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SCANNING TUNNELING MICROSCOPY CHARACTERIZATION OF AMMONIA SYNTHESIS CATALYSTS

F. BESENBACHER, E. LÆGSGAARD, I. STENSGAARD
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

P. STOLTZE [1] and H. TOPSØE
Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark

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The possibility of studying the texture of catalysts at the atomic level by Scanning Tunneling Microscopy (STM) is demonstrated. It is shown that high resolution pictures can be obtained even for a passivated ammonia synthesis catalyst using a scanning tunneling microscope operating in air. The STM results reveal that the catalyst has a spongy pore structure with both hole and slit shaped pores. The catalyst surfaces are observed to contain fine quite regular ridge structures with a direction that tentatively is related to the (110) direction of iron. The presence of the ridge structures is apparently the result of the topotactic nature of the reduction process and a preference to expose (111) Fe facets.

Keywords: Scanning tunneling microscopy (STM), ammonia synthesis catalysts, surface chemistry

1. Introduction

In order to understand the mode of operation of heterogeneous catalysts, it is important to have access to information about both the texture of the catalyst surfaces and the chemical and structural identity of the surface phases. While progress has been made on the last topic, it has been extremely difficult to obtain information on the texture of the catalyst at the atomic level. Thus, the origin of the textural promotion, the influence of structural promoters on the nature of structures present, and the stability of the catalytically active surfaces are still not fully understood. Using the classical ammonia catalyst as an example, the present paper will report the results of STM studies which illustrate how the much needed atomic resolution information may be obtained for *industrial* catalysts. Moreover, contrary to many other surface science techniques, it is shown to be possible to obtain the surface information with the catalyst in a gaseous environment.

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[1] Present address: Laboratory of Applied Physics, Technical University of Denmark.

The basic principle of a scanning tunneling microscope is electron tunneling between a sharp metal tip and a conducting surface. When the tip is positioned at a distance of 5–10 Å from the sample, the electron wave functions of the tip and sample overlap. The electron can then tunnel from the tip to the surface and vice versa, depending on the voltage ($\leqslant 3$ V) applied across the junction. The tunneling current depends exponentially on the width of the tunneling gap and the sample-to-dip distance is therefore very sensitive to the magnitude of the tunneling current. During scanning of the tip across the surface, the information of the surface topography is recorded by measuring the adjustments in tip-to-sample distance required to keep the tunnelig current constant. A raster image of structures extending to the atomic scale can thus be obtained [1,2].

The great excitement of the STM [1,2] is its capability to observe single atoms on surfaces of conducting materials, with a resolution close to 1 Å horizontally and 0.1 Å vertically. This is the feature that separates it from all other surface sensitive techniques and in fact has already lead to unprecedented insights into geometric and electronic structure of semiconductor and metal surfaces [2] under ultra high vacuum conditions. Very recently it was demonstrated that one can visualize dynamic processes on metal and semiconductor surfaces in real time and real space. This opens the possibility of studying the dynamics of model catalytic reactions [3].

An important area of application of the STM lies in its ability to image aperiodic or disordered surfaces with near-atomic lateral and vertical resolution, and thereby allowing the determination of the detailed surface structure and disorder. Heterogeneous catalysis is one field where the study of the local structure and texture at near atomic resolution by STM may be extremely useful.

The industrial ammonia synthesis catalyst is based on iron [4] to which promoters such as K and Al are added. The active state is produced by reducing an essentially non porous structure of magnetite to a highly porous structure with ~ 300 Å metallic iron crystallites [4–13]. Recent results [12,13] have provided evidence for a topotactic nature of the reduction process.

K is adsorbed on the surface of the metallic Fe particles [14–17] where it increases the stability of adsorbed N_2 [18,19] and thus increases the overall reaction rate [20]. Al has an important role in creating and maintaining the surface area of the iron. In the catalyst Al does not undergo reduction [14,17,21] but is present, at least in part as a thin layer covering a significant fraction of the catalyst surface [15,22–24]. The mechanism of stabilizing the surface area (textural promotion) is most likely related to the coverage of the surface by the textural promoter, Al, acting as spacers between Fe particles [6,13]. However, the presence of large amounts of promoter in the grain boundaries [4,23,25] has made it difficult to arrive at definite conclusions regarding the exact role of the textural promoter. Moreover, recent single crystal studies [26,27] have shown that Al may also contribute to the activity by restructuring the Fe surface to expose more active planes such as (111).

In the present letter we will emphasize the usefulness of STM in catalyst research by showing that high resolution pictures of a catalyst can be recorded by STM.

2. Experimental

The experiments were performed with a Topsøe KM1-type ammonia synthesis catalyst.

A large piece of catalyst was spark cut to a 25 × 25 mm rod. This rod was then spark cut into a number of slabs of uniform thickness from 2 to 10 mm. The resulting catalyst was reduced slowly at 1 atm in a $3H_2 + N_2$ mixture. Because of the unusual geometry and flow pattern, a temperature schedule could not be determined in advance from models [9] of the reduction of more conventional shapes. Instead the water concentration at the reactor exit was measured continuously and the heating rate was adjusted to keep the exit water concentration below a few hundred ppm. Because of the unusual flow pattern, the water concentration at and in the samples must have been somewhat higher. The sample was then cooled and passivated in a flow of 1% O_2 in N_2 at room temperature. In retrospect the sample preparation was unnecessarily elaborate. Fragments of prereduced catalysts a few mm large and exposing one reasonably plane face were very well suited for the recording of STM images.

In the present study we have taken advantage of the recent development of a high-stability STM [3,28,29] to produce STM images of actual catalysts. The key design features of our STM is the application of two piezoelectric ceramic tubes, one for the *x-y-z* motion of the tip and one for a linear motor used for coarse positioning of the tip relative to the specimen. This implies that the STM is fully controlled by electronic means. Furthermore, a combination with a small, rigid (lowest resonance frequency 16 kHz) and temperature compensated construction is able to reduce the sensitivity to mechanical and acoustical vibrations and temperature variations. This arrangement further allows easy tunneling on many different spots on the sample which proved to be crucial in the present experiments. However, in many cases high resolution could not be achieved as the tip was either damaged or blunted during the initial approach to the surface or at a very early stage in the recording of the picture. We presume that this happens because the tip initial happened to approach the surface near the mouth of a pore and suffered a mechanical collision with the wall of the pore at the start of the scan. Another possibility is that the tip may have approached a patch of the surface of high electrical resistivity such as promotor oxides located in grain boundaries resulting in a mechanical collision in an attempt to establish the desired tunnel current.

Images obtained by STM are composite data of topographic as well as electronic properties. The surface of the Fe crystallites in the passivated catalyst is covered with a thin oxide layer and one might think that this oxide layer would influence the tunneling process and degrade the resolution in the STM pictures. The result of the present study shows that this is not necessarily the case and pictures of high resolution can be obtained even for the catalyst in its passivated state. However, it should be kept in mind that the presence of the oxide layer makes recorded topographic heights somewhat uncertain. Furthermore, the correlation between features in the STM pictures and the topographic and electronic properties of the catalyst surface will be more complicated than for STM pictures of clean metal surfaces.

The experiments were performed with mechanically formed platinum-iridium tips. The sample bias varied between 1.0 and 1.5 V and the tunneling current was 0.7 nA. The dimensions of the images were recorded with 128 × 128 pixels. Post acquisition image processing consisted of a simple 9 point two-dimensional averaging of the raw data.

3. Discussion

The present STM investigation was performed in ambient air. Tunneling in air is in fact possible since in the very small working volume of the STM, 1000 $Å^3$, the effective number of molecules is only $\lesssim 10^{-2}$ even at atmospheric pressure, and thus we can still in a sense think of "vacuum tunneling". This feature should in principle also make it possible to perform in situ studies of catalysts while exposed to reactive gases.

The STM investigations of the reduced and passivated ammonia catalyst provide insight into both the porous nature of the catalyst and the topography, morphology and atomic features of the catalyst surfaces.

Mercury porosimetry and SEM studies have shown that the pores in the reduced ammonia catalysts have predominantly sizes in the 150–600 Å range with a few being above 1000 Å [8–10,12]. Thus, in the present study information about the pore structure is mainly obtained from the STM pictures with relatively low magnification. Fig. 1 shows a 1200 × 1200 Å region of the catalyst. A section of a slit shaped pore with a width of about 200 Å is noted. The existence of such slit or channel shaped pores is in agreement with the earlier SEM results [10,12] and is probably related to the tendency to form pores along certain crystallographic directions in the magnetite lattice [12,13] yielding in part plate-like structures. This is further substantiated by the data presented in fig. 2 where the shape and orientation of the pores appear to closely follow the ridge structures (to be discussed below) which, as observed in the atomic resolution STM pictures (figs. 2c, 2d and 3) probably are related to certain crystallographic features. The pores are seen to "penetrate" into the catalyst and the pore structure therefore to a large extent consists of a continuous network of channels and holes in a spongy iron structure (i.e. a "Swiss cheese"). This is different from the type of pore

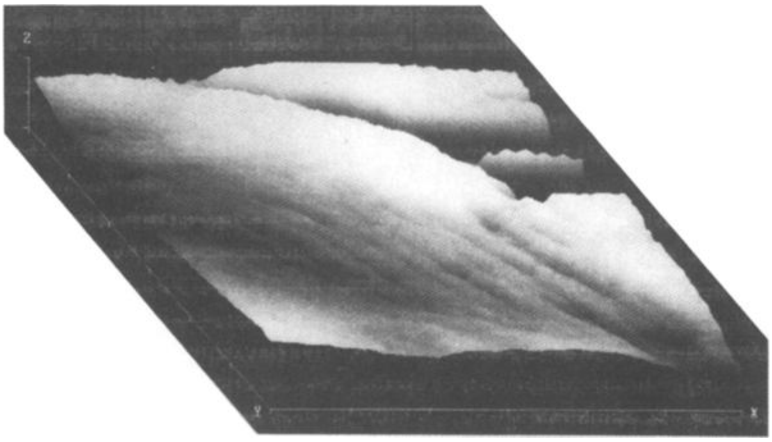

Fig. 1. STM grey-scale image of a 1200×1200 Å^2 region of the surface of a Topsøe KM1-type ammonia synthesis catalyst recorded with $I_t = 0.7$ nA and $V_1 = 1.2$ V. The z scale is 100 Å per division.

structure present in many catalysts where the pore structure represent the voids between agglomerates of particles. The special type of pore structure present in ammonia synthesis catalysts is most likely related to the genesis process in which the pores in the reduced catalyst are produced by removing oxygen from the essentially non-porous magnetite precursor structure.

Some difficulties were observed during the recording of the STM pictures at very low magnification scanning several thousands of Å. In certain cases, the difficulties were related to the tip reaching regions of the catalyst exhibiting low conductivity and low tunneling probability. These regions are probably low in iron and concentrated in promotor oxides. Thus, the above difficulty is reflecting the very heterogeneous nature of reduced ammonia catalysts [4,7,8,10,11,13] where a large fraction of the promoter oxides remains concentrated in regions corresponding to grain boundaries between magnetite grains.

Another difficulty encountered in the scans of large areas has to do with the presence of the pores. The STM tip tended to move deeply into the large pores leading to artifacts in the STM pictures and loss of resolution. The latter is due to shift in the point of closest contact between the tip and the catalyst surface. Consequently, it is difficult to provide very detailed information about the true three-dimensional nature of the pore system of the catalyst. Also the size of the smallest pores and features which can be probed will critically depend on the size and shape of the tip. Thus, while atomic resolution can be reached for the outer surfaces, the resolution for "interior surfaces" may be poorer (as for example seen in fig. 2a) and some small pores or cracks may not be pictured as such. In the present case the above limitation is apparently not very severe since as seen from the line scan in fig. 3, deep features only 10 Å wide are easily observed.

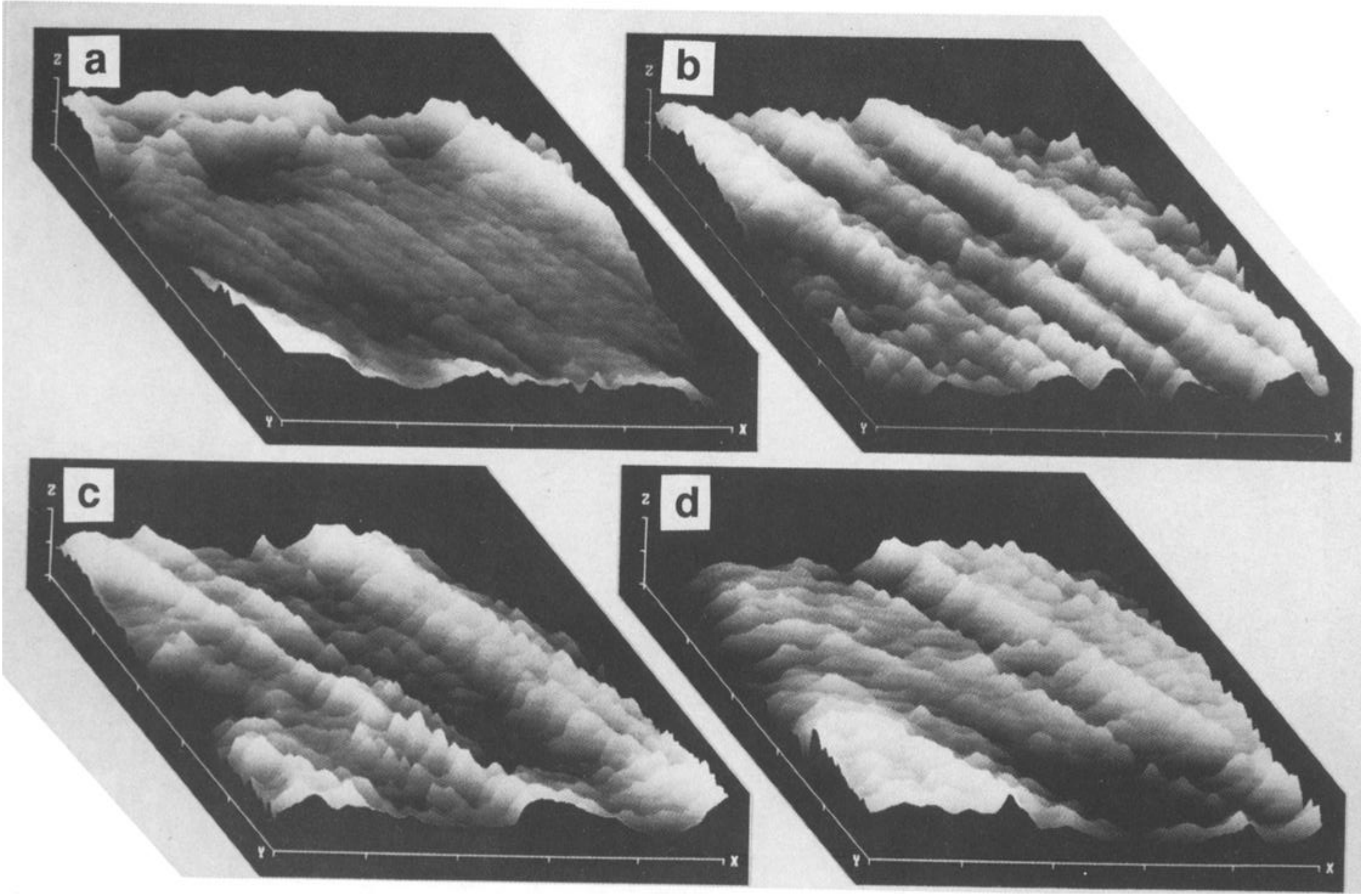

Fig. 2. Series of STM grey-scale images of the same region of the surface of a Topsøe KM1-type ammonia synthesis catalyst recorded with $I_t = 0.7$ nA and $V_1 = 1.2$ V. In the series of images from (a) to (d) we have in each case zoomed in, on the central part of the previous image. The x-y regions and the z-scale for the images are: (1) 800×800 Å^2, 50 Å/div; (b) 200×200 Å^2, 10 Å/div; (c) 100×100 Å^2, 10 Å/div; (d) 50×50 Å^2, 10 Å/div, respectively.

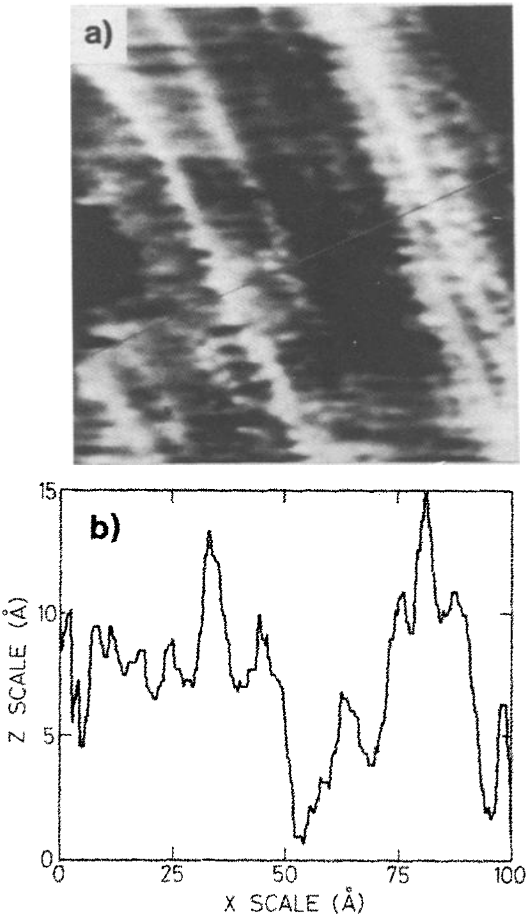

Fig. 3. (a): STEM grey-scale topograph of fig. 2(c) (100×100 Å^2). Surface protrusions are white while depressions are black. (b): Contourplot along the line marked in (a) crossing the ridges.

One of the most interesting features of the STM pictures is the marked corrugation of the catalyst surface giving rise to quite regular ridge-like features dominating most of the surfaces (figs. 1 to 3). The orientation of the ridges varies from region to region on the surface and the size of these regions appear to be greater than the typical iron particle size of about 200–300 Å as observed by XRD [4,5,11,13]. Thus the ridge structures most likely reflect the crystallographic orientations of the original magnetite grains and the topotactic nature of the reduction process. The observation (fig. 2a) that the orientation and shape of the pores may be related to the ridge structure further substantiates this and the recent investigations of Pennock et al. [12] and Schlögl [13] also show that the iron particles produced by reduction of a single magnetite grain will tend to be aligned. It is not expected that the passivation will greatly influence the above mentioned topographic features.

Figure 2 shows the same area of the catalyst surface at different magnifications. It is seen that the distance between the large ridges are typically about 40–60 Å and their height is about 15–40 Å (valley to top). From the pictures taken of the highest magnification atomic features are observed and the distance between atoms along the chains appears to be quite regular in many regions with a value of about 4.0 ± 0.5 Å. Regions with substantial disorder are also noted in agreement with the absence of a well ordered phases after passivation [30]. This distance of about 4.1 Å is close to that between Fe–Fe (or O–O atoms) in the (100) direction for FeO. FeO type structures which are formed upon passivation of iron have a tendency to grow epitaxially on iron such that the (100) direction in FeO is parallel to the (110) direction in Fe (the Fe–Fe distance along (100) direction in FeO (4.30 Å) is reasonably close to the Fe–Fe distance along the (110) direction in Fe (4.04 Å)). We thus tentatively suggest that the ridges correspond to the (110) direction of the Fe lattice. In situ XRD measurements [13,31] have in support of this shown that dimensions of the iron crystals are largest in the (110) direction. It therefore appears that the iron particles formed during the reduction grow in the (110) direction and this preference may be related to the (110) planes being closest packed of the iron planes.

During the reduction of the catalyst Al segregates out of the magnetite lattice [6,7,13] and the location of the promoter atoms is therefore also expected to be related to the ridge structures. However, from the present study on the passivated state of the catalyst, no firm conclusions can be made regarding the location of promoter atoms. The observation of changes in the ridge-like structure from region to region could be associated with local differences in promoter concentrations.

From STM line scans across the ridges (fig. 3) it can be estimated that the sides of the ridges form typically angles of about 70° with each other. This indicates that the sides could be related to the (111) planes of iron. Thus, this may be taken as evidence in favor of (111) surfaces being present in industrial ammonia catalysts after exposure to synthesis gas.

Several results in the literature have shown that (111) planes may form in such gas mixtures [32,33] and that such planes are important in ammonia synthesis [33,34]. A comparison [35] of the activity observed on (111) single crystals [34] with that of the KM1 industrial catalyst studied presently [36] also leads to the concusion that (111) planes dominate in industrial catalysts. The recent kinetic modeling work [20] is also in accord with this conclusion. Finally, it could be added that the presence of regular (111) sides on the ridges is in accord with an apparent low fractal dimension (surface roughness) measured by the adsorption of molecules of different size [37].

In conclusion, it has been found that high resolution STM pictures can be obtained for a real catalyst surface, while the catalyst is surrounded by a gas (in the present case air). The origin and structure of the ridges observed clearly need to be studied in greater detail preferably also by STM (and AFM) of the reduced catalysts. Such studies are planned and hopefully they may provide insight into the structure of the promoter atoms and the extent that these atoms may also show preferred orientations on the catalyst surface.

Acknowledgments

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References

[1] G. Binnig and H. Rohrer, IBM J. Res. Develop. 30 (1986) 355–369.

[2] P.K. Hansma and J. Tersoff, J. Appl. Phys. 61 (1987) R1–R23.

[3] F. Besenbacher, F. Jensen, K. Mortensen, E. Lægsgaard and I. Stensgaard, J. Vac. Sci. Technol. (in press).

[4] A. Nielsen, *An Investigation on Promoted Iron Catalyst for the Synthesis of Ammonia* (Jul. Gjellerup, Copenhagen, 3rd ed., 1968).

[5] A. Nielsen and H. Bohlbro, J. Am. Chem. Soc. 74 (1952) 963.

[6] H. Topsøe, J.A. Dumesic and M. Boudart, J. Catal. 28 (1973) 477–88.

[7] B.S. Clausen, S. Mørup, H. Topsøe, R. Candia, E.J. Jensen, A. Baranski and A. Pattek, J. Phys. (Paris) Colloq. (1976) pages 245–8.

[8] E.J. Jensen, H. Topsøe, O. Sørensen, F. Kragh, R. Candia, B.S. Clausen and S. Mørup, Scand. J. Metall. 6 (1977).

[9] A. Baranski, M. Lagan, A. Pattek, A. Reizer, L.J. Christiansen and H. Topsøe, in: *Preparation of Catalyst II*, eds. B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Elsevier, 1979) p. 353.

[10] G. Ertl, D. Prigge, R. Schlögl and M. Weiss, J. Catal. 79 (1983) 359.

[11] W.S. Borghard and M. Boudart, J. Catal. 80 (1983) 194.

[12] G.M. Pennock, H.M. Flower and S.P.S. Andrew, J. Catal. 103 (1987) 1–19.

[13] R. Schlögl, in: *Preparation and activation of the technical ammonia synthesis catalyst*, ed., J.R. Jennings, *Catalytic Ammonia Synthesis. Fundamentals and Practice* (Plenum Publishing Corp) in press.

[14] D.C. Silverman and B. Boudart, J. Catal. 77 (1982) 208: 20.

[15] S. Brunauer and P.H. Emmett, J. Am. Chem. Soc. 62 (1940) 1732–46.

[16] P.H. Emmett and S. Brunauer, J. Am. Chem. Soc. 59 (1937) 310–9.

[17] M. Weiss and G. Ertl, Stud. Surf. Sci. Catal. 11 (1982) 277–84.

[18] G. Ertl, S.B. Lee and M. Weiss, Surf. Sci. 114 (1982) 527–45.

[19] G. Ertl, M. Weiss and S.B. Lee, Chem. Phys. Lett. 60 (1979) 391–4.

[20] P. Stoltze and J.K. Nørskov, J. Catal. 110 (1988) 1–10.

[21] G. Ertl and N. Thiele, Appl. Surf. Sci. 3 (1979) 99–112.

[22] P.H. Emmett and S. Brunauer, J. Am. Chem. Soc. 56 (1934) 35.

[23] P.H. Emmett and S. Brunauer, J. Am. Chem. Soc., (1937) 1553–64.

[24] V. Solbakken, A. Solbakken and P.H. Emmett, J. Catal. 15 (1969) 90.

[25] C. Peters, K. Schafer and R. Krabetz, Z. Elektrochem. 64 (1960) 1194–9.

[26] D.R. Strongin and G.A. Somorjai, Catal. Lett. 1 (1988) 61–6.

[27] D.R. Strongin, S.R. Bare, and G.A. Somorjai, J. Catal. 103 (1987) 289, 301.
[28] F. Besenbacher, E. Lægsgaard, K. Mortensen, U. Nielsen and I. Stensgaard, Rev. Sci. Instru. 59 (1988) 1035–1038.
[29] E. Lægsgaard, F. Besenbacher, K. Mortensen and I. Stensgaard, Jour. Microscopy 152 (1989) 663–69.
[30] H. Topsøe, J.A. Dumesic and S. Mørup, in: *Application of Mössbauer Spectroscopy* (Academic Press, Vol. 2, 1980) p. 55.
[31] B. Fastrup, J. Villadsen, G. Steffensen, B.S. Clausen, W. Niemann and H. Topsøe, unpublished results.
[32] R. Brill, E.L. Richter and E. Ruch, Angw. Chem. 6 (1967) 882.
[33] M. Boudart, H. Topsøe and J.A. Dumesic, in: *The Physical Basis for Heterogeneous Catalysis*, eds. E. Drauglis and R.I. Jaffe (Plenum, 1975) p. 337.
[34] N.D. Spencer, R.C. Schoonmaker and G.A. Somerjai, J. Catal. 74 (1982) 129.
[35] M. Boudart and D.G. Löffler, J. Phys. Chem. 88 (1984) 5763.
[36] H. Topsøe, N. Topsøe, H. Bohlbro and J.A. Dumesic, in: *Proc. 7th Int. Congr. in Catalysis*, Part A, eds. T. Seiyama and K. Tanabe (Kodansha, Tokyo, 1981) p. 247.
[37] S.V. Christensen and H. Topsøe, to be published.