**DIMENSIONAL EFFECTS IN CONTROLLED STRUCTURE
SUPPORTED CATALYSTS DERIVED FROM LAYERED
SYNTHETIC MICROSTRUCTURES**

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Howard Saltsburg

**University of Rochester
Rochester, New York 14627**

DOE Patent Clearance Granted
MPD
Mark P Dvorscak
(630) 252-2393
E-mail mark.dvorscak@ch.doe.gov
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DOE Chicago Operations Office
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Dimensional Effects in Controlled Structure Supported Catalysts

Derived From Layered Synthetic Microstructures (LSMs)

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PI: Howard M. Saltsburg, University of Rochester

SUMMARY AND CONCLUSIONS

Several heterogeneous catalytic reactions show size dependence- whereby the specific rate (moles converted/area/time) changes with the average diameter of supported metal particles in the nanometer range. These size effects are known to depend on the catalyst preparation, purity, pre-treatment, and the nature of the metal-support interaction. However, the origin of these observed effects have not been fully explained. Geometric arguments relating the size dependence to the relative concentration of active sites on idealized crystal particles simply cannot account for all the observed results. Furthermore, the control of particle size and distribution is limited by standard preparation methods. High temperature pre-treatments used to increase particle size may be equivalent to altering two parameters at once. In an effort to overcome the geometric limitations of supported particles, we had created novel supported metal catalysts called Layered Synthetic Microstructures (LSMs) by the physical vapor deposition of alternating thin films of nickel and silica onto 3" silicon wafer substrates. Subsequent lithography followed by wet etching left an array of approximately 10^8 micron-sized towers with 1 cm^2 exposed metal. Relative catalytic rate measured for ethane hydrogenolysis in a recycle reactor (380 cc) showed that LSMs produce similar size effects as previously found with supported particles, indicating only one dimension needs to be nanosized to achieve size dependence.

In this study, experiments were accomplished using LSMs with a wider range of metals (Ni, Pt, Ir, Rh, Ru, etc.) and supports (SiO_2 and Al_2O_3). These combinations necessitated the use of dry etching with argon ions rather than wet etching to expose the metal layers. The metal thickness, the support, and the number of metal layers (i.e. metal-support interface length) were varied individually to study the corresponding effects on specific rates. Ethane hydrogenolysis rates on Ni/ SiO_2 LSMs had a maximum at 40Å thick nickel in agreement with the literature. However, no activity could be measured with Ni/ Al_2O_3 LSMs. The rates on Rh/ Al_2O_3 and

Ir/Al₂O₃ LSMs decreased with increasing metal layer size, but the rhodium samples were more active and had a sharper decrease in activity. Iridium LSM rates were proportional to the number of metal layers (i.e. scaled to the number of metal-support interfaces) indicating no true size dependence.

Carbon monoxide hydrogenation (methanation) rates on Ni/SiO₂ LSMs had a maximum between 40 and 100 Å nickel in agreement with one literature source, while rates on Ni/Al₂O₃ LSMs were proportional to the number of layers in the sample (i.e. the total metal-support interface length) rather than the thickness of the nickel layers. Many literature sources indicate that spillover of reaction intermediates occurs during methanation from nickel to alumina, but not to silica, and the results here support this finding. The rates on Ru/Al₂O₃ LSMs were not strongly dependent on the metal layer thickness or the metal-support interface length although previous studies found a size dependence for this system. Carbon monoxide oxidation was not found to exhibit a significant size effect with Pt/Al₂O₃ or Ir/Al₂O₃ LSMs as reported in some sources for supported clusters. However, the oxygen plasma used to remove the resist during the fabrication process resulted in non-steady reaction rates on the platinum samples where the rate was slow initially but jumped later in the reaction. This observation most likely resulted from atomic level reconstructions which are well described in the surface science literature. It can be concluded that a distinction can be made for the first time between several types of size effects due to the well-defined geometry of LSM catalysts. Rates in some systems are truly size dependent, while in other systems rates are clearly dependent on the metal-support interface. The advantage of the LSM catalysts is that several individual parameters can be varied keeping the pre-treatment the same.

In addition, a lift-off process has been developed for fabrication of all kinds of LSMs without resorting to either wet or dry etch techniques. The activity of the silica-supported silver LSMs for ethylene epoxidation showed the same dependence on silver layer thickness as did supported clusters for both rate and selectivity. The oxidation of hydrogen on platinum LSMs exhibited no size dependence in excess oxygen, and a size dependence in excess hydrogen, in accord with the observations using traditional supported cluster catalysts. Hydrogenolysis of ethane on rhodium LSMs demonstrated a strong size dependence again as on traditional cluster-supported catalysts. Combined with our previous results it can be concluded that the one-dimensional nanoscale aspect of the LSM catalyst is a sufficient condition for the size effects to

be exhibited. It was also found that by normalizing rates to metal-oxide interface length, classical structure-sensitive reactions can be divided into two categories: truly size-dependent reactions occurring on metal surfaces, such as ethane hydrogenolysis on rhodium LSMs; and "fake" size-dependent reactions or size independent reactions, which predominantly take place at the metal-support interface and are independent of metal surface area, such as ethane hydrogenolysis on silica or alumina-supported iridium LSMs.

Publications:

- (1) Mark Chaplin, "Structure sensitive catalyzed reaction studies on layered synthetic microstructures," Ph.D. thesis, University of Rochester, 1997
- (2) Zhujian Lu, "Size effects in heterogeneous reactions using layered synthetic microstructures," Ph.D. thesis, University of Rochester, 1997