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LDRD PROJECT NUMBER: 217050
LDRD PROJECT TITLE: Ion Imaging Near a Reactive Surface
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ABSTRACT:

In this project, resonance enhanced multi-photon ionization followed by spatial mode ion imaging (REMPI-SMII) has been developed as a new tool for *in-situ* monitoring of local catalytic activity near a chemically active surface. A prototype experimental setup was developed for the demonstration, and initial results indicate this approach is feasible as a new diagnostic for online monitoring of catalytic reactions. The catalytic conversion of H_2 and D_2 to form HD over a Pt surface was carried out using a dual-molecular beam arrangement with reactant beams impinging on a structured Pt surface. The catalytic production of HD was successfully detected through the REMPI-SMII approach, and next steps were identified to improve the experimental design for better spatial resolution and mapping of catalytic surface activity.

INTRODUCTION: In gas-surface heterogeneous catalysis, local surface structure is known to directly affect reaction rates, and complex reaction mechanisms that include feedback from one micro-domain of an active catalyst to the next are suspected. Yet, the measurement of local reaction rates over a polycrystalline sample with adequate time and spatial resolution to resolve crystallographic domains and time-varying kinetics remains an elusive yet foundational measurement need. The mechanism of communication between crystallographic domains of a heterogeneous catalyst via surface diffusion or gas phase transport has proven troublesome for experimentalists to tackle, but is hypothesized to be important for describing overall time-dependent catalytic reaction rates. In this project, our aim was to develop a completely new approach for spatially resolved on-line monitoring of local gas-phase reaction products over polycrystalline catalysts. We aimed to accomplish the goal of this project by combining resonance enhanced multi-photon ionization (REMPI) of target molecules with an optimized spatial-mode ion imaging apparatus.

The ion-imaging technique was first demonstrated by Chandler and Houston [1] to map the spatial distribution of photodissociation products. This approach was enhanced by the introduction of ion imaging lens in the apparatus [2]. In such devices, when the detector is placed at the focal plane of the ion lens, differing ion velocities for a given mass are mapped to different positions on the detector, allowing for high resolution measurements of ion velocities following collision or laser excitation. In the device developed in this project, we returned to the idea of spatial mode ion imaging, and extended it to be used to monitor the local catalytic gas-phase emission from solid heterogeneous catalytic samples. While several research groups have now reported the combination of a velocity mapped imaging apparatus for reactive surface scattering, none have utilized the ion lenses in spatial ion imaging mode to directly visualize

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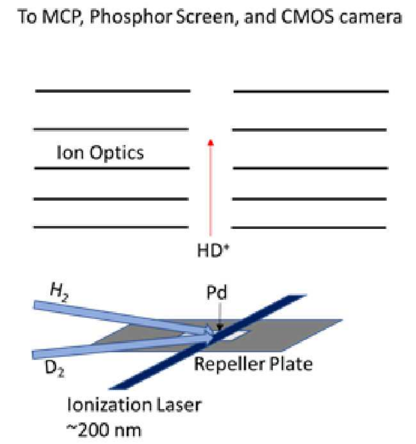

FIG. 1. Schematic of the spatial ion imaging experiment. Crossed molecular beams of H_2 and D_2 will impinge on a structured Pd sample. Catalytic production of HD will be monitored by selective REMPI ionization and spatial ion imaging.

spatially-dependent reaction rates over a multi-domain catalyst via selective REMPI excitation of desorbed surface reaction products. In this manner, the gas phase acts as a local reporter of catalytic activity and can be utilized to refine micro-kinetic models of combined gas-surface reactions. Our initial demonstration probed the conversion of molecular hydrogen and deuterium over structured Pt to form gas phase HD. Even though this is one of the most well-studied reactions in all of surface science, the understanding is far from complete, and unexpected behaviors are still found. Recently, a theoretical work predicted that, contrary to chemical intuition, stepped surfaces of Cu are less active for the cleavage of D_2 bonds than the flat (111) terrace sites [3]. We hypothesize that local surface structure modifies micro-kinetic reaction rates, and that spatially resolved, and quantified, measurement of gas phase product flux will reveal these structure-dependent rates for complex surface structures and improve micro-kinetic models. One key scientific question is the length scale over which surface chemical activity is imprinted into the gas phase, and the completed development of the REMPI-SMII approach demonstrated in these initial experiments will likely allow us to answer that question. In the future, this same technique may be used to answer further scientific questions, such as when and if gas phase reactions contribute in addition to surface reactions, during heterogeneous catalysis by measuring key gas-phase reactive intermediate concentrations.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD:

In these experiments, a crossed molecular beam chamber with baseline pressure of ~10^{-7} Torr was used. To form a skimmed molecular beam of H_2 (D_2), gasses were introduced via an Even-Lavie pulsed gas valve with a backing pressure of 30 psi. Gas pulses of 20 µs time duration were skimmed with a 2-mm diameter skimmer (Beam Dynamics) into the reaction chamber. The two molecular beams cross in the chamber perpendicularly to each other, as depicted in FIG. 1, and continue to two turbomolecular pumps oriented on the opposite sides of the chamber as the beam source, so as to capture the majority of the gasses after the interaction region to keep the operating pressure as low as possible. This allows a pressure of ~10^{-5} Torr during operation of the molecular beams. Where these two molecular beams intersect, a custom-designed repeller plate was incorporated. FIG. 2 displays photographs of this new plate after it was machined and polished. As seen in the left panel of FIG. 2, a ceramic insert was designed into which a UHV-compatible button heater was placed. This design allowed for independent electrical addressing of the button heater, isolated from the voltage applied to the repeller plate. The heater could heat the repeller plate to more than 500 °C if needed, although in practice the plate was never heated past 180 °C. As seen in the right panel of FIG 2, a notch of 2-mm depth and 1 cm X 1 cm lateral dimensions was machined into the repeller plate. This allowed for the placement of a catalyst sample deposited onto a conductive substrate. In our experiments, a 1 cm x 1 cm substrate of aluminum was used onto which a Pt layer with finger-like features was deposited through a mask using atomic layer deposition.

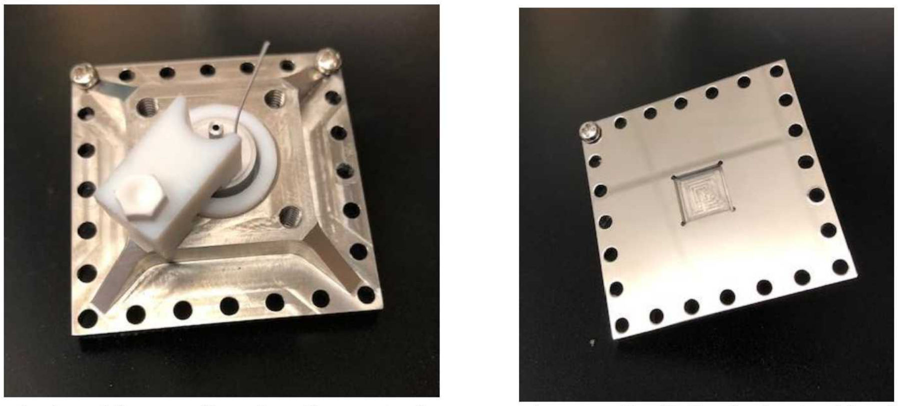

FIG. 2. Custom-designed ion repeller plate for use in these experiments. (Left) On the back-side of the repeller plate a ceramic insert allows for an electrically isolated button heater to be used. (Right) On the front face of the repeller plate, which faces the ion optics, a notch allows for a conductive subtstrate with deposited catalyst to be held at the same vertical plane as the rest of the repeller plate. Thus, the applied voltages accelerate ions over the catalyst as well as over the inert surface with the same potential.

During operation, a number density of ~10^{14} molecules/cm^3 was achievable in the near-surface region. If operating the reaction chamber as a static batch reactor, this would be analogous to a pressure of 10 mTorr. This pressure is well beyond those achievable with conventional surface science tools where experiments are conducted at near UHV conditions. Thus, this approach bridges the well-known “pressure-gap” in catalytic surface science.

The ion optics used in these experiments were also custom built, and consisted of 2 independently addressable plates: the repeller (as shown in FIG. 2) and the extractor. The repeller was held at a constant + 3,000 V. And the extractor was tuned to find two settings. The first setting places the “Fourier Plane” of the electron imaging device at the detector face, found in these experiments at +1,680 V. At this voltage, all ion velocities from across the surface are mapped to the same radial position on the detector. However, by increasing the voltage of the extractor, the ions travel through the Fourier plane before the detector, and by tuning the voltage the image plane may be focused onto the detector. At this voltage, the spatial distribution of near-surface generated REMPI ions is mapped onto the detector, providing “spatial mode imaging”. With the current plate arrangement, this voltage was found at + 2,400 V.

Because of a small concentration of HD impurities contained in both the H_2 and D_2 source cylinders, careful attention to background subtraction was required. During experiments, separate images were acquired with either Even-Lavie valve stopped, as well as with both stopped. Further images were acquired with the photoionization laser on and off.

The photoionization laser was tuned to be in resonance with the (0,0) rovibrational transition of the E,F ($^1\Sigma_g^+$) electronically excited state of HD, D_2, or H_2. The tunable ultraviolet radiation required for two-photon resonance with this state near 201 nm was generated by frequency tripling the output of a nanosecond tunable dye laser (Sirah PrecisionScan). A mixture of Rhodamine 610 and Rhodamine 640 was dissolved in methanol solvent in the dye laser to efficiently create tunable wavelengths in the vicinity of $\lambda = 600$ nm. The polarization of this radiation was verified by passing through a polarizing beam splitter cube, and controlled with a 200 nm half-wave plate. The HD^+ ions generated were accelerated through the ion lens system to a phosphor screen (Photonis USA, Inc.) coupled to a micro-channel plate (MCP) array and CCD camera (Andor Zyla).

RESULTS:

Ion trajectory simulations were carried out to determine the feasibility of the experimental approach. Specifically, the question to be answered was whether or not it is possible to image the spatial distribution of ions generated with different initial velocity vectors. The commercial SIMION ion trajectory software was used for these simulations.

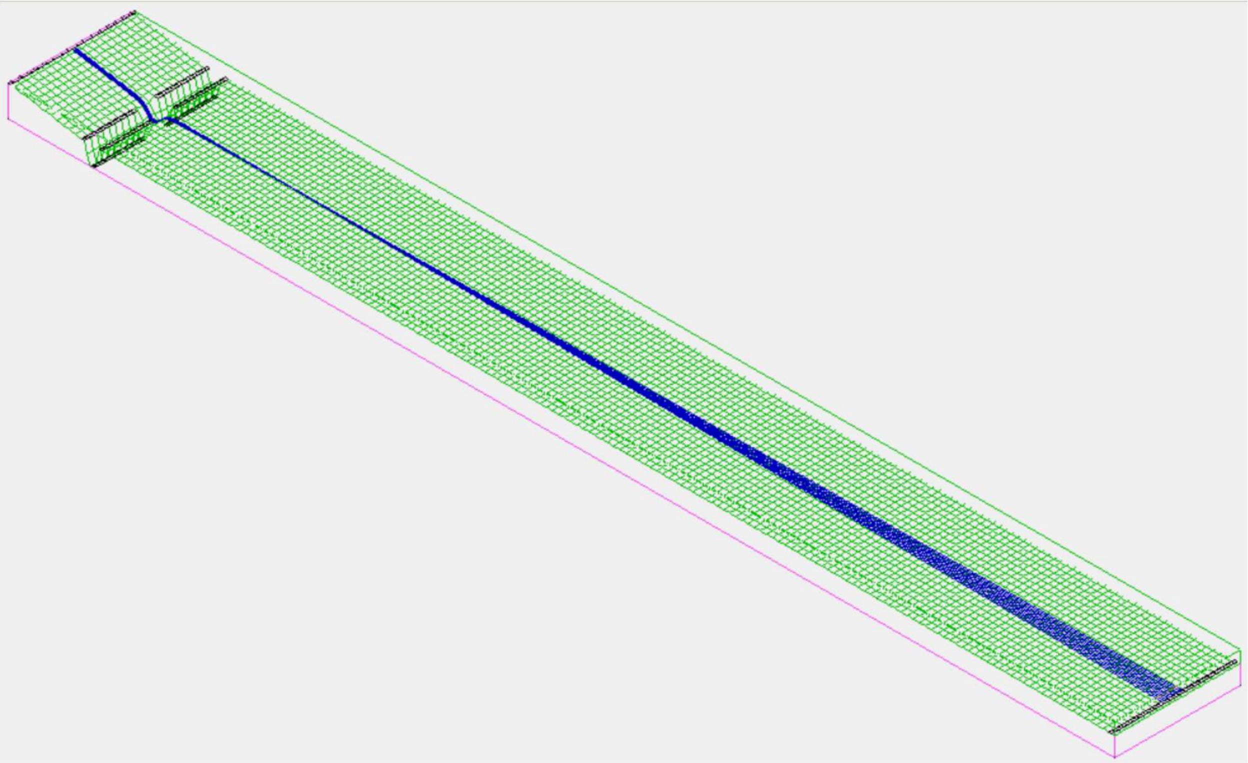

FIG. 3. SIMION simulation. In this simulation of the ion imaging lens arrangement, a series of equally spaced ion origination points from 1 mm to either side of the lens axis are projected to the detector. As can be seen, when velocities are imaged to the detector, a spatial image is recreated with 1:1 correlation to position at the sample.

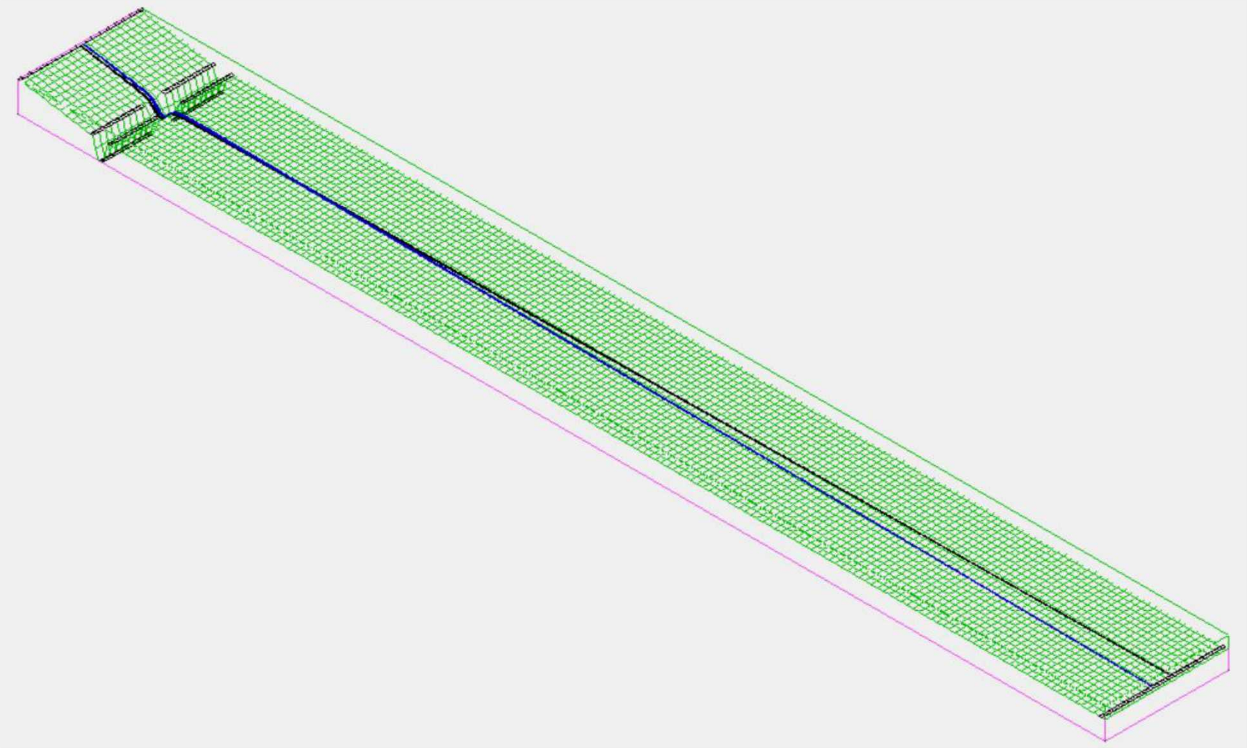

FIG. 4. SIMION simulation demonstrating two point-sources for HD^+ ions emanating with a cone of velocity vectors. When the voltage is set such that the imaging plane is at the detector, the ions from each point source are again focused to separate defined points at the detector. This demonstrates that spatial mode imaging is possible even though the initial velocity vectors of the created ions will have a distribution of angles.

As can be seen in FIG. 3 and FIG 4, simulation of the HD^+ ion trajectories through a model of our ion lens system shows that the fundamental idea of this approach is sound. A spatial imaging mode of an ion lens system, analogous to an optical imaging system, allows for ions with differing initial velocities and differing initial angle of the velocity vector is possible.

Experiments were carried out over a patterned Pt surface deposited onto an aluminum substrate. The substrate was cut and polished, and gold plated to ensure excellent conductivity while maintainaing no appreciable catalytic activity for H_2 or D_2 dissociative adsorption. A finger-like mask was created and Pt was deposited onto this surface in an atomic layer deposition chamber. The Pt "fingers" were 0.25 mm thick laterally, and separated by 0.50 mm. A structure was used to determine if our prototype device was capable of sensing modulation in the surface production of HD. Detecting such local modulation in gas-phase product formation caused by surface inhomogenieity of a catalytic surface has not yet been reported in the literature, and constitutes a major leap forward in diagnostics development for surface catalytic reactions. In FIG 5, a CCD image is displayed that resulted from collecting ionized HD molecules over the Pt surface held at 100˚C. The MCP was time-gated as the H_2, D_2, and HD ions have different mass, and thus the time-of-flight from the repeller plate to the detector allowed for an addiational axis of isolation of the HD molecules from other molecular species in addition to the selectivity of the resonant laser ionization process, eliminating the possibility for off-resonant ionization of reactant molecules adulterating the signal.

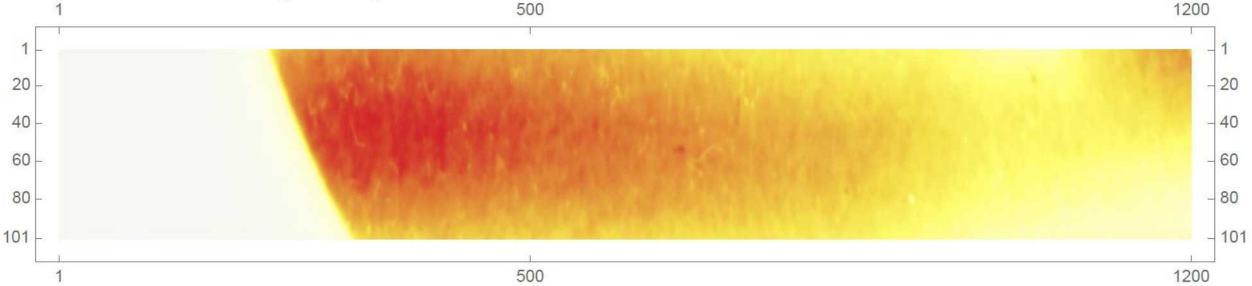

FIG. 5. CCD image of HD^+ generated catalytically. The ionization laser was focused just above the catalytic surface in the gas phase. Full background subtraction was achieved by removing the small signal present when either molecular beam was turned off. Thus, the observed signal originates from HD produced catalytically at the surface.

The sharp edge on the left side of the image in FIG. 5 is not caused by the sample, but by the edge of the clear aperature of the detection system. However, clear modulation of the signal originating from surface-produced HD is observed from left to right in this image. To further clarify this trend, FIG 6 displays a vertically integrated plot from the data in this image.

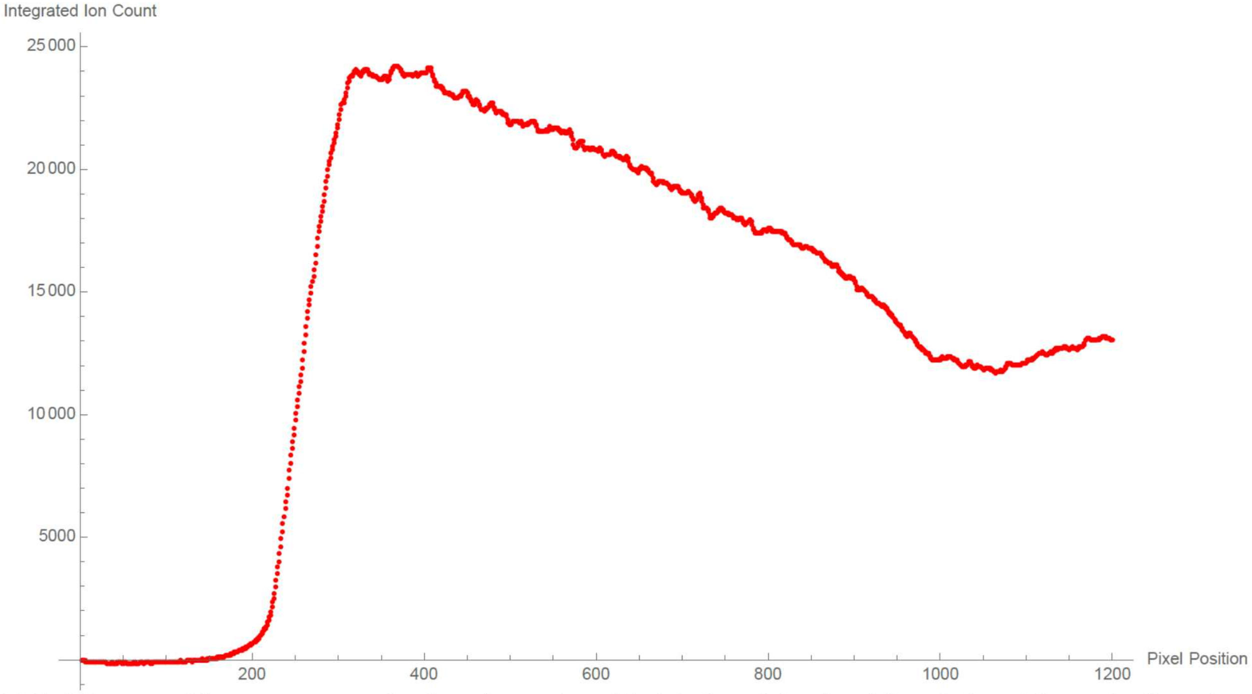

FIG. 6. Integrated ion count across the detection region. Modulation of the signal from left to right results from the magnified ‘fingers’ of Pt across the Au/Al substrate and represents a gas-phase measurement of direct local surface catalytic activity.

The data clearly demonstrate that firstly, we have successfully constructed a system where near-surface REMPI of product molecules results in measurable signals through the ion detection system. This is significant as this is a new diagnostic for surface reactions in and of itself, yielding a new method for near-field, as opposed to far-field or downstream, detection of catalytic activity. Secondly, we have demonstrated a clear modulation in the image of the ion production which supports the idea that near-surface imaging of the REMPI-SMII signals can yield spatial surface maps of catalytic activity.

DISCUSSION:

Our goal in this work was to demonstrate the possibility of a new cutting-edge methodology for detecting the local catalytic activity over a surface as it varies spatially. To first order, it was successfully demonstrated that the new REMPI-SMII technique for catalytic imaging is feasible. Clear signal from the near-surface gas phase was measured. This achievement already enables ground-breaking new measurements of catalytic activity *at* the surface, as opposed to downstream. In fact, the resolution here is only limited by the focused width of the laser pulse. Additionally, because the REMPI ionization wavelength is highly specific to the rotational and vibrational level, this approach allows the experimenter to map out the vibrational and rotational energy distribution of product molecules as a function of distance from the surface over a wide range of effective pressures. Any nonthermal distribution reveals information about the potential energy surface structure for the surface reaction and product desorption steps, depending on the mechanism.

The effective lateral resolution in the acquired ion image, as depicted in FIG. 5 and FIG. 6 above, suggests the need for improvement as the Pt features on the surface were quite sharp (on the μm length scale). Several factors in these preliminary experiments were detrimental to the overall spatial resolution of the ion image. First, the sample substrate was not ideally matched in thickness to the notch of the repeller plate. This issue has been easily rectified, and in future experiments a perfectly matched (in thickness) substrate will allow for the ionization laser to graze the sample to within 10 μm of the catalyst. As it was currently implemented, the focused laser beam was not able to approach closer than 1 mm from the catalyst surface. This will cause a blurring of the spatial imprint into the gas phase of the patterned catalytic surface structure. Additionally, the ion imaging lens arrangement does not *fully* image the distribution of initial molecular velocities to a single point on the detector. This also causes a degree of blurring in the image, as the angular velocity distribution thus causes points along the surface to be mapped to a distribution on the detector. This issue can be readily improved in future editions of the REMPI-SMII experiment. A recent discovery at Sandia-California has revealed a new ion lens arrangement (the subject of current work and a future publication) which acts as a nearly perfect lens. By incorporating this ion lens arrangement into the current apparatus, blurring by velocity distribution will be eliminated.

While careful attention was given in these experiments to background subtraction, the nonnegligible presence of HD in the reactants beams did provide difficulty and possible degradation of the measured signal. One possibility to overcome this in future experiments would be to search for signal from the v”=1 vibrational level of the product molecule. As the molecular beams are cool, no significant population of the v”=1 level should exist in the HD molecules that arise from reactant impurity.

With those suggested improvements, the REMPI-SMII catalytic imaging approach provides a robust and nearly universal method for imaging the surface emission of catalytic product molecules with chemical specificity and high spatial resolution. This is very important for the micro-kinetic modeling of catalysis as different crystallographic domains are known to have very different chemistry. Historically, the understanding of surface catalytic reactions was greatly enhanced when scientists began isolating single crystals of various terminations and carrying out catalytic reactions over crystals of varying miller indices. For instance, it became well known that surfaces with more defects, such as atomic step sites or kinks, are more active for most types of bond cleavage in hydrocarbons. This is, in part, caused by the very high surface free energy at such sites. However, real-world catalysts are not single crystals, and at a minimum, are composed of many crystallographic domains. Additionally, single crystal studies have tended to study a very small subset of naturally occurring surface terminations, particularly those of lowest surface free energy such as (111) or (100) surface of Pt, limiting our understanding of chemistry occurring at more diverse interfaces common in real world applications. Thus, experimental approaches, as the one explored in this project, that will allow for spatially resolved measurements of catalytic activity are paramount to understanding the behavior of such nonuniform catalysts.

ANTICIPATED OUTCOMES AND IMPACTS:

The most direct result of this work is the demonstration of a new experimental approach for monitoring *local* surface chemistry and product flux during solid-gas catalytic reactions. While this is important for catalysis science at large, there are several newly funded programs at Sandia that will directly benefit from the understanding gained here. The DOE Office of Science Basic Energy Sciences program in Gas Phase Chemical Physics has recently invested in a new core program at Sandia California to study gas-surface interactions during heterogenous catalysis. The focus of this project addresses the rarity of measurement techniques that probe the gas-phase near a reacting surface. In many gas-surface reactions, there exists an interplay between adsorption rate, surface diffusion and reactions, surface oxidation state, coverage (pressure), surface restructuring, product formation and desorption, and possibly even chemistry occurring in the gas phase via intermediates released from the surface. In some cases, this complicated kinetic system can give rise to time-varying or even oscillatory kinetics. In this project, Sandia proposed a novel suite of techniques including ambient pressure *imaging* XPS, surface sum-frequency generation, near-surface laser-induced fluorescence imaging and coherent Raman spectroscopy imaging of the gas phase. However, the idea explored in the current project, REMPI-SMII could have a direct impact on closing the kinetic picture for such surface catalytic systems. We intent to incorporate this new approach into this growing program, and include the methodology in the upcoming DOE renewal proposal for this program. This is significant because the idea of the current REMPI-SMII approach would have been too risky to propose as a future experiment directly to a DOE fundamental science program, but armed with this initial demonstration of feasibility, our new approach makes a natural addition to the suite of techniques already used and proposed for use in that program.

Additionally, a newly funded LDRD project at Sandia is aimed at exploring a complimentary approach for imaging near-surface molecules during heterogenous catalysis. The approach begins in an identical manner, with REMPI ionization of intermediates or product molecules over a catalytic surface, but instead of accelerating the ions through a home-built ion imaging apparatus, this experiment incorporates a commercial low energy electron microscope to image the REMPI-liberated electrons. This present short-term demonstration of the complimentary imaging of the generated ions has provided key insights that will aid the more powerful LEEM experiment. For instance, plans to incorporate molecular beams into the LEEM chamber have sprung from the topic of this ion imaging LDRD, and greatly enhance the probability for success in the new project.

Finally, a new project from DOE EERE explores the catalytic efficiency of catalysts with engineered defects. The fundamental idea is to create cheap catalysts tailored for a particular chemical conversion. Again, there are two fundamental questions that the approach demonstrated in this work could help answer. First, what is the heterogeneity and distribution of the catalytic efficiency for the engineered catalysts? Traditional far field measurements such as mass spectrometry or gas chromatography can not answer such questions. Second, are chemical intermediates released into the gas phase? The reduced efficiency of engineered catalysts, as compared to transition metal catalysts such as Pt or Pd, often necessitates increased temperatures. This increases the probability that gas-phase chemistry may play a role in the overall reaction mechanism. By measuring the near-surface concentrations of key intermediates through REMPI ionization and SMII imaging, this question can be answered.

Thus, while there are existing and planned projects that will directly benefit from the knowledge of the new approach demonstrated here, the impact of a new diagnostic approach is almost always widespread. We intend to publish this approach in a scientific publication. Because of the natural use for this diagnostic among the programs listed, we are continuing to implement the changes to the approach as outlined in the Discussion section above. Specifically, a newly designed ion lens system will be incorporated into the device allowing for more complete imaging of the velocity distribution and a clearer REMPI-SMII image. Once this is incorporated, the factors limiting the resulting spatial resolution will be identified, but it is suspected that a vast improvement in image quality will result. Further, catalyst substrates have been produced which exactly match the thickness of the sample holder within the repeller plate. This will allow the ionization laser to approach the catalyst at grazing incidence, improving the proximity to the catalyst structures we intend to image.

CONCLUSION:

In this project we have demonstrated a new approach that could revolutionize our capability to probe the *local* product flux and intermediate concentration emitted into the gas phase over real-world catalytic materials. Selective ionization of molecules in the near-surface region of an active catalyst followed by spatial-mode ion imaging maps, with high chemical specificity, the distribution of these molecules in the gas phase. Such a capability will likely allow for refinement of microkinetic models as the data acquired serves to provide mechanistic detail as well as serve as a benchmark for numerical simulation of catalytic reactions.

[1] D.W. Chandler, P.L. Houston, Journal of Chemical Physics, 87 (1987) 1445-1447.
[2] A. Eppink, D.H. Parker, Review of Scientific Instruments, 68 (1997) 3477-3484.

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[3] G. Fuchsel, K. Cao, S. Er, E.W.F. Smeets, A.W. Kleyn, L.B.F. Juurlink, G.J. Kroes, Journal of Physical Chemistry Letters, 9 (2018) 170-175.