High-pressure STM studies of oxidation catalysis
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Appendix I

NO reduction by CO on Pt (100)

In this appendix we present preliminary results obtained with High-Pressure Scanning Tunneling Microscopy on the catalytic NO reduction by CO on Pt(100) at atmospheric pressure and various temperatures. We found that the formation of the products N_2 and CO_2 strongly depends upon the temperature and surface structure.

A.I.1 Introduction

The study of NO reduction by CO on Pt(100) constitutes an intriguing research subject. First of all the catalytic reduction of NO_x is of great importance for reducing air pollution [1]. Secondly, there is still a controversy in the literature concerning the mechanism of the NO+CO reaction. Also, it has been shown experimentally that this reaction exhibits interesting dynamical behaviour such as multiple steady states and kinetic oscillations [2-6]. As a consequence the NO/Pt(100) and NO+CO/Pt(100) systems have been investigated using various techniques over the years as scanning tunneling microscopy [7-8], low energy electron diffraction [9-10], vibrational spectroscopies [11-12] or X-ray photoemission spectroscopy [13-14].

As pointed out in Chapter 5 the clean Pt(100) surface adopts a quasi-hexagonal structure. Upon adsorption of various gases (ethylene, H_2, O_2, NO and CO) this reconstruction is lifted. King and collaborators summarized the similarities between the NO and CO adsorption as following: gases adsorb with high initial sticking probabilities; both lift the reconstruction of the clan hex surface; and in both cases the adsorption is almost entirely nondissociative. But are also remarkable differences in saturation coverages, in ordered structures and adsorption sites [15].

The basic reaction equation for the interaction of NO and CO is:

$$NO + CO \rightarrow \tfrac{1}{2}N_2 + CO_2$$
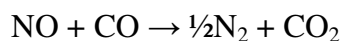
The key role in promoting the CO+NO reaction is played by the ability of the surface to dissociate NO [16]. Based on experimental observations by a variety of techniques it has been concluded that at room temperature NO adsorbs *molecularly* and that it lifts the hex reconstruction as we have already mentioned in the previous chapter. Upon heating above 390 K the molecularly adsorbed NO dissociates. The dissociation of chemisorbed NO, according to

$$NO_{ad} \rightarrow N_{ad} + O_{ad} \, ,$$

is immediately followed by the desorption of nitrogen,

$$2N_{ad} \rightarrow N_2 \, .$$
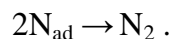
From the various models proposed to explain the reaction dynamics over Pt(100), we briefly describe only the two best known models in this section. One model is based on the fact that Pt(100) undergoes a surface reconstruction due to the adsorption of a few adsorbates, including NO and CO. King and co-workers have found that the hex $\rightarrow$ (1x1) surface phase transition depends non-linearly on surface coverage, and this nonliniarity is an essential ingredient in the dynamics of NO reduction on Pt(100) [17]. The other model is referred to as the so-called "vacancy model" and has been applied to the NO+CO reaction for the first time by Lesley and Schmidt [18]. The following reactions are used in this model in order to explain the autocatalytic behaviour of NO reduction (the square denotes an empty surface site):

$$CO + \square \leftrightarrow CO_{ads}$$
$$NO + \square \leftrightarrow NO_{ads}$$
$$NO_{ads} + \square \rightarrow N_{ads} + O_{ads}$$
$$N_{ads} + N_{ads} \rightarrow N_2 + 2 \square$$
$$CO_{ads} + O_{ads} \rightarrow CO_2 + 2 \square$$
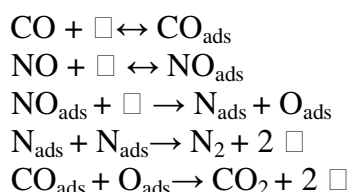
As can be seen the first two steps refer to the molecular adsorption of CO and NO on the surface. Both steps require an empty surface site. Due to the adsorption processes islands of adsorbates are formed and they grow until no more vacant surface sites are left. As a consequence the next step, dissociation of NO, is inhibited until one of the adsorbed species starts to desorb. When that is the case the dissociation can take place. This process is immediately followed by N_2 desorption and CO oxidation. The latter two reaction steps each produces two vacant sites, so that the process can continue until all CO and NO has reacted. This subprocess is autocatalytic in the sense that it produces more vacant surface sites than it requires [19].

Using our high-pressure STM, combined with mass spectrometry, we have performed a preliminary series of experiments on the NO+CO reaction on Pt(100), which we briefly present in the next section.

A.I.2 Results and discussions

The cleaning procedure for the Pt(100) sample has been described in Chapter 5. We have performed only three experiments, each at a different

temperature but all at the same total pressure of 1.25 bar. In this section we summarize our results, beginning with the lowest temperature.

T = 308 K

At this temperature we have not observed the formation of the two products, N_2 or CO_2. Image A from figure A.I.1 has been acquired after the sample had been heated to 308 K for 2h in an NO-rich gas flow. The quality of the original images was quite poor, so we differentially filtered them in order to enhance the contrast. As expected the exposure of clean hex-reconstructed Pt(100) to NO has led to the formation of square adatom islands corresponding to the unreconstructed Pt(100)-(1×1) surface. Image B has been recorded in a 1:1 mixture of NO and CO. These images clearly illustrate that when exposed to the gas mixture the surface has more adatom islands of different sizes and shapes.
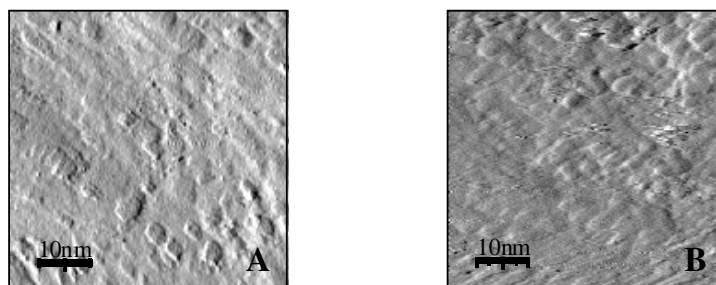

Figure A.I.1: *Differentiated STM images (50 nm × 50 nm) of the Pt(100) surface at 308 K, illustrating (A) the formation of (1×1) adatom islands due to exposure to 1.25 bar of NO and (B) the formation of a high density of islands of various shapes due to exposure to 1.25 bar of a 1:1 NO/CO mixture. V_t=0.2 V and I_t=0.2 nA.*

If a hex-reconstructed Pt(100) surface is exposed at room temperature to NO, the reconstruction is been lifted and c(2x4) structures are formed [7]. According to Miners et al. [20], if the NO-precovered surface is exposed to CO or a CO/NO mixture, two scenarios are possible. Either CO replaces NO and poisons the surface, or a mixture of CO and NO islands is formed. In both cases no reaction will take place at this low temperature of 308 K. Both scenarios could explain our experimental observations.

T = 383K

Figure A.I.2 displays the kinetics of NO+CO reaction as have been measured by the mass spectrometer at a constant total pressure of 1.25 bar and at 383 K. In order to differentiate between the CO and N_2 molecules that have the same molecular mass of 28 atomic mass units (amu), we have also followed the signals for ^{12}C, ^{16}O, ^{14}N, ^{15}N and $^{27}N_2$. We have further traced

in the spectrum mass 46, corresponding to the secondary reaction product NO_2. In order not to complicate our discussion we only show a selection of masses in Fig.A.I.2. The experiment of Figure A.I.2 started with a clean, hex-reconstructed Pt(100) surface that had been heated for 2 h in an Ar-rich flow. At a temperature of 383 K we have switched to an NO-rich flow at time t = 0. Accompanying the increase in NO signal we also noticed a significant increase in masses 28 (CO and/or N_2) and 44 (CO_2 and/or N_2O) and a small increase in the NO_2 signal. It is tempting to conclude from this that at this temperature, following the dissociation of adsorbed NO, the recombination of N_{ads} (which leads to the formation of N_2) and the reaction between $N_{ads}+O_{ads}$ (which leads to the formation of NO_2 and N_2O) took place.
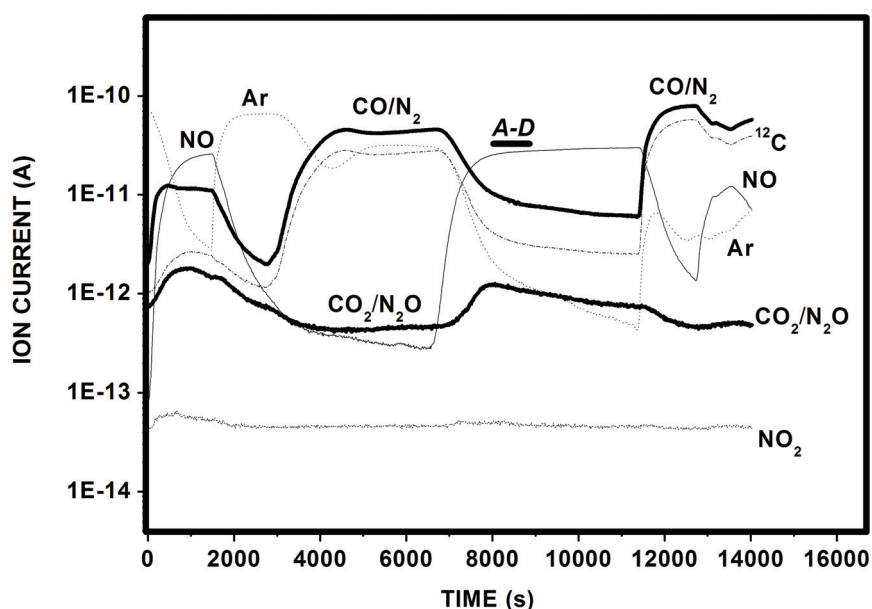

Figure A.I.2: *Kinetics of NO reduction by CO on Pt(100) at 383 K and 1.25 bar. First thick solid line in the figure corresponds to mass 38 amu, which can stand for one of the reactant gases-CO, but also for one of the desired reaction products N_2. The second ticker solid line corresponds to mass 44 amu that can correspond to the desired product CO_2, but also to a secondary product of this reaction N_2O.The thin solid line corresponds to the other reactant gas NO (mass 30 amu). The thin dotted line indicates the presence of Ar (mass 40 amu), while the dashed-dotted line corresponds to ^{12}C (mass 12 amu). The symbol A-B shows the time interval where the STM images presented in Fig.A.I.2 have been recorded.*

However, more experimental work is required to rule out the possibility that a dead volume in the NO gas line of residual oxygen from previous

experiments has reacted with the NO to form NO_2 and N_2O. At t = 1470 s we switched back to an Ar-rich flow. While the sample was in the pure Ar flow all other signals decreased. After this, at t = 32860 s, we slowly switched to a CO-rich flow. The CO-related mass signals (28 and 12) increased. In addition, only the signal of Ar, which shared its gas line with CO, increased. No other mass followed the increase in CO, which means that the adsorbed CO poisoned the surface. When we switched to an NO-rich flow at t = 6800 s, we found that after a short delay of a few hundred seconds the CO_2 signal increased. The fact that the signal that represents the masses of both CO and N_2 (28 amu) does not decrease as much as the ^{12}C signal (which corresponds to the CO molecules and not to N_2) constitutes a strong indication that N_2 is also formed. As we switched again to the CO rich flow at t = 11400 s, the CO_2 signal decreased. Also the N_2 signal ('difference' between the signals at masses 28 and 12) decreased. Assuming that prior to the increase in CO partial pressure the surface was NO-dominated, one might have expected the increase in CO pressure to be accompanied by a small increase in CO_2 and N_2 signals (at equal coverages of the reactants). However, it seems that CO reacted rapidly with the adsorbed NO and then poisoned the surface, as the reaction rate decreased really fast after switching to the CO-rich flow.

Figure A.I.3 shows a selection of STM images from a movie recorded simultaneously with the kinetics described above. As revealed by the images from figure A.I.3 the Pt(100) surface in an NO-rich flow shows the presence of vacancy islands, which disappear rapidly in time. Images B and C have been acquired consecutively after image A. The time interval required to record an image was approximately 1 minute. Image D shows a larger scale view of the surface and it has been recorded 6 minutes after image C. As can be seen there are still a few vacancy islands on the terraces. It seems that they prefer to appear on the wider terraces, but the wavy shapes of the steps indicate that vacancy islands close to steps (e.g. on narrow terraces) have coalesced with the steps. The shapes of the vacancy islands have a weak, hexagonal symmetry. We emphasize that we have not observed the formation of adatom islands, which we have observed when we exposed the hex-reconstructed surface to CO, as described in Chapter 6. One of the possible explanations for the presence of vacancy islands could be that NO did not lift the reconstruction but that it has led to an even higher-density structure of the first Pt layer than the original, hex-reconstructed surface.
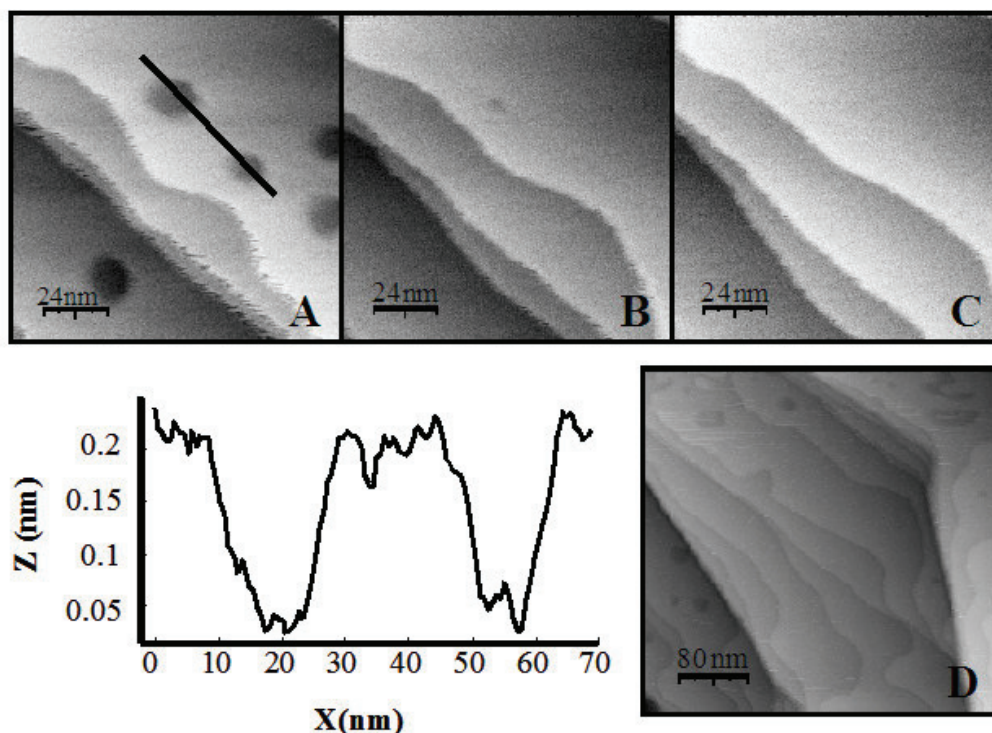
Figure A.I.3: STM images 100 nm × 100 nm (C-E) and 400 nm × 400 nm (F) showing the Pt(100) surface morphology in an NO-rich flow at a total pressure of 1.25 bar and at 383 K. The height profile along the line in image C indicates a depth of ~0.2 nm for the vacancy islands. V_t=0.8V and I_t=0.2 nA.

T=443 K

In the upper part of Figure A.I.4 the reaction kinetics at 1.25 bar and 443 K is depicted. Similar to the previous two experiments the sample has been heated for 2 h, but this time in a CO-rich flow. As indicated by arrow number 1 in figure A.I.4, at t = 3031 s we have switched to an NO-rich flow. The reaction rate for CO_2 production passed through a maximum, which we associate with the situation of equal coverages of the reactants on the surface (θ_{CO}=θ_{NO}). This behaviour is very reminiscent of Langmuir-Hinshelwood kinetics. Initially, the surface has been covered and poisoned by CO. At this temperature NO managed to adsorb on the surface and as the NO coverage increased beyond 50% there were less CO molecule to react with, so the reaction rate for CO_2 slowly decreased. At t = 8374 s (arrow number 2) we added again CO in the gas flow. This resulted in a modest, temporary increase in the CO_2 signal, which we again think corresponds to the situation of maximum reaction rate for equal coverages of NO and CO.
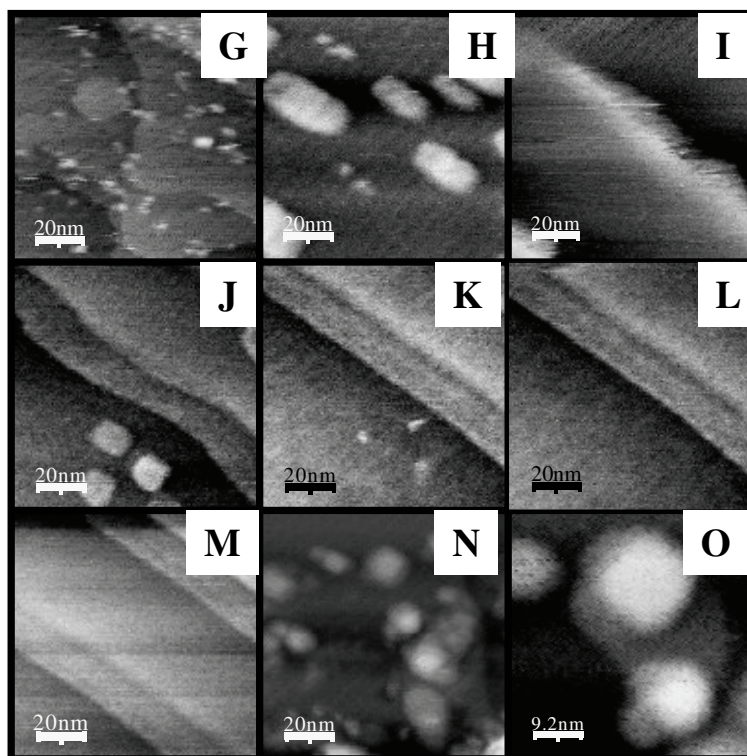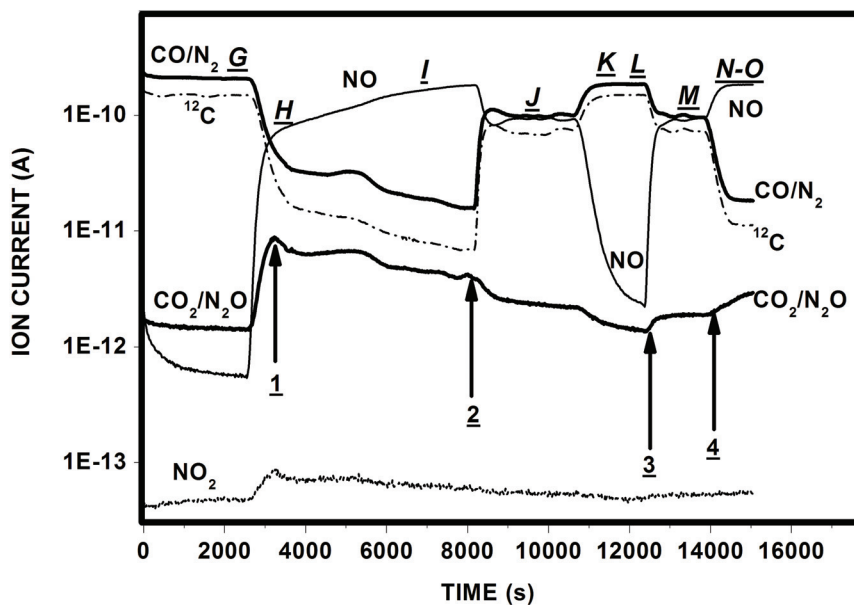
Figure A.I.4: *Reaction kinetics for the NO+CO reaction at 1.25 bar and 443 K (upper panel) and simultaneously recorded STM (lower panel) images reflecting the structural changes of the surface due to the exposure to NO, CO and NO/CO mixture (see text). The size of the images is 100 nm × 100 nm (J-N) and 46 nm × 46 nm (O). V_t=0.8V and I_t=0.2 nA.*

After this maximum, the CO_2 production rate decreased as the surface was exposed to a continuous flow of a 1:1 NO/CO mixture, which probably led to a slight over-population of the surface with CO. Adding more CO made the imbalance between adsorbed CO and NO more dramatic and decreased the rate of CO_2 production. At $t = 12678$ s (arrow 3) we added extra NO, so that the ratio NO:CO became again 1:1. This increased the CO_2 production rate again. The reaction rate increased further as we switched to a more NO-rich flow at $t = 13889$ s (arrow 4), thus approaching the maximum in the Langmuir-Hinshelwood mechanism again.

The STM images acquired simultaneously with the kinetics described above are shown in Figure A.I.4 (b). Image G corresponds to the CO-covered surface. It shows the presence of highly mobile, small adatom island structures. Image H has been acquired immediately after switching to an NO-rich flow. Under these conditions, the surface contains square adatom islands, which proves that NO also lifts the reconstruction. Similar to the case of CO exposure, longer exposure to NO at high temperature was found to result in the smoothening of the surface, as illustrated in image I, which was recorded after the surface had been in the NO-rich flow for a time interval of 1h. Image J was acquired in the 1:1 NO/CO mixture. The image shows the re-appearance of adatom islands that we have seen before (image H) when the surface was exposed to an NO-rich flow. Image K was recorded in a CO-rich flow. During the long exposure to CO the adatom islands were decaying and the surface became smoother, as is seen in image L, which was recorded 30 minutes after image K. The flat surface from image L seems to remain unchanged when exposed to an equal mixture of CO and NO, as indicated by image M. When we exposed the smooth surface to an NO-rich flow, adatom islands with height between 0.6 and 1.0 nm were formed as shown in images N and O.

A.I.3 Conclusions

Our preliminary experimental results regarding NO reduction by CO over Pt(100) at ambient pressures (1.25 bar) and various temperatures (ranging from 308 K to 443 K) show Langmuir-Hinshelwood type behaviour. The reaction strongly depends on the temperature. Although NO and CO are both thought to lift the hex-reconstruction and 'restore' a (1×1) surface structure, the STM images obtained at the highest temperature provide strong evidence that the density of Pt atoms in the CO-covered surface is not the same as that in the NO-covered surface.

A.I.4 References

[1]   K. C. Taylor, *Automobile catalytic converters* (Springer, Berlin, 1984)

[2]   M. Slinko, T. Fink, T. Löher, H. H. Maden, S. J. Lombardo, R. Imbihil and G.Ertl, *Surf. Sci.* **264** (1992) 157

[3]   T. Fink, J. P. Dath, M. R. Basset, R. Imbihl and G. Ertl, *Surf. Sci.* **245** (1991) 96

[4]   M. F. H.van Tol, J. Siera, P.D. Cobden and B. E. Nieuwenhuys, *Surf. Sci.* **274** (1992) 63.

[5]   P.D. Cobden, J. Siera and B. E. Nieuwenhuys, *J. Vac. Sci.Technol.,A* **10** (1992) 2487.

[6]   C. A. de Wolf and B. E. Nieuwenhuys, *Catal.Today* **70** (2001) 287.

[7]   E. Ritter, R. J. Behm, G. Pötschke and J. Wintterlin, *Surf. Sci* **181** (1987) 403.

[8]   M. -B. Song, K. Momoi and M. Ito, *Jpn. J.Appl.Phys.* **36** (1997).

[9]   H. P. Bonzel, G. Broden and G. Pirug, *J. Catal.* **53** (1978) 96.

[10] K. Masse and Y.Murata, *Surf.Sci.* **242** (1991) 132.

[11] G. Pirug, H. P. Bonzel, H. Hopster and H. Ibach, *J. Chem. Phys.* **71** (1979) 593.

[12] P. Gardner, M.Tüshaus, R. Martin and A. M. Bradshaw, *Surf. Sci.* **282** (1990) 112.

[13] S. Sugai, K. Takeuchi, T. Ban, H. Miki, K.Kawasaki and T. Kioka, *Surf. Sci.* **282** (1996) 67.

[14] E. D. L. Rienks, J. W. Bakker, A. Baraldi, S. A. Carabiniero, S. Lizzit, C. J. Weststrate and B. E. Nieuwenhuys, *Surf. Sci.* **516** (2002) 109.

[15] Y. Y.Yeo, L.Vattuone and D. A. King, *J. Chem. Phys.* **104** (1996) 3810.

[16] R. J. Gorte, L. D. Schmidt and J. L. Gland, *Surf. Sci.* **109** (1981) 367

[17] A. Hopkinson, D. A. King, *Chemical Physics* **177** (1993) 433

[18] M. W. Lesley and L. D. Schmidt, *Surf. Sci.* **155** (1985) 215

[19] A. Eichler and J. Hafner, *Journal of Cat.* **204** (2001) 118

[20] J. H. Miners et al., *Surf. Sci.* **547** (2003) 355