Flow Microcalorimetry: Applications in Catalysis

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Introduction

Characterization of heterogeneous catalysts has evolved in recent decades to provide great insight into the structure and performance of these valuable materials [1]. Methods focused on bulk, nanoscale and surface specific characteristics have all contributed to a greater understanding of mechanism and ability to optimize catalysts. Calorimetric measurements have been employed extensively to study gas chemisorption but use of liquid flow microcalorimetry is a relatively under-explored area in catalyst characterization [2]. In contrast, liquid flow microcalorimetry has been broadly employed for studies in adhesion [3], self-assembly [4], surfactant adsorption [5] and pigments [6]. From liquid flow microcalorimetry, one can determine strength of adsorbate interaction while differentiating between weak and strong (physisorption and chemisorption) binding sites on a catalyst surface. The acquired data can be utilized in modeling of reaction systems and understanding of mechanisms and optimization of catalyst materials.

Materials and Methods

Precious metal catalysts on supports such as silica, titania, alumina and carbon have been employed as purchased or prepared in-house by deposition of precursor salts and calcination. Solvents were purchased from Aldrich and handled in an inert atmosphere glove box to avoid influence of extraneous water in the adsorption process. Calorimetry measurements were conducted in the FMC Flow Microcalorimeter from Microsocal with a Waters 2414 Refractive Index (RI) Detector downstream of the calorimeter. Data were analyzed with CALDOS software. Catalyst samples were handled in sealed containers after calcination to limit exposure to humidity and then loaded to the instrument and held under active vacuum overnight before introduction of solvent. Typical measurements comprised: a) wetting the catalyst sample with pure flowing solvent (typically heptane), b) establishing a baseline for approximately 1 hour, c) switching to a 10 mM solution of the probe molecule in the same solvent and recording heat flow and RI response until the adsorption event reached saturation equilibrium, d) switching to pure solvent until the desorption event reached equilibrium, e) calibrating the heat flow response with a calibration heater and the RI response to establish a non-adsorbing reference molecule (decachydrornapthalene) to determine mass uptake by area difference.

Results and Discussion

FMC measurements were made for a series of molecules bearing diverse functional groups over a series of precious metal catalysts, relevant to hydrogenation catalysis. In one investigation focused on titania supported catalysts, a correlation of the substrate structure with the enthalpy of adsorption and quantity adsorbed suggested a functional group preference for adsorption and the likelihood of two types of sites for adsorption, Table 1. Notably, amines bind with low density but high enthalpy per adsorption site, whereas alcohols and ethers bind with higher density but low enthalpy. We will discuss the implications of these adsorption measurements in surface functionality, catalysis mechanistic studies and process optimizations for hydrogenation reactions.

Table 1. Adsorption on TiO2 catalysts and supports

<table>
<thead>
<tr>
<th>Support Qty Adsorbed μmol/g</th>
<th>Qty Chemisorbed μmol/g</th>
<th>ΔH Ads kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>THP TiO2 #1 (45 m2/g)</td>
<td>45</td>
<td>24</td>
</tr>
<tr>
<td>CyCmHM TiO2 #1 (45 m2/g)</td>
<td>121</td>
<td>72</td>
</tr>
<tr>
<td>CH3(CH2)11NH2 TiO2 #2 (7 m2/g)</td>
<td>5.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Significance

Fundamental thermochemical properties can be measured by liquid flow microcalorimetry to support mechanistic investigations, reaction modeling and to assist in process optimization. For the last point, competitive binding studies can be valuable to address issues of catalyst deactivation and yield loss from strong adsorption.

References