ACS SENSORS

pubs.acs.org/acssensors

Article

Microwatt-Resolution Calorimeter for Studying the Reaction Thermodynamics of Nanomaterials at High Temperature and Pressure

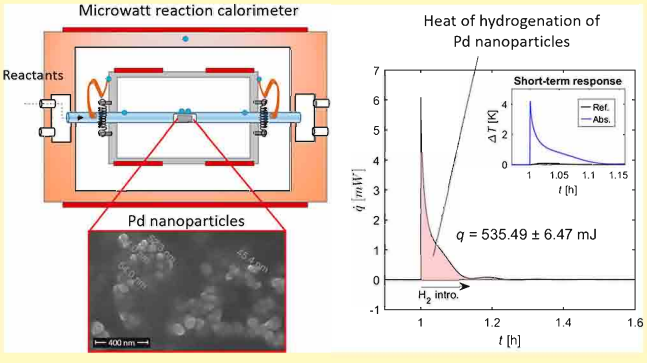
Amin Reihani, Ju Won Lim, David K. Fork, Edgar Meyhofer,* and Pramod Reddy*

Cite This: *ACS Sens.* 2021, 6, 387−398

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Calorimetry of reactions involving nanomaterials is of great current interest, but requires high-resolution heat flow measurements and long-term thermal stability. Such studies are especially challenging at elevated reaction pressures and temperatures. Here, we present an instrument for measuring the enthalpy of reactions between gas-phase reactants and milligram scale nanomaterial samples. This instrument can resolve the net change in the amount of gas-phase reactants due to surface reactions in an operating range from room temperature to 300 °C and reaction pressures of 10 mbar to 30 bar. The calorimetric resolution is shown to be <3 μW/$\sqrt{\text{Hz}}$, with a long-term stability <4 μW/hour. The performance of the instrument is demonstrated via a set of experiments involving H_2 absorption on Pd nanoparticles at various pressures and temperatures. For this specific reaction, we obtained a mass balance resolution of 0.1 μmol/$\sqrt{\text{Hz}}$. Results from these experiments are in good agreement with past studies establishing the feasibility of performing high resolution calorimetry on milligram scale nanomaterials, which can be employed in future studies probing catalysis, phase transformations, and thermochemical energy storage.



KEYWORDS: *reaction thermodynamics, calorimetry, nanoparticles, hydrogen absorption, palladium*

Knowledge of the thermodynamics of surface reactions and phase transformations in nanomaterials is of crucial importance to heterogeneous catalysis, sustainable production of fuels and chemicals,[1,2] as well as hydrogen storage and fuel cell applications.[3] In particular, nanomaterials, such as noble metal nanoparticles, are excellent candidates for these applications, as they provide a high surface to volume ratio and low resistance to reactant mass diffusion.[4] Further, in the context of hydrogen storage for renewable energy and transportation applications, metal hydride nanoparticles are considered to be a promising platform, as they enable storage of large amounts of hydrogen in the interstitial sites of crystal lattices and feature rapid kinetics at room temperature.[3]

Calorimetric reactors enable direct measurement of reaction thermodynamics and kinetics, and past work[5−9] has developed sensitive calorimeters to study surface reactions and catalysis. In Table 1 we summarize data from five representative studies, listing their operating range and main figures of merit. The instruments employ various temperature sensors, such as RTDs,[5] thermocouples,[6,7] and pyroelectric heat detectors.[8] In addition, they use several techniques for quantifying the mass of gas-phase reactants, such as pressure−concentration measurements,[5,6] molecular beams with known fluxes of reactants,[8] and gravimetric measurements using a microbalance.[9] Additionally, the specifications of two relevant, commercially available instruments are listed in Table 1. An important criterion for calorimetric measurements of chemical reactions is the amount of sample required for measurements. The amount and type of catalyst samples differ across previous studies: some use powdered samples, typically on the gram-scale,[5−7] while others use either thin-film single crystals or dispersed samples.[8,9] While the former group can achieve high temperature and pressure reaction conditions, the latter group is limited to low pressures and operates close to room temperature, largely due to use of microfabricated devices, sensors incompatible with high pressure or temperature, or the need for operation under vacuum environment. In addition, the high temperature and pressure operation of the calorimeters utilizing powdered samples is impeded by poor long-term temperature stability and low heat flow resolution due to high effective thermal

Special Issue: Commemorating NJ Tao

Received: July 27, 2020
Accepted: October 30, 2020
Published: November 23, 2020

https://dx.doi.org/10.1021/acssensors.0c01550
ACS Sens. 2021, 6, 387−398