

Synthesis of a Disperse Phase of Barium Oxide on Aluminum Oxide by Successive Ionic Layer Deposition

Thomas I Gilbert* and Johannes W. Schwank
University of Michigan, Ann Arbor, Michigan 48109 (USA)
*tomchem@umich.edu

Introduction

Heterogeneous catalyst design, synthesis, and characterization have been strongly influenced by recent advances in nanoscience [1]. Several recent studies suggest that a highly dispersed phase of barium oxide supported on γ -alumina is a better catalyst for NO_x storage in lean burn engine emissions than a bulk-like phase of supported barium oxide [2-5].

Successive ionic layer deposition (SILD), also known as successive ionic layer adsorption and reaction (SILAR), is an aqueous method which exploits the electric double layer effect to create thin solid films on supports. In SILD, submonolayers of desired cations and anions are alternately and selectively adsorbed on a support material to produce SILD nanoislands or nanolayers with controlled composition and morphology.

Much still remains to be understood about the SILD mechanism. It is unclear whether a precipitate is simply formed on the substrate with each SILD cycle or whether ionic or electrostatic forces persist through SILD layers. If the latter occurs, it is conceivable that these interactions play an important role in creating thermally stable dispersions at higher weight loadings.

A purpose of this study was to develop a SILD synthesis procedure which would allow the synthesis of a purely dispersed phase of barium oxide on aluminum oxide. Successfully synthesizing a purely disperse phase of catalyst on a support would enable a more detailed characterization of the effects of catalyst-support interactions on overall catalytic activity.

Materials and Methods

An apparatus consisting of an Automate Scientific ValveBank 8 perfusion system in combination with a Laurell WS-400B-6NPP/LITE spin coater was used for SILD on planar silicon wafers. SILD deposition on fused aluminum oxide crystallites was performed using a Buchner funnel and filter paper. The concentrations of the SILD and rinse solutions, the timing and sequence of the SILD steps, and the pretreatment and post-treatment of the support, each affect the properties of the oxide nanofilms synthesized by these methods.

NO_x was adsorbed on the $\text{BaO}/\text{Al}_2\text{O}_3$ materials as they cooled from 500°C in a stream of 1% NO_2 . Thermogravimetric analysis on a TA was performed in conjunction with an FT-IR from Thermo to analyze the evolved gases and determine the NO_x storage capacity.

XPS characterization was performed on a Kratos Axis Ultra using an Al $K\alpha$ x-ray source and a charge neutralizing flood gun. Cantilevers from Pacific Nanotechnology were used in AFM tapping mode with a NanoScope IIIa instrument. SEM characterization was performed on a FEI Nova Nanolab with a Schottky field emission electron gun.

Results and Discussion

SILD was used to deposit nanoislands of aluminum oxide on a silicon wafer, and then deposit even smaller nanoislands of barium oxide on the surface of the aluminum oxide nanoislands. Modifications to the conventional SILD procedure were necessary to achieve a successful synthesis. This disperse phase of barium oxide on aluminum oxide supported on a silicon wafer was thermally stable to 450°C .

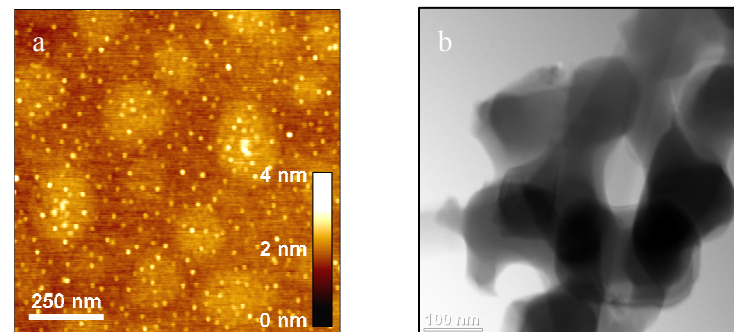


Figure 1. (a) AFM image of barium oxide nanoislands deposited on larger aluminum oxide nanoislands, supported on a silicon wafer; (b) TEM image of fused aluminum oxide crystallites

The average diameter of these BaO nanoislands is about 15 ± 2.0 nm, with an average height of approximately 1.3 ± 0.6 nm. The BET surface area of the fused aluminum oxide crystallites is $6.6 \text{ m}^2/\text{g}$. After 5 cycles of barium oxide were deposited using SILD techniques the BET surface area increased to approximately $7.0 \text{ m}^2/\text{g}$.

Significance

The synthesis of a purely disperse phase of catalyst on a support allows for a more detailed characterization of the catalyst-support interactions. We are currently investigating whether the SILD synthesis procedure can be used to maintain catalyst dispersion as catalyst weight loading increases.

References

1. Bell, A.T. *Science* 299, 1688-1691 (2003).
2. Chen, X., Schwank, J., Li, J., Schneider, W.F., Goralski, Jr. C.T., Schmitz, P.J. *Appl. Catal. B* 61, 164-175 (2005).
3. Chen, X., Schwank, J., Li, J., Schneider, W.F., Goralski, Jr. C.T., Schmitz, P.J. *J. Mater. Chem.* 15, 366-368 (2005).
4. Szanyi, J., Kwak, J.H., Kim, D.H., Burton, S.D., Peden, C.H.F. *J. Phys. Chem. B* 109, 27-29 (2005).
5. Kwak, J.H., Mei, D., Yi, C.W., Kim, D.H., Peden, C.H.F., Allard, L.F., Szanyi, J. *J. Catal.*, in press (doi:10.1016/j.jcat.2008.10.016).