COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Catalyst surface characterization in microfabricated reactors using pulse chemisorption

Chelsey D. Baertsch,[a,c] Martin A. Schmidt[b] and Klavs F. Jensen*[a]

[a] *Department of Chemical Engineering, Massachusetts Institute of Technology, 25 Ames Street, Cambridge MA 02139, USA. E-mail: kfjensen@mit.edu; Fax: 617-258-8224; Tel: 617-253-4589*

[b] *Microsystems Technology Laboratories, Massachusetts Institute of Technology, 60 Vassar Street, Cambridge MA 02139, USA*

[c] *Department of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette IN 47907, USA. E-mail: Baertsch@purdue.edu*

Received (in Cambridge, UK) 2nd July 2004, Accepted 10th August 2004
First published as an Advance Article on the web 4th October 2004

The metal dispersion of a Pt–Al_2O_3 catalyst was measured reproducibly using pulse CO chemisorption with 4 mg of sample in a silicon microfabricated packed-bed reactor, demonstrating the applicability of micoreactors for high-throughput catalyst characterization with quantitative comparison.

Combinatorial methods are now routinely employed in heterogeneous catalysis and have successfully been used for the rapid discovery of new catalytic materials.[1] Effective methods for combinatorial library synthesis, parallel infrared thermography, and scanning mass spectrometry for rate and selectivity measurement have been developed.[2,3] However, reactor systems for the simultaneous or sequential measurement of correlating structure and catalytic site properties are required for accurate catalyst comparison within the libraries using turnover rates. Methods for characterizing catalyst structure and quantifying active site densities of individual materials within a combinatorial library remain challenging and largely unaddressed in this field.

Silicon microfabrication methods arising from advances in microelectromechanical systems (MEMS) allow for the cost-effective replication of small chemical reactors with integrated sensors and actuators for automated high-throughput screening.[4] Microreactors can be used to accurately and reproducibly study catalytic rates, selectivities, and mechanisms using either high surface area powdered catalyst particles or catalyst coatings within submillimeter microchannels.[5–8] This study demonstrates that catalyst surface properties can also be characterized and quantified within silicon microfabricated reactors.

To compare the activity of supported metal catalysts within a combinatorial library, the number of available surface metal sites is required. Here, pulse CO chemisorption was used to quantify the metal dispersion of an alumina-supported Pt catalyst in an axial flow packed-bed microreactor. Pulse chemisorption was used as the quantification method because the adsorbent quantity can accurately be proportioned for small catalyst samples. Also, chemisorption is very adaptable; a wide variety of catalyst properties can be analyzed using this method depending on the adsorbent molecule and conditions.

The microreactors used in this study were fabricated out of silicon and glass substrates using a combination of photolithography, etch, and wafer bonding steps,[9] as reported previously.[8,10] In brief, single 20 mm long, 1 mm wide microreactor channels were etched ~350 μm into prime Si (100) wafers using an SF_6 deep reactive ion etch (DRIE) process to achieve high aspect ratio features.[11] 600 μm diameter gas inlet/outlet holes were etched through the wafer thickness. The surface fluorocarbon passivation layer remaining on the channel walls after DRIE was removed by wet oxidation followed by a buffered-oxide etch to obtain clean silicon reactor surfaces coated with only native oxide. Etched silicon wafers were sealed to form microchannels by anodic bonding to pyrex glass wafers. Fig. 1a shows a photograph of the silicon axial flow microreactor. Each 24.8 mm × 11.4 mm chip contains six distributed 400 μm wide by 350 μm deep etched thermocouple wells perpendicular to the main reactor channel for temperature measurement and control during chip heating. To retain catalyst particles within the channel during gas flow, 50 μm wide by 300 μm long slabs with 25 μm spacings are aligned across the exit of the reactor channel (Fig. 1b), as in previously reported packed-bed microreactor designs,[8,10] to retain 53–71 μm sieved catalyst particles.

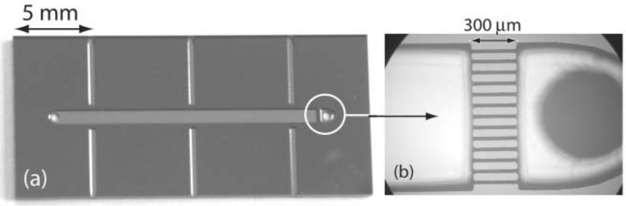

Fig. 1 (a) Optical image of the axial flow silicon packed-bed microreactor (b) detail of integrated catalyst retention posts.

The microreactor was packaged using a compression seal for fluidic connection to an aluminium chuck and heated using two cartridge heaters inserted into the compression plate. Powder samples were drawn into the microreactors using a vacuum line at the outlet of a packaged reactor. The catalyst capacity of fully loaded microreactors is ~4 mg. A conventional packed bed stainless tube reactor was used to analyze larger samples. The practical operating temperature for packaged microreactors was limited to approximately 523 K, above which the elastomeric gasket (Kalrez) degrades. In order to accommodate thermal expansion of the silicon/glass microreactor during temperature cycling, the compression plate was tightened after reaching 523 K in flowing He to obtain a hermetic seal, and continually tightened as the reactor was cooled to 308 K, ensuring constant flow through the reactor. Catalysts were dehydrated *in-situ* at temperatures up to 623 K in He ($\sim 8.3 \times 10^{-4}$ L s^{-1}, 1 h), reduced at the same temperature in a 5% H_2 in He mixture ($\sim 8.3 \times 10^{-4}$ L s^{-1}, 1 h) and purged in He prior to cooling the reactor to 308 K. Removal of oxygen, water, and hydrocarbon impurities from the UHP carrier gases was critical for reproducibility with the small catalyst samples.

Pulse chemisorption measurements were obtained for an Al_2O_3-supported Pt catalyst (178 m^2 g^{-1}, 1 wt.% Pt, Aldrich chemical) using an HP 5973 GC/MS for automated CO pulse injection and on-line mass spectrometry detection. 10–1000 μL pulses of 1% CO in He at 109–131 kPa were injected every 6 minutes into a continuous 2.35×10^{-4} L s^{-1} He flow through the catalyst bed. The pressure drop through the packed-bed microreactor at this flow rate was negligible. The cumulative mass abundance was monitored on-line for the duration of the injection sequence. Cumulative CO uptakes were determined using the eluted CO peak areas, and Pt dispersion was calculated assuming an adsorption stoichiometry of 1 CO/Pt. Catalyst loadings were obtained by

DOI: 10.1039/b410078f

Table 1 CO pulse chemisorption analysis at 308 K of 1 wt.% Pt–Al_2O_3 as a function of pretreatment temperature, reactor configuration, and catalyst quantity

Pretreatment temperature (K)	H_2O desorbed during pretreatment[a] (%)	Measured metal dispersion (%)			
		Tube reactor	Tube reactor	Microreactor	Microreactor
		~200 mg	~4 mg	~4 mg	<2 mg
298	0	12		no CO uptake detected	
523	63	30 ± 1[b]	22 ± 3[b]	21 ± 2[b]	no CO uptake detected
623	95	41			

[a] Ambiently adsorbed H_2O temperature programmed desorption; 201.9 mg Pt–Al_2O_3, 0.167 K s^{-1}, 1.67 L s^{-1} He. [b] Average and standard deviation from two measurements.

measuring the microreactor mass, with and without catalyst, with a 6-place Sartorius microbalance. All CO chemisorption measurements were performed at 308 K. Uptakes are reported in Table 1 as measured Pt dispersion and listed as a function of catalyst loading, reactor configuration (microfabricated *vs.* stainless tube), and pretreatment temperature.

Standard measurement capabilities of the home-built pulse chemisorption system used for quantitative analysis in this study were confirmed by comparing measurements to those obtained on a commercial Micromeritics Model 2910 temperature programmed pulse chemisorption analyzer. A metal dispersion of 41% for the investigated Pt–Al_2O_3 sample was obtained using both systems with approximately 200 mg catalyst, identical pre-treatment conditions (623 K), and a tube reactor.

The total CO chemisorption uptake and therefore reported Pt dispersion was found to be highly dependent on the catalyst dehydration and reduction temperature. Uptakes measured with ~200 mg of catalyst in a tube reactor linearly increase with the fraction of water desorbed during pre-treatment (Table 1; measured by temperature programmed desorption of ambiently adsorbed H_2O). CO uptakes are suppressed by residual H_2O either adsorbed on the surface or confined in the pore structure. This observation is significant for this study because the temperature of the packaged microreactor is limited to 523 K; therefore, the measured Pt dispersion using the microreactor is expected to be less than 41% due to this correlating effect.

Using only about 4 mg of catalyst in a silicon microreactor with a compression package at 523 K, CO uptakes were measured reproducibly. Pt dispersion was quantified at 21 ± 2%. As predicted, this is lower than the 41% dispersion measured on the same catalyst treated at 623 K. The Pt dispersion measured using a packed bed tube reactor loaded with ~4 mg catalyst is indistinguishable from that obtained using the microreactor after identical pre-treatments, confirming that no aberrations result from either the silicon surfaces and/or the microreactor package.

Sensitivity limitations of this system were reached when less than 2 mg of catalyst was used, or total CO uptakes were below about 2×10^{-8} mol. However, this doesn't represent an intrinsic limitation of pulse chemisorption measurements in microsystems, just of the mass spectrometer. In fact, this is a remarkable response using only a single mass filter quadrupole and Faraday cup detector (ppm sensitivity).

This study shows that quantitative analysis of metal surface sites in supported catalysts is possible using mg quantities of sample in microchemical systems. With this, microreactors are applicable for intelligent high-throughput characterization and materials screening using turnover rates. Pulse measurement approaches are also pertinent for activity and deactivation assessment of the performance of small catalyst samples in microreactors. Analysis of even smaller catalyst masses appears to be possible using on-line detectors with ppb sensitivity. Improved packaging for higher temperature analysis and temperature programmed studies will improve the data precision.

The authors gratefully acknowledge support from the Army Research Office and the MIT Microchemical Systems Technology Centre.

Notes and references

1 Y. Liu, P. Cong, R. D. Doolen, S. Guan, V. Markov, L. Woo, S. Zeyb and U. Dingerdissen, *Appl. Catal. A*, 2003, **254**, 59.

2 A. Hagemeyer, B. Jandeleit, Y. Liu, D. M. Poojary, H. W. Turner, A. F. Volpe, Jr. and W. H. Weinberg, *Appl. Catal. A*, 2001, **221**, 23.

3 F. Schuth, O. Busch, C. Hoffmann, T. Johann, C. Kiener, D. Demuth, J. Klein, S. Schunk, W. Strehlau and T. Zech, *Topics Catal.*, 2002, **21**(1–3), 55.

4 K. F. Jensen, *Chem. Eng. Sci.*, 2001, **56**, 293.

5 M. T. Janicke, H. Kestenbaum, U. Hagendorf, F. Schuth, M. Fichtner and K. Schubert, *J. Catal.*, 2000, **191**, 282.

6 T. McCreedy and N. G. Wilson, *Analyst*, 2001, **126**, 21.

7 Y. S. S. Wan, J. L. H. Chau, A. Gavriilidis and K. L. Yeung, *Chem. Commun.*, 2002, 878.

8 S. K. Ajmera, C. Delattre, M. A. Schmidt and K. F. Jensen, *J. Catal.*, 2002, **209**, 401.

9 M. Madou, *Fundamentals of Microfabrication*, CRC Press, 1997, Boca Raton, FL.

10 M. W. Losey, M. A. Schmidt and K. F. Jensen, *Ind. Eng. Chem. Res.*, 2001, **40**, 2555.

11 A. A. Ayon, R. Braff, C. C. Lin, H. H. Sawin and M. A. Schmidt, *J. Electrochem. Soc.*, 1999, **146**, 339.