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Studying Competing Reaction Pathways in Methanol Decomposition on Platinum Catalysts Under Ultra-High Vacuum (UHV) Conditions Using TPD and SFG Spectroscopy

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Introduction

- Catalysts are substances that increase the rate of chemical reactions, without undergo any permanent chemical change, and increase production of chemicals, minimize pollution, and reduce energy consumption in industry. The reaction of methanol decomposition on Pt proceeds through several steps: adsorption, dissociation, formation of surface intermediates, and desorption of reaction products. The reaction mechanism and surface intermediates depend on various factors: surface coverage, temperature, and pressure. Methanol adsorbs onto platinum surface at low temperature and dissociates through many steps to form gas phase products at higher temperatures. The main goal is to investigate the competing decomposition pathways of methanol on Pt(111), in which the behavior is opposite to what is expected.

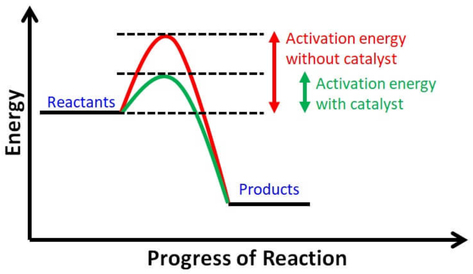

Figure 1: Reaction coordinate with and without presence of catalyst

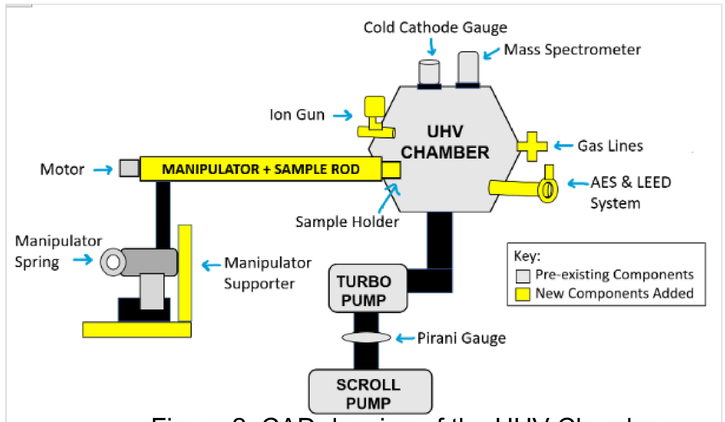

Figure 2: CAD drawing of the UHV Chamber

Method

- UHV conditions create a molecularly clean environment, isolating the chemical reaction where the base pressure is below 1 × 10^{-10} Torr. Temperature programmed desorption (TPD) measures gas products released from the surface as a function of temperature, allowing determination of reaction energies and gas product distributions. It will help identify which species come off the platinum surface. Sum-frequency generation (SFG) spectroscopy is a surface-sensitive vibrational technique that can study the molecular structure and orientation of adsorbates on the surface, involves shining two laser beams, one in the visible and one in the infrared region, onto the sample surface and measuring the nonlinear optical signal generated by the adsorbates. The data collected from TPD and SFG experiments can provide insights into the surface chemistry of materials, including the adsorption mechanism, reaction kinetics, and surface structure.

Conclusion

- TPD and TD-SFG spectroscopy were used to investigate the decomposition of methanol on flat platinum surfaces. The C-H bonds break between 180 and 200 K, and the O-H bond desorbed at 160 K and forming surface methoxy. The desorption of H2 occurs at a higher temperature (320 K), and the C-O bond breaks between 400 and 420 K. The research aimed to understand the chemical properties and mechanisms of catalytic reactions on metal surfaces to develop better catalysts for addressing global challenges, such as pollution and energy consumption.

Research and Discussion

- The surface structure of platinum impacts the distribution of gas products. Due to higher heating rates in TPD, the similar features are expected to be shifted to slightly higher temperatures in the TPD traces compared to the SFG spectra, with an estimated shift of 20 to 25K. All the C–H bonds break between 180 and 200 K. The disappearance of C–H resonance signals and suppression of the non-resonant background in the C–H region at 350 K indicate the decomposition of methoxy to CO and H. O-H bond desorbed at 160 K and forming surface methoxy. The desorption of H_2 occurs at a higher temperature 320 K. The C-O bond break between 400 and 420 K. CO desorbing from the surface between 450 and 500 K.

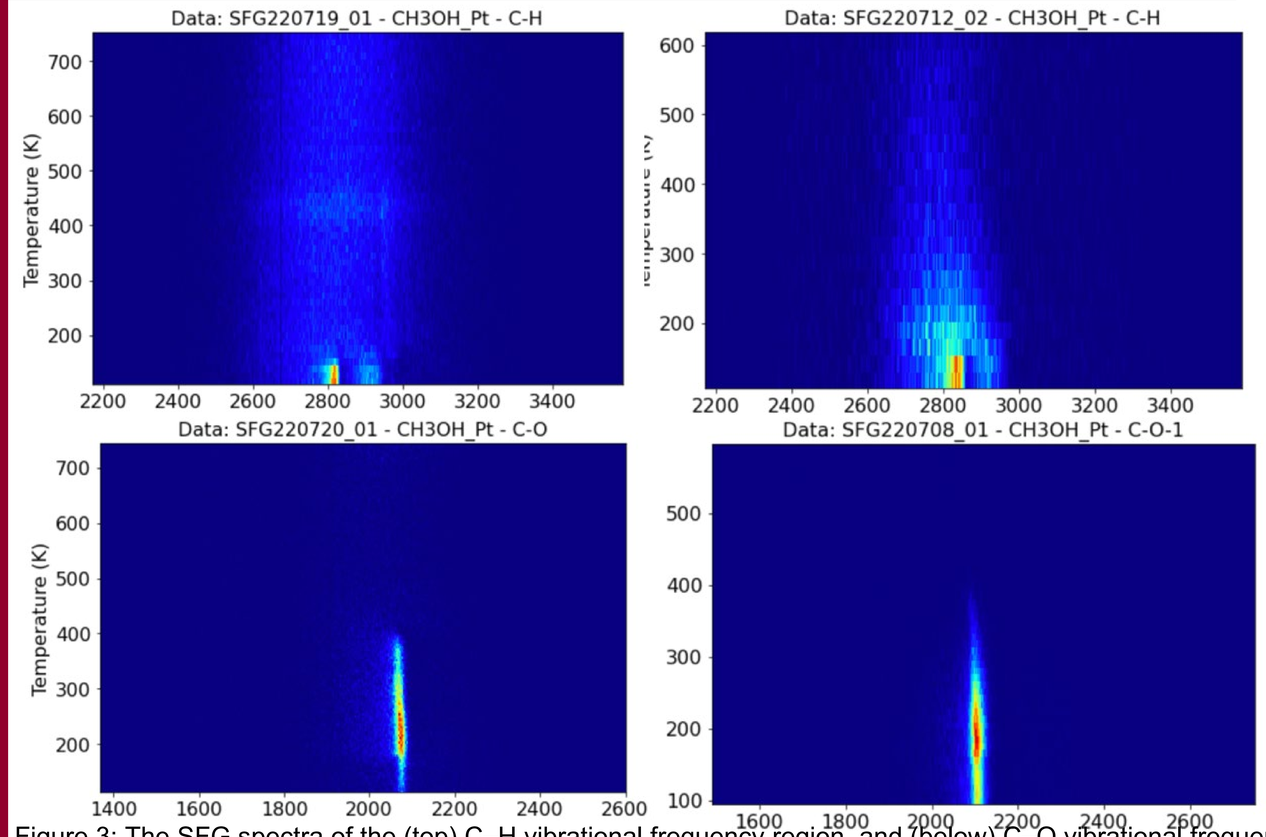

Figure 3: The SFG spectra of the (top) C–H vibrational frequency region, and (below) C–O vibrational frequency region, for methanol decomposition on Pt(111)

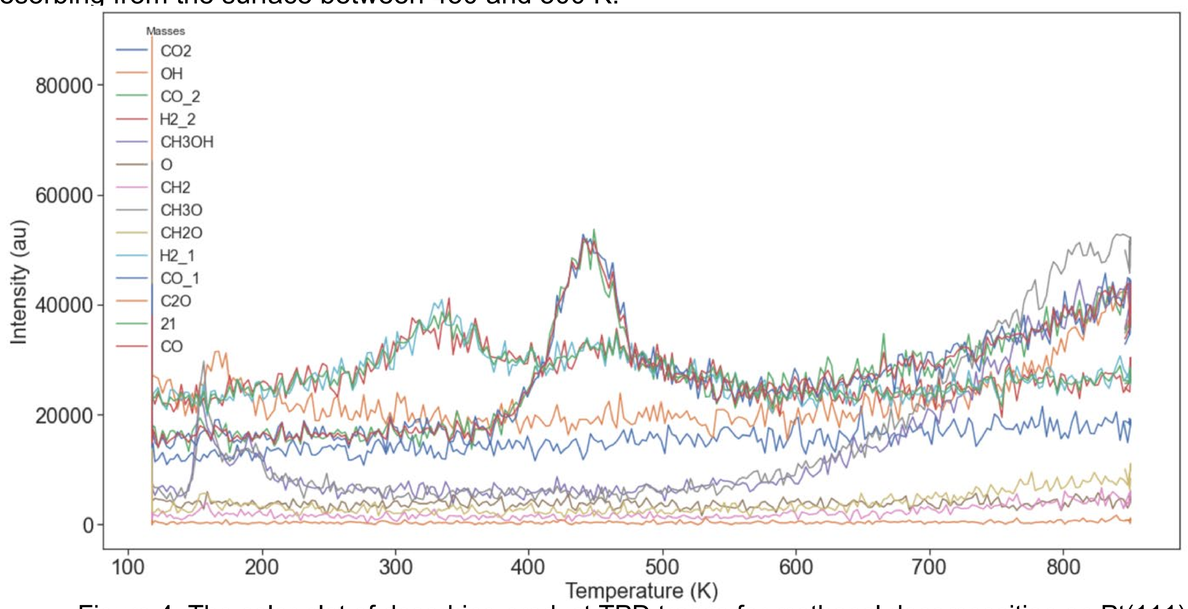

Figure 4: The color plot of desorbing product TPD traces for methanol decomposition on Pt(111)