Influence of oxidation-reduction treatment on the interaction of cobalt particles with silica support

D. POTOCZNA-PETRU, L. KĘPIŃSKI
W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950 Wrocław 2, Poland

The effect of oxidation–reduction treatment on the morphology of cobalt particles supported on SiO_2 and on the interphase interaction of cobalt with SiO_2 has been investigated by transmission electron microscopy and electron diffraction on model catalyst samples. It has been shown that the formation of Co–Si alloys may occur during the reduction of the Co/SiO_2 system with hydrogen at 773 K. The Co–Si alloying is observed only for small cobalt particles, which can be obtained by precalcination of the samples in air at 673 K.

1. Introduction

It is well known, that at higher temperatures reactive gases have a considerable influence on the evolution, dispersion and phase composition of systems comprised of a metal dispersed on a non-metallic substrate. This phenomenon is important in the application of this kind of system in catalysis and microelectronics.

In a previous study on the model Co/SiO_2 catalyst [1] we showed that the morphology of cobalt particles supported on silica is sensitive to the oxidation–reduction treatment and, at special conditions, the redispersion of cobalt particles was observed. It is known [2, 3] that the course of the oxidation and reduction processes of cobalt supported on silica is different from that for unsupported cobalt. This suggests that the silica is not an inert substrate in relation to cobalt.

The results of a transmission electron microscopy and electron diffraction study of the evolution of the structure of cobalt particles supported on thin SiO_2 films and of the $Co–SiO_2$ interaction induced by the oxidation–reduction thermal treatment, are reported.

2. Experimental procedure

Thin cobalt films about 3 nm thick were obtained by thermal evaporation of cobalt wire in vacuum on to the platinum microscopy grids covered with amorphous SiO_2 films. Details of the experimental methods and procedures were described previously [4, 5].

Following deposition, the samples were annealed at 573 K in a vacuum of 10^{-4} Pa for 4 h. Some of them were then calcined in air at 673 K for 4 h. The calcined and uncalcined thin films were heated in flowing hydrogen at 1 atm for 4 h at 523 and 773 K. After each stage of thermal treatment the samples were investigated by transmission electron microscopy (TEM) and electron diffraction (ED) to monitor changes in morphology and phase composition. We found that short contact of unannealed fine crystalline cobalt films with

air or their annealing in a vacuum lower than 10^{-4} Pa produced a small amount of crystalline oxide CoO detectable by ED. For annealed films with larger crystallites, the lines from the oxide phase could not be observed in ED. The exposure to air for several months caused complete oxidation of the unannealed films and the formation of a detectable amount of CoO in the annealed ones.

For the island films composed of separated particles, the particle-size distributions were constructed and the mean particle size was calculated using the formula $\bar{D} = \Sigma_i N_i \bar{D}_i / \Sigma_i N_i$, where N_i is the number of particles with diameter between D_i and $D_i + \Delta D_i$, and $\bar{D}_i = D_i + \Delta D_i / 2$.

3. Results

Transmission electron micrographs of thin cobalt films (~ 3 nm thick) supported on amorphous SiO_2 and heated in hydrogen at 523 and 723 K following pretreatment in vacuum or in vacuum and in air are shown in Figs 1 and 2, respectively. Electron diffractograms corresponding to these micrographs are presented in Figs 3 and 4. The successive micrographs in Fig. 1 correspond to samples heated for 4 h, in a vacuum of 10^{-4} Pa at 573 K (Fig. 1a), then in hydrogen at 523 K (Fig. 1b) and finally in hydrogen at 723 K (Fig. 1c). From Fig. 1a it appears that the film heated in a vacuum of 10^{-4} Pa after evaporation exhibited a quasicontinuous structure. Electron diffraction pattern also contained, in addition to rings from polycrystalline h c p and f c c cobalt, weak lines from CoO (Fig. 3a). The small amount of CoO was formed probably during heating of the sample in a vacuum of 10^{-4} Pa where oxygen is present in the residual gases. The reduction at 523 K in hydrogen caused the lines of CoO to disappear (Fig. 3b) but the morphology of the film did not change greatly (Fig. 1b). Upon heating at 773 K in hydrogen, the film broke up into separate
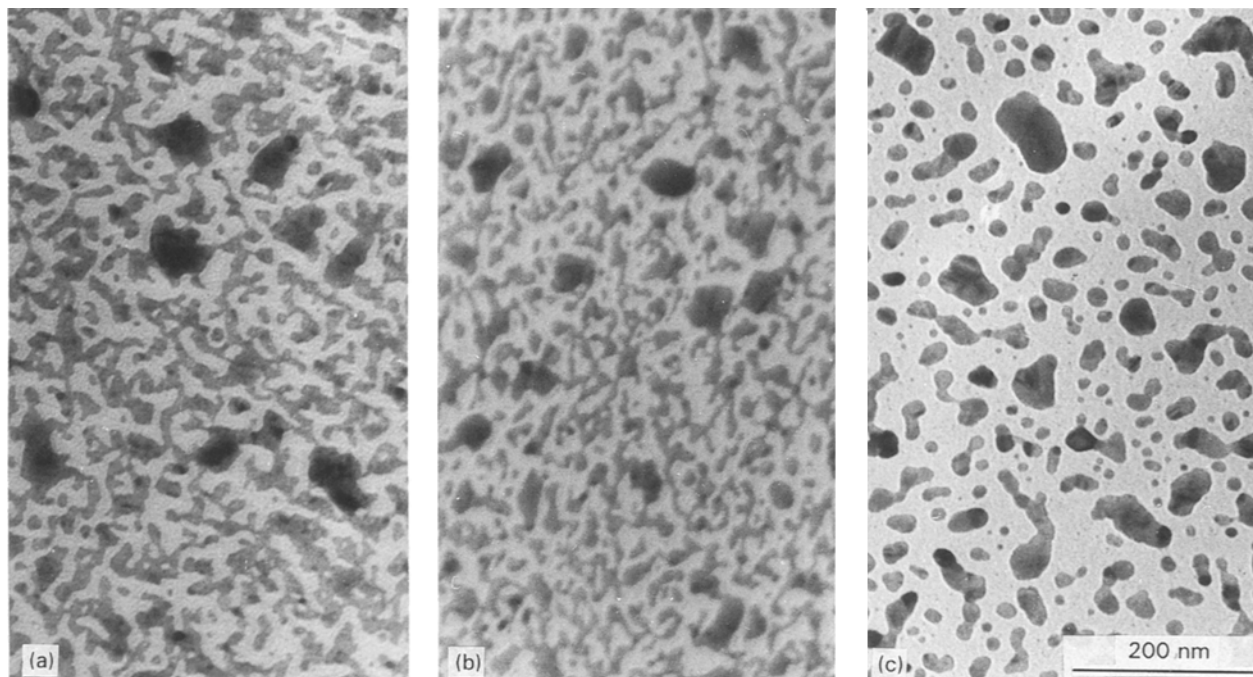
Figure 1 Electron micrographs of Co/SiO$_2$ films ($d \sim 3$ nm) heated (a) for 4 h at 573 K in vacuum, then (b) at 523 K in hydrogen, and then (c) at 773 K in hydrogen.
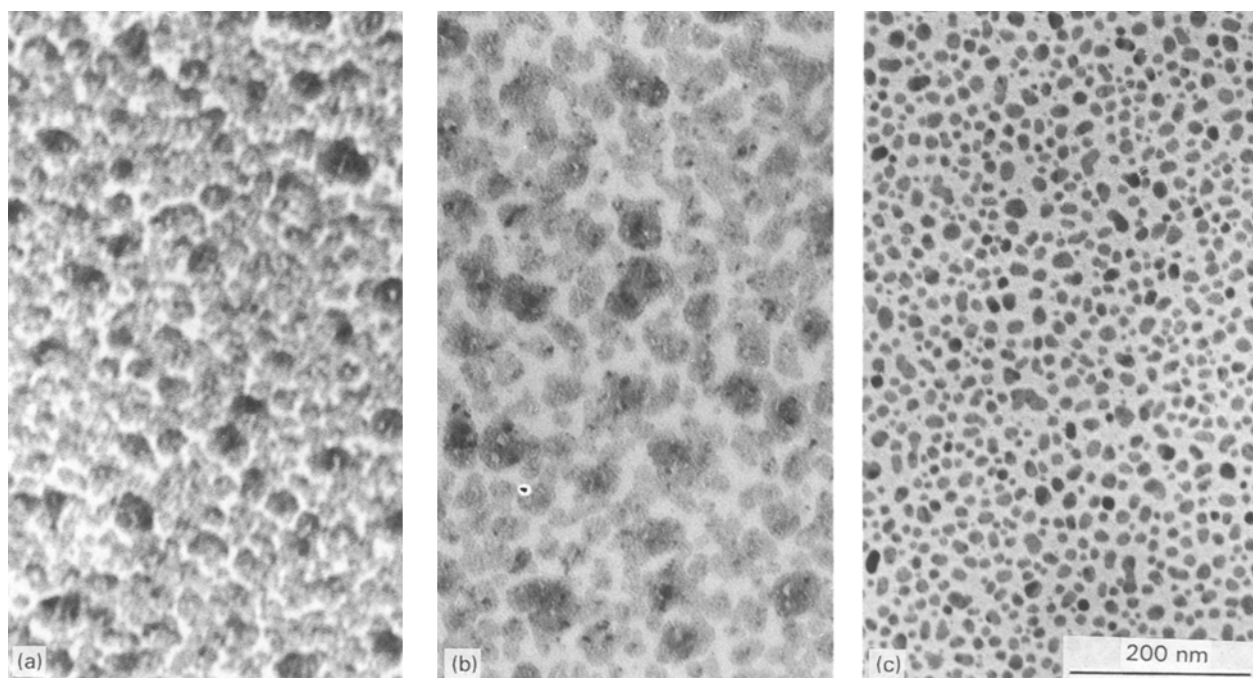

Figure 2 Electron micrographs of Co/SiO$_2$ films ($d \sim 3$ nm) heated (a) for 4 h at 673 K in air, then at (b) 523 K in hydrogen, and then (c) 773 K in hydrogen.

particles with irregular shapes, with a mean size of 19.1 nm (Fig. 1c). In the electron diffraction pattern of this specimen, only lines of h c p and f c c cobalt were identified (Fig. 3c).

The structure of the film calcined at 673 K in air for 4 h is shown in Fig. 2a. This treatment caused the spreading of the cobalt-containing phase identified by ED as Co$_3$O$_4$ (Fig. 4a). During heating of the calcined sample in hydrogen at 523 K, only part of the Co$_3$O$_4$ was reduced to CoO (Fig. 4b) and the film exhibited

a quasicontinuous picked structure (Fig. 2b). Reduction at 773 K caused the film to break into isolated particles with a mean size of 11.6 nm (Fig. 2c). The detailed analysis of the electron diffraction pattern from this sample (Fig. 4c) revealed that the lines from f c c cobalt were predominant and sharp and lines from h c p cobalt phase were much weaker. The results of the observed phase composition of the Co/SiO$_2$ systems after thermal treatment under various conditions are collected in Table I.
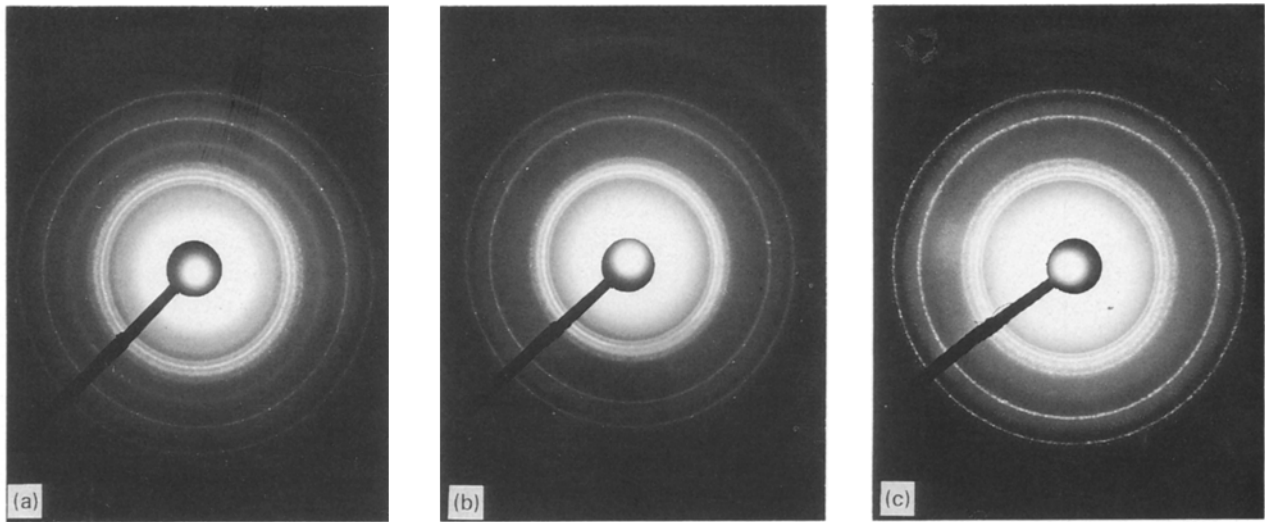
Figure 3 Electron diffraction pattern of Co/SiO₂ films (presented in Fig. 1) heated for (a) 4 h at 573 K in vacuum, then at (b) 523 K in hydrogen, and then at (c) 773 K in hydrogen.
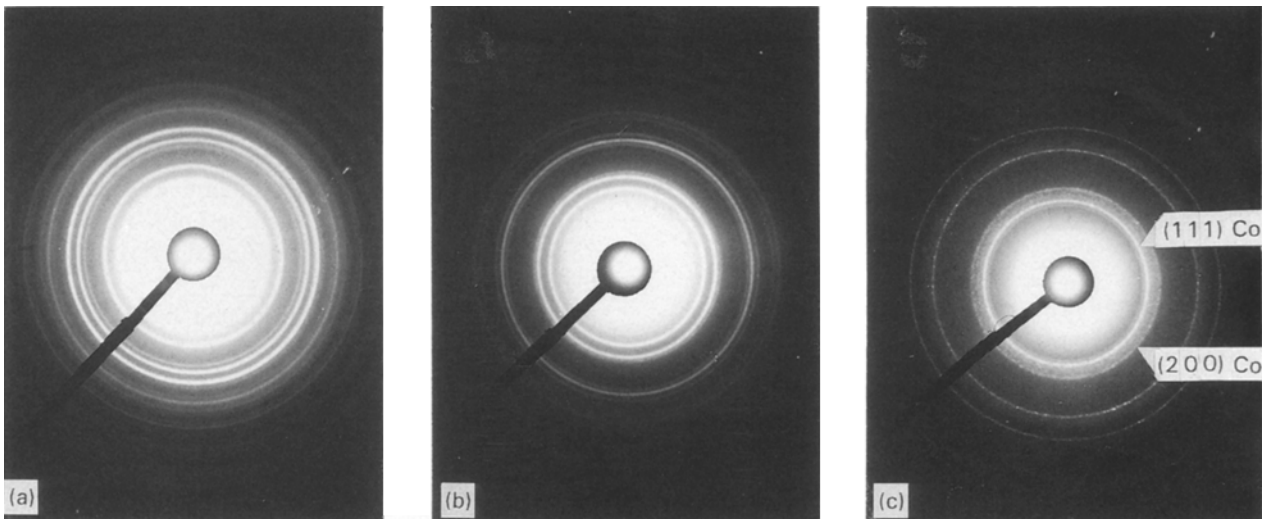

Figure 4 Electron diffraction pattern of Co/SiO₂ films (presented in Fig. 2) heated for (a) 4 h at 673 K in air, then at (b) 523 K in hydrogen, and then (c) 773 K in hydrogen.

TABLE I Composition of Co/SiO₂ systems after thermal treatment (for 4 h) under various conditions

Specimen	Treatment conditions		Components
	Atmosphere	Temperature (K)	
1.	Vacuum[a]	573	h c p, f c c Co, CoO trace
	H_2	523	h c p, f c c Co
	H_2	773	h c p, f c c Co
2.	Air	673	Co_3O_4
	H_2	523	CoO, Co_3O_4
	H_2	773	Co–Si alloys

[a] 10^{-4} Pa.

The particle-size distributions for the samples reduced in hydrogen at 773 K with and without precalcination are shown in Fig. 5.

4. Discussion and conclusions

From the present study it results that the precalcination of the thin cobalt films supported on SiO_2 in-

fluences the morphology of the reduced particles and the interaction between the metal and the support. The distinct effects observed in this work are the differences in the size distributions of particles (Fig. 5) and in ED patterns (Figs 3c and 4c) of samples calcined or no prior reduction. Complete oxidation of the samples to Co_3O_4 caused smaller particles to be obtained after reduction at 773 K (Fig. 5). The phase composition of the oxidized samples established in our work by ED confirmed previous results obtained by X-ray photoelectron spectroscopy (XPS) and temperature-programmed oxidation (TPO) [2, 6–9]. The 50 nm thick Co_3O_4 film was detected on the surface of the cobalt foil oxidized in air at 673 K for 5 min [6]. TPO profiles of the reduced Co/SiO₂ [2] and Co/Al₂O₃ catalysts [7] showed that the oxidation was already complete at 573 and 650 K, respectively. From the amount of consumed oxygen it was deduced that Co_3O_4 was formed during the course of TPO. Brundle *et al.* [8] observed the formation of CoO or $Co(OH)_2$ in cobalt films exposed at 300 K to oxygen or to air, respectively. In our study the hydroxide phase was not
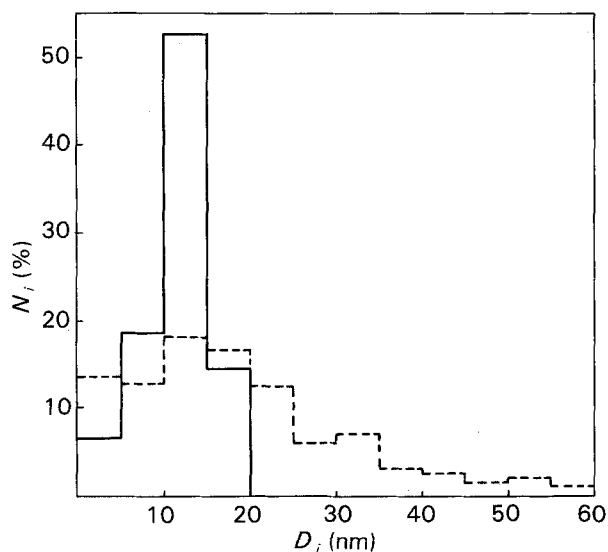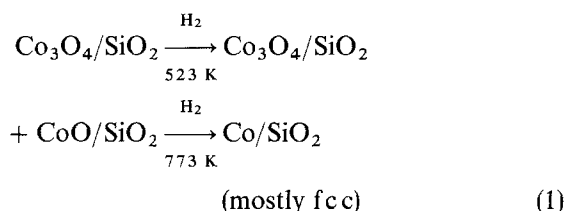
Figure 5 Particle-size distribution for Co/SiO_2 films $(d \sim 3\,nm)$ reduced with hydrogen at 773 K for 4 h (a) (———) after precalcination at 673 K in air and (b) (– – –) without calcination. (a) $\bar{D} = 11.6\,nm$, (b) $\bar{D} = 19.1\,nm$.

established by ED, but its formation on the surface in moist air could not be excluded.

We propose that in hydrogen the reduction of Co_3O_4 particles supported on SiO_2 proceeds according to the scheme:

$$Co_3O_4/SiO_2 \xrightarrow[523\,K]{H_2} Co_3O_4/SiO_2$$

$$+ CoO/SiO_2 \xrightarrow[773\,K]{H_2} Co/SiO_2$$

(mostly f c c)   (1)

This scheme agrees with the results reported for oxidized cobalt catalyst supported on various substrates [2, 3, 6, 7, 9] and for Co_3O_4 thin films [6]. For example, two peaks were observed in the temperature-programmed reduction (TPR) curves of pure Co_3O_4 and classical Fischer–Tropsch cobalt Kieselguhr catalyst [6]. According to the authors, the peak in the 523–573 K range corresponded to the reaction $Co_3O_4 \rightarrow CoO$ and the second one in the 573–973 K range was connected with the process $CoO \rightarrow Co$. For the catalyst, the width of the second peak was dependent on promoters, while for Co_3O_4 the reduction was completed at about 673 K. The increase in the reduction temperature for supported and promoted catalysts may be caused by the formation of the new phase between cobalt and the promoters or the substrate. In our study, Co_3O_4/SiO_2 sample reduced at 773 K exhibited significantly intensified lines of f c c cobalt in the ED pattern (Fig. 4c). We suppose that the predominance of the f c c cobalt phase, which is an equilibrium form only above 700 K, is caused by the formation of the Co–Si solid solution. For Co/SiO_2 samples reduced under even more severe conditions (higher temperatures and longer times) only f c c phase or, in some cases, Co_2Si silicide was present in electron diffraction patterns [10]. From the XRD study by Luo *et al.* [11] on the $Co_{1-x}Si_x$ alloy it is known that

for $x = 0.04$–0.115, the strong reflections corresponding to f c c cobalt phase and weak ones of h c p cobalt were observed; for $x = 0.13$ only reflections of f c c cobalt and for $x = 0.15$ reflections of f c c cobalt and weak lines probably from Co_2Si appeared. SiO_2 is usually considered an inert substrate in relation to the group VIII metals, except for temperatures above 1200 K [12]. Recent investigations have shown however, that under specific conditions (dispersed phases, reduction atmosphere) the strong metal–SiO_2 interaction can occur, eventually bringing about the formation of intermetallic compounds or alloys at much lower temperatures, as has been observed, for example, for palladium [13–16] and nickel [17, 18]. Similarly to the above systems, in the case of Co/SiO_2 also, some reduction of the substrate by atomic hydrogen generated as the result of dissociative chemisorption of hydrogen on the small cobalt particles, can be expected, despite the fact that under standard conditions (without the metal), SiO_2 cannot be reduced to silicon with hydrogen. Considering the fact that both strong lines from f c c cobalt and weak lines corresponding to h c p cobalt were visible in our sample calcined at 673 K and reduced at 773 K (Fig. 4c), we can expect (based on [11]), that the amount of silicon dissolved in cobalt did not exceed 11 at %. The presence of distinct and equally intense h c p and f c c cobalt lines in the uncalcined samples reduced at 773 K demonstrated the lack of Co–Si alloying detectable by ED.

The different behaviour exhibited by cobalt particles on SiO_2 in samples calcined or no prior reduction, may be rationalized if one considers the difference in the particle-size distributions (Fig. 5) observed for these samples. For the calcined sample consisting of fine particles, the Co–SiO_2 interface area is large, providing optimum conditions for the metal–support reaction and for diffusion of silicon into cobalt. For larger, three-dimensional particles in the noncalcined sample, the Co–SiO_2 reaction is more difficult mainly due to diffusion limitation.

The formation of Co–Si alloys in small cobalt particles supported on SiO_2 reported in this work, can account for the decrease in activity for CO hydrogenation with increasing dispersion observed by Ruel and Bartholomew for Co/SiO_2 catalyst [19].

In summary, the formation of Co–Si alloys during thermal treatment of a Co/SiO_2 model system in hydrogen at 773 K was observed by electron diffraction. The preliminary calcination of the samples facilitated this process by improving the metal dispersion and increasing the Co–SiO_2 interfacial area.

References

1. D. POTOCZNA-PETRU and L. KEPIŃSKI, *Catal. Lett.* 9 (1991) 355.
2. H. F. J. VAN'T BLIK, D. C. KONINGSBERGER and R. PRINS, *J. Catal.* 97 (1986) 210.
3. T. PARYJCZAK, J. RYNKOWSKI and S. KARSKI, *J. Chromatogr.* 139 (1977) 349.
4. D. POTOCZNA-PETRU, *Carbon* 29 (1991) 73.
5. *Idem, Polish. J. Chem.* 59 (1985) 885.

6. B. A. SEXTON, A. E. HUGHES and T. W. TURNEY, *J. Catal.* **97** (1986) 390.
7. H. F. J. VAN'T BLIK and R. PRINS, *ibid.* **97** (1986) 188.
8. C. R. BRUNDLE, T. J. CHUANG and D. W. RICE, *Surf. Sci.* **60** (1976) 286.
9. J. H. A. MARTENS, H. F. J. VAN'T BLIK and R. PRINS, *J. Catal.* **97** (1986) 200.
10. D. POTOCZNA-PETRU, in preparation.
11. H. L. LUO and P. DUWEZ, *Canad. J. Phys.* **41** (1963) 758.
12. H. SCHULZ, K. RITAPAL, W. BRONGER and W. KLEMM, *Z. Anorg. Allg. Chem.* **357** (1968) 299.
13. R. L. MOSS, D. POPE, B. J. DAVIS and D. H. EDWARDS, *J. Catal.* **58** (1979) 206.
14. W. JUSZCZYK and Z. KARPIŃSKI, *ibid.* **117** (1989) 519.
15. R. LAMBER, N. JAEGER and G. SCHULZ-EKLOFF, in "Structure and Reactivity of Surfaces", edited by C. Morterra, A. Zecchina and G. Costa, (Elsevier, Amsterdam, 1989) p. 559.
16. L. KĘPIŃSKI and M. WOŁCYRZ, *Appl. Catal.* **73** (1991) 173.
17. H. PRALIAUD and G. A. MARTIN, *J. Catal.* **72** (1981) 394.
18. R. LAMBER, N. JAEGER and G. SCHULZ-EKLOFF, *Surf. Sci.* **227** (1990) 268.
19. R. C. RUEL and C. H. BARTHOLOMEW, *J. Catal.* **85** (1984) 78.