

Ar⁺ assisted carbidization of TiO₂ (1 1 0) supported Mo nanoparticles by decomposition of C₂H₄

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Abstract

Ar⁺ assisted carbidization of Mo nanoparticles supported on TiO₂ (1 1 0) is studied by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). In order to activate the diffusion of carbon into the bulk of Mo nanoparticles we applied Ar ions (1 keV) during the exposure of C₂H₄. XPS exhibited that the decomposition of C₂H₄ at 850 K accompanied by ion bombardment results in an almost complete carbidization of nanocrystalline Mo while this treatment performed without ion bombardment results only in the carbidization of the particle surface. The modification of the crystallinity of the Mo-carbide particles was deduced from STM measurements.

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1. Introduction

Mo-oxide and -carbide supported on different oxides are very effective catalysts in hydrocarbon cleaning and reforming processes like aromatization of alkanes or selective oxidation of olefins [1,2]. The combination of Mo-carbide with reducible oxide supports, like titania, can result in catalysts with very particular properties. The thermal stability and reaction of Mo with the bulk oxygen of TiO₂ have been studied on both polycrystalline [3,4] and single crystal supports [5–9]. The carbidization of Mo or MoO_x is the key process for the fabrication of supported Mo-carbide catalysts. The elementary steps of this reaction are well characterized for Mo [10–13] and Mo₂C [14–20] solids. The application of low energy ions for the nanostructural treatment of surfaces is also a well known procedure [21,22].

In this work Mo grown on TiO₂ (1 1 0) were converted into Mo-carbides by Ar⁺ assisted decomposition of C₂H₄.

The conversion was followed by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM).

2. Experimental

The STM measurements were performed in an ultrahigh vacuum (UHV) system equipped with an STM-head, a quadrupole mass spectrometer (QMS) and a cylindrical mirror electron energy analyzer (CMA) for Auger electron spectroscopy (AES). The XP spectra were collected in separate experiments using the ELETTRA synchrotrone light source facilities (Sincrotrone Trieste, Materials Science Beamline). For all experiments polished TiO₂ (1 1 0) probes (dark gray color) were used with nearly the same pretreatments [6].

The XP spectra were recorded at the ELETTRA bending magnet beamline with a plane grating monochromator based on the SX700 concept and at the primary photon energy of 550 eV [23]. The photoemitted electrons were collected by a SPECS PHOIBOS HSA150 analyzer. The following parameters were applied during the experiments:

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constant energy (FAT) resolution mode, high point transmission lens mode, acceptance area of 2–3 mm², acceptance angle of 8°, emission angle of 30°, incidence of photons 60°. The STM imaging was performed by W-tips (+2 V, 0.05 nA).

3. Results and discussion

The main difficulty of the carbidization of Mo supported on TiO₂ originates from the fact that the temperature needed for the diffusion of the C into the bulk of Mo takes place above 1100 K at which temperature the reaction with the oxygen is also very fast [19,20]. The decomposition of hydrocarbons requires a temperature of 850 K [14]. In

order to produce bulk carbide at 850 K, we used an accompanying bombardment of Mo nanoparticles with Ar⁺ beam (1 keV, 5 × 10¹³ Ar⁺ cm⁻² s⁻¹). The impinging ions cause thermal spikes in the particles selectively and in this way the formation of bulk carbide is activated.

Fig. 1 shows the Mo-3d, C-1s and Ti-2p regions where the curves denoted by (i) exhibit the state measured on a TiO₂ (1 1 0) surface deposited by 2.0 ± 0.2 eqML (equivalent monolayer) of Mo at room temperature and annealed at 950 K for 10 min. The Mo-3d levels at 228.2 and 231.35 eV can be attributed to metallic Mo. The C-1s signal exhibits that no carbon is present in the metallic film. The peaks at 458.9 and 464.6 eV refer to the Ti⁴⁺ state of the substrate; the shoulder at 456.4 eV indicates the presence of

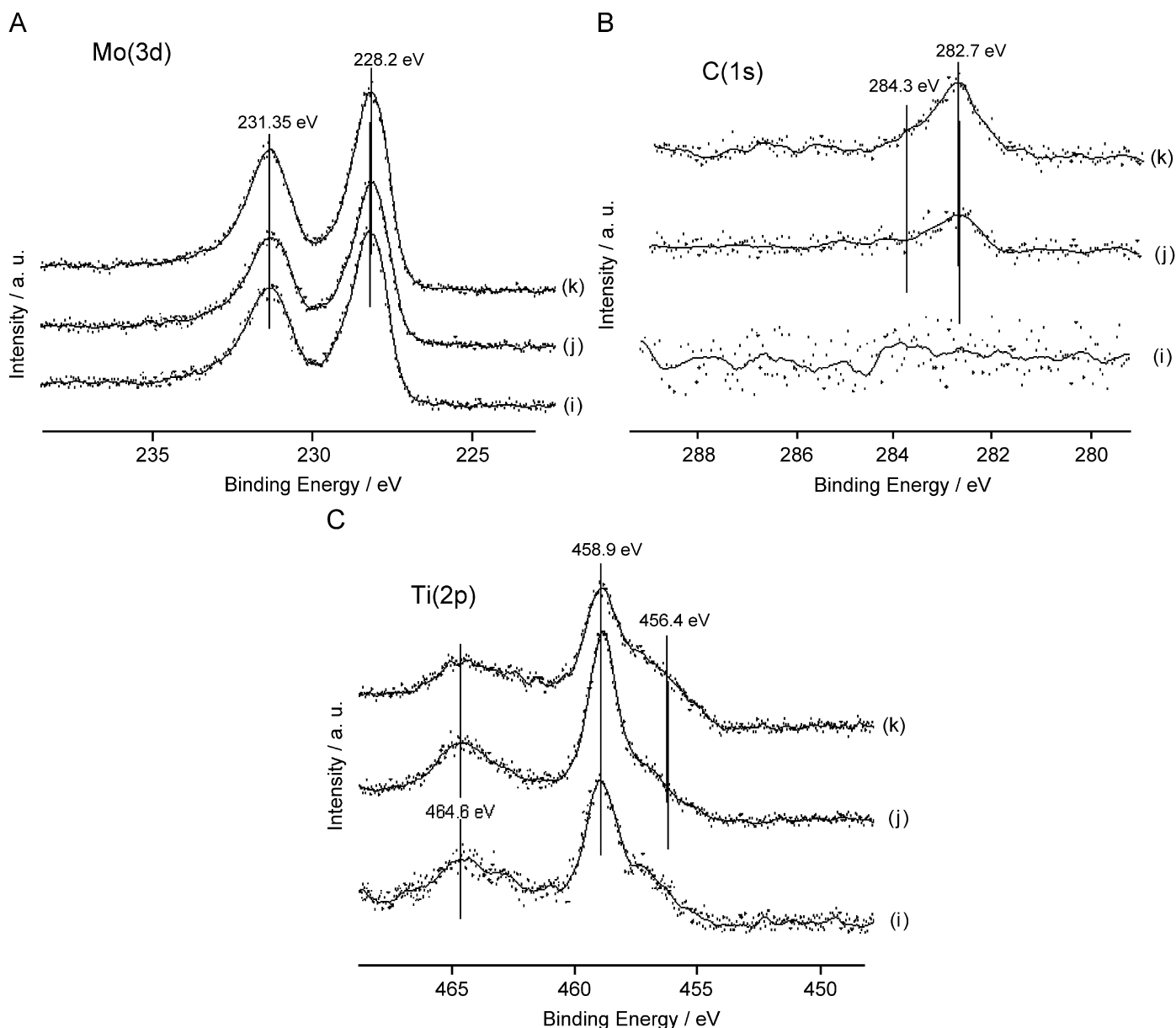


Fig. 1. XPS spectra of: (A) Mo-3d; (B) C-1s; and (C) Ti-2p regions recorded after the following treatments: (i) deposition of 2 eqML of Mo on TiO₂ (1 1 0) surface followed by annealing at 950 K; (j) exposure to C₂H₄ (10⁻⁶ hPa, 850 K, 1 min); (k) same as (j) accompanied with Ar⁺ bombardment (1 keV, 5 × 10¹³ ion cm⁻² s⁻¹).

Ti³⁺. The spectra (*j*) show the different energy regions after the exposure to 10⁻⁶ hPa C₂H₄ for 10 min at 850 K. Only a slight change can be observed in the spectra of Mo-3d and Ti-2p, however, a new peak appeared at 282.7 eV in the C-1s region (carbide state). It is known that the position of

Mo-3d is not very sensitive to the carbidization and the stoichiometric titania support is inactive in the decomposition of C₂H₄. Nevertheless, the decrease of the Ti³⁺/Ti⁴⁺ ratio suggest some adsorption of these molecules on the oxygen defect sites. The curves (*k*) in Fig. 1 exhibit the XPS

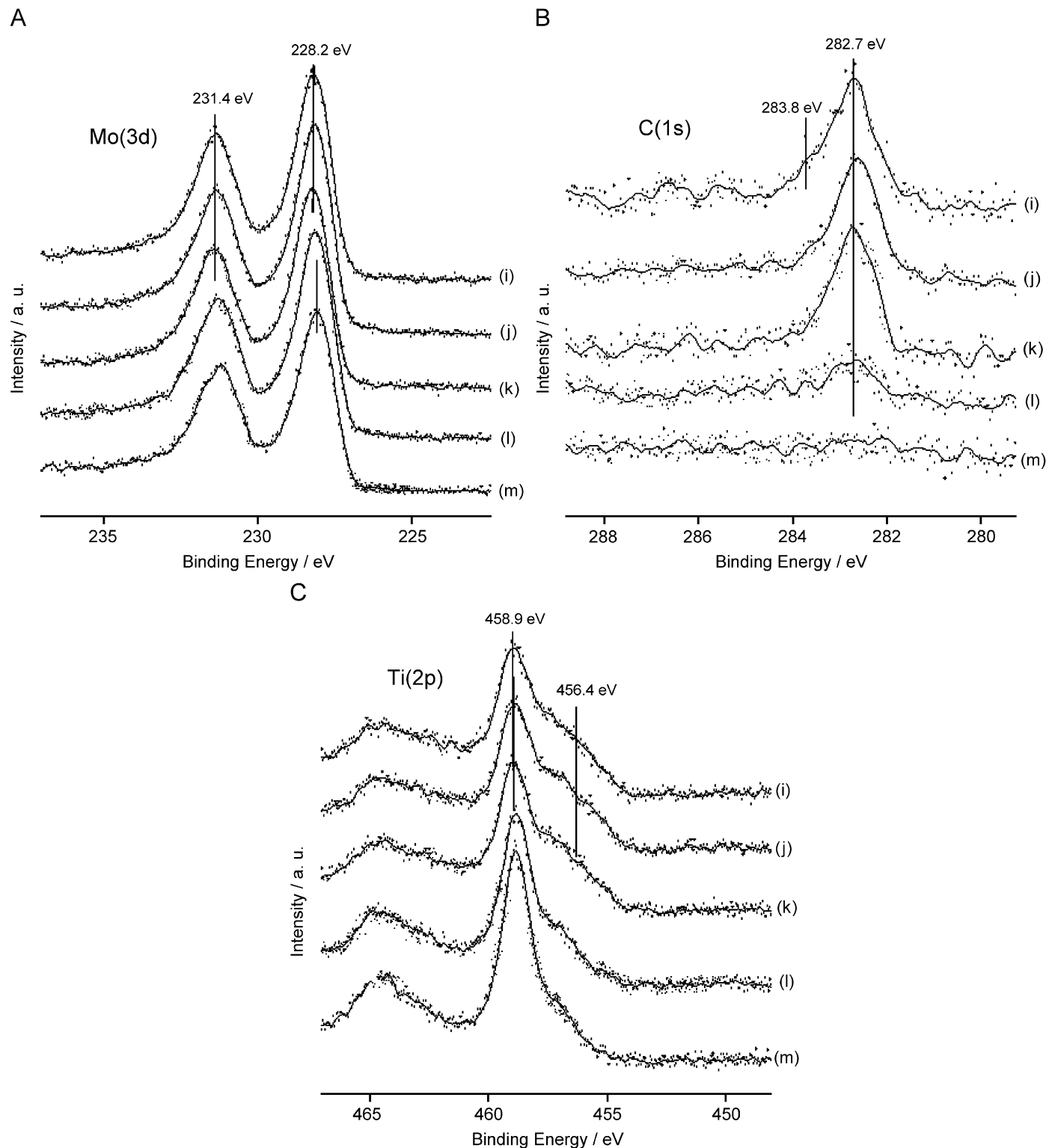


Fig. 2. Effects of annealing at different temperatures on the XPS regions of Mo-3d, C-1s and Ti-2p: (*i*) after the carbidization procedure presented also in Fig. 1 (*k*); after annealing at (*j*) 850; (*k*) 900; (*l*) 950; (*m*) 1000 K for 10 min.

spectra taken after exposing the Mo/TiO₂ (1 1 0) surface to 10⁻⁶ hPa C₂H₄ for 1 min at 850 K accompanied by Ar⁺ bombardment. It can be seen that the C-1s signal characteristic of carbide has increased by a factor of 3–4. The Mo-3d signal did not change, at the same time the Ti-2p signal indicates an enhanced concentration of Ti³⁺ states. These results suggest that the Ar⁺ assisted deposition of C₂H₄ leads to accumulation of carbon also in the Mo crystallites. A shoulder appearing in the C-1s signal at 284.3 eV refers likely to the formation of graphitic C. The comparison of the intensity of C-1s and Mo-3d orbitals, taking into account the sensitivity factors for these peaks, revealed a similar amount of C and Mo on the surface.

Fig. 2 shows the Mo-3d, C-1s and Ti-2p signals after the annealing at higher temperatures. The curves (i) exhibit the state after the preparation, the curves (j, k, l, m) show the characteristic XPS signals after 10 min thermal treatments. It can be seen that the annealing at 850 K causes the disappearance of the shoulder at 284.3 eV (C-1s), which refers to the oxidation of the graphitic C. The annealing at 900 K does not cause any substantial change, however, the increase of the temperature to 950 K leads to a significant decrease of the carbidic C-1s signal and also of the low energy shoulder at 456.4 eV on the Ti-2p signal characteristic of Ti³⁺. A very slight shift (approximately 0.2 eV) to lower binding energies was also detected in the Mo-3d signal. After annealing to 1000 K for 10 min, the C-1s signal disappears completely indicating the oxidation of the C-content of the Mo-carbide particles by the bulk oxygen of TiO₂ [14].

The STM images (Fig. 3 A, B) demonstrate the TiO₂ (1 1 0) surface exposed to 2 eqML of Mo at RT and annealed at 950 K for 10 min. The lateral extension of the rectangular particles is 4–6 nm and their height varies in the range of 0.6–1.2 nm. The lateral aspect ratio of the elongated particles is different from 1. This morphology may be explained by the formation of metallic Mo crystallites with the (0 0 1) facet parallel to the support plane and a wetting thin MoO_x interface [11]. This surface was exposed to C₂H₄ (10⁻⁶ hPa, 1 min, 850 K) accompanied by Ar⁺ bombardment and annealed at 900 K in UHV for 10 min (Fig. 3C and D). According to the XPS measurements discussed above, the supported Mo is in carbidic form in this state. Comparing the morphology and the distribution of the nanoparticles before and after this treatment, the following conclusions can be made: (i) the surface density of the particles decreased; (ii) the size distribution became wider; (iii) they have a rather round outline and their lateral aspect ratio is close to 1. The Fourier analysis of the shape of the particles exhibited rather a rectangular than a hexagonal symmetry. The effect of a further annealing at 950 K is shown in Fig. 3E and F. The XPS measurements in Fig. 2 indicated that the removal of surface carbon proceeds mainly in the 900–950 K temperature range. In harmony with this observation, the shape of the particles changed, they exhibit clearly rectangular outline. The average volume of

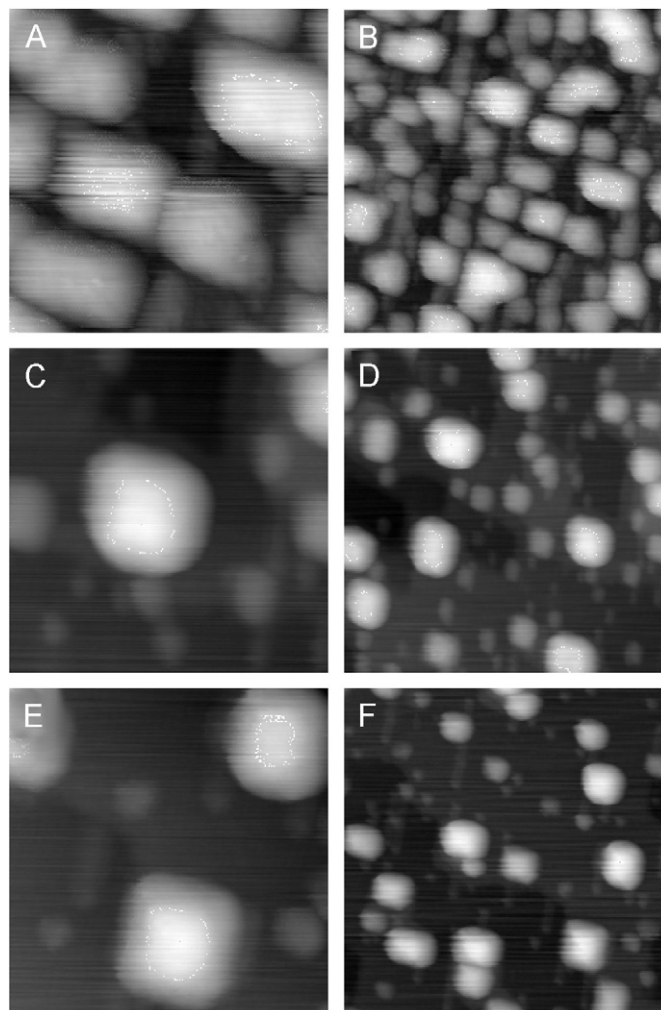


Fig. 3. Characteristic STM images (A, C, E) of 20 × 20 nm² and (B, D, F) of 50 × 50 nm² recorded after the different treatments: (A, B) deposition of 2 eqML of Mo on TiO₂ (1 1 0) followed by annealing at 950 K; (C, D) exposure to C₂H₄ (10⁻⁶ hPa, 850 K, 1 min) accompanied by Ar⁺ bombardment followed by annealing at 900 K; (E, F) annealing at 950 K.

the particles decreased by 35–40% calculated by the evaluation of the three largest particles on the images of 50 × 50 nm². This reproduced feature (a large attention was paid for the true imaging) may be explained by the loss of C content of the particles. By taking the bulk properties of these materials, the ratio of the volumes of Mo₂C and Mo assuming similar Mo content is 1.2. From this fact we may conclude that the procedure presented in this work leads to the formation of Mo_xC nanocrystallites, where 1 < x < 2. We may assume also that the different shapes of the supported Mo and Mo_xC nanoparticles detected in this work can be explained by the different wetting abilities of these materials: Mo wets the TiO₂ surface more strongly than Mo_xC does. Comparing the initial state to the final morphology after the treatments, it can be seen that the total amount of the Mo significantly decreased and the elongation of the particles almost disappeared. Both of these features can be easily explained

by the effect of the energetic Ar ions impinging in the particles.

4. Conclusions

The XPS results clearly show that the supported rectangular Mo nanoparticles (Mo (1 0 0)/[1 0 0]//TiO₂ (1 1 0)/[0 0 1]) can be transferred into Mo-carbide nanoparticles by the deposition of C₂H₄ at 850 K accompanied by Ar⁺ (1 keV) bombardment. The Mo-carbide nanoparticles produced in this procedure are stable up to 950 K, above this temperature they lose carbon and became partially oxidized.

Acknowledgments

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References

- [1] Solymosi F, Németh R, Széchenyi A. *Catal Lett* 2002;82(3–4):213.
- [2] Solymosi F, Szőke A. *Appl Catal A* 1998;166:225.
- [3] Chary KVR, Bhaskar T, Seela KK, Lakshmi KS, Reddy KR. *Appl Catal A* 2001;208:291.
- [4] Reddy BM, Chowdhury B, Reddy EP, Fernández A. *Appl Catal A* 2001;213:279.
- [5] Asakura K, Ijima KJ. *Electron Spec Rel Phenomena* 2001;119:185.
- [6] Berkó A, Magony A, Szökő J. *Langmuir* 2005;21:4562.
- [7] Domenichini B, Rizzi GA, Krüger P, Negra MD, Li Z, Petukhov M, et al. *Phys Rev B* 2006;73:245433.
- [8] Kitchin JR, Barteau MA, Chen JG. *Surf Sci* 2003;526:323.
- [9] Chun W-J, Asakura K, Iwasawa Y. *Catal Today* 2001;66:97.
- [10] Schroeder T, Zegenhagen J, Magg N, Immaraporn B, Freund H-J. *Surf Sci* 2004;552:85.
- [11] Chang Z, Song Z, Liu G, Rodriguez JA, Hrbek J. *Surf Sci* 2002;512:L353.
- [12] Biener MM, Friend CM. *Surf Sci* 2004;559:L173.
- [13] Santra AK, Min BK, Goodman DW. *Surf Sci* 2002;513:L441.
- [14] Óvári L, Kiss J, Farkas AP, Solymosi F. *J Phys Chem B* 2005;109:4638.
- [15] Edamoto K, Sugihara M, Ozawa K, Otani S. *Appl Surf Sci* 2004;237:498.
- [16] Fukui K-I, Lo R-L, Otani S, Iwasawa Y. *Chem Phys Lett* 2000;325:275.
- [17] Edamoto K, Sugihara M, Ozawa K, Otani S. *Surf Sci* 2004;561:101.
- [18] Clair TPSt, Oyama ST, Cox DF. *Surf Sci* 2000;468:62.
- [19] Schöberl Th. *Surf Sci* 1995;327:285.
- [20] Reinke P, Oelhafen P. *Surf Sci* 2000;468:203.
- [21] Valbusa U, Boragno C, Bautier de Mongeot F. *J Phys Cond Matter* 2002;14:8153.
- [22] Süle P, Menyhárd M. *Phys Rev B* 2004;71:113413.
- [23] Vašina R, Kolařík V, Doležel P, Mynář M, Vondráček M, Cháb V, et al. *Nucl Instrum Methods Phys Res A* 2001;467–468:561.