

reduction occurs in the Mn cluster upon the S_3 -to- S_0 transition, presuming that the valence change of Mn is the main cause for this K-edge energy downshift. The simulated data also indicate that the K-edge energy upshifts by 1.0 eV upon the S_0 -to- S_1 transition. The extent of the upshift of the simulated K-edge energy is coincident with those upon the S_1 -to- S_2 and S_2 -to- S_3 transitions, suggesting that an oxidation of Mn(III) to Mn(IV) might be involved in the S_0 -to- S_1 transition as well.

The present study demonstrates that the valence or structure or both of the Mn cluster oscillates period-four during the cycling of the Joliot-Kok's oxygen clock, showing directly that the so-called S-states reflect mainly the differences in redox states or configurations or both of the Mn cluster during the four-electron cyclic reaction.

REFERENCES AND NOTES

1. P. Joliot, G. Barbieri, R. Chabaud, *Photochem. Photobiol.* **10**, 309 (1969).
2. B. Kok, B. Forbush, M. McGloin, *ibid.* **11**, 457 (1970).
3. A. W. Rutherford, *Trends Biochem. Sci.* **14**, 227 (1989).
4. Govindjee and W. J. Coleman, *Sci. Am.* **262**, 50 (February 1990).
5. D. B. Goodin *et al.*, *Biochim. Biophys. Acta* **767**, 209 (1984).
6. V. K. Yachandra *et al.*, *Biochemistry* **26**, 5974 (1987).
7. G. N. George, R. C. Prince, S. P. Cramer, *Science* **243**, 789 (1989).
8. M. Kusunoki *et al.*, *J. Biochem.* **108**, 560 (1990).
9. R. D. Guiles *et al.*, *Biochemistry* **29**, 486 (1990).
10. G. C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci. U.S.A.* **78**, 274 (1981).
11. J. P. Dekker, H. J. Van Gorkom, J. Wensink, L. Ouwehand, *Biochim. Biophys. Acta* **767**, 1 (1984).
12. Ö. Saygin and H. T. Witt, *ibid.* **893**, 452 (1987).
13. T. Ono *et al.*, *Biochemistry* **30**, 6836 (1991).
14. M. Kusunoki, in *Progress in Photosynthesis Research*, J. Biggins, Ed. (Nijhoff, Dordrecht, 1987), vol. 1, pp. 729–732.
15. G. W. Brudvig and R. H. Crabtree, *Proc. Natl. Acad. Sci. U.S.A.* **83**, 4586 (1986).
16. R. D. Guiles *et al.*, *Biochemistry* **29**, 471 (1990).
17. C. F. Fowler, *Biochim. Biophys. Acta* **462**, 414 (1977).
18. S. Saphon and A. R. Crofts, *Z. Naturforsch. Teil C* **32**, 617 (1977).
19. P. Marchand and L. Marmet, *Rev. Sci. Instrum.* **54**, 1034 (1983).
20. T. Ono and Y. Inoue, *Biochim. Biophys. Acta* **806**, 331 (1985).
21. W. F. J. Vermass *et al.*, *ibid.* **764**, 194 (1984).
22. S. Styring and A. W. Rutherford, *Biochemistry* **26**, 2401 (1987).
23. G. T. Babcock and K. Sauer, *Biochim. Biophys. Acta* **325**, 483 (1973).
24. Supported by a grant for Photosynthetic Science and Biodesign Research Program (to T.O.) at the Institute of Physical and Chemical Research (RIKEN) by the Science and Technology Agency of Japan and by a grant-in-aid for Scientific Research on Priority Areas (04225234) (to T.O.) from the Ministry of Education, Science and Culture. We thank the staff of the Photon Factory for their kind help during our experiments.

22 June 1992; accepted 29 September 1992

Linear Metal Nanostructures and Size Effects of Supported Metal Catalysts

Ioannis Zuburtikudis* and Howard Saltsburg†

Nickel metal catalysts composed of nanometer by micrometer strips have been produced with solid-state microfabrication techniques. The strips are actually the edges of nickel-catalyst thin films, which are sandwiched between separating support layers, which are also nanometers thick. These linear nanostructures constitute well-defined and well-controlled catalytic entities that reproduce the size of traditional supported metal clusters in one dimension, thus separating size from total number of atoms in the catalyst. Examination of their catalytic activity showed that they duplicate the behavior of conventional supported clusters. A specific rate maximum was observed for the hydrogenolysis of ethane at a nanoscale dimension similar to the cluster size at which the rate is maximum in the case of the supported cluster studies, whereas the hydrogenation of ethylene shows no such size dependency. The results suggest that the surface-to-volume ratio or the number of atoms in the catalytic entity cannot be the source of these size effects and that either support effects or nonequilibrium surface structures are the determining factors.

The need for maximizing the effective surface area of catalytically active metals in heterogeneous systems led to the extensive use of highly dispersed metals in the form of clusters supported on a variety of carrier materials. The rates of certain reactions,

when normalized to unit surface area of the clusters, as well as the selectivities of some of them, depend on the overall metal cluster size under otherwise similar reaction conditions (1, 2). If one characterizes the size of the supported metal cluster by an equivalent average diameter, clusters smaller than ~10 nm exhibit such size dependence. The phenomenon is of considerable technological and scientific importance: (i) it suggests that one could produce catalyst

structures that show greater normalized (specific) reaction rates or affect the selectivity in a favorable way or both (2), (ii) it furnishes data for testing electronic and geometrical models of catalysis (2), and (iii) it can be used to probe chemically the transition from atoms to bulk solids (3).

Traditionally, supported metal catalysts are produced through chemical routes (such as impregnation and coprecipitation). The catalytic activity of the resulting supported clusters is examined, and the reaction results are correlated with theoretical calculations that provide the structural and electronic features of idealized and unsupported metal clusters as a function of their total number of atoms. This number is taken to be representative of the measured average size of the produced clusters and serves as a metaphor for structure. The problems with using supported clusters (nonuniform shapes and sizes, possible existence of adventitious surface species, very difficult direct characterization of their surfaces, and failure to distinguish between size and total number of atoms in the cluster) have led to studies with simpler model systems: single crystals and unsupported metal clusters. However, the results from these studies are at best indicative of what may happen on supported clusters. They address only certain issues of the whole problem; for example, the single crystal studies investigate the role of specific surface structures on the origin of the phenomenon. There is a need for developing a scheme that allows the investigation of the size effects without so many limitations. We describe a new class of supported metal catalysts that are much more carefully defined, illustrate their use in addressing the origin of the size effects, and demonstrate the inappropriateness of the metaphor of the "number of atoms."

By vacuum-depositing alternating layers of metal catalyst and support material on a suitable substrate, one can fabricate a layered synthetic microstructure (LSM) whose edge exhibits a compositionally modulated surface that consists of catalyst and support (Fig. 1). The topmost layer is made out of support material so that the only exposed metal catalyst is in the form of strips between those of the support. The thickness of the metal layers can be controlled, is in the nanometer scale, and is comparable to the size of supported metal clusters. Although the width of the catalyst strips is of the order of nanometers, the length of the strips is macroscopic (micrometer scale or larger). In effect, the catalyst is created as a linear microstructure that preserves only one dimension in the nanometer range. As a result, the number of connected metal atoms in this linear structure is orders of magnitude greater than in the typical cluster and separation of dimension from the

Department of Chemical Engineering, University of Rochester, Rochester, NY 14627-0166.

*Present address: Eastman Kodak Research Labs, Rochester, NY 14650-2022.

†To whom correspondence should be addressed.

number of atoms is achieved. In order to provide sufficient metal surface area for reaction studies at atmospheric pressures, conventional lithographic and etching techniques are used to etch the initial LSM in a repetitive pattern in the direction perpendicular to the top surface of the layers. A forest of micrometer-sized towers of given shapes is produced (Fig. 1). Each tower is essentially identical to every other and has a lateral surface that is also identical to the edge of the initial LSM. The metal catalyst is present as micrometer-long, nanometer-wide metal strips on the edges of each tower. Because all edges are identical, all metal strips are identical and nonuniformities in the shape and size of the catalytic entities are reduced to a minimum. Furthermore, and unlike typical catalyst preparations, there is complete control over thickness, composition, and spacing of both catalyst and support layers. In addition, all of the towers are attached to a single support wafer, making handling very convenient. The edges of the towers located on the perimeter of the forest are representative of all of the surfaces of interest and are readily accessible for experimental observation, in contrast to clusters within a porous matrix.

We used electron beam evaporation and a conventional vacuum system for wafer coating to prepare four different Ni/SiO₂ LSMs on top of oxidized 3-inch (7.5-cm) Si wafers. The Ni layer thicknesses ranged between 2 and 10 nm, whereas the SiO₂ thickness was fixed at 4.1 nm. Photolithog-

raphy and chemical etching resulted in the creation of $\sim 10^7$ towers per Si wafer with a total Ni surface area of 1 to 2 cm², depending on the specimen. A laser interferometric micrograph of the forest with the 2-nm-thick Ni and the 4.1-nm SiO₂ layers (specimen 1) is shown in Fig. 2. The Ni linear catalyst strips are on the edges of these towers, but they are too thin to be resolved optically. Due to limitations of the optical interference measurement, the vertical scale of the micrograph can only be calculated to within a quarter of a wavelength and hence is inaccurate. The overall pattern of the forest, however, is represented correctly. The as-deposited LSMs were x-ray amorphous. In addition, no diffraction peaks were observed corresponding to the LSM superlattice. Because it was not possible in our vapor coating system to deposit exactly the same thickness for every individual layer (Ni or SiO₂) during the course of the LSM fabrication (4), the characteristics of the LSM samples were not derivable from x-ray studies. Multilayers can be formed with sufficient accuracy to permit their use as x-ray filters (5), and the thickness distribution in the LSMs was very narrow (4). No further attempts were made to provide a detailed characterization of the LSMs because the initial objective of the research was to determine whether the catalytic size effect would be observed. The

structure of the LSM layers has not yet been studied, but typical thin film studies show that island formation or clustering is not a factor in layers thicker than 2 nm (5). The uniformity and complete accessibility of a representative reaction surface on the wafer perimeter should allow the full range of surface science techniques to be used to characterize these surfaces. Optical channels are readily prepared for in situ studies.

A simple batch, external recirculation reactor was used to study one of the classical reactions that exhibit size effects, the hydrogenolysis of ethane: $C_2H_6 + H_2 \rightarrow 2CH_4$. The LSMs, blank wafers, and the reactor were subjected to extensive oxidation and reduction to ensure that the LSM edges (catalyst) were clean and that Ni was present as metallic Ni. The protocol followed was similar to that used to prepare conventional supported metal clusters for catalytic studies (4). The observed rate, corrected for background and normalized to the calculated geometrical exposed area of the LSM edges, exhibited a maximum as a function of the Ni layer thickness. The maximum occurred at a thickness very close to the diameter reported for a rate maximum on traditional Ni on silica clusters. The results over the Ni LSM catalysts are summarized in Fig. 3 (curve 1) and compared with large cluster data (curve 2), small cluster data (curve 3), and bulk foil

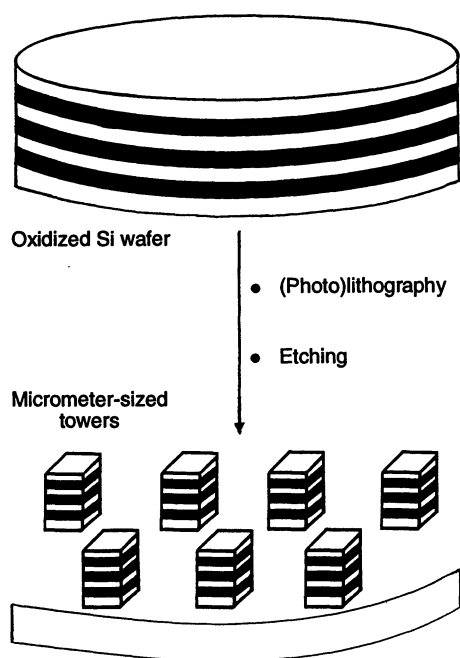


Fig. 1. The initial LSM and the forest of micrometer-sized towers. Shaded areas are metal layers. Ideal picture; dimensions not to scale.

Fig. 2. Laser interferometric micrograph of the manufactured forest for specimen 1.

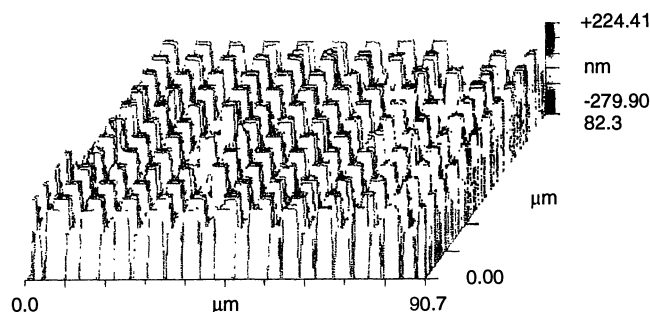
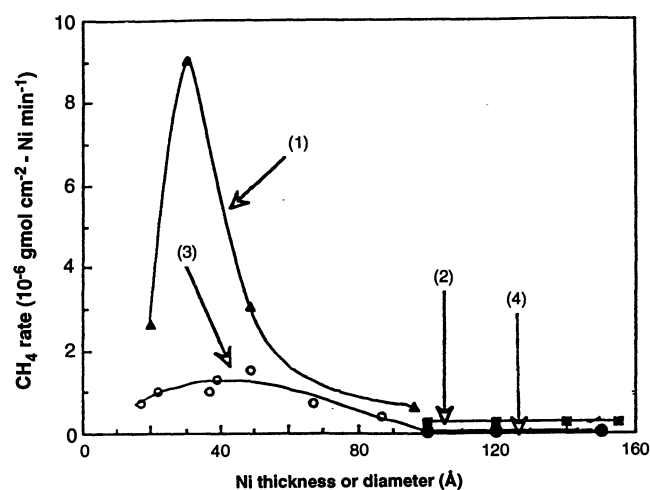


Fig. 3. Specific rate of CH₄ production during the hydrogenolysis on Ni catalysts: curve 1, Ni LSMs; curve 2, large clusters of Ni on SiO₂ (10); curve 3, small clusters of Ni on SiO₂ (11); and curve 4, Ni foil (12).



data (curve 4) under the same reaction conditions. Note that the data converge at large thickness or diameter, suggesting that the calculations of the LSM surface areas, based on ideal geometry of the layers, are not significantly in error. Furthermore, the hydrogenation of ethylene ($\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$) on the Ni LSMs showed no thickness dependence of the specific rate, in agreement with observations made with traditional supported clusters. These results imply that only one dimension need be in the nanometer scale to produce the size effects. The LSM layer thickness is the relevant parameter. Since the surface-to-volume ratio in the LSMs is orders of magnitude smaller and the number of connected Ni atoms is orders of magnitude larger than in traditional supported catalysts, that ratio or number cannot be the source of the size effects.

The origin of the size effects must be sought in explanations that are independent of the total number of connected atoms in the metal but are dependent on the configuration of the atoms in at least one nanometer-scale dimension. Two possible explanations can be proposed, although neither can be proven at this time. One is the result of a support effect, because the metal support contact area parallel to the nanoscale dimension is essentially the same in both LSM edges and clusters. It is known that Ni and SiO_2 do not mix in the bulk, but even if that occurs on the nanometer scale in the LSMs the same effect would be present in the clusters due to similar postpreparation processing. The stoichiometry of the silica layers is not known since SiO_x may be present in the vapor-deposited layer. However, if that stoichiometric variation is the origin of the support effect, it must be present also in the cluster supports, which are prepared in a very different manner. Alternatively, the cluster and LSM surface structures could be the same. Because it is unlikely that the minimum free energy surface structure of the supported cluster matches that of the minimum free energy surface structure of the LSM edge, the LSM result suggests that neither are equilibrium structures, thus excluding those derived from the model potentials for unsupported clusters with a specific total number of atoms in them. Recent calculations of the structure of smaller unsupported clusters, made with the use of metal interaction potentials more appropriate to metals, also suggest that the surface structures in real systems could be significantly different from those previously calculated (6, 7). Limited studies of supported cluster catalyst topography with tunneling microscopy further suggest that very nonideal structures are present (8). Although increased rates of catalytic reactions

have been reported for amorphous catalysts (9), the larger maximum absolute rates reported here, relative to clusters, are more likely due to the narrower size distribution in the LSM edges. Finally, size-constrained surface reconstruction as a result of reaction could occur both on clusters and LSMs.

REFERENCES AND NOTES

1. M. Boudart, *Adv. Catal.* **20**, 153 (1969).
2. M. Che and C. O. Bennett, *ibid.* **36**, 55 (1989).
3. R. S. Averback, J. Bernholc, D. L. Nelson, *Clusters and Cluster-Assembled Materials*, vol. 206 of the *Materials Research Society Symposium Proceedings* (Materials Research Society, Pittsburgh, 1991).
4. I. Zuburtikudis, thesis, University of Rochester (1992).
5. T. W. Barbie, *SPIE J.* **563**, 1 (1985).
6. A. Sachdev and R. Masel, paper presented at the American Institute of Chemical Engineers 1991 Annual Meeting, Los Angeles, November 1991.
7. D. G. Vlachos, L. D. Schmidt, R. Aris, *J. Chem. Phys.* **96**, 6880 (1992).
8. P. A. Thomas, W. H. Lee, R. I. Masel, *J. Vac. Sci. Technol. A* **8**, 3653 (1990).
9. A. Molnar, G. V. Smith, M. Bartok, *Adv. Catal.* **36**, 329 (1989).
10. D. J. C. Yates, W. F. Taylor, J. H. Sinfelt, *J. Am. Chem. Soc.* **86**, 2296 (1964).
11. A. Sárkány and P. Tétényi, *React. Kinet. Catal. Lett.* **12**, 297 (1979).
12. J. H. Sinfelt, J. L. Carter, D. J. C. Yates, *J. Catal.* **24**, 283 (1972).
13. Sincere thanks to L. Fuller and D. Casilio of the Rochester Institute of Technology (Department of Microelectronics Engineering) for their decisive role in the lithography and etching work. The financial support of the Elon Huntington Hooker Fellowship to I.Z. is gratefully acknowledged.

24 June 1992; accepted 24 September 1992

Viscoelastic Dynamics of Confined Polymer Melts

Hsuan-Wei Hu and Steve Granick

The frequency-dependent shear response of an ultrathin polymer melt (polyphenylmethylsiloxane) confined between adsorbing surfaces (parallel plates of mica) is described. The sinusoidal deformations were sufficiently small to give linear response, implying that measurement did not perturb the film structure. A remarkable transition was observed with decreasing thickness. When the film thickness was less than five to six times the unperturbed radius of gyration, there emerged a strong rubber-like elasticity that was not characteristic of the bulk samples. This result indicates enhanced entanglement interactions in thin polymer films and offers a mechanism to explain the slow mobility of polymers at surfaces.

From biology to tribology, prominent interfacial processes involve polymers. With regard to surface mobility, the sharp inconsistency between theory and experiment emphasizes the prominence of some kind of trapped state in this problem (1–3). In this report, we are concerned with the dynamics of molten polymer of thickness comparable to the radius of gyration; other examples of unexpectedly slow surface mobility concern the spreading of polymer melts (4) and the adsorption-desorption dynamics of polymers in solution (5). Theoretical studies of the confining forces needed to maintain thin polymer films show that essentially zero force is required at equilibrium (6) down to a film thickness of two to three segment dimensions (7). Experimentally, strong repulsion is observed starting when the films are significantly thicker, several times the unperturbed radius of gyration (8–10). Dynamic experiments also indicate a slowing down of near-surface dynamics (11, 12). However, the forced deformations in those studies caused nonlinear responses and the experiments were not designed to measure associated elastic effects. The is-

ssues raised are clearly relevant to many diverse physical phenomena, especially polymer-filler interactions in rubbers and composites (13), polymer adhesives, lubrication, and problems concerning the wall boundary conditions for transport during polymer processing (14).

We report on the linear viscoelasticity of thin polymer films. The significance of linear response (obtained with shear amplitudes $< 2 \text{ \AA}$) is that measurement did not perturb the film structure. A remarkable transition was seen with diminishing film thickness. At a thickness less than five to six times the unperturbed radius of gyration (5 to $6 R_G$), the viscoelastic behavior crosses from viscous relaxation, which is characteristic of single chains in the bulk liquid, to a predominantly elastic and rubber-like response. This latter response indicates enhanced steric constraints on motion, which may be construed as enhanced entanglement interactions.

The experimental approach has been reported elsewhere (15, 16). In brief, the polymer fluids were confined between atomically smooth, step-free single crystals of muscovite mica that were configured as parallel plates and that were surrounded by a droplet reservoir. To measure shear

Materials Research Laboratory and Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801.