Catalysis Letters Vol. 106, Nos. 1–2, January 2006 (© 2006)
DOI: 10.1007/s10562-005-9182-7

Kinetic and spectroscopic studies of vinyl acetate synthesis over Pd(100)

D. Kumar[a], Y.-F. Han[a,b], M.S. Chen[a], and D.W. Goodman[a,*]

[a]*Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX, 77843-3012*
[b]*Institute of Chemical and Engineering Sciences, Singapore, 627833*

Received 8 August 2005; accepted 28 September 2005

A kinetic study of vinyl acetate (VA) synthesis over a Pd(100) catalyst is described, and the effect of particle-size on this reaction ascertained by comparing the single crystal data with data from supported Pd catalysts (5 wt% Pd/SiO_2, $d_{Pd} = 4.2$ nm, and 1 wt% Pd/SiO_2, $d_{Pd} = 2.5$ nm). A negative reaction order with respect to ethylene and a positive order with respect to oxygen were found for the model and supported catalytic systems, whereas the catalytic stability was strongly dependent on the particle size. The mechanism for VA synthesis is proposed to be identical on all catalysts studied based on the similarities of the kinetic parameters. Carbon-containing species on the poisoned Pd(100) catalyst were investigated by X-ray photoelectron spectroscopy (XPS), and the coverage was estimated to be approximately 1.5 ML after VA synthesis.

KEY WORDS: kinetics of vinyl acehate synthesis; Pd(100) catalysts.

1. Introduction

Vinyl acetate (VA) monomer is an important feedstock for the production of polymers such as, polyvinyl acetate and vinyl acetate copolymers [1]. Currently, VA is commercially produced mainly via gas-phase acetoxylation, as shown in eq. 1.

$$C_2H_4 + CH_3COOH + \frac{1}{2}O_2 \rightarrow C_2H_3OOCCH_3 + H_2O \quad (1)$$

Supported Pd catalysts are typically used for this reaction operating between 413 and 453 K and at pressures between 5 and 10 atmospheres [2–7]. A limited number of studies during the last 20 years have shown that the performance of Pd catalysts can be significantly affected by several factors, such as Pd dispersion, Pd chemical states and catalyst additives [5–11].

The present study was undertaken to examine in detail the kinetics of VA formation over a Pd(l00) single crystal and to compare the results with data from high-surface-area Pd supported on SiO_2. The present results are discussed in the context of previous data reported from our laboratories for VA synthesis [12–14].

2. Experimental

2.1. Surface analysis and reactor system

A system combining a commercial PHI 5500 surface analytical instrument and a preparation chamber, both with base pressures of 10^{-10} Torr, was used for these experiments. The surface analytical chamber is equipped with a dual Mg/Al anode X-ray source, an Auger gun, a quadruple mass spectrometer, a differentially pumped ion gun and a hemispherical analyzer. The catalyst was mounted on a retraction bellows allowing translation from the surface analysis section to the reactor that could be pressurized from 2×10^{-10} Torr to ~1000 Torr. The surface composition and cleanliness of the model catalysts were confirmed with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), For XPS analysis, Mg–$K_\alpha$radiation (300 W, pass energy 58.7 eV) was used, and the spectra referenced to sputtered Au and Cu foils.

A Varian Star 3400 CX series gas chromatograph (GC) with a thermal conductivity (TCD) and a flame ignition detector (FID) is attached to the reactor. A sample aliquot was injected into the GC after liquid N_2 condensation following a reaction, e.g., 2.0 h, and separated using Porapak-Q and Haysep R columns. Research grade ethylene (99.999%) and ultra-high purity oxygen (99.98%) were obtained from Matheson and used as received; glacial acetic acid (99.99%) was obtained from Aldrich further purified by triple distillation. The purity of the gases was verified by GC and mass spectroscopy (MS).

2.2. Catalyst preparation and kinetic measurements

2.2.1. Single crystal catalyst

The single crystal Pd(100) catalyst used in this study was a 1.0 cm diameter, 0.1 cm thick disk. A W/5% Re-W/26% Re thermocouple spot welded to the back of the sample was used to monitor the temperature; the sample

* To whom correspondence should be addressed.
E-mail: goodman@mail.chem.tamu.edu

was resistively heated via Ta leads. The catalyst was cleaned in UHV using Ar ion sputtering and annealing to 1000 K.

A typical reaction time was 2 h at a total pressure of ~15 Torr. After reaction, the products were condensed in a sample loop and introduced into the GC for analysis. The reactor was then evacuated and the catalyst transferred into the surface analysis section for XPS analysis. The turnover frequencies (TOF's) (molecules of VA produced per surface Pd site per second) were calculated from the number of VA molecules produced during the reaction (total conversion $<0.5\%$) using a Pd(100) atom density of 1.7×10^{15} atoms/cm^2 [15].

2.2.2. Supported catalysts

Pd/SiO_2 catalysts with a metal loading of 5.0 and 1.0 wt%, denoted as Pd-5 and Pd-1, respectively, were prepared by incipient wet-impregnation of high surface area (600 m^2/g) SiO_2. The reaction was carried out in a micro fixed-bed reactor connected to an online GC. The methodology for preparation of the supported catalyst and carrying out the reactivity measurements have been described in detail elsewhere [12,14]. The morphology, particle size, and chemical composition of the Pd catalysts, both fresh and used, were determined using transmission electron microscopy (TEM), X-ray diffraction (XRD) and XPS. TEM and XRD showed the average particle size of the Pd-1 and Pd-5 catalysts to be 2.5 and 4.2 nm, respectively.

3. Results and discussion

3.1. Kinetics

A stable VA reaction rate was observed for the Pd(100) catalyst after ~60 min of reaction at 413 and 433 K (figure 1), however, it is noteworthy that an induction period is apparent in the first few minutes of the reaction. The Pd-5 and Pd- 1 catalysts, at 443 K and $p_{O_2}=7.6$ Torr, $p_{C_2H_4}=57.0$ Torr, $p_{AcOH}=12.0$ Torr, showed a ~120 min induction period after which the rates became stable. TEM shows the average particle size of Pd to be 4.2 and 2.5 nm for the Pd-5 and Pd-1 catalysts, respectively [12]. These results show that the stability of the catalysts is independent of the Pd particle size.

The temperature-dependent reaction rates for the three catalysts studied are shown in figure 2. The reaction rate for the Pd(100) catalyst over the entire temperature range is much lower than the corresponding rates for the supported catalysts. The Pd-1 catalyst shows a higher activity compared with Pd-5 as reported previously [12].

The reaction rates as a function of O_2 and ethylene partial pressure at 433 K are displayed in figures 3 and 4, respectively. As evident in figure 3, changing p_{O_2} from 2.0 to 6.0 Torr while maintaining $p_{C_2H_4}$ and p_{AcOH} constant at 9.0 and 4.0 Torr, respectively, the reaction

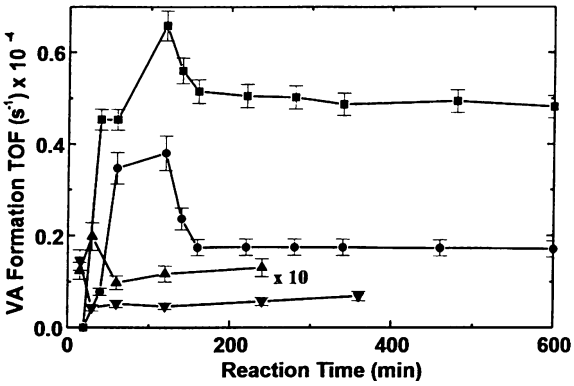

Figure 1. VA reaction rate as a function of time on Pd(100) catalyst at 413 (▲) and 433 K (▼); $p_{O_2}=5.2$ Torr, $p_{C_2H_4}=21.0$ Torr, $p_{AcOH}=8.0$ - Torr; on Pd-l (■) and Pd-5 (●) catalysts at 443 K;$p_{O_2}=7.6$ Torr, $p_{C_2H_4}=57.0$ Torr, $p_{AcOH}=12.0$ Torr, the remainder is N_2; flow rate: 30–60 ml/min; catalyst weight: 0.1-1.6 g.

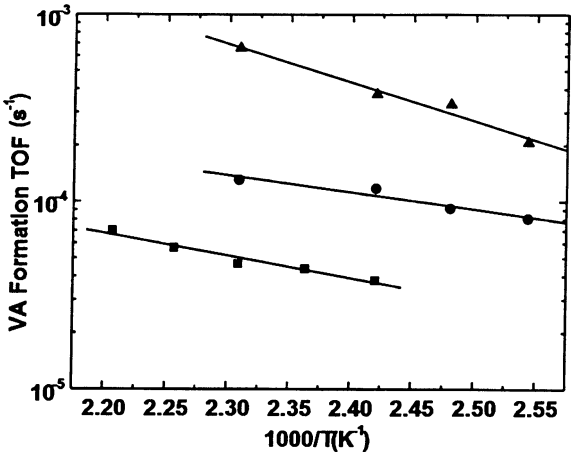

Figure 2. Arrhenius plot of VA formation rate on Pd(100) (■), Pd-5 (●) and Pd-1 (▲) at various temperatures. For Pd(100) $p_{O_2}=2.0$ Torr, $p_{C_2H_4}=9.0$ Torr, $p_{AcOH}=4.0$ Torr; for Pd-5 and Pd-1 catalysts $p_{O_2}=7.6$ Torr, $p_{C_2H_4}=57.0$ Torr, $p_{AcOH}=12.0$ Torr, the remainder N_2; flow rate: 30–60 ml/min, catalyst weight: 0.1-1.6 g.

rate increased from 4.5×10^{-5} to 7.5×10^{-5} s^{-1} at 423 K. Similarly, in changing $p_{C_2H_4}$ from 2.0 to 7.0 Torr (figure 4) while maintaining p_{O_2} and P_{AcOH} constant at 8.5 and 3.2 Torr, respectively, the reaction rate decreased from 7.5×10^{-5} to 5.0×10^{-5} s^{-1} at 433 K. Varying p_{AcOH} from 3.0 to 5.0 Torr (not shown) has little effect on the reaction rates for the Pd(100) catalyst [7,14], consistent with a similar behavior with respect to p_{AcOH} reported earlier for Pd-5 and Pd-1 catalysts [12]. The reaction orders with respect to C_2H_4 and O_2, as summarized in table 1, were calculated by fitting the data to a power rate law:

$$r_{VA}=k\cdot p_{C_2H_4}^{a}\cdot p_{O_2}^{\beta} \quad (2)$$

Although the reaction rates are clearly dependent on the Pd particle size, the reaction orders with respect to

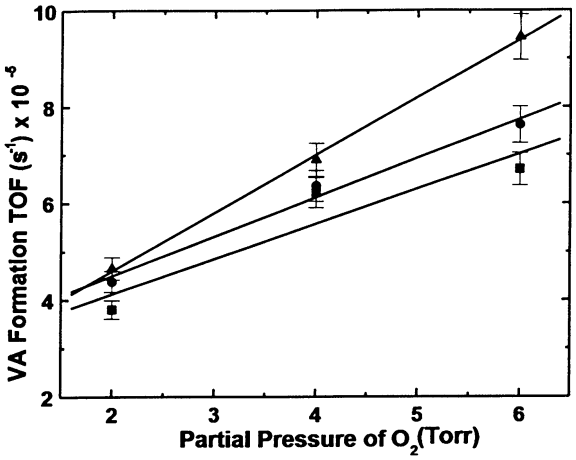

Figure 3. Dependence of VA formation TOF on partial pressure of O_2 at 413 K (■), 423 K (●), 433 K (▲) on Pd(100); $p_{C_2H_4} = 9.0$ Torr, $p_{AcOH} = 4.0$ Torr.

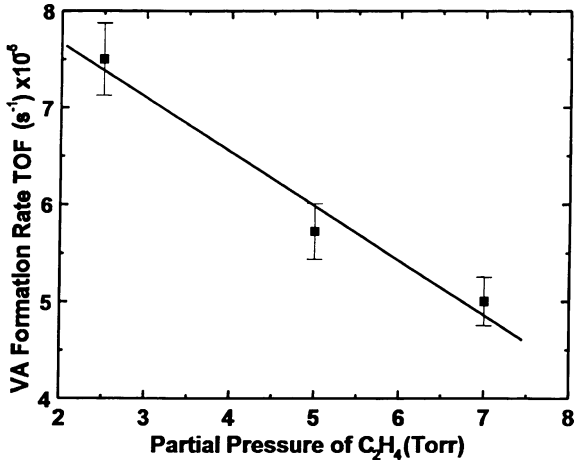

Figure 4. Dependence of VA formation rate on partial pressure of C_2H_4 at 433 K (■) on Pd(100); $p_{O_2} = 2.0$ Torr, $p_{AcOH} = 4.0$ Torr.

ethylene and oxygen are not. A negative reaction order with respect to C_2H_4 and a positive order with respect to O_2 imply that the reaction can be fit to a Langmuir–Hinshelwood mechanism. The negative order for C_2H_4 may be due to the stronger adsorption of ethylene and its derivative surface species, such as ethylidyne and ethylidyne. The coverages of these ethylene species increase with increasing C_2H_4 pressure, which inhibit or decrease the coverages of other species like acetate and oxygen required for VA synthesis, inducing the decrease of the overall VA formation rate. An increase in O_2 pressure facilitates an increase in the coverage of active surface oxygen species that then leads to an increase in the VA formation rate. In summary, the kinetic parameters for VA synthesis over Pd(100) are similar to those observed for supported Pd/SiO_2, particularly noteworthy being E_a and the reaction order with respect to ethylene.

CO_2 is the main by-product formed via combustion of the reactants/products. Selectivities for VA of 90% and 92% were observed for the Pd-5 and Pd-1 catalysts, respectively, at 413 K ($p_{C_2H_4} = 57$ Torr, $p_{O_2} = 7.5$ Torr and $p_{AcOH} = 12.0$ Torr). The selectivity of the Pd(100) catalyst for VA could not ascertained because of the relatively low surface area of the catalyst and small amounts of CO_2 produced compared to the background CO_2.

3.2. XPS

Under reaction conditions, acetic acid and water are the primary surface species during VA synthesis as determined by isotopic transient methods [8,16]. Previous results from our laboratories have shown the formation of PdC_x on Pd-5 and Pd-1 catalysts during VA synthesis [17,18], with Pd-5 showing the greater tendency to form PdC_x. C 1s XPS of the Pd(100) catalyst subsequent to reaction (figure 5) can be resolved into three distinct peaks with binding energies (BE) centered at 284.2, 285.5 and 288.0 eV. The more intense peak at 284.2 eV is assigned to a surface CH_x ($x = 0$–3) species formed from the dissociation of an ethylenic and/or acetate species. The features at 285.5 and 288.0 eV are assigned to CO and an acetate species, respectively [19–22].

CO at saturation coverage was used to calibrate the absolute quantity of carbon on the surface of Pd(100) after reaction. The C_{1s} XP spectra show a primary feature centered at 285.5 eV for various coverages of CO (as shown in the lower panel of figure 5), which is in excellent agreement with the observations by Jones *et al.* [23,24]. Madix *et al.* [25], have reported that the saturation coverage for CO on Pd(100) at room temperature is 0.53 ML. By comparing the peak area of the C_{1s} is

Table 1
Kinetic parameters for the synthesis of VA over Pd/SiO_2 catalysts, power rate law: $r_{VA} = k \cdot \left(\frac{p_{C_2H_4}}{P_{Total}}\right)^{\alpha} \cdot \left(\frac{p_{O_2}}{P_{Total}}\right)^{\beta}$

Catalysts	$k \times 10^{-3}$ (s^{-1})	α	β	E_a (kJ/mol)
Pd(100)[a]	0.4–0.8	-0.40 ± 0.04	0.50 ± 0.05	23.00 ± 3.0
5% Pd/SiO_2[b]	0.8–1.4	-0.60 ± 0.02	0.12 ± 0.01	17.3 ± 2.0
1% Pd&SiO_2[b]	2.4–5.1	-0.34 ± 0.02	0.18 ± 0.01	39.0 ± 2.0

[a]The p_{O_2} and $p_{C_2H_4}$ in the reaction mixture were varied (p_{O_2}: 2.5–9.0 Torr and $p_{C_2H_4}$: 2.0–8.5 Torr, respectively) while the p_{AcOH} was kept constant at 3.2 Torr.

[b]The reactant gas consisted of p_{O_2}: 7.5–63.0 Torr, $p_{C_2H_4}$: 56.3–101.3 Torr and p_{AcOH}: 12.0 Torr with N_2 as the remainder. Characterization of the reaction kinetics is described elsewhere [14].

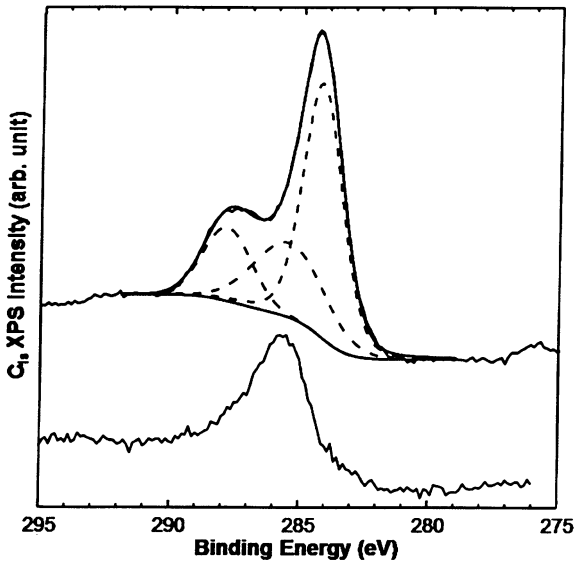

Figure 5. C_{1s} XPS spectrum after VA reaction on Pd(100) at 433 K; $p_{O_2}=2.0$ Torr, $p_{C_2H_4}=9.0$ Torr, $p_{AcOH}=4.0$ Torr; the lower panel is the C_{1s} XPS spectrum of CO at saturation on Pd(100) at 300 K.

region after VA reaction to that for saturated CO shown in figures 6a and b, the amount of C on Pd(100) after reaction is estimated to be approximately 1.5 ML. This carbon coverage is in agreement with the results of Bowker *et al.*, who have estimated the carbon coverage on Pd(110) following exposure to ethylene [19] and acetic acid [26] to be approximately 1.5 ML. These authors report that of this 1.5, 0.5 ML is on the topmost surface while the remainder is interdiffused into the top several layers of the catalyst [18,19,26].

Figure 6a shows C_{1s} XPS spectra acquired at room temperature after reaction and after flashing the Pd(100) catalyst to various temperatures. Each of these spectra can be deconvoluted into three surface species, CH_x, CO and acetate, as shown in figure 5. The intensities for each component as a function of annealing temperature are plotted in figure 6b, After a flash to 380 K the intensity of the carbon features at 284.3 and 288.5 eV decreases rapidly. This reduction in intensity is likely due to desorption of ethylene and acetate species, in agreement with previous studies [26–28], showing desorption of acetate species at approximately 350 K. Flashing to much higher temperatures, i.e., >500 K, removes adsorbed CO (at 285.5 eV), and at still higher temperatures, the feature at 284.2 eV, assigned to amorphous carbon and CH_x species, disappears. Note that during this transformation no apparent change was observed in the binding energy of the Pd 3d feature. These XPS results show that carbon-containing species formed during VA synthesis reaction are stable on Pd(100) to 350–500 K.

Additional questions, remain regarding the adsorption behavior of ethylene and acetic acid in the presence of oxygen and the suppression of ethylene combustion during VA synthesis. Current work is underway to address these and related issues of VA synthesis over Pd and Au-Pd catalysts.

4. Conclusions

The kinetics of vinyl acetate (VA) synthesis over Pd(100) catalyst have been explored. The Pd particle size-dependence of the reaction rates is assessed by comparing the single crystal kinetics with those of supported Pd catalysts. Negative order with respect to ethylene and positive order with respect to oxygen were observed for all the catalysts, neither being dependent on the Pd particle size. Deactivation of the supported and unsupported catalysts was comparable. XPS showed that the carbon level following reaction on the Pd(100) catalyst was approximately 1.5 ML.

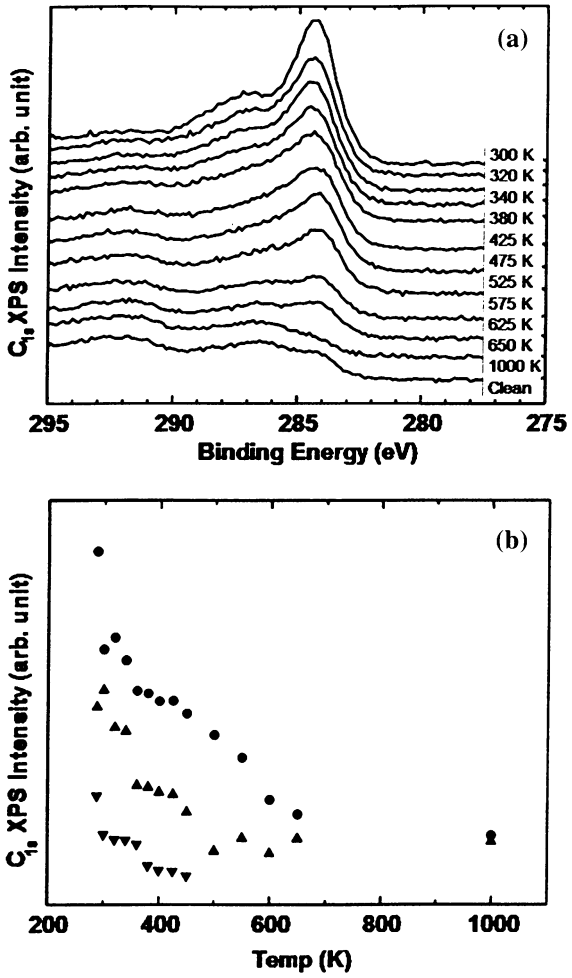

Figure 6. (a) C_{1s}XPS spectra on Pd(100) after reaction at 433 K and after annealing to temperatures as indicated; $p_{O_2}=2.0$ Torr, $p_{C_2H_4}=9.0$ Torr, $p_{AcOH}=4.0$ Torr; (b) C_{1s} XPS peak intensity for CH_x (●), CO (▲) and acetate (▼) species plotted versus the annealing temperature.

Acknowledgments

We would like to thank Dr. Les Wade of Celanese Chemical Company for useful discussions. We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Science and the R.A. Welch.

References

[1] H.F. Rase, *Handbook of Commercial Catalysts: Heterogeneous Catalysts*, (CRC Press LLC, 2000).
[2] C.T. Bissot, US Patent, 4,048,096 (1977).
[3] D. Kragten, R.A. van Santen, M. Crawford, W. Provine and J. Lerou, Inorg. Chem. 38 (1991) 331.
[4] T. Kawaguchi and T. Wakasugi, Appl. Catal. 36 (1988) 67.
[5] W.D. Provine, P.L. Mills and J.J. Lerou, Stud. Surf. Sci. Catal. 101 (1996) 191.
[6] S. Nakamura and T. Yasui, J. Catal. 17 (1970) 366.
[7] B. Samanos, P. Bountry and R. Montarnal, J. Catal. 23 (1971) 19.
[8] E.A. Crathorne, D. MacGowan, S.R. Morris and A.P. Rawlinson, J. Catal. 149 (1994) 254.
[9] S. Nakamura and T. Yasui, J. Catal. 23 (1971) 315.
[10] Sennewald, US Patent, 3,631,079 (1971).
[11] W.J. Bartley, S. Jobson, G.G. Harkreader, M. Kitson and M. Lemanski, US Patent, 5,274,181 (1993).
[12] Y.-F. Han, D. Kumar and D.W. Goodman, J. Catal. 230 (2005) 353.
[13] Y.-F. Han, D. Kumar, C. Sivadinarayana and D.W. Goodman, J. Catal. 224 (2004) 60.
[14] Y.-F. Han, J.-H. Wang, D. Kumar, Z. Yan and D.W. Goodman, J. Catal. 232 (2005) 467.
[15] D. Bürgler, G. Tarrach, T. Schaub, R. Wiesendanger and H.-J. Güntherodt, Phys. Rev. B. 47 (1992) 9963.
[16] S.M. Augustine and J.P. Blitz, J. Catal. 142 (1993) 312.
[17] Y.-F. Han, D. Kumar, C. Sivadinarayana, A. Clearfield and D.W. Goodman, Catal. Lett. 94 (2004) 131.
[18] M. Bowker and C. Morgan, Catal. Lett. 98 (2004) 67.
[19] M. Bowker, C. Morgan, N. Perkins, R. Holroyd, E. Fourre, F. Grillo and A. MacDowall, J. Phys. Chem. B 109 (2005) 2377.
[20] Z. Bastl and T. Sarapatka, Collect. Czech. Chem. Commun. 63 (1998) 1793.
[21] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg (ed), *Handbook of X-ray Photoelectron Spectroscopy*, (Perkin-Elmer Corporation, Physical Electronics Division, 1979).
[22] M. Sock, A. Eichler, S. Surnev, J.N. Andersen, B. Klötzer, K. Hayek, M.G. Ramsey and F.P. Netzer, Surf. Sci. 545 (2003) 122.
[23] I.Z. Jones, R.A. Bennett and M. Bowker, Surf. Sci. 439 (1999) 235.
[24] J.N. Andersen, M. Qvarford, R. Nyholm, S.L. Sorensen and C. Wigren, Phys. Rev. Lett. 67 (1991) 2822.
[25] E.M. Stuve, R.J. Madix and C.R. Brundle, Surf. Sci. 146 (1984) 155.
[26] M. Bowker, C. Morgan and J. Couves, Surf. Sci. 555 (2004) 145.
[27] X.-C. Guo and R.J. Madix, J. Am. Chem. Soc. 117 (1995) 5523.
[28] R.D. Haley, M.S. Tikhov and R.M. Lambert, Catal. Lett. 76 (2001) 125.