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Gold, silver and copper catalysts supported on TiO_2 for pure hydrogen production

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Abstract

A catalytic study of the hydrogen production by CO water gas shift reaction (WGSR) on gold, silver and copper particles supported on TiO_2 has been carried out. A deep characterisation of the catalysts by TPR and FTIR has been performed. Silver catalyst exhibits no catalytic activity, copper and gold catalysts show intermediate and very high performances, respectively. These strong differences have been interpreted on the basis of FTIR data of CO adsorption at 90 K and on the effect of coadsorbed species. Gold and copper catalysts, either oxidised or reduced, are able to adsorb CO. Reduced silver catalyst does not adsorb CO at all, while oxidised silver catalyst does quite strongly. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pure hydrogen production; Gold, silver and copper catalysts; Water gas shift reaction

1. Introduction

The water gas shift reaction (WGSR) is one of the oldest methods for pure hydrogen production. Recently, the interest to WGSR has been renewed due to the possibility to use pure hydrogen in fuel-cells or in other reactions related to environmental protection and clean technologies.

Copper-based catalysts are well known low temperature WGSR catalysts [1]. Quite recently, it was established that also nano-sized gold catalysts supported on TiO_2 and Fe_2O_3 are very active at low temperatures in the WGS reaction [2]. Some results, concerning a FTIR study of WGS reaction on Au/TiO_2 and Au/Fe_2O_3 catalysts, have already been reported by some of us [3]. Here a comparative study of IB metals on titania will be presented. The chemisorption and catalytic properties of the IB metals have been already the object of some comparative studies [4]. In this paper, we will present a TPR, FTIR and catalytic study mainly devoted to understand the strong differences in the catalytic activity of the three title catalysts in the hydrogen production by CO WGSR.

2. Experimental

2.1. Materials

The samples were prepared by the deposition–precipitation method [2] in a ‘Contalab’ laboratory reactor (ContravesAG, Switzerland) under complete control of all parameters (temperature, pH, stirrer speed, reactant feed flow rates, etc.). The deposition–precipitation method involves the deposition on titania, preliminarily suspended in water by the ultrasounds technique,

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of the corresponding metal hydroxide or hydrocarbonate through chemical interaction of initial metal salts and Na_2CO_3 in aqueous solution. The samples were calcined at 673 K after the preparation. All the chemical used, $Cu(NO_3)_3{\cdot}3H_2O$, $AgNO_3$, $HAuCl_4{\cdot}H_2O$, Na_2CO_3 and $TiCl_4$ were analytical grade. The anatase was prepared by the hydrolysis of $TiCl_4$ with ammonia at pH 9, at low temperature. The samples containing 3 wt.% IB metals on TiO_2 will be labelled as Cu/Ti, Ag/Ti Au/Ti.

2.2. Methods

The catalytic activity of the samples in the WGS reaction was measured in a flow reactor at atmospheric pressure under the following conditions: catalyst bed volume 0.5 cm^3 (0.63–0.80 mm pellets), space velocity 4000 h^{-1}, and vapour/gas ratio = 0.7. The samples were reduced for 1 h in the same mixture at different temperatures: Cu/Ti at 493 K, Ag/Ti and Au/Ti at 373 K. The reactant gas mixture feed into the reactor contained 4.498 vol.% CO, the rest being argon. Analysis of the converted mixture at the reactor outlet was carried out on an 'Infralyt 2000' gas analyser with respect to CO and CO_2 content. The catalytic activity was expressed by the degree of conversion of CO. TPR measurements were performed using the apparatus described in Ref. [5] under the following conditions: gas mixture, hydrogen–argon (10% H_2); flow rate, 24 ml min^{-1}; sample amount, temperature rise: 15 K min^{-1}; sample amount: 0.050 g of Cu/Ti, 0.100 g of Ag/Ti and 0.150 g of Au/Ti, respectively. Additional experiments concerning reoxidation with purified air were performed after the TPR peaks of the fresh samples were registered. The reoxidation was carried out at two different temperatures. In the first case, the H_2–Ar flow was switched over to air flow at the temperature just after the corresponding TPR peak of the fresh sample (483 K for Cu/Ti, 423 K for Ag/Ti and 403 K for Au/Ti). The sample was kept at this temperature for 15 min. The TPR measurement was performed after cooling to RT. In the second case, the sample was cooled to RT and reoxidised in air for 15 min at this temperature and then the TPR spectrum was recorded. The FTIR spectra have been taken on a Perkin-Elmer 1760 spectrometer, with the samples in self-supporting pellets introduced in a cell allowing thermal treatments in controlled atmospheres and spectrum scanning at controlled temperatures (from 90 K up to RT). The FTIR spectra of the three samples were normalised on the weight of the pellets.

3. Results and discussion

3.1. Catalytic activity

The catalytic activity data are summarised in Fig. 1. The samples were reduced in a 1% H_2 in argon feed, at 493 K as for the Cu/Ti sample and at 373 K as for the Au/Ti and the Ag/Ti samples, before the measure. The silver catalyst remains almost completely inactive in all the examined temperature range, with a maximum conversion of 6% at 520 K, while gold gets a CO conversion of 80% at the same temperature and copper exhibits an intermediate behaviour, by getting a 30% conversion. We have undertaken a TPR and FTIR characterisation of these samples to understand the origin of these differences.

3.2. TPR results

The results are summarised in Fig. 2. The TPR peak of fresh Cu/Ti is composite (Fig. 2A, curve 1) and it consists of two overlapping peaks at 433 and 448 K. Two peaks were detected by the TPR technique also on Cu/ZrO_2 catalysts prepared by the coprecipitation

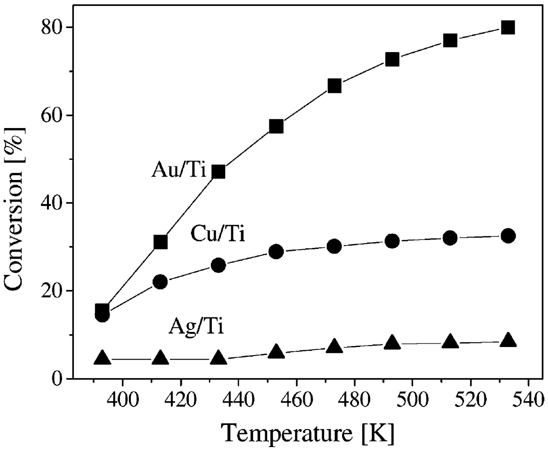

Fig. 1. Temperature dependence of the catalytic activity (degree of CO conversion) of the samples: (■): Au/Ti; (●): Cu/Ti; (▲): Ag/Ti.

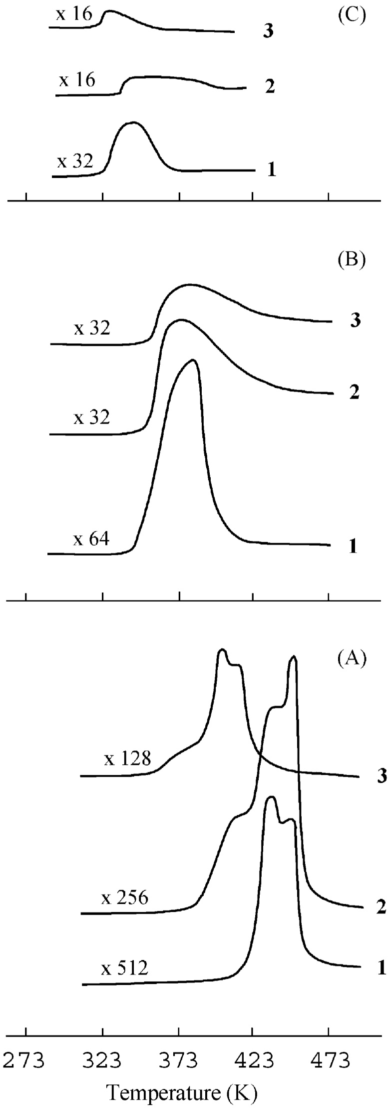

Fig. 2. TPR spectra of the studied samples: (A) Cu/Ti; (B) Ag/Ti; (C) Au/Ti. Curves 1—TPR of the fresh samples; curves 2—TPR after reoxidation with purified air by switching the H_2–Ar flow over to air flow immediately after the TPR peak of the fresh sample (483 K for Cu/Ti, 423 K for Ag/Ti and 403 for Au/Ti), the samples were left at this temperature for 15 min; curves 3—after the first TPR experiment the sample was cooled to RT and reoxidised in air for 15 min at this temperature, after which a new TPR experiment was recorded.

method [6]. The authors assigned the peaks observed to the reduction of Cu(I) oxide (high temperature peak) and of Cu(II) oxide (low temperature peak). The two reduction peaks reported in Fig. 2A, curve 1 are in the same temperature region of those that some of us observed on Cu/Ti samples prepared by the chemisorption–hydrolysis procedure [7] and assigned to CuO crystallites of different dimensions. The same assignment can be applied, in our opinion, also to the peaks reported in Fig. 2A. Two differences on the TPR profile of the Cu/Ti sample after reoxidation at 483 K (Fig. 2A, curve 2) respect to the one detected on the fresh Cu/Ti (Fig. 2A, curve 1) are evident. A shoulder from the low temperature side, that indicates the formation of more easily reducible species and an higher intensity of the high temperature peak, that can be explained assuming a different size distribution of the CuO crystallites, have been observed. The peaks are weaker and shifted towards lower temperatures after reoxidation at RT (Fig. 2A, curve 3). At this temperature, the oxidation treatment is less effective and produces more easily reducible species. As for Ag/Ti, the TPR peak of the fresh sample (Fig. 2B, curve 1) is quite broad and asymmetric, $T_{\max} = 383\,\mathrm{K}$, and can be ascribed to the reduction of oxygen species on finely dispersed silver and to the reduction of Ag_2O [8].

The TPR spectrum of the fresh Au/Ti sample (shown in Fig. 2C, curve 1, $T_{\max} = 350\,\mathrm{K}$) can be detected only if during the achievement of the steady-state conditions of the hot-wire detector the sample is cooled to 263 K. The spectra run after reoxidation at 400 K (Fig. 2C, curve 2) and after reoxidation at RT (Fig. 2C, curve 3) have been registered in the same experimental conditions described above. In this case, the reduction process occurs already at RT and can be ascribed to the reduction of oxygen species adsorbed on very small gold clusters.

3.3. FTIR spectra of CO adsorption at 90 K on Au/Ti, Cu/Ti and Ag/Ti

A comparison between the spectrum produced by the interaction with 2 mbar of CO at 90 K on the fresh Au/Ti oxidised sample (Fig. 3A, dotted curve) and the spectrum of the same sample put in contact with 2 mbar of CO at RT and cooled again in CO to 90 K (solid curve) is shown in Fig. 3A. In the high frequency range, in addition to a very strong band at $2179\,\mathrm{cm}^{-1}$ and to a weak one at $2205\,\mathrm{cm}^{-1}$, both the spectra are characterised by weaker bands at 2165 and $2157\,\mathrm{cm}^{-1}$. These absorptions, by comparison with

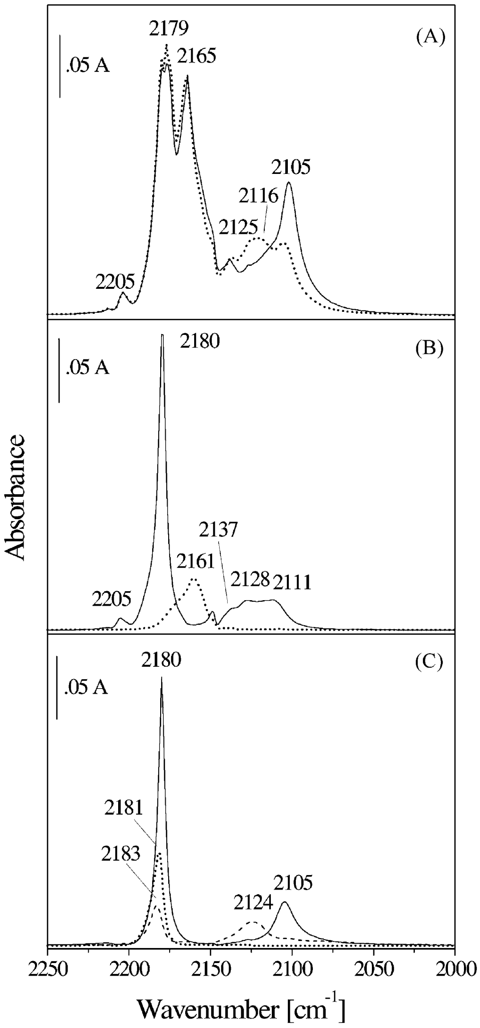

Fig. 3. FTIR spectra of CO interactions on the three samples. (A): 2 mbar of CO at 90 K on the freshly Au/Ti oxidised sample (dotted curve), 2 mbar of CO at RT on the same sample, followed by cooling to 90 K (solid curve). (B): 0.03 mbar of CO at 90 K on Au/Ti (solid curve) and on Ag/Ti (dotted curve), both calcined and pre-treated in pure oxygen at 673 K (normalised spectra). (C): 0.03 mbar of CO at 90 K on Au/Ti (solid curve), Cu/Ti (dashed curve), and Ag/Ti (dotted curve) reduced samples (normalised spectra).

the spectroscopic features reported in literature for TiO_2 [9,10], can be ascribed to CO adsorbed on different support Ti^{4+} cations. The main peak at 2179 cm^{-1} is assigned to full coverage of CO σ-bonded on coordinatively unsaturated ions located on extended patches of the anatase (0 1 0) face, the 2205 cm^{-1} one is assigned to a few more uncoordinated and defective sites and the band at 2165 cm^{-1} is assigned to CO adsorbed on Ti^{4+} sites more efficiently shielded by the surrounding oxygen atoms, possibly inward displaced. Finally, the band at 2157 cm^{-1} can be ascribed to CO hydrogen bonded to surface OH groups. Moreover, some significant differences between the two spectra are evident in the range 2150–2000 cm^{-1}. On the sample put in contact with 2 mbar of CO at RT and cooled again in CO to 90 K, the components at 2125–2116 cm^{-1} (oxidised gold sites) [11] show a reduced intensity respect to those observed in the spectrum produced by interaction of 2 mbar of CO at 90 K, while the component at 2105 cm^{-1} (metallic gold step sites) is strongly increased [3,12]. This experiment clearly indicates that on the freshly oxidised sample, in agreement with the TPR results previously presented, there are some oxidised gold sites that can be easily reduced by contact with reducing molecules, hydrogen or CO, already at RT. These already reduced or easily reducible gold sites, exposed at the surface of very small gold particles, can be able to activate CO for the WGS reaction.

Fig. 3B shows the normalised spectra produced by adsorption of 0.03 mbar of CO at 90 K on Au/Ti and on Ag/Ti catalysts, both calcined and pre-treated in pure oxygen at 673 K. At this CO pressure, in the 2210–2180 cm^{-1} range, only the 2180 and the 2205 cm^{-1} components are present on the Au/Ti sample. At lower frequencies, bands at 2137, 2128 and 2111 cm^{-1}, assigned to CO on oxidised and metallic gold, are evident (Fig. 3B, solid curve). No bands are detected in the 2210–2180 cm^{-1} range or in the 2140–2090 cm^{-1} range for the Ag/Ti sample, only an absorption band at 2161 cm^{-1} with a shoulder at higher frequency is produced (Fig. 3B, dotted curve). This absorption falls at an intermediate frequency between that typical of metallic silver films, absorbing in the range 2148–2120 cm^{-1} [13], and that typical of Ag^{+} cations, observed in the range 2190–2230 cm^{-1} [14] and can be ascribed to CO adsorbed on $Ag^{\delta+}$ sites exposed at the surface of a Ag_xO layer fully covering the support. The absorption bands ascribed to CO adsorbed on support cations are completely absent on the oxidised silver catalysts (Fig. 3B, dotted curve), while a band at 2181 cm^{-1} is present in the spectrum of Ag/Ti sample reduced in hydrogen at 423 K (Fig. 3C, dotted curve). By reduction of the

Ag_xO layer to silver metallic particles, some of the support sites are regenerated, as observed by other authors [15]. The absence of any new band in the reduced sample indicates that metallic silver sites do not adsorb CO at all, in agreement with the very low strength of the Ag–CO bond, calculated and experimental, as reported in [16]. By reoxidation of the sample at 673 K, the absorption band at 2161 cm^{-1} with the shoulder as on the initial oxidised sample reappears (not shown for sake of brevity), indicating that the reduction does not produce any irreversible sintering of the metallic phase. Therefore, the very low catalytic activity of Ag/Ti cannot be related to a low dispersion of the silver phase, but to the incapability of silver in the CO chemisorption and activation.

On Au/Ti reduced sample, mainly two absorption bands are detected at 2180 and at 2105 cm^{-1} (Fig. 3C, solid curve). The band at 2105 cm^{-1}, on the basis of previous works [12], is assigned to CO adsorbed on metallic, step gold sites. On Cu/Ti reduced sample, mainly two absorptions are detected. The first band, assigned to CO adsorbed on support cations, is centred at 2183 cm^{-1}, the second absorption, with a weak component at 2099 cm^{-1}, is observed at 2124 cm^{-1} (Fig. 3C, dashed curve).

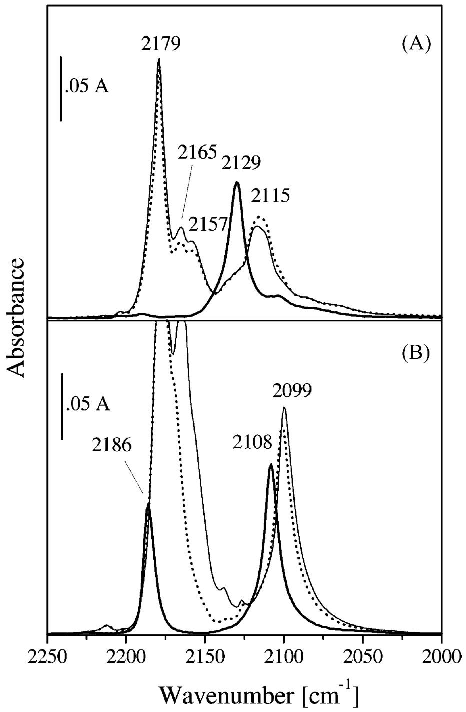

Fig. 4. FTIR spectra of Cu/Ti (A) and Au/Ti (B) produced by interaction of 2 mbar of CO adsorbed at 90 K on the freshly reduced sample (thin curve), after subsequent outgassing up to RT (bold curve) and again at 90 K after readmission of CO (dotted curve).

Fig. 4A shows the comparison between the spectrum produced by interaction of 2 mbar of CO adsorbed at 90 K on the freshly reduced Cu/Ti sample (Fig. 4A, thin curve), the spectrum of the same sample outgassed up to RT (Fig. 4A, bold curve) and the spectrum obtained after readmission of CO at 90 K (Fig. 4A, dotted curve). In the high frequency range, on the freshly reduced sample at full coverage (Fig. 4A, thin curve), bands at 2165, 2179 and 2205 cm^{-1} are present. Moreover, the spectrum exhibits also a band centred at 2157 cm^{-1} and a quite broad and complex absorption with the maximum at a 2115 cm^{-1}. As observed for the Au/Ti sample, the high frequency bands are related to CO adsorbed on different sites of the support. By decreasing the CO pressure at 90 K and outgassing up to RT (Fig. 4A, bold curve), the high frequency components gradually reduce their intensities, blue shift and finally disappear. At the same time, the band at 2157 cm^{-1} is easily depleted during the outgassing at 90 K and the absorption centred at 2115 cm^{-1} significantly changes, becoming sharper and shifting up to 2129 cm^{-1}. Looking at the behaviour of the 2157 cm^{-1} band and also of the component centred at 2115 cm^{-1}, the observed features can be explained assuming that in presence of an high pressure of CO, two CO molecules are coordinated on copper. By decreasing the CO pressure, the 2157 cm^{-1} and the 2115 cm^{-1} bands are simultaneously depleted and at the same time the 2129 cm^{-1} band is formed. On the basis of the literature data [17], the 2115 and 2157 cm^{-1} bands can be assigned to the symmetric and asymmetric modes of bicarbonylic species on copper. A band centred at 2129 cm^{-1} has been already observed in some of our previous works of CO chemisorption at RT on Cu/Ti sample [7] and it has been assigned to CO adsorbed on Cu^0 isolated atoms or two-dimensional small clusters. Absorption bands at these frequencies were also observed by de Jong et al. [18] on well-reduced Cu/SiO_2 samples and by He et al. [19] on ultra-thin Cu films on Rh(1 0 0). In all cases, the results of

Moskovits and Hulse [20] on copper carbonyl complexes, isolated in an argon matrix are the guide for the interpretation. Recently, in a study [21] concerning the determination of the nature of the copper sites in Cu/TiO_2 catalysts, a band at ≈2130 cm^{-1} has been assigned to CO adsorption at Cu^+ sites. However, on our sample, the absorption centred at 2129 cm^{-1} is fully reversible to the outgassing (not shown for the sake of brevity). This behaviour is unusual for Cu^+ sites, that adsorb irreversibly and strongly CO at RT. Moreover, the 2129 cm^{-1} band reduces its intensity, becomes broader and red-shifts back to 2115 cm^{-1}, giving rise to the spectrum of the bicarbonylic species almost identical to the initial one (Fig. 4A, thin curve), after readmission of CO at 90 K (Fig. 4A, dotted curve). These experimental features indicate that the surface composition, the coordination and the oxidation state of copper are not modified during the experiment.

As for the similar experimental features concerning the Au/Ti sample and presented in Fig. 4B, the spectrum of the fresh sample in contact with 2 mbar of CO (Fig. 4B, thin curve) is characterised by the strong bands at 2179 and at 2165 cm^{-1}, already assigned to CO adsorbed on (1 0 1) and on more oxygen shielded Ti^{4+} sites. A strong band at 2099 cm^{-1}, previously observed at 90 K on a fully hydrated Au/TiO_2 sample [22] and assigned to CO adsorbed on Au^0 step sites exposed at the surface of gold particles is present. By decreasing the CO pressure at 90 K and by outgassing up to RT, the 2179 and 2165 cm^{-1} bands gradually reduce their intensity, blue-shift and are finally depleted. At the same time, the maximum of the absorption assigned to CO adsorbed on Au^0 sites significantly blue-shifts up to 2108 cm^{-1} (Fig. 4B, bold curve). This frequency is usually observed in the FTIR experiments of CO adsorption on different gold samples [12]. By readmission of 1 mbar of CO at 90 K (Fig. 4B, dotted curve), a spectrum very similar to the initial one is produced. These experimental features indicate that, in presence of an almost complete monolayer of CO adsorbed on titania, as in presence of an almost complete monolayer of water [22], the gold sites exposed at the surface of the metallic particles are modified by the species adsorbed on the neighbouring titanium sites. In both the cases, the shift can be ascribed to a work function and/or to a ligand effect of the adsorbed molecules.

4. Conclusions

From the comparative study of the three IB metals nano-dispersed on titania it can be concluded that:

- The gold reduced catalyst activates CO molecules on surface step sites. The FTIR absorption band red-shifts if CO or water are coadsorbed on the support cations. The red-shift of the band may be ascribed to an electronic effect of coadsorbed species. This mutual effect, evidenced by the FTIR technique, can be also at the origin of the enhanced reactivity of water and CO already discussed or Au/TiO_2 samples [16,22].
- On the atomically dispersed copper present on the reduced catalyst, bicarbonylic species are formed by interaction with high CO pressures, while by decreasing the pressure, monocarbonylic species are observed.
- The silver catalyst is almost completely inactive because the metallic silver is completely unable to adsorb and activate CO molecules already at 90 K and therefore no reaction with coadsorbed water can occur.

References

[1] G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 4, 1997, p. 1831.
[2] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, R. Giovanoli, Appl. Catal. A 134 (1996) 275;
D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, R. Giovanoli, Bulg. Chem. Comm. 30 (1998) 64.
[3] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, J. Catal. 188 (1999) 176.
[4] A. Baiker, M. Kilo, M. Maciejewski, S. Menzi, A. Wakaun, in: L. Guczi, et al. (Eds.), New Frontiers in Catalysis, Elsevier, Amsterdam, 1993, pp. 1257–1272.
[5] N. Kotsev, D. Shopov, J. Catal. 22 (1971) 297.
[6] R.A. Koeppel, A. Baiker, Appl. Catal. A 84 (1992) 77.
[7] F. Boccuzzi, A. Chiorino, G. Martra, M. Gargano, N. Ravasio, B. Carrozzini, J. Catal. 165 (1997) 129.
[8] L.J. Kundakoovic, M. Flyzani-Stephanopoulos, Appl. Catal. A 183 (1999) 35.
[9] G. Cerrato, L. Marchese, C. Morterra, Appl. Surf. Sci. 70–71 (1993) 200.
[10] G. Martra, Appl. Catal. A 200 (2000) 275.
[11] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal. 202 (2001) 256.
[12] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. 100 (1996) 3625;

G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319 and references therein.

[13] P. Dumas, R.G. Tobin, P.L. Richards, Surf. Sci. 171 (1986) 555.

[14] B. Liang, L. Andrews, J. Phys. Chem. A 104 (2000) 9156 and references therein.

[15] K. Hadjiivanov, E. Vassileva, M. Kantcheva, D. Klissuski, Mater. Chem. Phys. 28 (1991) 367.

[16] M.S. Liao, Q. Er Zhang, J.C.S. Faraday Trans. 94 (1998) 1301.

[17] D. Scarano, S. Bordiga, C. Lamberti, G. Spoto, G. Ricchiardi, A. Zecchina, C. Otero Areàn, Surf. Sci. 411 (1998) 272.

[18] K.P. de Jong, J.W. Geus, J. Joziasse, Appl. Surf. Sci. 6 (1980) 273.

[19] J.W. He, W.K. Kuhn, L.W.H. Leung, D.W. Goodman, J. Chem. Phys. 93 (1990) 7463.

[20] M. Moskovits, J.E. Hulse, Surf. Sci. 61 (1976) 302.

[21] F. Colonna, F. Marquez, C.H. Rochester, J.A. Anderson, PCCP 2 (2000) 5320.

[22] F. Boccuzzi, A. Chiorino, J. Phys. Chem. B 104 (2000) 5414.