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Gas-Phase Hydrogen-Atom Measurement above Catalytic and Non-Catalytic Materials during Ethane Dehydrogenation

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ABSTRACT

The role of a solid surface for initiating gas-phase reactions is still not well understood. Hydrogen atom (H) is an important intermediate in gas-phase ethane dehydrogenation and is known to interact with surface sites on catalysts. However, direct measurements of H near catalytic surfaces have not yet been reported. Here, we present the first H measurements by Laser Induced Fluorescence in the gas-phase above catalytic and non-catalytic surfaces. Measurements at temperatures up to 700 ºC show H concentrations to be at the highest above inert quartz surfaces, compared to stainless steel and a platinum-based catalyst. Additionally, H concentrations above the catalyst decreased rapidly with time on stream. These newly obtained observations are consistent with the recently reported differences in bulk ethane dehydrogenation reactivity of these materials, suggesting H may be a good reporter for dehydrogenation activity.

1. Introduction

Understanding the interactions between heterogenous catalysts and the gas-phase poses a significant scientific challenge. While the nature of adsorbed species on a catalytic surface can be studied using various analytical methods, less is known about the gas phase, especially the concentration of short-lived radical species. These species become important during the study of reactions such as ethane dehydrogenation, where gas phase reactions can dominate over surface reactions at elevated temperatures. The local chemistry can vary spatially due to differences in gas-phase composition, active site availability, temperature, and pressure. The conventional approach for the study of heterogenous catalysts involves a study of catalyst performance through analysis of downstream products, for example, by detailed speciation with gas chromatography (GC)[1]. Studies of catalyst surfaces are often done at low pressures using surface science tools since these conditions, however unrealistic, provide simpler, more easily characterized systems. Bridging the so-called "pressure gap" has been critical to catalyst development[2]. The need for improved characterization of catalyst surfaces, their active sites, and their surface chemistry at relevant conditions has led to significant development of operando diagnostics[3]. While surface diagnostics at realistic conditions have received much attention, there have been limited in-situ studies of the gas-phase and its interaction with catalysts, despite its importance. Here, we use Laser Induced Fluorescence (LIF) as a tool to explore local hydrogen atom (H) production over surfaces, applying the process to characterization of industrially-important ethane dehydrogenation reactions.

Rosén and coworkers used LIF to measure OH radical over Pt during hydrogen oxidation[4–8]. Zetterberg and coworkers have done significant work combining in situ LIF in the gas-phase with High Energy X-Ray Diffraction and Surface Optical Reflectance to study catalytic CO oxidation[9–

[20]. Deutschmann and coworkers have used local gas sampling[21] and LIF[22,23] to study catalytic oxidation and reduction reactions. Most recently, Zhou et al.[24] have combined LIF, Raman, and near-surface MS to characterize a catalytic methanol oxidation system. In each of these studies, key gas-phase species serve as local reporters of catalytic activity. These studies show that the application of near-surface gas-phase measurements can be an invaluable tool for catalyst development. The current work seeks to extend this concept to an alkane dehydrogenation system.

Olefins are important chemicals in a number of industries. In order to meet growing demands, dehydrogenation of alkanes (e.g. ethane) as route to industrial alkenes (e.g. ethylene) has received significant attention[25,26]. Currently, high-temperature (850-900 ºC), energy-intensive steam cracking is the most common method of ethane dehydrogenation[26]. However, catalytic alternatives have also been the focus of significant research[1,26,27], seeking to reduce the energy requirement of the dehydrogenation process, typically through reduced operating temperatures. A significant challenge in catalyst development is suppression of side reactions, which can often lead to contamination of the catalyst, and numerous additives are being explored[25,26].

A recent study by Riley et al. demonstrated high ethylene yield at reduced temperatures, but without catalyst, through ethane dehydrogenation in a quartz tube reactor[28]. The thermally driven reaction avoids the problems of catalyst contamination and regeneration, while significantly reducing operating temperatures to 700 ºC. The authors note that the introduction of catalyst reduced reactor performance at this temperature. Additionally, a quartz tube reactor outperformed a stainless steel reactor [28]. Understanding the nature of these differences, however, is difficult using traditional bulk effluent analysis, such as GC-FID/TCD. Here, we explore LIF as a method to characterize local gas-phase measurements near the reactor and catalyst surfaces, potentially providing additional insight into this promising reactor system.

Dehydrogenation or pyrolysis of ethane involves a number of important radical species, such as methyl (CH_3) and hydrogen-atom (H) [29,30]. The importance of H in dehydrogenation makes it an attractive candidate as a gas-phase reporter of dehydrogenation chemistry. Additionally, hydrogen abstracted on reactive sites on a catalyst can “spillover” onto inactive sites on the substrate [31]. This surface-bound H can participate in surface-based reactions, including the formation of H_2. However, the transport of this H into the gas-phase, and participation in gas-phase reactions, is still not well understood. Baumgarten and coworkers[32–37] indirectly observed gas-phase H-atom transport through measurement of detector species or reaction products downstream. To our knowledge, no direct measurement of H-atom in the gas-phase has been made near a catalytic surface.

The purpose of this study was to investigate H concentration in the gas-phase near catalytic and non-catalytic surfaces during ethane dehydrogenation. This is accomplished by three-photon LIF. Idealized surfaces are investigated in a stagnation reactor geometry in order to provide a well characterized flow field and well controlled temperature.

2. Materials and Methods

Stainless steel and quartz samples were commercially obtained (Goodfellow). The steel is 316 stainless and is in the form of 0.5 mm thick, 10 mm diameter disks. The quartz (SiO_2) samples are 0.5 mm thick, 10 mm × 10 mm sheets. The catalyst contains platinum-manganese bimetallic nanoparticles supported on silica with nominal 2 wt% Pt loading (PtMn). The PtMn catalyst was prepared according to the procedure used by Wu et al.[38] using sequential incipient wetness of pH-adjusted manganese (II) nitrate solution and tetraamine platinum nitrate solution. The catalyst has been characterized via x-ray diffraction (XRD), x-ray fluorescence (XRF), Brunauer Emmett Teller (BET) surface area analysis, and transmission electron microscopy (TEM)[28]. XRD analysis determined the crystalline phases present within the Pt-based catalyst and was conducted with a Bruker D2 Phaser operating in Bragg-Brentano geometry. XRF elemental composition measurements were taken with an Orbis Micro-XRF using a 30 μm spot size, 20 kV voltage, and 800 μA current. Surface area measurements were taken with a Micromeritics Gemini 2360 Surface Area Analyzer. Samples were outgassed overnight at 120 ºC in flowing nitrogen prior to analysis. A JEOL JEM 2010 F field emission microscope was used for TEM imaging. Surface characterization results can be found in the supplementary materials of[28]. The catalyst powder was formed into 1 mm thick, 6.35 mm diameter pellets with a press (Retsch PP 25, 1000 MPa pellet pressure).

Samples were placed in a vacuum-capable stainless steel cell, as shown in Figure 1. Each side of the cell is equipped with 3 mm thick UV-grade windows. A half-inch ceramic button heater (model 101275-28, HeatWave labs) was used to heat materials to specified temperatures up to 700 ºC. Measurements were limited to 700 ºC as coke formation on heater leads would cause heater malfunction at higher temperatures. Reactants (controlled by mass flow controllers, MKS) flow into the cell from a 9.4 mm inner diameter tube and impinge on the heated material in a stagnation flow configuration. The outlet of the tube was a distance, h, of 20 mm from the heated material surface. The cell is vented to an exhaust stream, and all measurements are carried out at ambient pressure. The reactant stream was 10% ethane, by volume, with the balance as nitrogen. The total volumetric flowrate, Q, was 100 sccm (0 ºC reference), to produce similar gas velocities to[28]. Given the differences in system configurations, however, residence times cannot be directly matched, though the results of Riley et al[28] showed limited sensitivity to residence time.

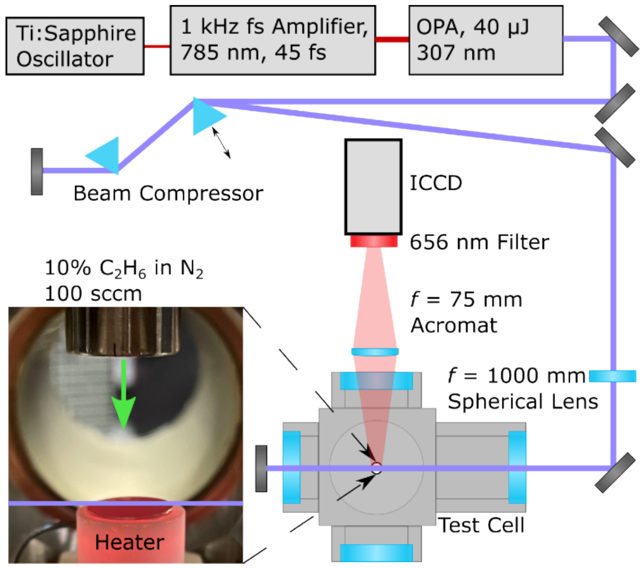

Figure 1. Test cell and LIF diagnostic.

Hydrogen atom concentration was measured by femtosecond (fs) three-photon Laser Induced Fluorescence[39]. 307 nm radiation was produced by an Optical Parametric Amplifier (OPA, HE-TOPAS Prime, Light Conversion). The OPA was pumped by 8 mJ, 45 fs pulses at 1 kHz (Legend Elite Duo, Coherent). The 307 nm beam pulse energy was reduced by an ND filter to 40 µJ to limit plasma generation at the beam focus[39], and had a bandwidth of approximately 5 nm. The inherent and window-induced first-order chirp of the fs UV beam was compensated for with a two-prism compressor.

The UV beam was focused by a 1 m focal length lens to approximately 250 µm diameter, and the edge of the beam passed over the materials at a distance of less than 50 µm. The entire cell is mounted on a translation stage allowing the relative position between the surface and the fixed beam to be adjusted. Fluorescence was collected normal to the beam propagation direction by a 2-inch, 75 mm focal-length acromatic doublet lens. Hydrogen atom excited by the 307 nm beam fluoresces at 656 nm[39]. Collected LIF was passed through a 656 nm narrowband filter (656FS03-25, Andover). The lens imaged LIF to an intensified CCD with a 3rd generation intensifier (iCCD, iStar, Andor). The intensifier gain was set to 75% and gated to 10 ns. Each image consists of 800 intensifier gates accumulated on-chip. 100 images were averaged for each measurement. Background signals were acquired by removing ethane from the reactant stream.

A rich (equivalence ratio = 1.2) methane/air flame was used to reliably produce H-atom for the purpose of system optimization and calibration. It should be noted that H-LIF intensities in these experiments are two orders of magnitude lower than those in the flame. Krypton gas, which has similar transition energies to H-atom[40], was also used as a measure of day-to-day performance of the system.

The presence of H atom was first confirmed by coupling the iCCD to a spectrometer (Shamrock 500i, Andor). The spectrally resolved LIF signal above SiO_2 at 700 ºC is shown in Figure 2. With the narrowband filter removed, a peak in fluorescence emissions is detected at 656 nm, confirming the presence of H atom. Figure 2 also shows the spectral response of the narrowband filter used in all H-LIF measurements. It is worth noting that there is some broadband LIF not associated with H atom collected at each condition. However, evaluation of the spectral response shown in Figure 2 provides an upper bound of this interference of about 5%.

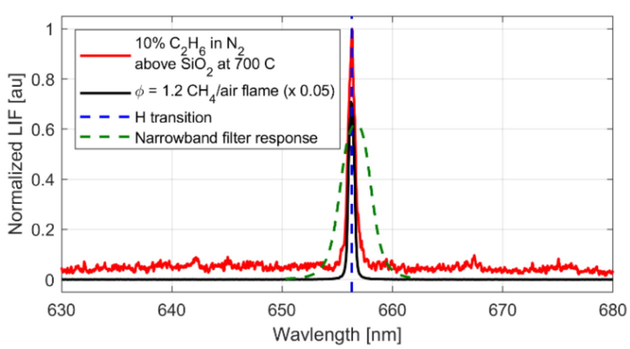

Figure 2. LIF spectrum.

The sensitivity of the system to h and Q was evaluated by comparing LIF signals over SiO_2 at 700 ºC. These results are summarized in Figure 3. Negligible differences in H-LIF were found with h varying from 6 to 20 mm. An order of magnitude increase in Q from 100 to 1000 sccm, thereby decreasing residence time, reduced overall LIF signals by approximately 30%.

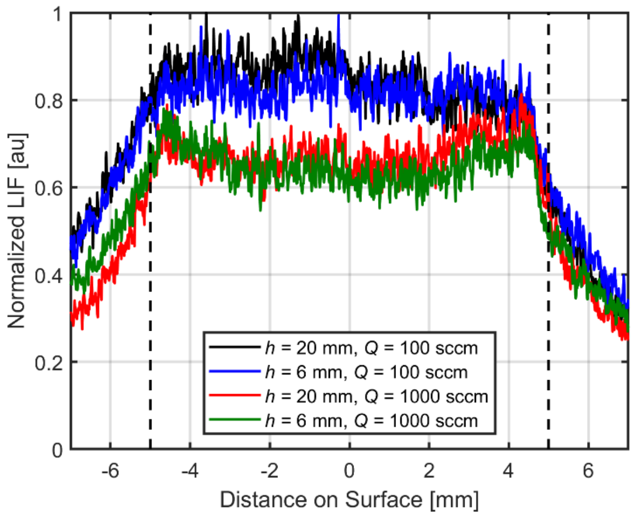

Figure 3. H-LIF above SiO_2 at 700 ºC with reactant tube distances of 6 or 20 mm, and overall flowrates of 100 or 1000 sccm. Dashed lines indicate locations of the surface edge.

3. Results and Discussion

Signals are integrated along the width of the beam and the length over the material. Signal for the C_2H_6/N_2 mixture is normalized by the signal in Kr to account for changes in laser energy or system response. It should be noted that the response in Kr was found to be insensitive to temperature above 300 ºC. It is assumed that bulk gas composition above the different surfaces are comparable enough that there are negligible differences in quantum efficiency and fluorescence lifetime. With this assumption, H-LIF responses for different materials can be compared, and H-LIF intensities assumed proportional to H number density. Measurements were made at successively increasing temperatures. Between each measurement, the cell was purged with pure nitrogen for measurement of the background largely comprised of the heated surface blackbody radiation. Additionally, as the temperature is increased, small surface or beam position changes were tracked by measurements of LIF in krypton, and the surface was moved to keep a consistent measurement distance.

This technique was subsequently applied to assess hydrogen production, and thereby ethane dehydrogenation, above several material surfaces. Normalized hydrogen-atom LIF signals over each of the materials are summarized in Figure 4. Error bars represent the standard deviation of repeat measurements combined in quadrature with the 5% uncertainty due to broadband interference. For both quartz and steel, increases in surface temperature result in increased H-LIF just above the surface. The increases are monotonic with temperature, consistent with a thermally driven production of H. Notably, the concentration of H above quartz is about a factor of 2 higher than stainless steel at 700 ºC. This difference in H concentration is consistent with the higher fraction of bulk ethane conversion observed in a quartz reactor, compared to a steel reactor[28]. It is worth noting, no presence of coke deposition is observed on either quartz or steel over the entire temperature range.

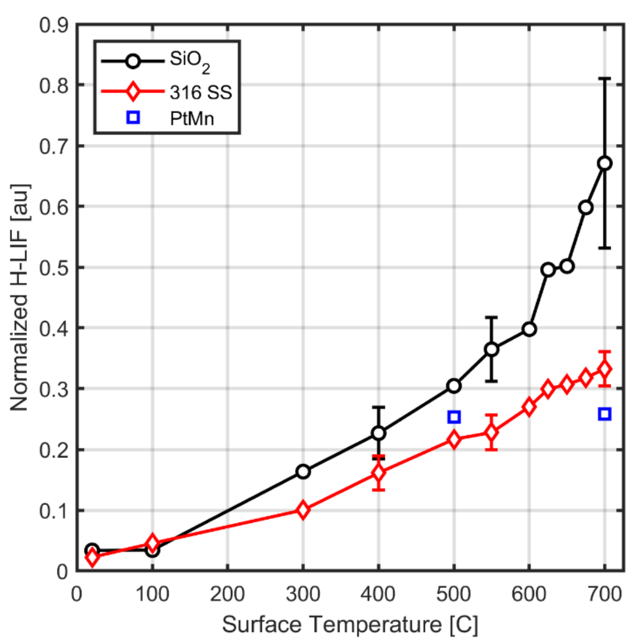

Figure 4. Normalized H-LIF above surfaces over a range of temperatures. Measurements are made 125 μm from the surface.

Riley et al.[28] compared the performance of a blank quartz tube reactor to a system containing PtMn catalyst. The PtMn catalyst performed relatively poorly at 700 ºC, generating significant coking that was believed to degrade the catalyst performance. At lower temperatures, (< 600 ºC), however, coking was less pronounced, and the catalyst outperformed the blank quartz tube at the same temperatures. The present LIF technique was therefore applied to explore potential local dehydrogenation above PtMn catalyst at 500 ºC, where the catalyst is expected to outperform quartz, and 700 ºC, where the quartz is expected to outperform the coking catalyst. Immediately before testing, the catalysts were reduced in 10% H_2 in N_2 at 400 ºC for 1 hour. Measurements for the catalyst are limited to two temperatures as coking and deactivation of the catalyst is a known problem, and fresh catalyst was used for each test. As indicated in Figure 4, at 500 ºC, H-LIF concentrations above the PtMn are comparable to those of the non-catalytic materials, within uncertainties. This observation suggests that there are not significant amounts of H atom desorbed from the catalyst and transported these short, localized distances (50-300 μm) away from the surface despite H being known to form on the surface[31]. At 700 ºC, H-LIF above the catalyst does not increase significantly (unlike quartz and steel), and H-LIF is noticeably lower than either non-catalytic surface, which again mirrors the reduced bulk dehydrogenation performance of the catalysts at elevated temperatures. It is worth noting that since H production over quartz is expected to be driven by thermal pyrolysis of ethane, even if the catalyst were completely deactivated at this temperature, one might expect the thermal production of H would be the same as that of the quartz. The observation of reduced concentrations of H over PtMn suggests the catalyst acts more as a H sink rather than source for gas-phase H.

As coking and deactivation is a known problem for dehydrogenation catalysts, the temporal response of the PtMn catalyst was also measured, and the results are shown in Figure 5. For these experiments, a freshly reduced catalyst was heated to the desired temperature in pure nitrogen. Once ethane was introduced to the reactant stream, LIF measurements are made every few minutes. Measurement for each data point takes 1-2 minutes. H atom concentrations are comparable in the first two minutes of ethane introduction at both 500 ºC and 700 ºC. Notably, the concentration of H-atom over the PtMn surface drastically drops within minutes. While the measured H-LIF reduces significantly over the course of an hour at both 500 ºC and 700 ºC, the reduction is much faster at 700 ºC. These rapid changes in local chemical composition highlight one of the challenges of catalytic dehydrogenation. In principle, the reduction in H atom could be due to reduced gas temperatures, changes in local mass transport, or changes in surface activity. It is unlikely the surface temperature will change significantly enough to cause the observed reduction in H atom, and mass transport near the surface will be dominated by the fixed flow conditions and should not change. Therefore, the observed changes are reasonably attributed to changes in surface activity. This change in activity likely includes significant coking of the catalyst at this temperature and may include increased adsorption/absorption of H in the "H-sink" mentioned above, though the mechanism is uncertain. Clearly, however, these results confirm that PtMn is not as effective at higher temperatures. Reduction of H-LIF to negligible quantities after 60 minutes also precludes the possibility that H is being photolytically produced in the reactants in these experiments.

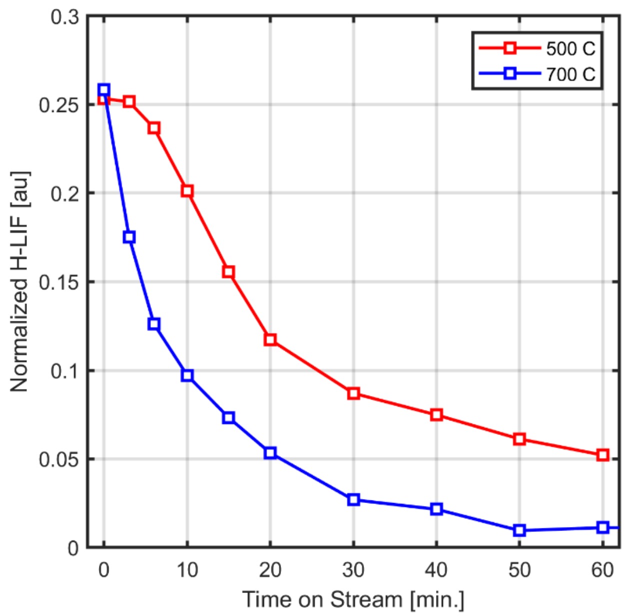

Figure 5. Temporal profiles of H-LIF over PtMn catalyst at 500 ºC and 700 ºC.

One key virtue of this characterization technique is the ability to locally assess reaction activity as a function of distance from the heated surface. Figure 6 shows these results for all three materials at 700 ºC. For quartz, H-LIF remains high near the surface (within 400 µm) before dropping off gradually by about 35% 1 mm from the surface. As H production over this inert surface is driven by gas-phase reactions, the H-LIF profile suggests a gradual reduction in gas temperature going away from the surface, as would be expected. Interestingly, H-LIF over steel remains more consistent, dropping by about 15% over 1 mm, though starting at a lower amount. The convergence in H-LIF between quartz and steel over 800 µm from the surface may be representative of a consistent gas-phase temperature at this distance. The lower concentration of H near the surface of steel, relative to quartz, then indicates surface chemistry that inhibits formation of H or consumes H. Steel surfaces have been shown to promote radical recombination within a few mm in reacting flows[41]. More interestingly, H-LIF over PtMn increases at an increased distance from the surface. Figure 6 shows measured H-LIF 125 µm from PtMn after 1 hour, where the signal has dropped to negligible levels. However, probing 375 µm away from the surface 2 min later shows higher levels of H atom. This observation indicates that the surface inhibition or consumption effect is even stronger on the catalytic surface. Though consumption of H through radical recombination may occur near the surface, reduced formation of H is also expected based on the observed reduced dehydrogenation performance[28]. Gas-phase temperature measurements are necessary to determine the extent to which the surfaces affect the local temperature field. However, these highly-localized observations provide new insights into the possible mechanisms behind the observed differences in dehydrogenation efficiency above these varied surfaces and are uniquely identified by H-LIF studies.

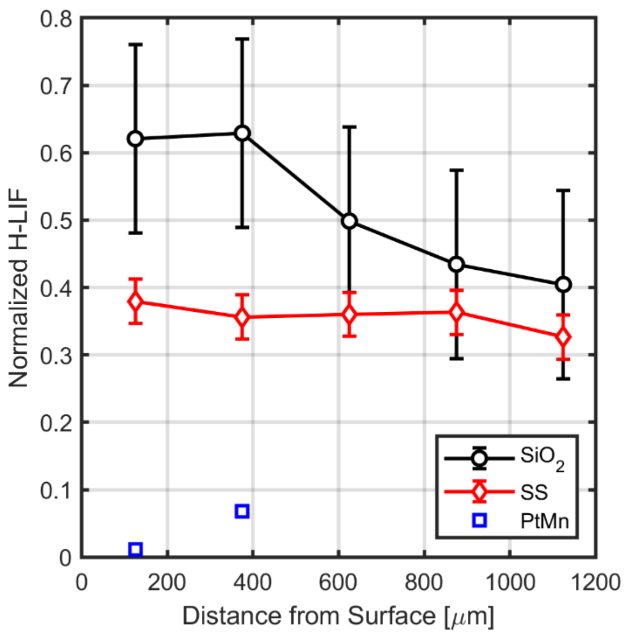

Figure 6. Normalized H-LIF above quartz, stainless steel, and PtMn catalyst at 700 ºC. Data for PtMn at 125 µm and 375 µm are taken 60 and 62 minutes after ethane introduction, respectively.

4. Conclusions

This report details the first near-catalyst gas-phase hydrogen atom measurements by Laser Induced Fluorescence. Local hydrogen atom measurements above heated quartz, stainless steel, and PtMn-based catalyst in an ethane/nitrogen stagnation flow between room temperature and 700 ºC showed hydrogen concentrations above quartz were higher than steel or PtMn with the difference in concentration more significant at higher temperatures. Using H atom as a reporter of ethane dehydrogenation, the results are consistent with previously observed superior performance of quartz as an ethane dehydrogenation reactor material[28]. Local LIF measurements provide new insights about the possible mechanisms behind these differences. In particular, surface chemistry which inhibits H formation, or increases H consumption, may alter dehydrogenation chemical pathways. Meanwhile, rapid catalyst deactivation from coking or H consumption by PtMn catalyst appears to diminish H concentrations locally above the surface. This study exemplifies the potential value of highly-localized, surface specific measurements of gas reaction chemistry enable by H-LIF spectroscopy.

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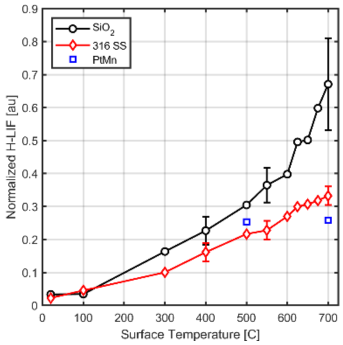
TOC Graphic



SiO2
316 SS
PtMn
Normalized H-LIF [au]
Surface Temperature [C]
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
600
700