Catalysis Letters 27 (1994) 43–51

A novel microfabricated Pd / SiO_2 model catalyst for the hydrogenation of 1,3-butadiene

A.C. Krauth [a], K.H. Lee [a], G.H. Bernstein [b] and E.E. Wolf [a,1]

Departments of [a] Chemical Engineering and [b] Electrical Engineering,
University of Notre Dame, Notre Dame, IN 46556, USA

Received 1 November 1993; accepted 6 April 1994

The hydrogenation of 1,3-butadiene was successfully demonstrated using a microfabricated catalyst. The reaction was carried out at atmospheric pressure and 100°C with a hydrogen to hydrocarbon ratio of 125. Data from a thin film Pd/silica catalyst is also presented for comparison. The conversion for the microfabricated catalyst is more stable and slightly lower than that for the thin film catalyst; however, the geometric surface area of the thin film catalyst is 7.5 times greater than that of the microfabricated catalyst. The selectivity of the reaction products is greatly different between the two catalysts. The microfabricated catalyst has a much lower selectivity for 1-butene and favors the 2-butenes more so than does the thin film catalyst.

Keywords: microfabricated catalyst; thin film catalyst; Pd; hydrogenation of 1,3-butadiene

1. Introduction

Microfabrication of integrated circuits has been common practice for many years and the techniques and processes developed have led to the rapid growth in the microelectronics industry. This paper demonstrates the use of microfabrication techniques for preparing a model catalyst and reports its catalytic ability during 1,3-butadiene hydrogenation. The main advantage of microfabricating a catalyst is that it is possible to construct the catalyst in a reproducible and predesigned manner. Using this technology should allow one to prepare a catalyst with predetermined size, shape, spacing and composition. Other applications of this technology have already appeared in the area of catalytic research, from the production of solid-state catalytic gas sensors [1] to the study of size effects in supported metal catalysts [2]. The previous work done on studying size effects used microfabricated columns of alternating metal and support layers. The width of the strips, or the thickness of the metal layers, was the variable used to study the size effects. This

---

[1] To whom correspondence should be addressed.

paper presents a catalyst that is comprised of a well defined array of catalytic particles supported on SiO$_2$ and compares its activity with that of a thin film catalyst.

The main disadvantage of the microfabricated catalyst is that it does have a low surface area compared to conventional industrial catalysts. The reaction chosen to characterize the activity of the catalyst is the hydrogenation of 1,3-butadiene, because reasonable conversions may still be obtained with a low surface area catalyst. This reaction has been used as a test reaction for other research groups, mainly for evaluating Pd [3,4] and Pt [5,6] catalysts. This communication outlines the preparation method as well as initial results concerning the hydrogenation of 1,3-butadiene in a flow system.

2. Experimental

2.1. CATALYTIC PREPARATION

The preparation procedure described below is only a partial description of the complete procedure, which involves other aspects now under a pending patent application. The procedure presented, however, describes completely the results presented in this work. Except for the photomasks, the microfabricated catalyst was prepared in the Microelectronics Laboratories in the Electrical Engineering Department at the University of Notre Dame.

The silica support was obtained by oxidizing a clean, n-type ⟨100⟩ silicon wafer. Oxidation conditions were 1200°C and 24 h duration in a dry oxygen environment, which yielded a silica layer with a thickness of 1 μm. A few drops of a mixture composed of DuPont Pyralin VM651 Adhesion Promoter (2 drops), methanol (40 cm^3) and water (3 cm^3) was applied to the wafer and it was spun until dry. The mixture acted as an adhesion promoter for the spin-on dielectric material (DuPont Pyralin PI-2613 Polyimide Coating). The wafer was spun at 3000 rpm for 30 s to produce an even layer. The polyimide film was partially cured for 30 min at 145°C. The thickness of the polyimide layer shrunk to 0.25 μm after the film was completely cured.

The next step was to transfer the desired pattern for the catalytic particles to the polyimide layer. A positive photoresist (Shipley Microposit S1400-27 Photoresist) was applied to the surface of the wafer and spun at a speed of 5000 rpm for 30 s, which resulted in a layer of approximately 1.2 μm thick. The wafer was then "soft" baked at 90°C for 30 min to evaporate a portion of the solvents in the photoresist. The wafer was next brought into contact with a glass photomask, which had the pattern of the catalytic particles imprinted on it, using a contact mask aligner. The pattern was 4 μm transparent squares separated by 4 μm opaque spaces. The wafer was exposed to an ultraviolet light source (350 W mercury arc lamp, i-line, 365 nm) through the photomask and then immersed in a developing solution of one part water and one part Shipley Microposit Developer Concentrate. The positive photoresist depolymerizes when exposed to UV light; therefore, the resist underneath the transparent square areas washed away when immersed in the developer. The polyimide is also photosensitive and is affected in the same manner as the positive resist.

The catalytic metal, Pd (99.997% pure, Johnson Matthey AESAR/ALFA), was deposited onto the wafer by vacuum thermal deposition. A deposition using 0.566 g resulted in a film thickness of approximately 3000 Å. Afterwards, the wafer was immersed in acetone to lift off the remaining photoresist and the Pd on top of the resist. The Pd that remained filled the squares previously opened in the polyimide layer. The final step was to completely cure the polyimide dielectric by baking the wafer at 400°C for 30 min.

A thin film catalyst, used as a reference for comparison with the microfabrication catalyst, was prepared by the evaporation of Pd onto a silica surface. A silicon wafer was oxidized at 1100°C for 3 h in dry oxygen to yield an oxide layer about 2000 Å thick. Then a film of 12 nm was deposited onto the silica using 15.7 mg of Pd in a vacuum evaporator.

2.2. ACTIVITY MEASUREMENTS

The hydrogenation of 1,3-butadiene was carried out in a 3/8″ i.d. quartz tube at atmospheric pressure. The tube was heated using a flexible, electrical heating jacket (300 W/120 V, BriskHeat).

Both the thin film and the microfabricated catalyst were studied under the same reaction conditions. The catalysts were reduced in hydrogen flow for 8 h. The microfabricated catalyst was reduced at 250°C, while the thin film catalyst was treated at 450°C. After the treatment, the temperature was set to the reaction temperature of 100°C. The flow of reactants introduced into the reactor consisted of hydrogen (partial pressure of 500 Torr), 1,3-butadiene (4 Torr) and nitrogen to produce a constant flowrate of 110 cm^3/min. Ultra high purity grade nitrogen and hydrogen were supplied by Mittler Supply, Inc. and the 1,3-butadiene (99.5% purity) was supplied by Matheson Gas Products.

The reaction products were analyzed using a Varian Aerograph (Series 1400) FID detector and separated by a 7 foot chromatographic column packed with 0.19% picric acid/graphpac packings (Alltech Associates, Inc.).

3. Results and discussion

A scanning electron micrograph of the finished microfabricated catalyst is shown in fig. 1. The photograph displays four rows of Pd particles, each of which is roughly a 4 μm square. As it can be seen, the edges of the particles are much sharper than the corners. This is due to diffraction effects during the exposure step. This

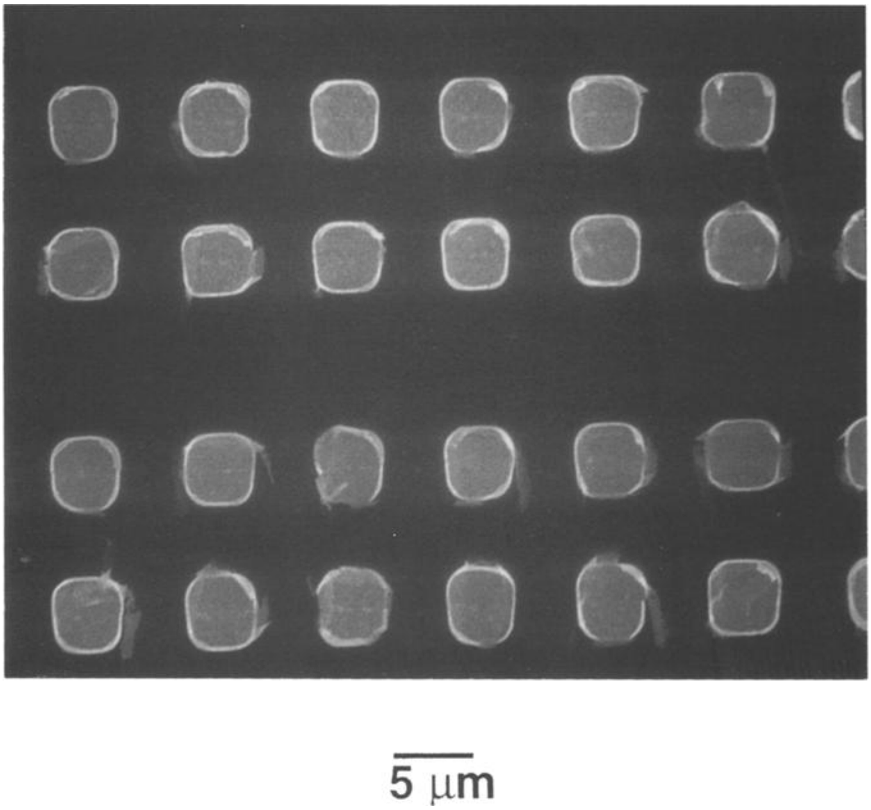

Fig. 1. Scanning electron micrograph of the Pd/SiO$_2$ microfabricated catalyst. Scale bar = 5 µm.

particular image was obtained on a catalyst that has been used and regenerated, and so does not appear as clean as the fresh catalyst.

The conversion and selectivity versus time on stream for the microfabricated and thin film catalysts are displayed in figs. 2a–2c. The data shown is for a fresh piece of catalyst in both cases. The microfabricated catalyst compares favorably with the more conventional thin film catalyst, which has a larger surface area. The thin film catalyst has a geometric surface area of 1.5 cm^2; whereas, the geometric surface area of the microfabricated catalyst is roughly 0.2 cm^2. The initial conversion of the microfabricated catalyst is 51.9% and remains relatively stable over the 60 min reaction period as shown in fig. 2a. Initially, the thin film catalyst has a higher conversion, 78.9%, but it deactivates much faster over time. After 1 h, the conversion of the thin film catalyst drops by 23.1%, compared to a decrease in conversion of only 5.7% for the microfabricated catalyst. It is reasonable to expect that if the microfabricated catalyst has the same surface area as the thin film catalyst, it would yield a higher conversion than the thin film catalyst. Since the size of the microfabricated particles is relatively large, 4 µm, one would expect the turnover frequency to be comparable to the thin film catalyst. At 27°C (near zero con-

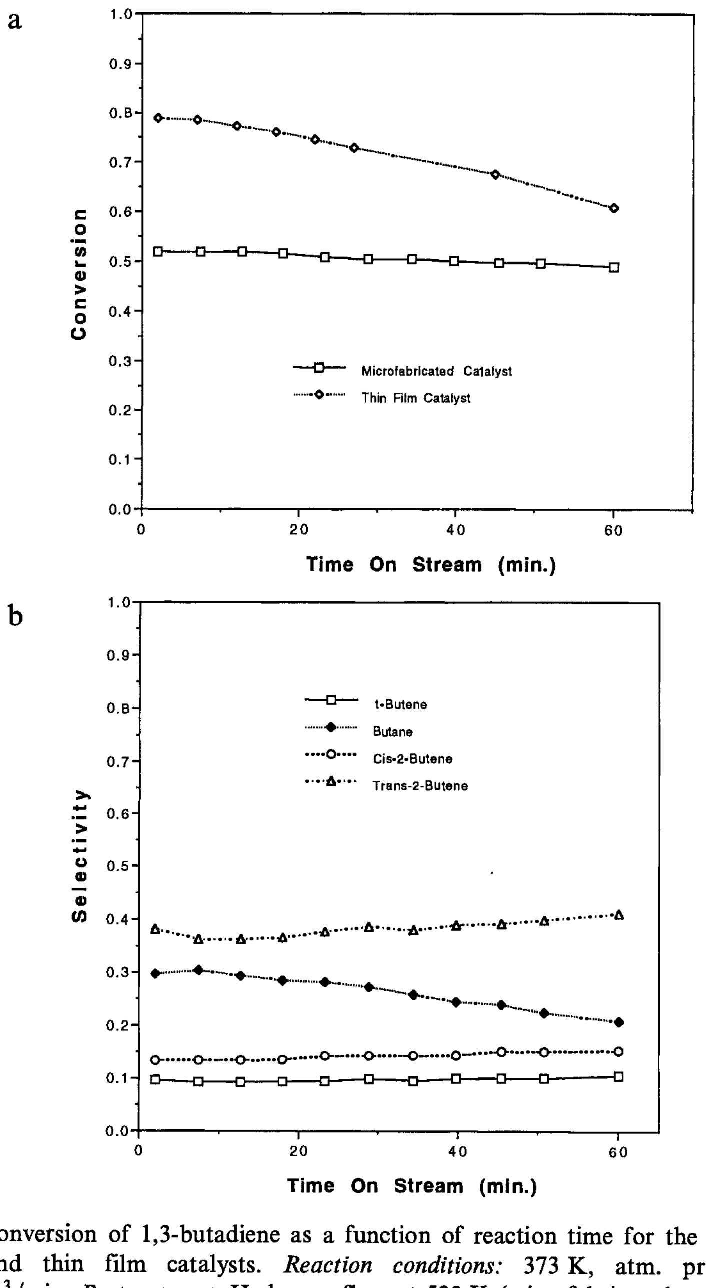

Fig. 2. (a) Conversion of 1,3-butadiene as a function of reaction time for the Pd/SiO$_2$ microfabricated and thin film catalysts. *Reaction conditions:* 373 K, atm. pressure, $H_2/HC = 125, 110$ cm^3/min. *Pretreatment*: Hydrogen flow at 523 K (microfabricated catalyst) or 723 K (thin film catalyst) for 8 h. (b) Selectivity of the Pd/SiO$_2$ microfabricated catalyst as a function of reaction time for the hydrogenation of 1,3-butadiene. *Reaction conditions:* 373 K, atm. pressure, $H_2/HC = 125, 110$ cm^3/min. *Pretreatment*: Hydrogen flow at 523 K (microfabricated catalyst) or 723 K (thin film catalyst) for 8 h. (c) Selectivity of the Pd/SiO$_2$ thin film catalyst as a function of reaction time for the hydrogenation of 1,3-butadiene. *Reaction conditions:* 373 K, atm. pressure, $H_2/HC = 125, 110$ cm^3/min. *Pretreatment*: Hydrogen flow at 523 K (microfabricated catalyst) or 723 K (thin film catalyst) for 8 h.

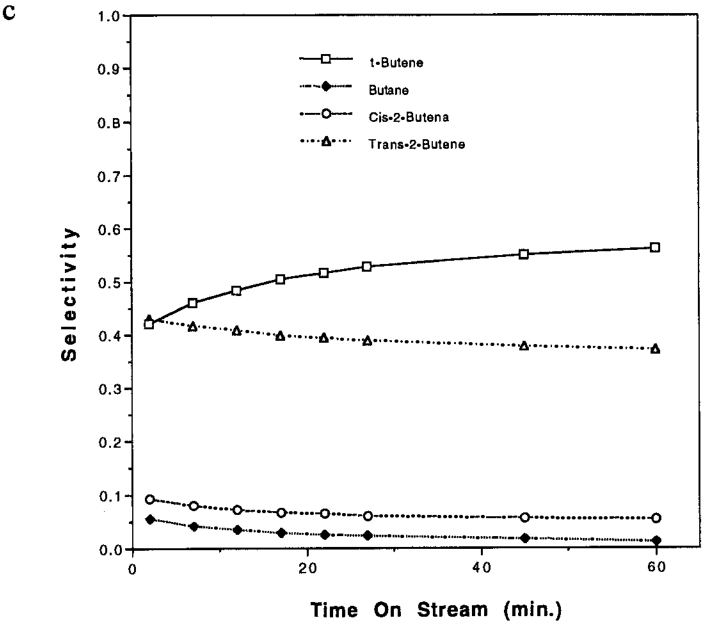

Fig. 2. (continued).

version) the turnover frequency of the microfabricated catalyst is 20.8 s^{-1} and 33.2 s^{-1} for the thin film catalyst. However, at 100°C the microfabricated catalyst is more active. One possible explanation for the difference in conversion between the two samples may be due to the surface morphology. Initial studies using atomic force microscopy (AFM) have shown that the 4 μm particles are in fact composed of much smaller Pd grains. AFM micrographs of the fabricated sample, fig. 3, show that the average particle size of the microfabricated catalyst is approximately 65 nm. The AFM micrographs for a Pd thin film catalyst treated for 8 h in H_2 at 450°C appear in a recent publication by Lee and Wolf [7]. For comparison, the thin film sample had a much more uniform morphology with a slightly larger particle size of 75 nm. Since the particle size distribution for the microfabricated catalyst appears to be much wider, including a larger number of smaller particles, this difference may explain the higher relative activity over the thin film catalyst at the reaction conditions stated. One method being investigated to obtain better control of the surface is electron beam lithography. By using electron beam lithography to create smaller openings in the resist layer, we hope to prepare a catalyst with a more uniform and pre-determined particle size.

There are also differences between the selectivities of the two catalysts. The selectivities of the microfabricated and thin film catalysts are shown in figs. 2b and 2c, respectively. The microfabricated catalyst is initially very selective towards trans-2-butene and butane; whereas, 1-butene and trans-2-butene are favored in the thin film catalyst. The fabricated catalyst is also slightly more selective towards cis-2-butene (initially 13.4%) than is the thin film catalyst (initially 9.3%). The selectivity

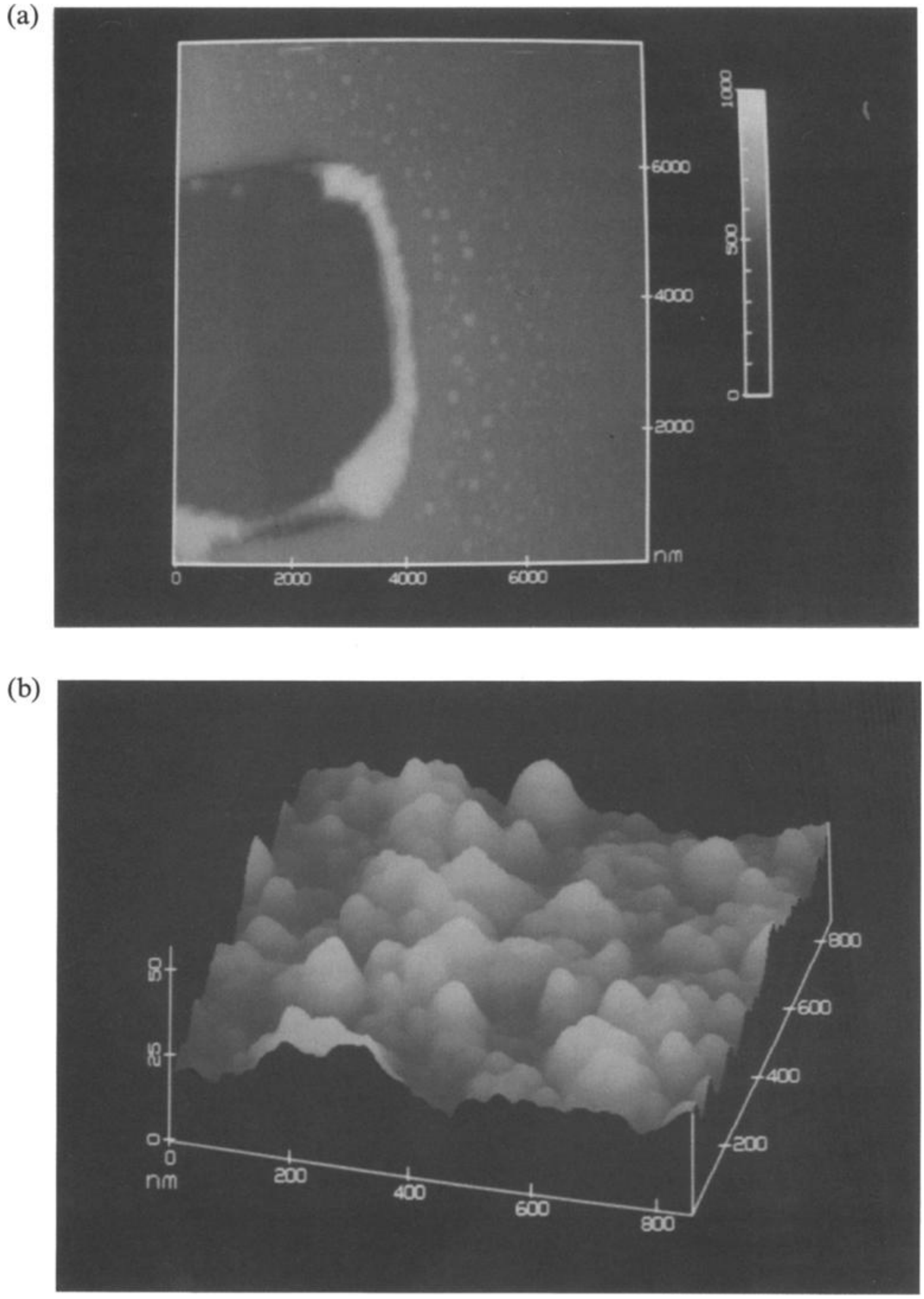

Fig. 3. AFM images of the Pd microfabricated catalyst. (a) Top view showing part of one microfabricated particle (8000 × 8000 nm^2), (b) surface view of the microfabricated particle (800 × 800 nm^2).

of the 2-butenes increases with respect to time for the microfabricated catalyst and decreases for the thin film catalyst. The selectivity of trans-2-butene is initially less in the microfabricated catalyst (43.0% versus 38.1%), but after the 1 h reaction, the selectivity becomes greater than that for the thin film catalyst (41.1% versus 37.2%). The microfabricated catalyst also has a higher selectivities for butane than does the thin film catalyst.

The main difference in selectivity between the two catalysts is with respect to 1-butene. The microfabricated catalyst has an initial 1-butene selectivity of 9.6%, compared to a selectivity of 42.1% for the film catalyst. The difference in selectivity is not due to the difference in conversions, since as the conversions converge towards each other for the two catalysts in fig. 2a, the 1-butene selectivities do not. The difference in 1-butene selectivity initially is 32.5% and grows to 45.6% after 1 h as the difference in conversions decreases from 27.0 to 11.8%.

Since the difference in selectivity cannot be solely attributed to the difference in conversion, there must be different types of active sites present on the two catalysts. As time on stream passes, the microfabricated catalyst increasingly favors the formation of 2-butenes over 1-butenes as compared to the thin film catalyst. The perimeter of the catalytic particles of the microfabricated catalyst may have sites that are more active and selective to a di-π adsorption of butadiene, as described by Sautet and Paul [8], that leads to the 2-butene formation. It is also possible the differences noted earlier between the two catalysts in surface morphology may also be the reason. Thus, at this point we cannot specifically ascertain the cause of the activity–selectivity differences. Further work is underway to investigate parameters of the microfabricated catalyst, such as the size, shape, spacing and composition of the catalytic particles. As mentioned previously, while the particles in the pattern reported here are very large, use of electron beam lithography will lead to the design of particles that are closer to the same range as that of supported catalysts.

It should also be noted that the flow reactor used with the microfabricated catalyst did not accommodate it well and it lay at an angle of about 60° with respect to the flow. Since the microfabricated catalyst is one sided, there was a possibility of some of the gas bypassing the catalyst. The flow patterns were not identical when evaluating the activity of both catalysts; however, the differences in conversion and selectivity are too large to be attributed to the bypass of reactants along the catalytic wafer. New catalysts with different patterns are being prepared and refinements in reactor design are underway to eliminate this potential effect from the activity results.

4. Conclusion

A microfabricated catalyst has been prepared and its activity compares favorably to a thin film catalyst and exhibits different selectivity in the hydrogenation of 1,3-butadiene. The microfabricated catalyst converts more 1,3-butadiene per surface area than the thin film sample at the reaction conditions used. Differences in surface morphology between the two catalysts may be the reason for the differences in activity.

Acknowledgement

Financial support from NSF grants (NSF CTS 92-15339 and NSF EC592-53580) and the Graduate Assistance in Areas of National Need Program (GAANNP) through Notre Dame's Center for Bioengineering and Pollution Control is gratefully acknowledged. Furthermore, we would like to thank the National Nanofabrication Facility at Cornell for technical assistance and for supplying the photomasks.

References

[1] P.T. Moseley and B.C. Tofield, *Solid State Gas Sensors* (Hilger, Philadelphia, 1987) p. 227.
[2] I. Zuburtikudis and H. Saltsburg, Science 258 (1992) 1337.
[3] B. Tardy, C. Noupa, C. Leclercq, J.C. Bertolini, A. Hoareau, M. Treilleux, J.P. Faure and G. Nihoul, J. Catal. 129 (1991) 1.
[4] A. Sarkany, Z. Zsoldos, B. Furlong, J.W. Hightower and L. Guczi, J. Catal. 141 (1993) 566.
[5] M. Primet, M. El Azhar and M. Guenin, Appl. Catal. 58 (1990) 241.
[6] C.M. Pradier, E. Margot, Y. Berthier and J. Oudar, Appl. Catal. 43 (1988) 177.
[7] K.H. Lee and E.E. Wolf, to be published.
[8] P. Sautet and J.F. Paul, Catal. Lett. 9 (1991) 245.