluting the IR peak for different surface sites.

3. Results and Discussion

Figure 1 shows the CO desorption curves from Pt. Without plasma exposure, the under-coordinated sites (steps and edges) bind CO more strongly (1.6 eV) compared to the well-coordinated site (terraces, 1.4 eV). Under plasma exposure, these values converge to 1.2 eV, for a simple argon-plasma at a density of 10¹⁰ cm⁻³. Density Functional Theory (DFT) calculations confirm that the combination of charging and electric fields has a strong effect on the binding energy of CO to under-coordinated sites and a negligible effect on well-coordinated sites, in qualitative agreement with the in-situ FTIR measurements.[3]

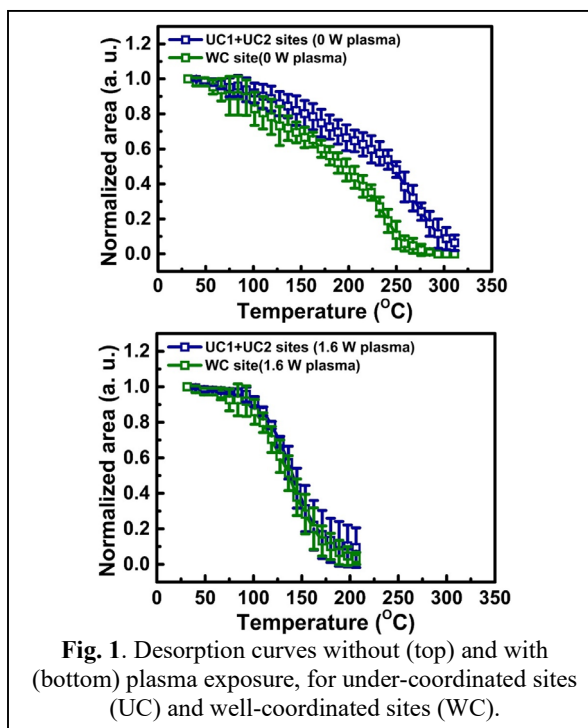


Fig. 1. Desorption curves without (top) and with (bottom) plasma exposure, for under-coordinated sites (UC) and well-coordinated sites (WC).

4. Conclusion

Plasmas not only activate molecules in the gas phase (dissociation and vibrational excitation), but also strongly affect the chemistry of adsorbates.

Acknowledgment

This work has been supported by the U.S. Department of Energy, National Energy Technology Laboratory (DOE-NETL) under award number DEFE0032091.

References

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