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**MODELING AND PERFORMANCE ANALYSIS OF DEB BASED HYDROGEN
GETTERS**

BY

**JOHN ANTHONY MATTESON
BS CHEMICAL ENGINEERING**

THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

Chemical Engineering

The University of New Mexico
Albuquerque, New Mexico

August, 2022

MODELING AND PERFORMANCE ANALYSIS OF DEB BASED HYDROGEN GETTERS

by

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B.S., Chemical Engineering, University of New Mexico, 2015

M.S., Chemical Engineering, University of New Mexico, 2022

ABSTRACT

Hydrogen getter materials are used to irreversibly absorb hydrogen gas in sealed environments. The DEB based getter system, despite finding widespread use in this application, still poses challenges with respect to experimental performance analysis and fundamental understanding of reaction mechanism. The second chapter of this report addresses the experimental challenges of this getter system by demonstrating the utility and experimental strengths of a custom magnetic suspension balance (MSB) based gravimetric sorption system. This apparatus enables performance evaluation in process relevant conditions including dilute mixed gas environments which our results indicate is necessary for accurate performance evaluation of getter systems. Chapter three of this report posits a parallel-series reaction mechanism for DEB hydrogenation and uses kinetic expressions developed from this framework to model the reaction in terms of intermediate and fully hydrogenated DEB species. The kinetic framework modeled in this report suggests considerable hydrogen mobility in the getter system. Furthermore, the shift in selectivity with hydrogen pressure indicates that the hydrogen exposure history of the getter material, and by extension the containment structure, may be ascertained by analyzing the relative concentration of DEB and its hydrogenation products.

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CHAPTER 1

INTRODUCTION

Hydrogen gas buildup in sealed containers is an undesirable but frequently observed phenomena, particularly in vacuum applications, lead-acid batteries and sealed environments containing radioactive materials [1]. The hydrogen originates from several sources including outgassing of hydrogen from metal hydrides, reaction of trace gases on catalytic surfaces, corrosion and radiation induced hydrolysis of water and organics. This gradual accumulation of hydrogen gas can have detrimental impacts on the integrity of the containment structure materials, embrittle solder joints of electronic components and can pose a potential explosion hazard in the presence of residual O₂ [2]. Due to the abovementioned concerns, materials which are capable of irreversibly reacting with and binding hydrogen are frequently included in such containers to preempt hydrogen accumulation, these materials are commonly referred to as hydrogen getters.

Hydrogen getters are chemical systems capable of irreversibly binding hydrogen (referred to as gettering) at low partial pressures. Several classes of hydrogen getter materials exist including recombination catalysts, metal hydrides, and unsaturated organics in combination with a hydrogenation catalyst. Recombination catalysts such as Pt, Pd and Rh react hydrogen and oxygen to create water are one type of system that can be employed for preventing hydrogen accumulation. These systems show very high capacity, kinetics, temperature and pressure stability, however, there are significant drawbacks that prevent use of this type of getter in sealed environments such as the buildup of water in the containment structure, the added heat of reaction from water formation (68 kcal/mol H₂) and the requirement of sufficient oxygen to drive the reaction [2]. There also exist several

metals and intermetallic compounds that react with hydrogen to form metal hydrides, e.g., Mg, ZrCo, Mg₂Ni, and LaNiAl. While metal hydrides do not produce water or require the presence of other gasses, the primary concern with this platform is that the hydriding reaction is reversible with temperature, giving the possibility to the release of hydrogen under high temperature conditions which can potentially create a dangerous reaction environment. Due to the issues associated with recombination catalysts and metal hydrides the material commonly employed in sealed containers for getting hydrogen is an unsaturated organic molecule paired with a hydrogenation catalyst. This material functions

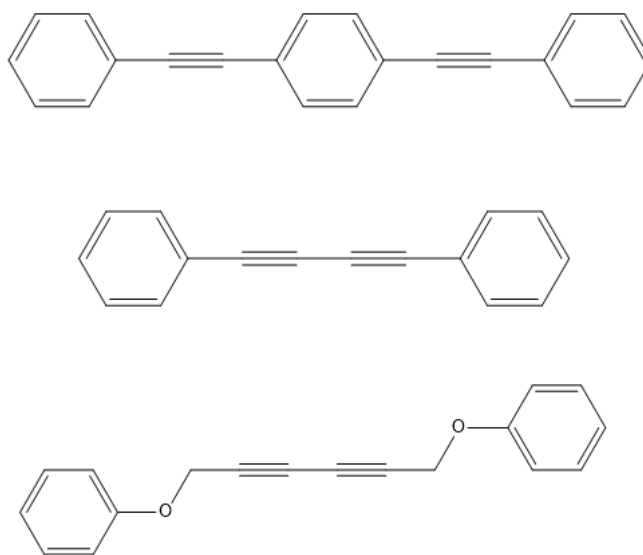


Figure 1 Structure of 1,4-bis(phenylethynyl)benzene (DEB) (top) and predecessor materials DPB (middle) and DPPE (bottom)

by metal catalyzed dissociation of hydrogen gas followed by hydrogenation of unsaturated carbon bonds in the organic molecule which irreversibly binds the hydrogen. This platform, pioneered by Sandia researchers Courtney and Harrah in 1975 [3] originally utilized dimerized phenyl propargyl ether (DPPE) and represented an attractive hydrogen getter solution due to numerous features, such as: its ability to be handled in air, minimal to no

activation requirement, substantial hydrogen capacity and low equilibrium hydrogen overpressure. Subsequent evolutions of this system migrated to diphenyl butadiyne (DPB) and ultimately to 1,4-bis(phenylethynyl)benzene (DEB) (see figure 1) as its melting point (179°C) is substantially greater than DPPE and DPB (80 and 87°C respectively) which reduces the potential for material migration and contamination of the sealed environment with getter material [4].

The getter platform investigated in this report falls into the *unsaturated organic with hydrogenation catalyst* class of materials and is comprised of the organic molecule DEB combined with a heterogeneous palladium on carbon (Pd/C) catalyst. This getter platform was first described in a 1990 report by researchers with Allied Signal Aerospace in Kansas City MO. In this report researchers found that the DEB-Pd/C platform is capable of getting 8 moles of H₂ per DEB molecule or 241.7cm³ H₂/g_{getter} and has a melt temperature of 179°C and 87°C in its fully hydrogenated form (compared to 52.5°C for fully hydrogenated DPB).

Since its disclosure in 1990 the DEB based getter system has become one of the most commonly utilized systems of its class for hydrogen getting applications [5]. Several reports have been published on this material over the last 30 years notably, Balooch in 1999 [6] investigated the thermochemical properties of the material as well as the hydrogenation kinetics at 100mT and subsequently demonstrated the first application of rubberized DEB materials in 2001 [7]. Pri-Bar conducted several studies in the early 2000's aimed at understanding the mechanism for catalyzed hydrogenation in this solid solvent free getter system and also published the only report on reaction product speciation in 2006 [8]. Dinh investigated the reaction mechanism by kinetic modeling of the DEB getter

system in 2015 [9], interrogating pressures from 5-20Torr and temperatures ranging from 20-50°C. Powell similarly conducted a detailed kinetic analysis of predecessor Diphenyl butadiene (DPB) based getter materials at 17°C over the range of 750-0.75mT [4]. Recently, Sharma published a detailed report on thermochemical and materials properties of DEB and its reaction products [10].

Current research has been dominated by investigating and improving the performance of DEB getter material incorporated into various polymers. The ultimate aim of these efforts is to produce a getter material with dual functionality as both hydrogen getter and gasket material. The barrier properties of the polymer matrix also act to protect the getter from atmospheric contaminants such as O₂ and H₂O which can reduce getter performance. Ortiz-Acosta demonstrated the use of direct ink writing techniques to 3D print a getter impregnated elastomer into a high surface area face centered-tetragonal (FCT) lattice structure in 2018 [11]. In 2020 Sangalang and Dinh investigated the performance of a getter system composed of DEB-Pd/C in a rubber matrix with porous silicone foam which was obtained from a commercial collaborator [12]. Tan, in 2021 published a report the performance of DEB-Pd/C incorporated into a porous low density polyethylene (LDPE) composite produced via mixing and melt pressing of getter, LDPE and poly(ethylene oxide) (PEO) powders into a dense sample and subsequently creating microporosity by removing the PEO by solvent extraction with water [5].

While these next generation composite getter materials are actively being investigated there still exist significant challenges which have yet to be adequately addressed. These challenges can be broadly defined to fall under the category of *experimental* or *fundamental* challenges.

Experimentally, performance evaluation of getter materials has not been adequately standardized to facilitate direct comparison across experiments and materials. This results in potentially misleading performance evaluation data as qualitatively disparate behavior can be observed depending on reaction conditions, detailed further in *Gravimetric Based Performance Evaluation of DEB Hydrogen Getters*. This is particularly relevant to experimental next generation composite getter systems as because of barrier properties and diffusion effects, these materials are significantly prone to demonstrating misleading experimental performance data. While initial results of these experimental compounds appear promising a notable commonality identified of this research is the ubiquitous use of pure H₂ *frequently* at high (circa atmospheric) pressures for performance evaluation. Experimental evidence is presented in Chapter 1 of this report demonstrating that in mixed gas environments boundary layer diffusion limitations can become the dominant rate limiting mechanism, which drastically impacts observed performance particularly in systems incorporating a selectively permeable matrix or barrier materials. Thus it is highlighted in this report that performance evaluation studies utilizing pure gas at elevated pressures may not be representative of hydrogenation kinetics in many use environments where the sealed container is backfilled with inert gas.

The *fundamental* challenge with regard to this getter platform lies in the lack of consensus on governing reaction mechanisms. Despite modeling efforts indicating that hydrogen spillover should not be evident at low partial pressures [13], Dinh reports that this phenomena is observed experimentally [9]. Furthermore, there is still no consensus on the mechanism by which solid unsaturated organic molecules spatially distanced from the catalyst surface become hydrogenated. The two dominant theories are that either via lattice

diffusion effects unreacted DEB migrates toward the catalyst displacing reacted DEB, or that there exists a mechanism by which dissociated hydrogen atoms diffuse away from the catalyst through the heavily π - π bonded supramolecular structure of the organic crystal to react with unsaturated C-C bonds. At present however little experimental evidence exists to support either theory. Due to this uncertainty, kinetic modeling of getter performance has leaned heavily on the use of empirical kinetic expressions without fundamental mechanistic underpinnings. Additionally, aside from Pri-Bar's work in 2006 there has been no attention given to reaction product speciation in these systems, with all kinetic modeling efforts expressing the reaction in terms of conversion α (the extent of theoretical uptake assuming 8H/DEB). It has been observed experimentally that a complex mix of reaction products are present in the organic matrix over the course of the reaction which may be exerting influence on the observed kinetics. Thus, it is hypothesized in the report *Kinetic Modeling of Intermediate Reaction Product Formation in DEB based Hydrogen Getters* that insight into the reaction mechanism may be gained by understanding and modeling the evolution of reaction products in the getter system over the course of the reaction.

CHAPTER 2

GRAVIMETRIC BASED PERFORMANCE EVALUATION OF DEB HYDROGEN GETTERS

INTRODUCTION

Sealed environments containing radioactive materials have been found to generate hydrogen gas from radiation-induced hydrolysis of water and organics present inside the container [2]. As hydrogen accumulation is known to lead to embrittlement of metals and alloys, this can have deleterious impacts on the structural materials and electrical components of sealed radioactive-containing environments. In order to alleviate these risks, hydrogen getter materials are introduced into the sealed container to irreversibly react generated hydrogen gas, by saturating solid organic molecules. In particular, one organic hydrogen getter formulation used in the DOE complex is that composed of 1,4-bis(phenylethynyl) benzene (DEB) mixed with carbon-supported Pd catalyst (Pd/C). The hydrogenation of the DEB molecule occurs through a complex mechanism that could result in various hydrogenated products (Fig. 2).

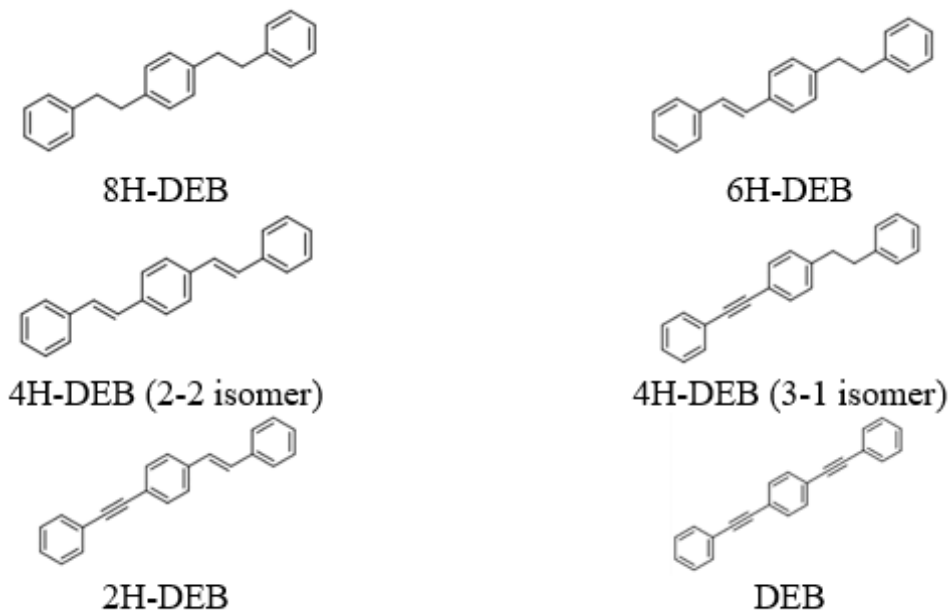


Figure 2. Molecular structures of DEB hydrogenation reaction products and isomers.

A particular system which employs hydrogen getters is the Transuranic Package Transporter (TRUPACT)-II waste container [4]. For the TRUPACT-II system, the Nuclear Regulatory Council (NRC) has imposed upper safety bounds of 5% v/v hydrogen as the maximum allowable concentration. Following this guidance, the NRC has listed a number of considerations to take into account related to the use of hydrogen getters for transuranic waste sealed containers. These considerations include hydrogen getter capacity, getter performance under different operating pressures, effects of poisons on getter performance, best location considering stratification of gasses, as well as temperature and humidity effects. Kinetic measurements of these hydrogen getter materials have been used as a means to evaluate their performance under the different conditions that need to be considered according to the NRC. This kinetic analysis can provide valuable information regarding specific reaction rates and sorption capacity, which is critical to identify required hydrogen getter quantities, their placement, as well as to model and predict performance of new hydrogen getter systems. Historically, performance analysis of these systems has been conducted manometrically in batch-type reactors [4] [9] [12]. However, while these reactors have been suitable for interrogating hydrogen uptake in pure gas environments, they are difficult to adapt to dilute, mixed gas environments at low partial pressures of interest (below 1Torr). In order to address the challenges associated with mixed gas environments, a custom sorption system needs to be designed and implemented in order to more accurately evaluate hydrogen getter performance under process-relevant conditions.

In this work, we describe the design and operation of a magnetic suspension balance (MSB)-based gravimetric sorption system for evaluating the performance of the DEB-Pd/C hydrogen getter. The designed MSB system has a notable advantage in that it can maintain

an isobaric reaction environment by constantly flowing gas while the pressure is being maintained by an upstream flow control valve and a downstream turbo pump for the case of pure gas experiments, or via an upstream mass flow controller and a downstream control valve and dual-diaphragm pump for the case of mixed gas experiments. Our results will show that our custom-design system facilitates isobaric reaction conditions over the wide pressure range of 1mTorr to 1000Torr, while also permitting kinetic evaluation in dilute mixed gas environments. The simultaneous control of mixed gases and partial pressures is critical to the understanding and more suitable evaluation of hydrogen getter performance at system-relevant conditions. Further, experimental considerations for the evaluation of the adequate baseline at relevant pressure and gas environment (pure vs. mixed gas) are investigated. We believe that our work reported here showcases both the unique advantages of the experimental apparatus as well as demonstrates the necessity for mixed gas performance analysis of getter systems which may exhibit diffusion limited uptake (e.g., assemblies and getter impregnated platforms).

MATERIALS

The hydrogen getter materials studied in this work were obtained from the Kansas City National Security Campus (KCNSC). These materials consist of cylindrical getter pellets (lot x201) comprised of 75wt% 1,4 bis(phenylethynyl) benzene (DEB) and 25wt% Pd/C catalyst. The Pd/C catalyst consists of 5wt% Pd supported on activated carbon. The DEB organic molecule is capable of reacting with 1-4 mols of H₂/mol DEB, producing various hydrogenation products as shown in Figure 2. The cylindrical pellet dimensions were approximately 3.7mm (L) by 3.2mm (D), with each pellet weighing approximately 30 mg. Additionally, getter pellet mini-assemblies were investigated to interrogate mass transfer

limitations imposed by the containment structure. These mini-assemblies (Fig. 3), also obtained from KCNSC, consisted of the same getter pellets (x201) contained in a fluorinated ethylene-propylene (FEP) tube. The pellets were secured with end plugs, largely restricting gas admission to the 254 μ m diameter center hole (the permeability of the relatively thick FEP tube at these conditions has been previously measured and confirmed to be negligible) [14]. All getter materials were stored in an inert enclosure prior to performance evaluation.

THE MAGNETIC SUSPENSION BALANCE SYSTEM

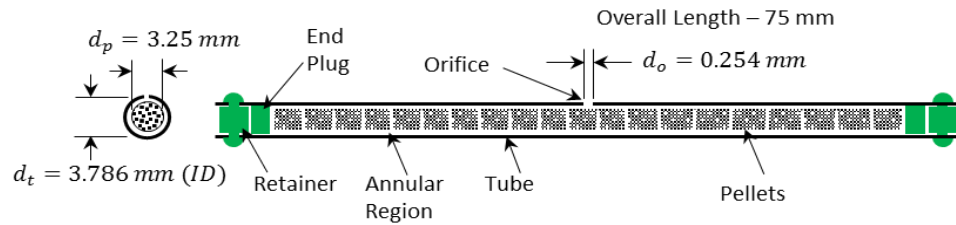


Figure 3. Getter pellet mini-assembly with system component pedigree, obtained from KCNSC, consisting of 20 getter pellets confined in a FEP tubing with a 254 μ m diameter center hole, mini-assembly OD=4.14mm

Typical deployment conditions for hydrogen getter systems include sealed containers backfilled with inert gas in which hydrogen gas is slowly evolved from radioactive nuclear materials therein. In order to more properly evaluate process-relevant conditions, such as mixed gases and low partial pressure hydrogen, a custom MSB-based sorption system has been designed and evaluated for gravimetric hydrogen uptake experiments at isobaric conditions (Fig. 4). The MSB system magnetically suspends the sample holder assembly and measures the mass with an external electromagnet attached to the microbalance. This design allows hermetic separation of the balance from the reaction chamber, enabling gravimetric sorption experiments over a wide range of pressures, temperatures, and also enabling the utilization of toxic or corrosive reaction gasses such as

hydrogen and CO. An initial balance zeroing and zeroing throughout each experiment are always conducted as this zero-point (ZP) can drift over the course of an experiment due to changes to laboratory conditions including temperature, pressure, and humidity. The MSB system utilizes an automatic sample decoupling feature (ASD) to correct for any observed drift. The ASD feature periodically decouples the sample from the internal magnet such that only the weight of the free-floating magnet is measured, termed here as ZP. After the ZP is recorded, the magnet is raised, recoupling the sample to the levitating magnet, which is referred to as the measuring point (MP). For our experiments, the ZP is measured every 5 minutes and an OriginPro® script is utilized to extract the ZP points from the data set for background subtraction, yielding a highly stable sample mass over the duration of the experiment as shown in Fig. 5. The construction of this system is designed to facilitate both pure and mixed gas experiments over pressures ranging from 1mTorr to 1000Torr with a flowthrough reaction chamber in which isobaric conditions are maintained via an upstream flow control valve and a downstream turbo or a dual-diaphragm pump, depending on the target pressure. For all studies, the system was maintained at a constant temperature of 23°C using a thermostatic sample chamber and magnetic coupling assembly. Purity of the H₂ and He gases used was 99.999%. Additionally, the MSB gravimetric sorption system was integrated into a commercial inert glovebox to preserve sample integrity, facilitating getter material loading and removal from the sorption system without exposing the material to atmospheric contaminants (PureLab HE 2GB, Inert Technology).

Prior to H₂ exposure, the samples are pre-treated in an inert enclosure by heating to ca. 65°C for 24 hours for removal of any physisorbed water or any other adsorbed atmospheric contaminants. Following this pre-treatment, the hydrogen getters were

introduced into the MSB system and evacuated with an unrestricted turbo pump (hiCube 80, Pfeiffer) for an additional 24 hours (Ion gauge [355 Micro Ion, Granville Phillips], pressure ca. $2\mu\text{Torr}$ after 24 hours) to stabilize the system and remove any additional loosely sorbed water that may have accumulated during the brief exposure window during sample incorporation. Lastly, the system was brought to the desired experimental pressure and allowed to react to the desired reaction extent, e.g., completion.

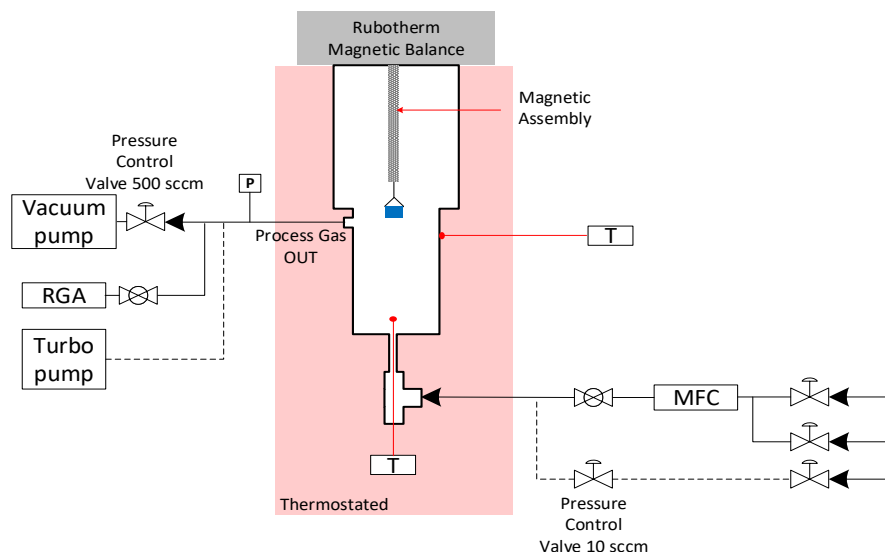


Figure 4. MSB System Schematic. Suspension balance and sample chamber are temperature-controlled using a recirculating chiller. For low pressure experiments, the reaction chamber pressure is controlled using a control valve along with a turbo pump. For high pressure or mixed gas experiments, control is achieved from a mass flow controller, a control valve, and the dual diaphragm vacuum pump.

DISCUSSION

Stability of Gravimetric Measurements in Vacuum

One concern often raised with the increased hydrogenation of organic molecules, specifically regarding gravimetric sorption measurements of DEB-based hydrogen getters, is the intuition that increased hydrogenation should lead to increased volatility of DEB's hydrogenated reaction products [9] [15]. However, a recent study published by Sharma et al. revealed that even the most volatile hydrogenated DEB product, 8H-DEB, showed

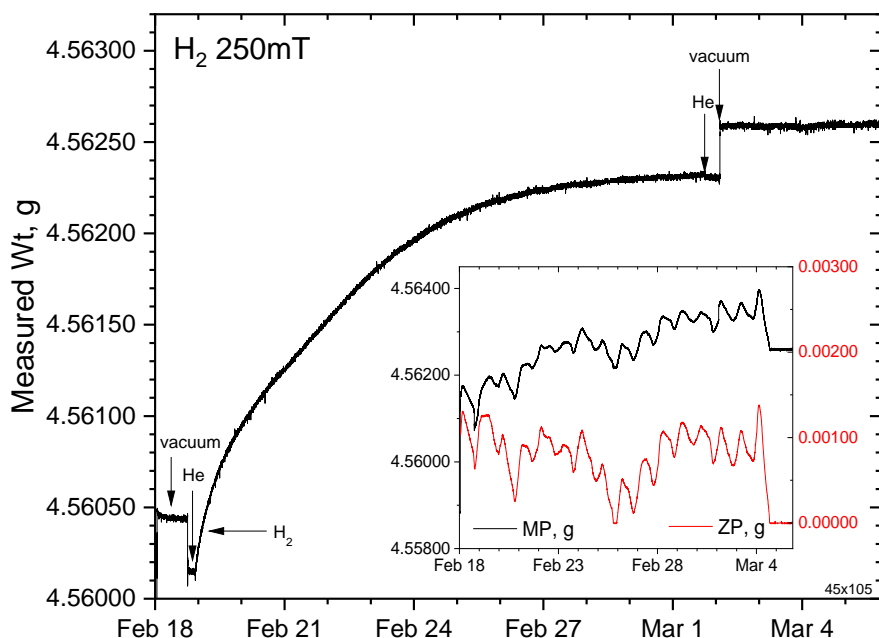


Figure 5. Pure gas 250mT MSB gravimetric experiment. Inset. Drift in background and measured point data, its subtraction yields the precise gravimetric uptake curve shown in the main figure. A stable weight over the course of 4 days in vacuum is for the fully reacted DEB-based getter pellet.

microTorr level equilibrium vapor pressures for temperatures as high as 353 K [10]. Nevertheless, to further interrogate this phenomenon in our MSB gravimetric system, 4 getter pellets were reacted to complete conversion and then evacuated using an unrestricted turbo pump for several days (Fig. 5). As seen in Fig. 5, the sample weight of the hydrogenated DEB under vacuum conditions is stable over the course of 4 days at 23°C, indicating that the volatility of a sample comprising a high concentration of the highest vapor pressure reaction product, 8H-DEB, is not sufficient to cause measurable weight loss over the course of the ambient temperature experiment thereby corroborating the findings reported by Sharma et al. These results indicate that our gravimetric-based experiments for performance analysis should not be convoluted by mass loss even at elevated temperatures mirroring the upper bound of anticipated environmental conditions (ca. 50°C).

Establishment of Relevant Analysis Pressure for Performance Evaluation

As hydrogen is slowly evolved in the sealed environments in which getter systems operate, the pressure range of interest is constrained to low hydrogen partial pressures, i.e. <1Torr. While we understand that isobaric experiments are required for a range of pressures and temperatures to ascertain rate laws and reaction mechanisms, the determination of the most relevant baseline pressure for evaluating the performance of new hydrogen getter systems is critical. With this purpose, hydrogen uptake experiments were

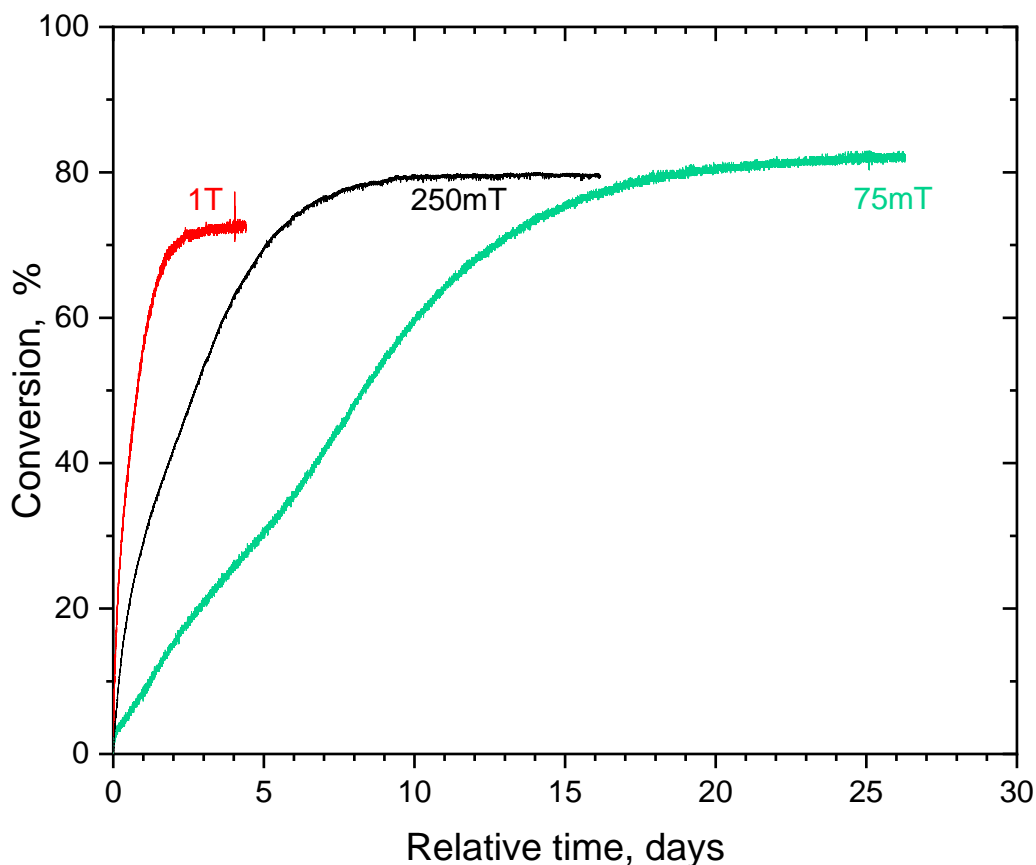


Figure 6. Conversion versus time data for x201 getter pellets in pure gas environments. Samples reacted at various pressures for establishment of appropriate baseline evaluation pressure.

conducted across a range of low pressures of pure hydrogen gas (75mTorr to 1Torr) to better understand hydrogen getter performance at relevant pressures with respect to both kinetics and capacity (Fig. 6). As can be observed from fig. 6, at 75 and 250 mTorr, a similar full conversion of $82\pm 1\%$ and $79\pm 3\%$ respectively was reached, however, kinetics for the 75mTorr system were much slower, reaching full conversion only after 16 days, vs. 7 days for the 250 mTorr system. A different behavior was observed at 1Torr, showing much faster kinetics but with an ultimate conversion value of only $72\pm 1\%$. The exact mechanism of this observed difference in hydrogen uptake capacity is currently being explored, but we hypothesize that it might be due to a difference in self-diffusivity or permeability of hydrogenated DEB products. Pri-Bar et al. showed that the distribution of reaction products varies as a function of reaction pressure [8]. In their work, the authors investigated the reaction product distribution of DEB-Pd/C hydrogen getters reacted to 10% of theoretical uptake capacity at three different reaction pressures (0.1, 12, and 150Torr). Their results showed that lower pressures favor 4H-DEB whereas higher pressures favor the fully hydrogenated 8H-DEB. Given that each system was reacted to the same conversion extent, their results indicate that lower pressures exhibit a more spatially diffuse reaction whereas higher pressures show a dense reaction front near Pd particles. This difference in both reaction products and their spatial distribution is hypothesized to result in a diffusion limited condition due to the disparate materials properties (eg. crystal packing density and C-H dipole interaction) of 4H relative to 8HDEB [sharma] which could prohibit self-diffusion or hydrogen mobility. Further investigation of this phenomena is currently underway utilizing materials characterization techniques such as X-ray diffraction (XRD) and hydrogen nuclear magnetic resonance (H-NMR) spectroscopy to

examine reaction products of partially and fully reacted samples as correlated to reaction pressure. The goal is to identify the relationship between kinetics/conversion and reaction product speciation. Pending this analysis, our current studies indicate that pressures below 1Torr are more optimal for obtaining greater ultimate conversion values in getter system performance evaluations. Thus, in order to facilitate experimental throughput, while also obtaining use relevant and reproducible performance information, 250mT was selected as the baseline pressure for hydrogen uptake and sorption analyses.

Mitigation of Boundary Layer Effects in Mixed Gas Sorption Analysis

Heterogeneous reactions in dilute gas streams have the potential to become diffusion limited. This occurs when the rate of reaction exceeds the rate of convective mass transfer to the catalyst surface. The net result of this phenomenon is the formation of a concentration boundary layer which limits the rate of the reaction to the rate of diffusion through the stagnant boundary layer. The boundary layer thickness decreases with increases in the bulk gas velocity and the rate of convective mass transfer. Thus, increasing the experimental volumetric gas flowrate can be utilized to alleviate diffusive mass transfer limitations. Thus, sorption analysis on different sample sizes as a function of flow rate were performed with results shown in Fig. 7. A flowrate of 100sccm of 1000ppm H₂ equates to a rate of 52,560 cm³/y of H₂ flow which is 1.5x the maximum rate achievable for 0.6g (20 pellets) of getter. However, as can be seen from fig. 7 (inset), 20 getter pellets under a flowrate of 100sccm appears to be initially diffusion limited with a relatively constant reaction rate until about 30% conversion which lies in contrast to pure gas experiments which show a steadily decreasing reaction rate over this range. As mentioned when comparing the hydrogen flowrate (100sccm@1000ppm H₂ = 52,560cm³ H₂/year) to the

anticipated initial reaction rate ($\sim 60,000 \text{ cm}^3 \text{ H}_2 \text{ year}^{-1} \text{ g}^{-1}$) this indicates a H_2 surplus ratio of 1.5 (H_2 flow rate/max H_2 reaction rate), decreasing the sample size to 2 pellets or 4 pellets at 100sccm yields a surplus ratios of 14.6 and 7.3 respectively which both result in identical kinetics. Furthermore, increasing the flow rate to 290sccm for 20 pellets (surplus ratio of 4.2) also yields identical results. This demonstrates that boundary layer impacts can be effectively mitigated by increasing the flow rate of hydrogen relative to the anticipated maximum reaction rate for a given quantity of getter material. Further, fig. 8 shows a comparison between mixed gas performance (1000ppm H_2/He) to that of pure H_2

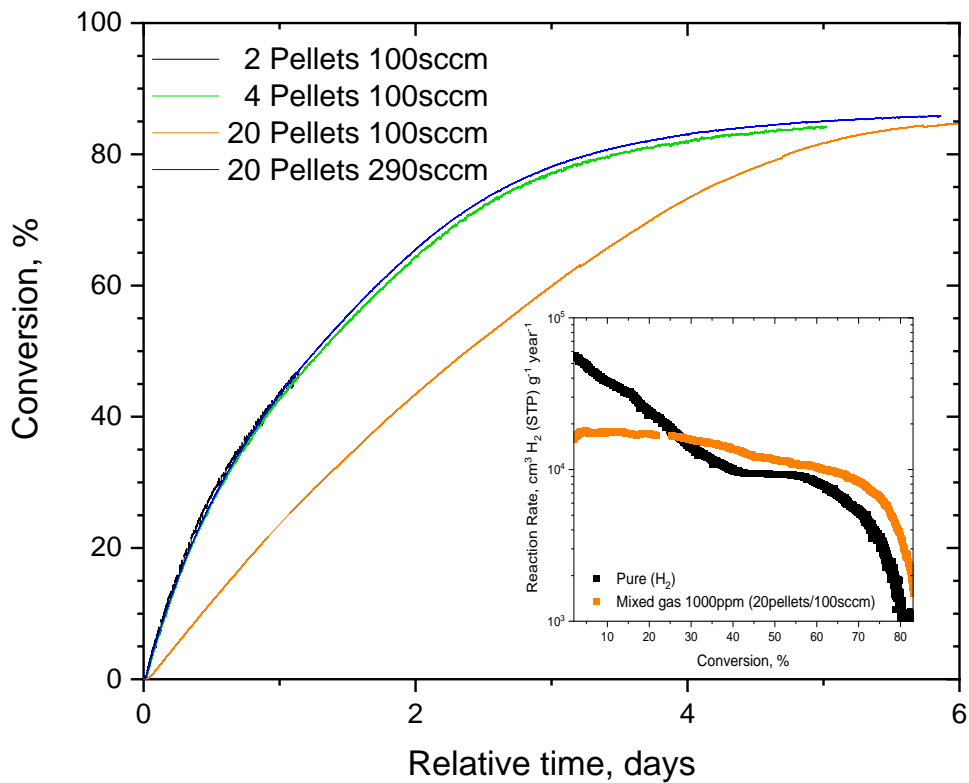


Figure 7. Example of boundary layer impacts on measured kinetics in mixed gas environments. Experiments conducted utilizing 1000ppm H_2 in He at 250T absolute pressure. Inset shows reaction rate in boundary layer diffusion limited scenario compared to kinetics of pure gas experiment.

gas experiments. As can be seen the performance of getter material in mixed gas environments is statistically identical to that of pure gas experiments. This result confirms

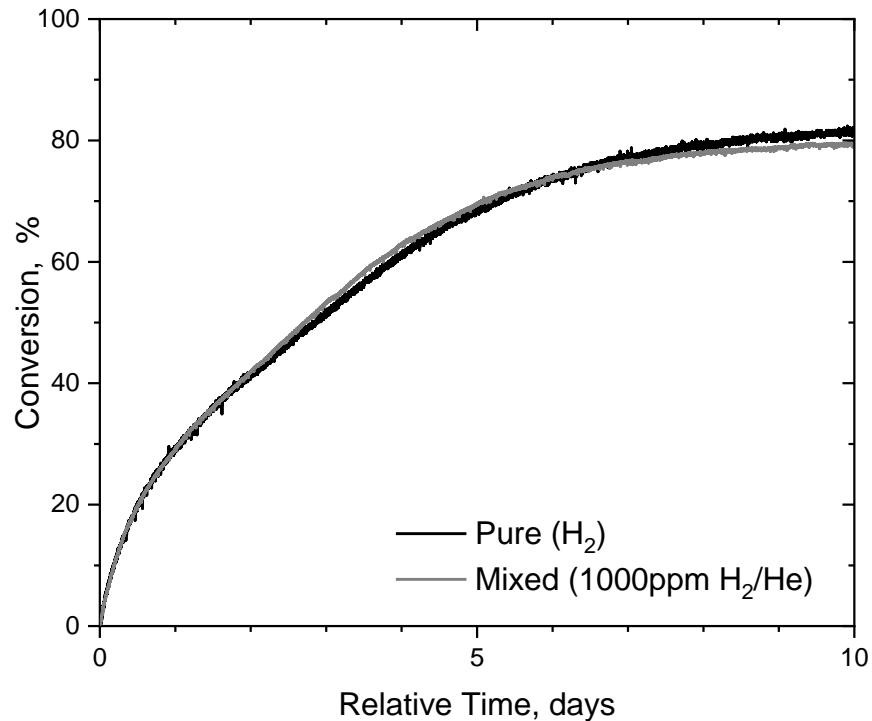


Figure 8. Performance Analysis of mixed gas versus pure gas experiments on loose x201 pellets at 250mT hydrogen pressure. Mixed gas utilizes 1000ppm H₂/He. As can be seen reaction rates are negligibly impacted by boundary layer effects with adequate mixed gas flow rate

that the convective mass transfer used in the mixed gas experiment (100sccm/4-pellets) is adequate for interrogating the specific reaction rate while mitigating boundary layer effects in a loose or unconstrained sample thereby enabling evaluation of idealized getter material performance as a function of both absolute and partial hydrogen pressure.

Comparison of Gravimetric to Manometric Analysis Results

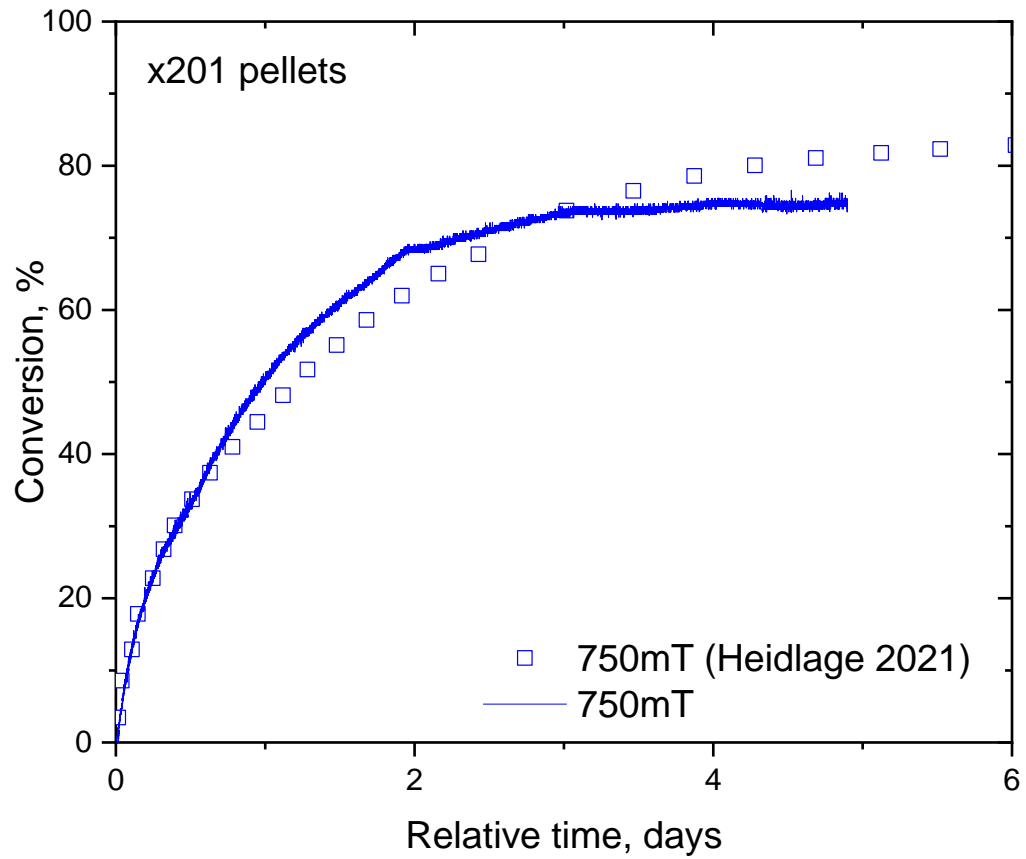


Figure 9. Comparison of gravimetric sorption results to manometric results published in literature on x201 getter materials 750mT pure hydrogen

Results obtained using our gravimetric based method were compared to published results in literature. Heidlage et. al. utilized a manometric-based system to interrogate the performance of identical x201 getter pellets under *pseudo-isobaric* conditions at 750mT [16]. As can be seen in figure 9, excellent agreement was found with regards to reaction kinetics for the first 40% of the reaction. While slight differences exist in the later stage kinetics and ultimate conversion the agreement between the two methods highlights both the consistency in performance analysis data as well as the complementary nature of these

two disparate methods of analysis for pure gas evaluations in ultra-low-pressure environments.

Mass Transfer Limitations in Mixed Gas Environments

The primary objective for conducting mixed gas analysis is to interrogate getter systems which may intrinsically possess significant mass transfer limitations, for example, containment structures with flow restricting orifices or novel getter systems which utilize selectively permeable membrane materials or microporous polymers as getter encapsulants. For this investigation, model getter system assemblies (schematic depicted in fig. 3) were evaluated for hydrogen uptake in both pure and mixed gas (H₂/He) environments. Performance evaluation of the assembly in pure hydrogen at 250mTorr showed similar performance to that of the same getter materials without the containment structure (pellets), as seen in Fig. 10. This shows that in the pure gas environment, the reaction rate of the hydrogen getter is not fast enough to exhibit an appreciable absolute pressure differential across the mini-assembly. This finding is supported by molecular flow calculations, applicable in the pure gas environment at a pressure of 250mTorr, in which the mean free path (λ , Eq. 1) is approximately 332 μ m. Compared to the 254 μ m diameter of the mini-assembly orifice, yields a Knudsen number of 1.3 (Eq. 2), meaning that at these conditions, the hydrogen gas is not governed by viscous forces but rather free molecular flow. Calculating molecular impingement (ϕ , Eq. 3) upon the orifice based on a Maxwell-Boltzmann distribution shows that the rate of molecular impingement is 3.6E20 cm⁻² s⁻¹, normalized to the orifice diameter, this corresponds to 215,000cm³ H₂ (STP) y⁻¹ or 6x greater than the maximum rate of reaction seen for 0.6g of loose getter pellets (36,000cm³

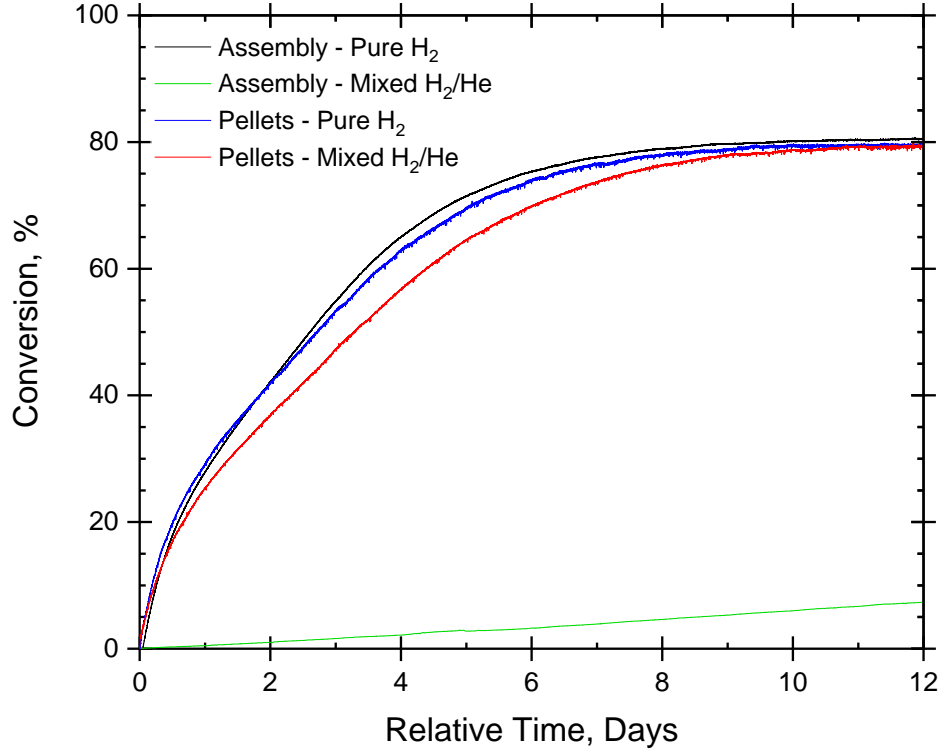


Figure 10. Pure and mixed gas experiments on loose x201 getter pellets as well as x201 getter pellet mini-assemblies. Results reveal orders of magnitude reduction in hydrogen uptake for mini-assemblies under mixed gas environments due to binary gas diffusion limitations

H₂ (STP) y⁻¹). This excess of random molecular flux into the mini-assembly indicates that this system will not show mass transfer limitations in a 250mT pure gas environment.

$$\text{Equation 1: } \lambda = \frac{k_B T}{\sqrt{2} \pi d^2 P}$$

$$\text{Equation 2: } Kn = \frac{\lambda}{L}$$

$$\text{Equation 3: } \varphi = \frac{1}{4} n \sqrt{\frac{8 k_B T}{\pi m}}$$

As shown in fig. 10, the performance of loose getter pellets in mixed gas environments was similar to that observed to that in pure gas environments. However,

getter pellet mini-assemblies were observed to be substantially impacted by the mixed gas reaction environment with the mini-assembly exhibiting a constant reaction rate 1-2 orders of magnitude lower than the uncontained material. Given that the Knudsen number is $1.3E-3$ in the mixed gas scenario, mass transport is governed by viscous forces and the flow is treated as a continuum. As demonstrated previously at 290sccm the ratio of hydrogen flow to the predicted maximum reaction rate for 0.6g of getter (4.2) indicates that ample hydrogen is supplied to the system to facilitate the reaction. Assuming a hydrogen gas concentration at the mini-assembly surface equivalent to the bulk concentration (1000ppm) and a hydrogen concentration of zero at the getter surface, calculation of the molecular flux using Fick's law (Eq. 4) and Chapman-Enskog theory (Eq. 5) for the binary diffusion coefficient yields a hydrogen flux of $542 \text{ cm}^3(\text{STP})/\text{year}$ compared to a measured value of $351 \text{ cm}^3(\text{STP})/\text{year}$ for the mini-assembly reaction rate. These results are in agreement given that the 1D diffusion calculation assumes a maximum concentration gradient between the bulk gas and getter surface.. This agreement between the measured reaction rate and the calculated binary diffusion limited mass flux is indicative that the getter mini-assembly containment structure is likely imposing a significant mass transfer limitation on hydrogen uptake the impact of which can be quantified by analysis of getter systems in dilute mixed gas reaction environments.

$$\text{Equation 4: } J_{H_2} = -D_{H_2He} \frac{dC_{H_2}}{dx}$$

$$\text{Equation 5: } D_{H_2He} = \sqrt{\frac{1}{M_{H_2}} + \frac{1}{M_{He} P \sigma_{H_2He}^2 \Omega_{H_2He}^{\{1,1\}*}(T^*)}} \cdot 0.0018583 T^{3/2}$$

CONCLUSION

The design and operation of a MSB-based gravimetric sorption system for performance evaluation of DEB-based hydrogen getters in both pure and mixed gas environments has been demonstrated. Our experimental results revealed that pure gas performance data is in alignment with pseudo-isobaric manometric methods reported by others, indicating that gravimetric sorption analysis provides a valuable complementary avenue for analysis of hydrogen getter systems with the distinct advantage of being able to analyze performance in highly dilute mixed gas environments.

Our interrogation of hydrogen getter performance as a function of reaction pressure revealed that high pressure (≥ 1 Torr) performance analysis of getter materials does not provide reliable information representative of the getter material behavior and performance characteristics at the lower hydrogen partial pressures more commonly encountered in sealed environments. This is demonstrated by the reduced conversion capacity observed at 1Torr compared to the 75mTorr and 250mTorr experiments. Furthermore, the necessity of conducting dilute mixed gas performance evaluation on getter materials has been demonstrated, by performance analysis of model getter pellet mini-assemblies which restricts gas admission to the 254 μ m center orifice. Our experiments showed that this system has exhibited orders of magnitude lower gettering performance in mixed gas evaluation compared to pure hydrogen gas environments. This result appears to be due to experiments being governed by free molecular flow (Knudsen ~ 1) at low pure hydrogen gas pressures, which calculations reveal does not impose a mass transfer limitation. While, on the other hand, dilute (1000ppm) mixed gas experiments (Knudsen ~ 0.001) are governed by continuum flow and are significantly diffusion limited with molecular flux

calculated via Fick's law and Chapman-Enskog theory yielding values in alignment with the measured hydrogen uptake.

The significant diffusion limitation shown in the model mini-assembly system, which possesses a macroscopic (0.254mm) scale orifice, indicates that specific attention should be paid to performance analysis of materials which could exhibit similar diffusive limited performance. This phenomenon is of particular importance in the design of getter impregnated platforms which utilize selectively permeable membrane materials or microporous polymers as getter encapsulants, as these systems would be similarly susceptible to diffusion limitations, the impact of which can be observed and quantified via dilute mixed gas performance analysis. Given the demonstrated necessity of conducting performance analysis in dilute mixed gas environments, the MSB based gravimetric sorption system described in this report possesses a distinct advantage in its ability to obtain precise uptake data in isobaric dilute mixed gas streams approaching single ppm H₂ concentration levels.

CHAPTER 3.

KINETIC MODELING OF INTERMEDIATE REACTION PRODUCT FORMATION IN DEB-BASED HYDROGEN GETTERS

INTRODUCTION

Hydrogen getters, which are materials capable of irreversibly binding trace hydrogen gas (H_2) to prevent accumulation, are commonly used in high vacuum applications and sealed systems susceptible to H_2 evolution. Unsaturated organic molecules such as 1,4-bis(phenylethynyl)benzene (DEB) are excellent H_2 getters due to their fast and irreversible reaction with dissociated hydrogen. In the DEB-based H_2 getter system, shown in Figure 11, DEB is mixed with a high surface area palladium/carbon (Pd/C) catalyst to enable molecular H_2 dissociation. After H_2 dissociation, H atoms migrate from the Pd surface to the carbon support via surface diffusion and spillover effects enabling reaction with DEB molecules [9]. However, the mechanism facilitating hydrogenation of DEB molecules not in contact with the catalyst surface is still poorly understood. This is where the peculiarity of this getter system arises; in conventional catalysts which operate in a solution or gas phase the reactant is in molecular form and its mobility enables catalyst-reactant collisions, however in a solid system there is no such molecular mobility. Thus alternative hypotheses have evolved to explain the nature of the reaction between the solid reactant and dispersed catalyst. The two most common hypotheses are lattice diffusion within the organic crystal with unreacted DEB displacing hydrogenated DEB at the catalyst surface [15] [12] or alternatively atomic hydrogen diffusion through the supramolecular crystal structure of DEB enabling hydrogen to react with DEB away from the catalyst surface [8] [17].

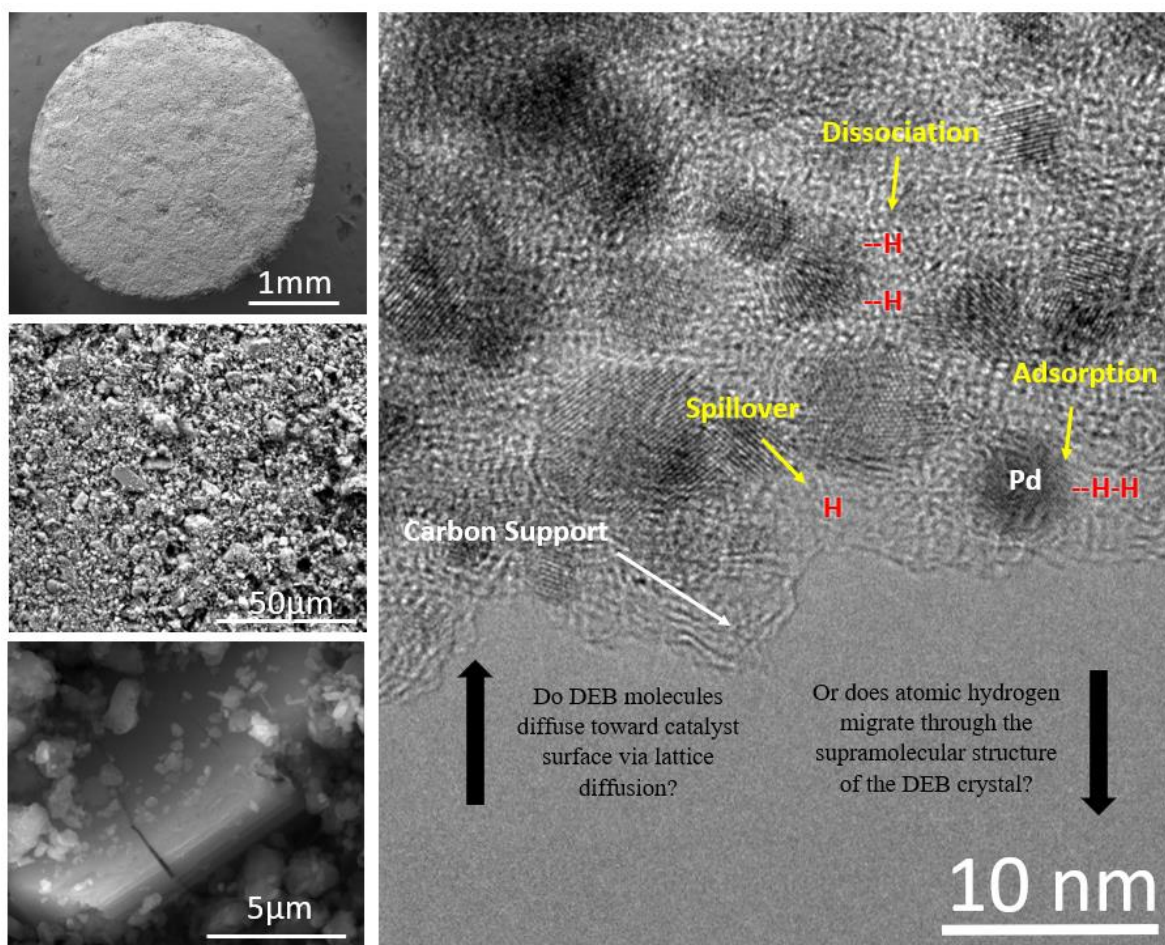


Figure 11. Top and Middle Left: SEM Images of getter pellet Bottom Left: SEM image of large DEB crystal present in getter material Right: TEM image of Pd/C catalyst

Hydrogen uptake analysis measured at high pressure has demonstrated that these materials are capable of reacting to up to 50% of theoretical capacity in under 30 minutes [14]. Given the large DEB crystals present in these materials (Fig. 11 Bottom Left) this seems to suggest an exceptionally rapid rate of crystal lattice diffusion with unreacted DEB molecules diffusing several microns in a matter of minutes. This result suggests that another mechanism may be active in the getter system enabling the hydrogenation of DEB molecules away from the catalyst surface. An alternative theory behind this reaction mechanism was posited by Pri-Bar et al. (2000). In this work, Pri-Bar explains the solid

phase catalyzed hydrogenation as being facilitated by the supramolecular chemistry of the organic crystal material. DEB and other phenylalkynyl derivatives have the capacity to form self-assembled molecular stacks due to strong π - π interaction between adjacent phenyl rings, which is observable in their highly crystalline structure seen in x-ray diffraction (XRD). Pri-Bar analyzed the contribution of molecular structure toward solid phase hydrogenation by comparing the reaction rates of similar organic molecules, particularly diphenylacetylene (DPA) and *trans*-stilbene (TS) (Fig. 12), mixed with Pd/C catalyst. His results revealed that getter materials made with DPA crystals were capable of rapid hydrogenation to 95.2% of theoretical capacity whereas the use of *trans*-stilbene (TS) at the same 16:1 ratio of Organic: Pd results in a system that reacts very sluggishly and only reaches hydrogenation levels comparable to a monolayer coating (~4% of theoretical capacity).

Given the uncertainty in the mechanism of hydrogen gettering with solid DEB-Pd/C materials, kinetic analysis is typically conducted using modified semi-empirical expressions. While these semi-empirical expressions have proven acceptable for predicting

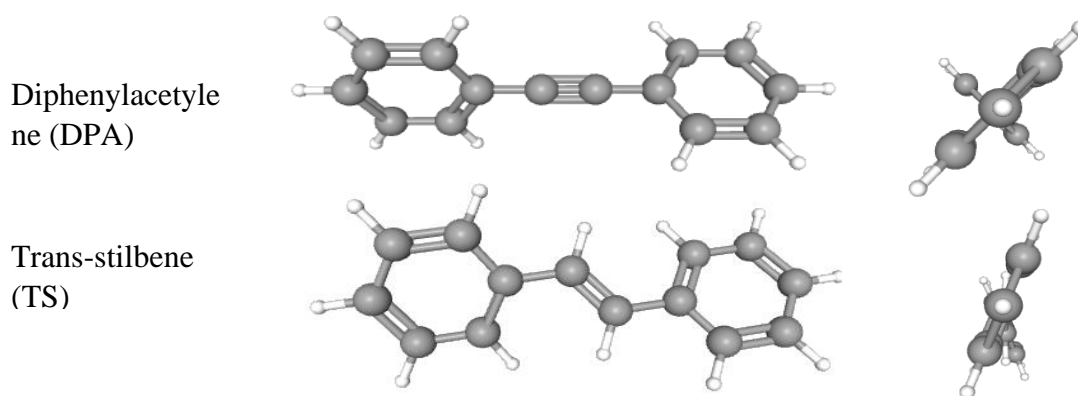


Figure 12. 3D ball-and-stick molecules of diphenylacetylene (DPA) and *trans*-stilbene (TS) used for the investigation of supramolecular structure contribution on their solid-phase catalyzed hydrogenation. Structure of DPA is conducive toward T-shaped π - π stacking of adjacent phenyl rings.

kinetics within narrow parameter sets, the equations lack mechanistic underpinnings and, frequently rely on multiple equations to cover the full range of reaction conditions (pressure and conversion extent) relevant to these type of systems [9] [4]. Additionally, it should be noted that thus far, all of the equations developed for modeling DEB hydrogenation kinetics, only model the reaction in terms of *conversion* extent and not in terms of *concentrations* of DEB and its intermediate and final hydrogenation products (fig. 13). Thus, in this work, we present kinetic modeling of individual reaction products using equations developed from fundamental rate law expressions, which may prove to be an invaluable tool for bridging the gaps in fundamental understanding of reaction mechanisms as well as aid in explaining phenomena observed in experimental kinetic data.

MODEL DEVELOPMENT

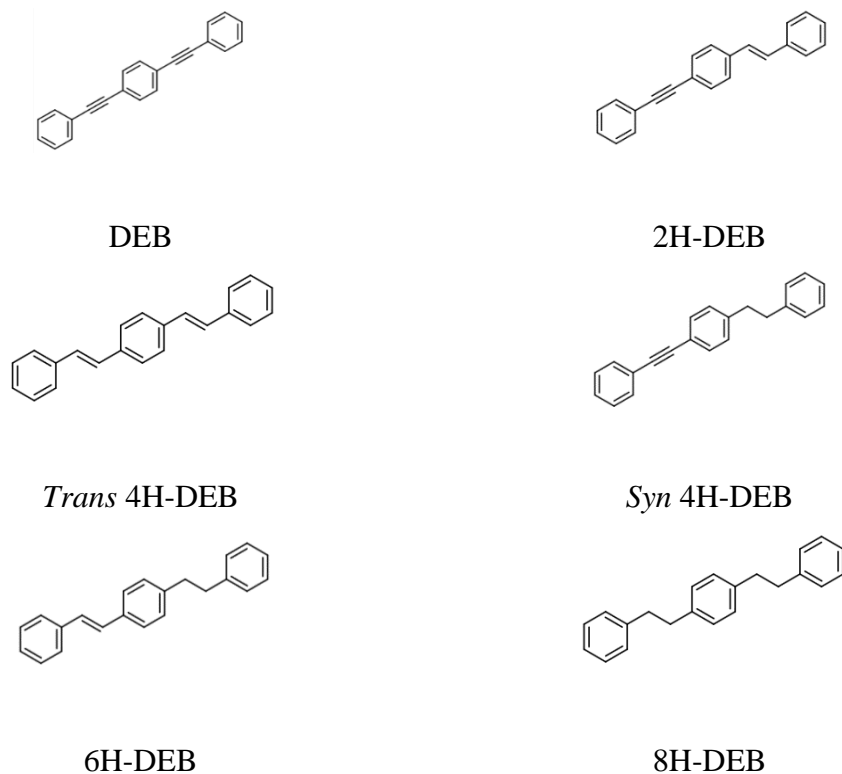


Figure 13. Molecular structures of DEB and hydrogenated products

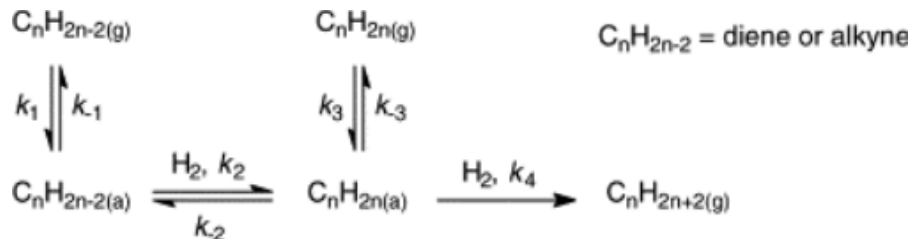


Figure 14. Rake mechanism typically used to describe hydrogenation of alkynes or dienes.

As observed from figure 13, hydrogenation of DEB occurs by hydrogen addition to the DEB alkyne and subsequently alkene moieties. Traditionally, this is thought of as a stepwise 2H addition, analogous to the rake mechanism used to describe acetylene hydrogenation on supported Pd catalysts [18] (Fig. 14). The rake mechanism involves a series of hydrogenation steps with reversible adsorption/desorption reactions at each step. While this mechanism has been used for two-phase heterogeneous catalysis, the DEB system is a solid-phase getter with products and reactants considerably less mobile. Given this lack of mobility, the gas-phase adsorption/desorption steps of the rake model can be ignored.

With regards to the reversibility of hydrogenation, experimentally it has been observed that getters reacted to completion do not show mass loss upon removal of hydrogen. This indicates that the reverse reaction is either not observed or has negligible influence on reaction kinetics and therefore is not considered in this analysis.

Additionally, in the solid state reaction scenario, where intermediate alkenes are not desorbed, one has to consider the potential of a direct reduction of alkynes to alkanes on Pd supported catalysts, as demonstrated by Al-Ammar et al. [19]. In this study authors

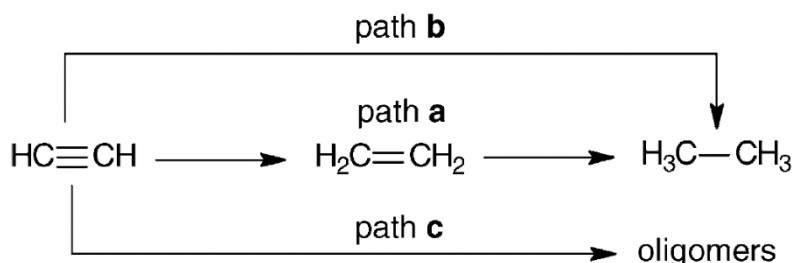


Figure 15. Competing paths in acetylene hydrogenation

observed that distinct paths exist for acetylene hydrogenation over Pd catalysts. Path A follows a multi step sequence of 1) acetylene adsorption 2) hydrogenation to ethylene 3) desorption (note: binding energy between ethylene/Pd is lower compared to acetylene/Pd [20]) 4) re-adsorption of ethylene 5) hydrogenation to ethane. Alternatively, path B involves reactive adsorption of acetylene to produce multiply bound intermediates followed by direct hydrogenation to ethane. Given the numerous π orbitals present in unreacted DEB and its strong interaction with both active sites on the catalyst as well as the π cloud of the activated carbon support combined with the lack of mobility present in the solid system (desorption of intermediates is considerably less likely compared to gas or solution phase reactions) the possibility of path B (reactive adsorption and direct hydrogenation of triple bonded to single bonded carbons) needs to be considered in kinetic modeling. When considering the potential for both hydrogenation paths the overall reaction can be described as a *series-parallel* route of hydrogenation.

Thus, in order to develop fundamental rate equations for the individual species the series reaction (DEB \rightarrow 2H-DEB \rightarrow 4H-DEB \rightarrow 6H-DEB \rightarrow 8H-DEB) as well as the

parallel reactions of alkyne to alkane moieties (DEB \rightarrow 4H-DEB, 2H-DEB \rightarrow 6H-DEB & 4H-DEB \rightarrow 8H-DEB) are considered.

The series reduction of DEB proceeds as follows:



And the parallel direct hydrogenation of alkyne DEB to alkane DEB can be expressed as:



While the direct hydrogenation of the triple bond to single bonded carbon can only occur on DEB 2H-DEB and *syn* 4H-DEB, the lack of quantitative data on the *syn* and *trans* isomers of 4H-DEB stemming from the difficulty in separating these particular constituents from partially reacted samples, limits both the ability and utility of modeling the kinetics of this individual isomer. Thus, no distinction is made between *syn* 4H and *trans* 4H-DEB in the kinetic expressions developed in this work.

Developing rate expressions from stoichiometry yields an overall rate equation that is 4th order with respect to hydrogen. However, this has not been found to be the case in published studies [9] [4]. DEB getter materials are typically observed to exhibit kinetics with circa first order dependence on hydrogen for the initial (non-diffusion limited)

reaction. Thus, normalizing the individual reactions to be no greater than first order in hydrogen yields the following differential forms for DEB and its hydrogenation products

$$\frac{d[\text{DEB}]}{dt} = -k_{04}[\text{DEB}][\text{H}] - k_{02}[\text{DEB}][\text{H}]^{1/2} \quad [8]$$

$$\frac{d[2\text{HDEB}]}{dt} = k_{02}[\text{DEB}][\text{H}]^{1/2} - k_{22}[2\text{HDEB}][\text{H}]^{1/2} - k_{24}[\text{DEB}][\text{H}] \quad [9]$$

$$\frac{d[4\text{HDEB}]}{dt} = k_{04}[\text{DEB}][\text{H}] + k_{22}[2\text{HDEB}][\text{H}]^{1/2} - k_{42}[4\text{HDEB}][\text{H}]^{1/2} - k_{44}[4\text{HDEB}][\text{H}] \quad [10]$$

$$\frac{d[6\text{HDEB}]}{dt} = k_{42}[4\text{HDEB}][\text{H}]^{1/2} + k_{24}[\text{DEB}][\text{H}] - k_{62}[6\text{HDEB}][\text{H}]^{1/2} \quad [11]$$

$$\frac{d[8\text{HDEB}]}{dt} = k_{44}[4\text{HDEB}][\text{H}] + k_{62}[6\text{HDEB}][\text{H}]^{1/2} \quad [12]$$

With the overall rate of hydrogen uptake being the sum of the individual hydrogenation reactions:

$$\begin{aligned} \text{rate}_{\text{H}_2}(t) = & k_{02}[\text{DEB}][\text{H}]^{1/2} + 2k_{04}[\text{DEB}][\text{H}] + k_{22}[2\text{HDEB}][\text{H}]^{1/2} + \\ & k_{24}[2\text{HDEB}][\text{H}] + k_{42}[4\text{HDEB}][\text{H}]^{1/2} + 2k_{44}[4\text{HDEB}][\text{H}] + \\ & k_{62}[6\text{HDEB}][\text{H}]^{1/2} \end{aligned} \quad [13]$$

Also, the initial concentration of DEB is treated as 1 and hence the following equation applies

$$[\text{DEB}] + [2\text{HDEB}] + [4\text{HDEB}] + [6\text{HDEB}] + [8\text{HDEB}] = 1 \quad [14]$$

The coupled differential equations were solved numerically using the computational software (Wolfram Mathematica) with individual reaction constants determined by fitting the output to experimental data published by Pri-bar et. al at low

levels of conversion (up to 13%) and over pressures spanning three decades in magnitude [8].

RESULTS

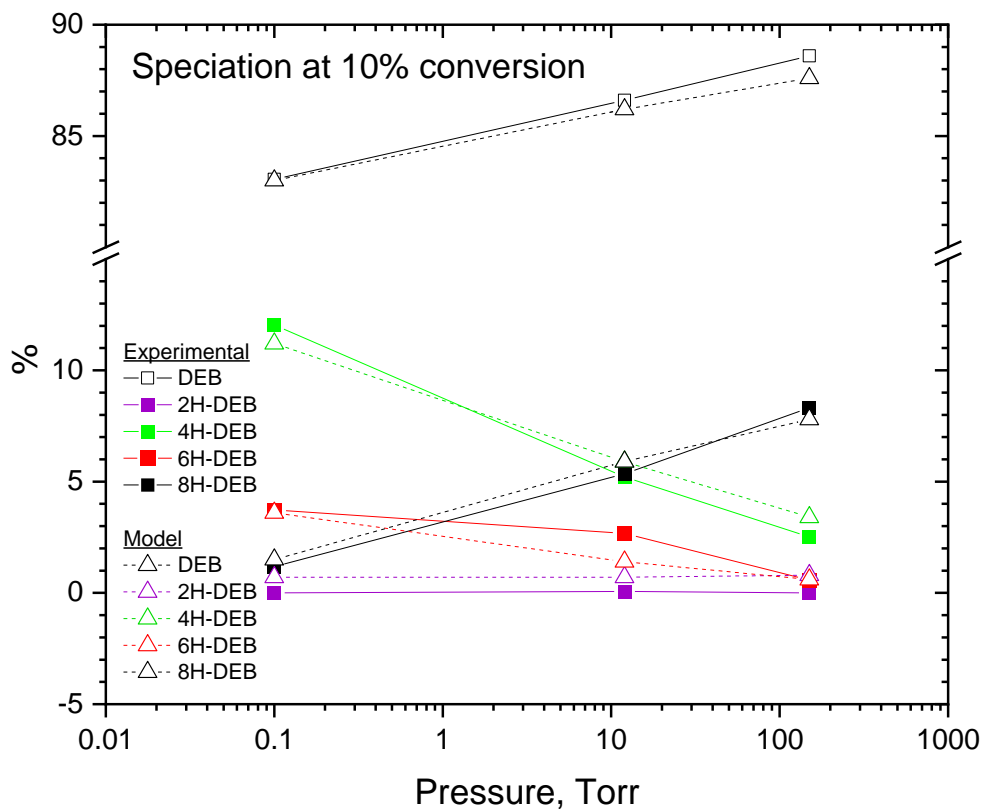


Figure 16. Comparison between experimental fit data and model prediction. Speciation of getter systems at 10% conversion as a function of hydrogen pressure.

The conversion of DEB into hydrogenated species predicted from the derived series of rate equations provides a good fit to the experimental data when comparing the speciation at 10% hydrogenation over a range of pressures spanning over three decades of magnitude (Fig. 16). The accuracy in the predicted speciation using the equations developed from this hypothesized mechanistic framework are found to be on average within $\pm 0.6\%$ absolute deviation from experimental data.

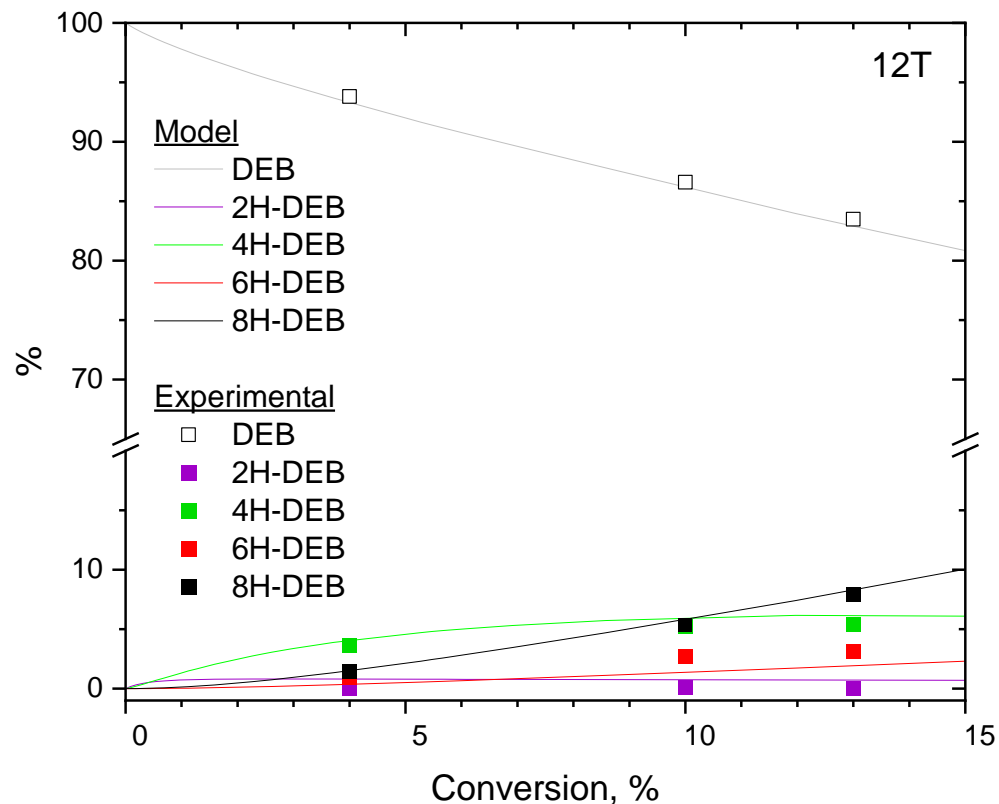


Figure 17. Speciation as a function of conversion at 12T. Comparison between experimental data and model prediction

Figure 17 depicts the evolution of hydrogenated product intermediates as a function of percent conversion. Given the uncertainty in the mechanism by which hydrogen reacts with DEB away from the catalyst surface, the fitting of the rate constants was done using only data at low $\leq 13\%$ conversion as data at higher levels of conversion *may* have the potential to be influenced by DEB lattice diffusion. As can be seen in figure 17, the model captures intermediate product development with the exception of 6H-DEB which is slightly underpredicted at 12T (10% & 13% conversion). However, as figure 16 reveals, 6H-DEB evolution at 10% conversion accurately fits the experimental data at both 0.1T and 150T.

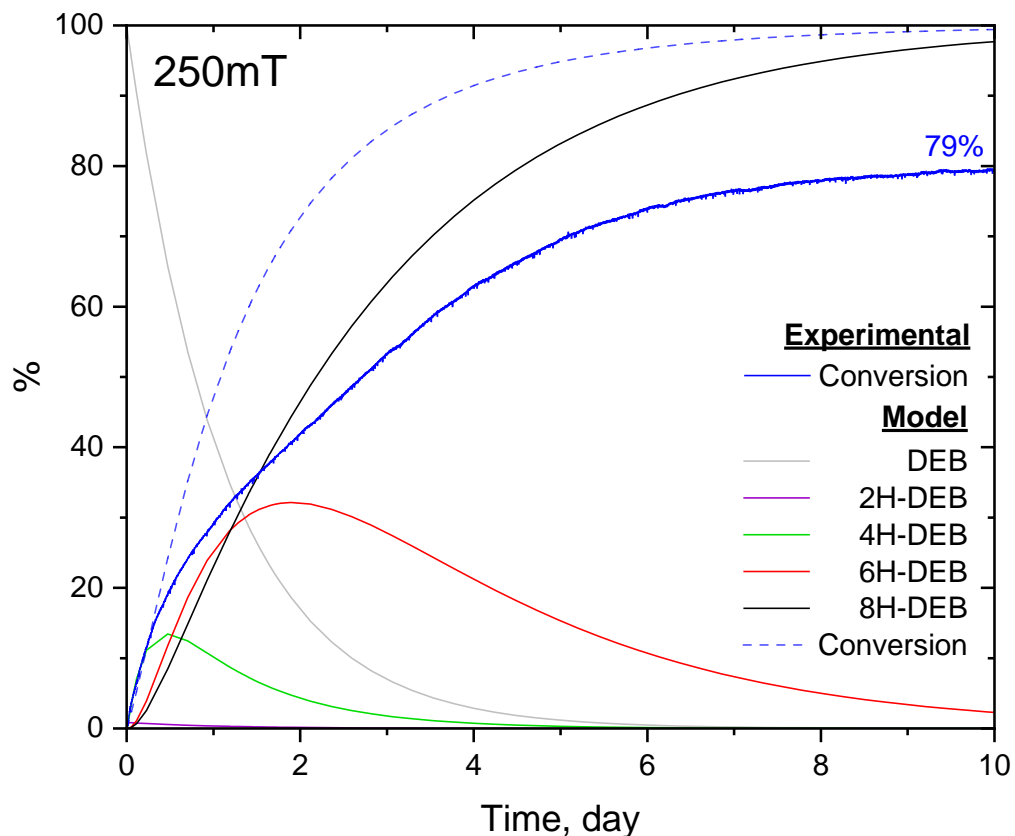


Figure 18. Comparison of experimental gravimetric uptake data with model predicted kinetics and reaction product evolution at 250mT

Comparing the model to experimental gravimetric hydrogen uptake (figure 18) shows good agreement at low levels of conversion for which the rate constants were derived. However, experimental data shows a substantial slowdown in kinetics as the reaction progresses above 15% conversion, only reaching approximately 79% of theoretical uptake. At 250mT hydrogen partial pressure, the model predicts 4H-DEB to peak after approximately 12 hours and 6H-DEB to peak at approximately 45 hours with considerable intermediate reaction products predicted to be present in the system over the course of the reaction. This lies in contrast to the speciation predicted at higher pressures, as evidenced in figure 19, where at 150T the getter system shows considerably suppressed intermediate species production compared to 75mT.

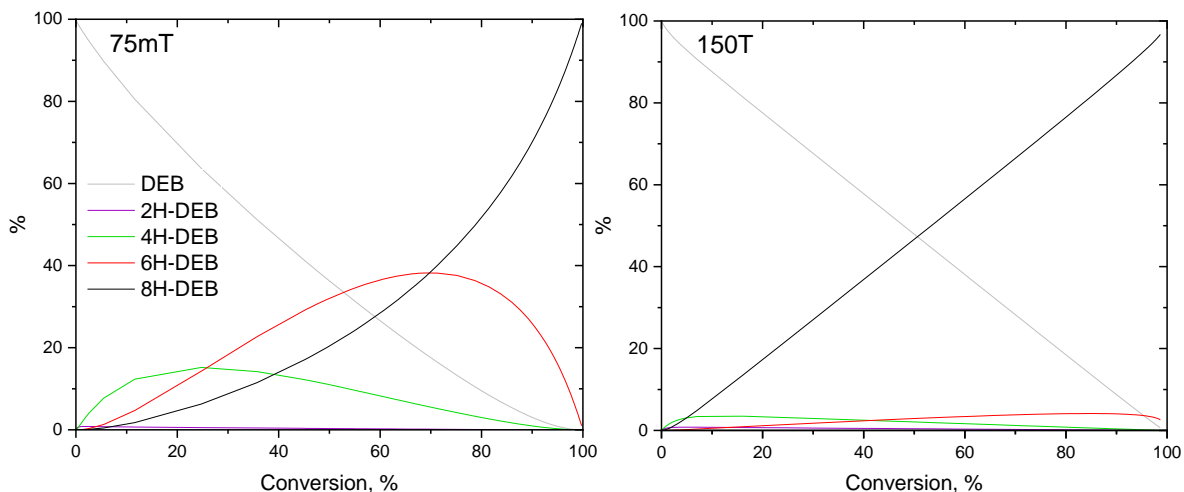


Figure 19. Comparison of predicted speciation as a function of conversion at 75mT (left) and 150T (right)

DISCUSSION

Shift in reaction product distribution as exposure analysis tool

Another way to analyze the shift in reaction product speciation as a function of pressure is shown in figure 20. Figure 20 depicts the preference for 8HDEB as a product from the calculation of the percent of hydrogen stored in 8H-DEB

8HDEB Preference, %

$$= \frac{8 * 8HDEB}{2 * 2HDEB + 4 * 4HDEB + 6 * 6HDEB + 8 * 8HDEB} * 100$$

This shows that when exposed to *trace* concentrations of hydrogen gas (75mTorr), the getter will store hydrogen predominantly as intermediate species (4H and 6HDEB), whereas, if the getter system encounters a high-pressure hydrogen environment (150Torr) this will result in a rapid shift toward 8HDEB due to both fast kinetics and speciation preference. This result may potentially be of use to analyze the exposure history of sealed environments containing getter materials as the observed speciation of reaction products

present in unsaturated getter material will yield information regarding the hydrogen pressure seen by the getter.

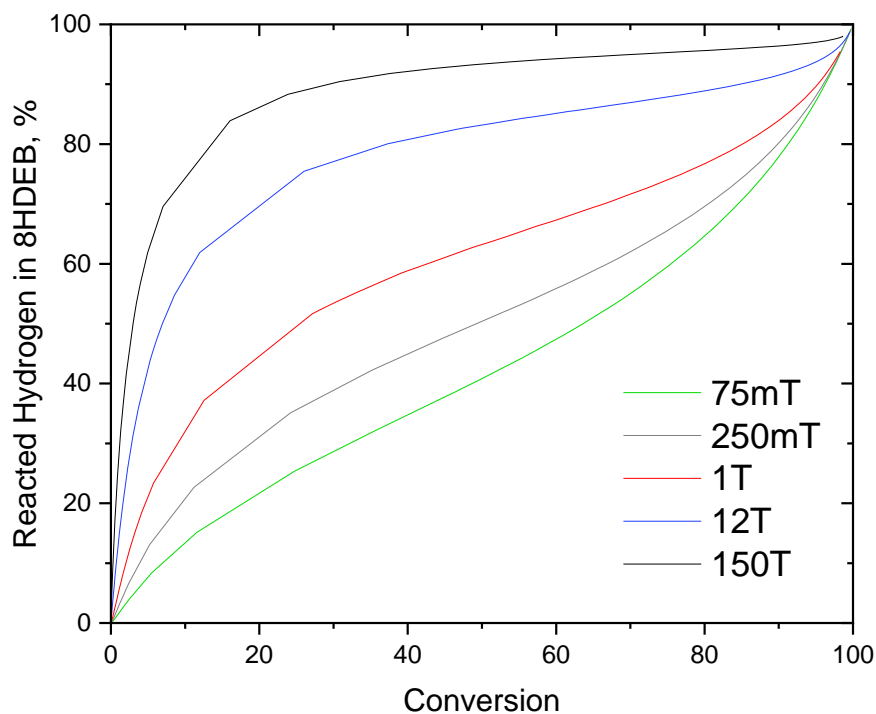


Figure 20. Reacted hydrogen in 8H-DEB as a function of conversion and pressure
Final conversion and speciation

One aim of this modeling effort is to elucidate how reaction product speciation as a function of pressure and conversion may explain some of the phenomena observed in experimental uptake data and how this correlates to the proposed mechanism of DEB hydrogenation. One particular observation in experimental uptake data, seen in figure 21, is a downward trend in final conversion as a function of hydrogen pressure. From the standpoint of DEB lattice diffusion, there is no reason *a priori* to assume the shift in preference of reaction product to 8H-DEB would have a negative influence on the ability for DEB to diffuse toward the catalyst surface. In fact, the analysis of properties of DEB and hydrogenation products by Sharma et. al. [10] proposed that CH dipole interactions of

carbons linking the phenyl rings for DEB, Trans 4H-DEB, and 8H-DEB have 0, 8 attractive, and 8 repulsive dipole interactions (per molecule), respectively. Furthermore, Sharma et. al. also observed of 8H-DEB that it has the lowest melting temperature, highest vapor pressure and largest d-spacing compared to virgin DEB and other intermediates. Given this information, one would assume that the repulsive dipole interactions, decreased density and decreased crystal binding energy of 8H-DEB would likely facilitate lattice diffusion, whereas the attractive dipole interactions and higher density and higher binding energy of 4H-DEB would hinder a lattice diffusion limited reaction. Given that greater 8H-DEB preference at high hydrogen pressure corresponds with *reduced* final conversion this suggests that crystal lattice diffusion may not be responsible for limiting ultimate conversion.

However, if one assumes hydrogen mobility is enabled by the supramolecular structure of the organic crystal, DEB and intermediate trans 4H-DEB would facilitate hydrogen diffusion away from the catalyst while 8H-DEB, which is unreactive, exhibits a lower density crystal structure and possesses repulsive CH dipole interactions between molecules would likely prohibit hydrogen diffusion. Given this proposed relationship one would anticipate to see an influence of 8H-DEB accumulation on observed reaction kinetics and final conversion. Figure 21 (left) depicts the model predicted *reactive fraction* of the system versus conversion which is defined below as the ratio of reactive species to unreactive species.

$$\text{Reactive fraction} = \frac{DEB + 2HDEB + 4HDEB + 6HDEB}{8HDEB}$$

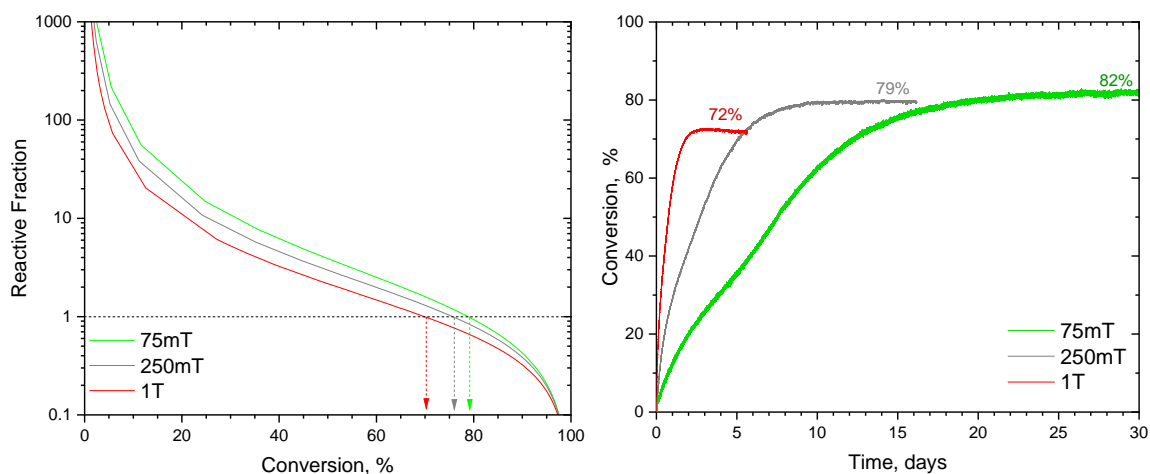


Figure 21. Experimental gravimetric uptake data on getter materials as a function of reaction pressure (Right), reactive fraction calculated from model speciation data as a function of conversion (Left) arrows indicate level of conversion where reactive fraction = 1

Based on the equation, reactive fraction values greater than 1 indicate a system composed of predominantly reactive DEB species conducive toward hydrogen mobility whereas a reactive fraction <1 indicates that the system is mostly 8H-DEB which is unreactive and, due to decreased crystal density and repulsive dipole interactions, prohibits hydrogen mobility through the supramolecular structure. Comparing the reactive fraction with conversion data reveals that the ultimate conversion observed experimentally is in alignment with where the model predicts the system shifts from being *conductive* to *prohibitive* of hydrogen diffusion (final conversion observed experimentally: $82\pm 1\%$, $79\pm 3\%$ & $72\pm 1\%$ for 75mT, 250mT and 1T respectively). This result, while purely theoretical, appears to support the hypothesis of hydrogen mobility within the supramolecular crystal structure enabled by strong interactions between adjacent DEB molecules.

CONCLUSION

Modeling of reaction product species evolution was conducted with kinetic expressions developed assuming a mechanism of parallel and series hydrogenation. A system of partial differential equations was developed from this mechanistic framework and fit to experimental GCMS data at low levels of conversion (<14%). The model exhibits considerable intermediate species production when the getter system is reacted at low partial pressures of hydrogen, whereas reacting at high pressures produces primarily fully reacted 8H-DEB. There are three primary implications of this work. First, the ability for the model, developed using fundamental rate law expressions assuming series and parallel hydrogenation of DEB, to fit experimental data strongly supports this proposed reaction mechanism observed previously in high pressure acetylene hydrogenation over Pd catalysts. Secondly, comparing the model predicted speciation with experimental uptake data appears to suggest that hydrogen mobility within the supramolecular crystal framework of DEB is responsible for hydrogenation of triple or double bonded carbons away from the catalyst surface. Finally, it is posited that the observed shift in product speciation as a function of reaction pressure may potentially represent a means to interrogate the history of DEB getter containing sealed environments, as an *unsaturated* getter would possess information regarding its history of hydrogen exposure in the observed product speciation. This could potentially provide a means of both detecting evidence of a spike in hydrogen pressure or quantifying the mean atmospheric concentration of hydrogen seen by the getter in the sealed environment over time. Work is currently underway utilizing XRD to quantify reaction product speciation in partially

reacted samples which would provide a facile and non-destructive means of quantifying product speciation in getter samples as a means of validating the aforementioned hydrogen exposure analysis application.

SUPPLEMENTAL

Reaction constants obtained from fitting model to experimental data

Reaction Constant	Value	Units
K02	1.967E-5	Torr ^{-1/2} second ⁻¹
K04	1.736E-6	Torr ⁻¹ second ⁻¹
K22	2.310E-3	Torr ^{-1/2} second ⁻¹
K24	1.50E-3	Torr ⁻¹ second ⁻¹
K42	6.366E-5	Torr ^{-1/2} second ⁻¹
K44	7.639E-5	Torr ⁻¹ second ⁻¹
K62	9.259E-6	Torr ^{-1/2} second ⁻¹

CHAPTER 4

CONCLUSION

The findings in this report yield valuable information relevant to both *experimental* performance evaluation as well as *fundamental* and mechanistic understanding of hydrogen getter materials. The system investigated in this report consists of an unsaturated organic molecule 1,4-bis(phenylethynyl)benzene (DEB) and a hydrogenation catalyst (5%Pd/C). This getter system has emerged as the most commonly utilized material of its class for hydrogen gettering applications in sealed environments [5]. While this system has found widespread application in preventing hydrogen accumulation in environments prone to off gassing, corrosion or catalytic production of hydrogen gas, there still exist both *experimental* and *fundamental* challenges related to this material which have yet to be adequately addressed.

Experimentally, performance evaluation of hydrogen getter materials has been conducted utilizing numerous techniques and methods. Manometric methods used to measure hydrogen uptake are typically done in either a *pseudo*-isobaric or batch type (Sieverts) reaction environment which, while highly relevant to certain use conditions, possess inherent challenges for obtaining idealized getter behavior due to the dynamic pressure conditions. Additionally, manometric methods possess unique challenges when obtaining uptake data in highly dilute mixed gas environments which are observed in many use conditions [2]. The experimental apparatus and method described in *Gravimetric Based Performance Evaluation of DEB Hydrogen Getters* addresses both of these challenges. The apparatus has been custom designed to operate in a flow through condition maintaining a constant *absolute* pressure in the reaction chamber, moreover by utilizing specialty mixed gasses a constant *partial* pressure of reactive gas can be maintained in the chamber thereby

enabling interrogation of idealized getter performance in highly dilute mixed gas environments. One of the primary advantages of this novel apparatus is its ability to interrogate and isolate the impact of *diffusive* mass transfer limitations in getter systems. The results presented in this report highlight the significant diffusive mass transfer limitation imposed by the 254 μ m center-hole in the fluorinated ethylene-propylene (FEP) mini-assembly containment structure (Chapter 1, figure 2). However, the implication of this finding is of particular relevance to next generation composite getter systems which are currently the subject of numerous investigations [5] [11] [12] [21]. Getter impregnated polymeric materials or composites utilizing selectively permeable barrier materials have attracted much attention recently due to the potential bi-functional nature of these materials as both hydrogen getter and gasketing material. These novel composite systems would be particularly susceptible to diffusive mass transfer limitations due to solution-diffusion (Henry's law) related phenomena as well as to the tortuosity or microporosity of these materials having a similar effect to the observed center-hole imposed diffusion limitation seen in chapter 1. These diffusion limitations imposed by matrix, barrier or containment structures are found to be both observable and quantifiable in mixed gas experiments. This result indicates that pure gas performance evaluations, the standard in published getter literature, may not fully account for diffusive mass transfer limitations which have been found to be the rate limiting mechanism in certain use conditions. Hence it is stressed in this report that mixed gas performance evaluation should be conducted on new getter materials susceptible to mass transfer limitations in order to accurately model their performance in (non-vacuum) use environments as well as to adequately account for and improve the mixed gas diffusivity of the composite system.

Fundamentally, it is found in the published literature on DEB based hydrogen getters that the contribution of intermediate reaction products on the kinetics and mechanism of hydrogenation is largely ignored. The two triple bonds of DEB are capable of reacting with up to four H₂ molecules, this implies the presence of 2H, 4H and 6H-DEB intermediate hydrogenation products before fully hydrogenated (8H-DEB) is formed. These intermediate hydrogenation products have been experimentally verified to not only exist but also, under certain conditions, represent the *dominant* reaction product found in partially reacted getter materials [8]. Furthermore, materials property analysis conducted by Sharma et. al. has revealed highly disparate thermodynamic properties of DEB and its intermediate and final hydrogenation products. In fact Sharma's results find that, contrary to intuition, the thermodynamic properties such as volatility and melting temperature do not increase monotonically with degree of hydrogenation and that the major factor influencing these properties is the local attractive or repulsive carbon-hydrogen dipole interaction between adjacent getter molecules in their crystal structures. Given the disparate properties of hydrogenated intermediates it is surprising that the body of literature concerning the mechanism and kinetics of DEB hydrogenation do not account for intermediate species production and only model hydrogenation in terms of mols of hydrogen uptake or more commonly α , % of theoretical uptake. In chapter 2 of this report we develop a kinetic rate expression for DEB hydrogenation based on reaction fundamentals describing the reaction with a *consecutive-parallel* mechanism with both 2H as well as 4H additions being possible. This kinetic modeling enables prediction of reaction kinetics and functions as a model of intermediate species production over the course of the reaction. The *consecutive-parallel* mechanism for DEB hydrogenation is observed to

explain the shift in reaction product selectivity as a function hydrogen pressure with high pressures favoring 8H-DEB while low pressures ($<1T$), relevant to use conditions, show considerable intermediate species (4H and 6H-DEB) production. The novelty of this report lies in the construction of a kinetic expression for DEB hydrogenation based on reaction fundamentals as opposed to the empirical fitting used in literature. Furthermore, it is identified that the observed shift in intermediate product selectivity with reaction pressure has potential application for interrogating the history of hydrogen exposure for partially hydrogenated getter materials as the extent of conversion and speciation present in the sample can yield information regarding historical hydrogen pressure seen in the sealed environment.

The future direction of hydrogen getter work is envisioned to utilize our unique experimental apparatus to probe the performance of next generation composite getter systems. As discussed the gravimetric based approach enables isolation of diffusive mass transfer limitations inherent in the material which will prove invaluable toward accurate performance analysis, materials development as well as engineering of said next generation getter materials. Likewise, further refinement of the model for intermediate species development will be conducted in order to interrogate fundamental reaction mechanisms present in these, as well as composite, getter systems and to explore the potential for observed DEB product speciation to function as a novel analysis method for interrogating the hydrogen exposure history of a sealed environment. Calibrating the model going forward intends to utilize highly accurate X-ray crystallography to identify and quantify the concentration of individual hydrogenation products which are observed to possess unique crystal diffraction patterns [10]. This approach is envisioned to significantly

increase experimental throughput enabling the production of a high fidelity model for hydrogenation product speciation as a function of reaction pressure and conversion extent which, as mentioned, may prove to be an invaluable new methodology for analysis of getter material hydrogen exposure history.

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