Oxygen induced direct hydrogenation of CO on Ni(100) surface

Hong He and Ken-ichi Tanaka

The Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

Received 20 July 1993; accepted 27 November 1993

A trace amount of oxygen in H_2 promotes a new type of direct hydrogenation reaction of adsorbed CO on Ni(100) surface. The formation of H_xCO_y was suggested by high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). HREEL spectra showed the formation of surface hydroxyl (OH) and the C–H bonds of H_xCO_y species but no carbonyl (C=O) loss peak was detected although thermal desorption yielded large amount of CO. The H_xCO_y undergoes the decomposition at 400–450 K on the hex-OH Ni(100) surface, which yielded CO, CO_2, H_2 and H_2CO. It was confirmed that no C–H bond formation occurs on c(2 × 2)-O, p(2 × 2)-O Ni(100) and hex-OH Ni(100) as well as on clean Ni(100) surfaces. This fact indicates that the gas phase oxygen may induce the direct hydrogenation of CO to form H_xCO_y, which is analogous to the hydrogenation of O to form hex-OH on Ni(100).

Keywords: Hydrogenation of CO; direct hydrogenation of CO; intermediates of CO hydrogenation; Ni(100)

1. Introduction

Coadsorption of CO and H_2 on low index nickel surfaces has been studied to get insight into the mechanism of the catalytic methanation reaction and Fischer–Tropsch synthesis [1–3]. It has been shown that the presence of gas phase hydrogen induces the low temperature displacement of chemisorbed CO on Ni(100) surface by the adsorption of hydrogen [3–5]. However, so far the formation of C–H and/or O–H bonds by the reaction of CO with hydrogen has never been proven on a nickel surface, and the methanation reaction on nickel has been explained by the hydrogenation of carbidic carbon intermediates.

On the other hand, direct hydrogenation of CO molecules has been proposed on some catalysts, and the Rh catalyst supported on SiO_2 is a typical example [6]. In this case, the catalytic properties of the Rh catalyst are undoubtedly influenced by the supporting oxides, that is some oxides seem to promote the hydrogenation of CO to yield oxygen containing products such as alcohols and aldehydes. If direct

hydrogenation of CO occurs, such intermediate species as H_xCO_y should be formed on the surface during the catalytic hydrogenation of CO or CO_2 with H_2. In fact, HCOO was found on a Co/SiO_2 surface at 490 K during the hydrogenation reaction of CO_2 with H_2 [7,8]. The formation of HCOO was also reported on a Rh(100) surface [9], where the reaction between OH and CO was proposed as a key reaction to yield HCOO. An interesting fact is that the OH species on the Rh(100) surface were preferentially formed by the reaction of O with H_2O, and the reaction of O and H gave no OH species. In addition, an inverse isotope effect of rate constant ($k_H/k_D = 0.75$) observed in the methane formation on Ni/SiO_2 catalyst was explained by prehydrogenation of CO molecules [10].

In contrast to this, the reaction of CO with H_2 on nickel catalysts gives only methane and so far the formation of such species as H_2CO, HCO or COH have never been detected on the nickel surface. Taking these facts into account, it is interesting that the thermal desorption spectrum of methanol yielded only H_2 and CO on either clean or modified Ni(110) [11–13], but partial dehydrogenation of methanol occurs on Ni(100) modified with sulfur. That is, the selectivity was changed with sulfur coverage; the dehydrogenation to CO and H_2 at $\theta_s < 0.25$ to the partial dehydrogenation giving H_2CO and H_2 at $\theta_s = 0.38$ [14]. This selectivity change was explained by the stabilisation of the adsorbed methoxy intermediates on the sulfided Ni(100) surface.

In this paper, we report evidence for the direct hydrogenation of CO on the Ni(100) surface which was observed by HREELS during the hydrogenation of CO in the presence of a trace amount of O_2.

2. Experimental

All experiments were performed by using a two-tiered stainless steel UHV chamber with base pressure $< 5.0 \times 10^{-10}$ Torr, which was previously described [15]. A clean Ni(100) surface was obtained by repeating oxidation in 10^{-8} Torr O_2 at 800 K and argon-ion bombardment at room temperature, and annealing at 1000 K. H_2 and D_2 were purified by diffusing through a hot Pd–Ag alloy thimble, but the other gases from commercial cylinders or glass ampules (CO: 99.95%, O_2: 99.99%) were used without further purification. Hydrogenation of the adsorbed CO on clean Ni(100) surface was performed by using hydrogen containing a trace of O_2; $H_2 + O_2$ ($\sim 1 : 10^{-5}$) or $D_2 + O_2$ ($\sim 1 : 10^{-5}$). Electron energy loss spectra were obtained at room temperature in the off-specular direction. The incident beam energy was fixed at 5 eV, and the resolution was 110–130 cm^{-1} before reaction and 140–200 cm^{-1} after reaction.

3. Results and discussion

When a clean surface of Ni(100) was predosed with 0.2 Torr CO and postdosed

with 1.0 Torr H_2 containing 10 ppm of O_2 for 5 min at room temperature, a characteristic HREEL spectrum such as shown in fig. 1a was obtained. Energy loss peaks appeared at 3670 cm^{-1} (O–H stretching mode) and at 2700–3100 cm^{-1} (C–H stretching mode), but no distinctive peaks corresponding to adsorbed CO (1900–2050 cm^{-1}) were observed. Phonon peaks originating from the Ni–O lattice smear the low frequency range loss peaks. When the surface for spectrum a in fig. 1 was heated, the dominant peak at 3670 cm^{-1} disappeared at 550–600 K and the peaks for the C–H stretching mode disappeared at 440–490 K as shown in figs. 1b–1f. It should be pointed out that the surface corresponding to the spectrum a in fig. 1 gave necessarily the characteristic hexagonal LEED pattern. Similar LEED pattern was also observed on Ni(100) after being exposed to $O_2 + H_2$ as well as O_2 alone. By time resolved experiments combining the AES, LEED and HREELS, it was deduced that O(a) and OH(a) overlayers were sequentially formed on Ni(100) surface in the order of p(2 × 2), c(2 × 2), and hex [16,17].

The TDS spectrum from the surface corresponding to fig. 1a is shown in fig. 2. Five different masses (m/e = 2, 18, 28, 30, 44) were monitored, which may correspond to H_2, H_2O, CO, H_2CO and CO_2. As was mentioned above, the energy loss peaks for adsorbed CO are undoubtedly very weak in fig. 1a, but the TDS spectra

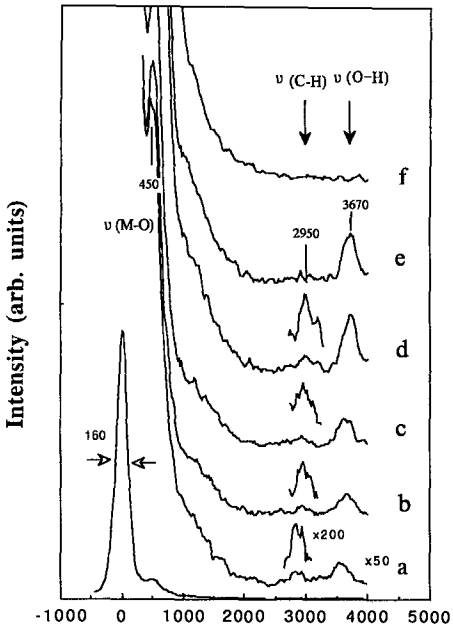


Fig. 1. (a) HREEL spectra from Ni(100) after predosing with 0.2 Torr CO and postdosing with $H_2 + O_2$ ($1 : 10^{-5}$) 1.0 Torr at 300 K for 5 min. Annealing sample (a) to (b) 330 K, (c) 360 K, (d) 420 K, (e) 450 K, (f) 550 K. In all cases the crystal was cooled to 300 K for recording the spectra.

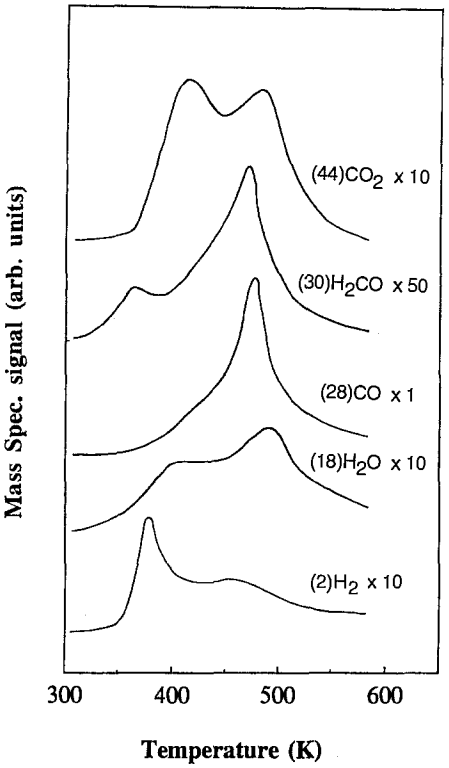


Fig. 2. Thermal desorption spectra from fig. 1a. The heating rate was 10 K s^{-1}.

gave a dominant desorption peak of CO at 480 K. The desorption peak of CO is close to the disappearance temperature for the C–H species (450 K) as shown in figs. 1b–1f. This fact indicates that the CO molecules desorbed at 450 K may originate from such species as H_xCO_y, and they contain no C=O bond or the C=O is parallel to the surface [7,18–20]. The TDS up to 550 K induced the LEED pattern change from the hexagonal to a c(2 × 2) pattern. Taking account of the facts that the reaction of C(a) + O(a) → CO(g) on Ni(100) occurs at around 600 K and that the CO molecules adsorbed on the c(2 × 2)-O Ni(100) desorb at room temperature [21], we can conclude that the CO peak in the TDS spectrum at about 480 K originated from neither the desorption of adsorbed CO nor the oxidation of carbon.

The disproportionation reaction of CO, CO(a) + CO(g) → C(a) + CO_2(g), was reported to occur on the p(2 × 2)-O Ni(100) surface at 300 K [21], but we did not detect any carbon deposition on either the p(2 × 2)-O or c(2 × 2)-O Ni(100) surface. It is worthy of note that H_2CO ($m/e = 30$) and CO ($m/e = 28$) give the same desorption temperature (470–480 K) as shown in fig. 2, although the peak for the H_2CO is very small compared to the desorption peak of CO [22].

The blank experiments were carefully performed by exposing the Ni(100) to 0.3 Torr of CO and then treating with 2 Torr of H_2 (or D_2) containing no O_2. The

peaks for the adsorbed CO were detected by HREELS, but no C–H and C–D peaks were visible at all. When a clean Ni(100) was exposed to O_2 alone, a weak O–H stretching loss peak was detected but no C–H and C–D peaks appeared. In order to confirm the assignment for the peaks again, D_2 was used for H_2. It should be pointed out that the Ni(100) used in the experiments was pretreated with D_2 at 800 K, because a lot of H atoms absorbed in the bulk should be replaced with D atoms. As shown in fig. 3, when Ni(100) was exposed to 0.3 Torr of CO, the strong peaks for the adsorbed CO were detected (fig. 3a). Upon dosing of 2 Torr of H_2, the C–O stretching loss peak decreases significantly, but not any new surface species were formed on Ni(100) (fig. 3b). When the Ni(100) was exposed to 0.3 Torr of CO and then treated with 1.7 Torr of D_2 containing 10 ppm O_2 for 5 min, the energy loss peak for the OD stretching mode was observed at 2660 cm^{-1} and that for the C–D stretching mode at 2150 cm^{-1}. This fact indicates that the loss peaks for the C–H and C–D did not originate from organic contaminants in the gases used. The TDS spectra of the sample represented in fig. 3c is shown in fig. 4. If we compare the spectra in fig. 4 to those in fig. 2, we can recognise rather large isotopic effects in the desorption of D_2 and D_2O, although the desorption of D_2CO and CO has only a small isotopic effect and there is no isotopic effect in the desorption of CO_2. The surface after the TDS experiment gave also a c(2 × 2) LEED pattern. From these results, we deduced that the chemical processes yielding OH or OD and H_xCO_y or D_xCO_y species occur on the Ni(100) surface only when a trace amount of oxygen (~ 10 ppm) exists in H_2.

In our previous paper, it was shown that when a Ni(100) surface was exposed

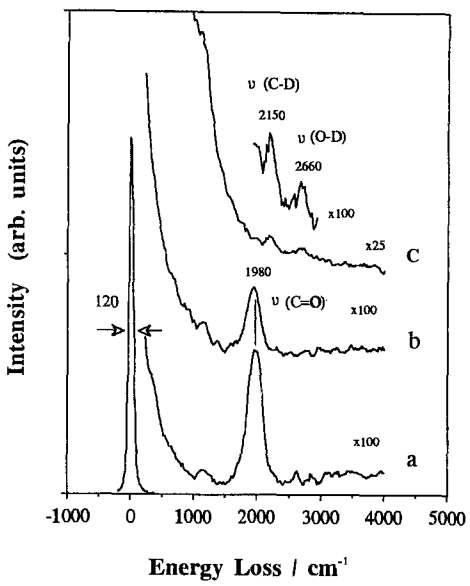


Fig. 3. HREEL spectra from Ni(100) surface (a) after dosing 0.3 Torr CO at 300 K for 5 min, (b) after exposure of (a) to 2 Torr H_2 at 300 K for 5 min and (c) after predosing with 0.3 Torr CO and postdosing with $D_2 + O_2(1 : 10^{-5})$ 1.7 Torr at 300 K for 5 min.

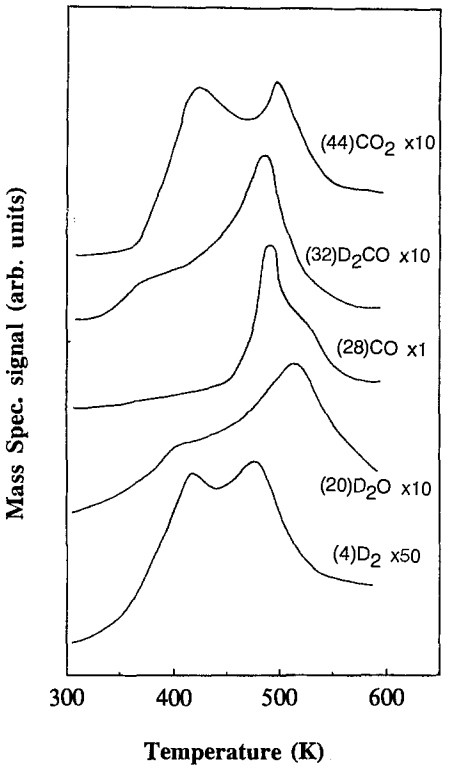


Fig. 4. Temperature desorption spectra from fig. 3. The heating rate was 10 K s^{-1}.

to D_2 containing a trace amount of O_2, a characteristic hexagonal OH-overlayer instead of the OD is predominantly grown on the Ni(100) surface [16,17]. That is, the hydrogen absorbed in the bulk of Ni, which might be protonic hydrogen, undergoes selective reaction with oxygen to yield OH species, and formation of H_xCO_y might be reaction analogous to the formation of OH.

The thermal stability of H_xCO_y species formed on Ni(100) is apparently different from that of the CH_x species given by the hydrogenation of carbidic carbon on Ni(100) surface [23]. The thermal decomposition of the CH_x and that of the H_xCO_y species are shown in fig. 5, where the H_xCO_y species undergo decomposition at 450–500 K on the hex-OH/Ni(100) surface, but CH_x on p4g-carbidic Ni(100) undergoes decomposition at about 370 K.

Contrary to this, the H_xCO_y species formed on Ni(110) by adsorption of CH_3OH are unstable at above room temperature so that the methoxy group is detectable only at low temperature and no other intermediates such as H_2CO, HCO, HCOO or COH are detected even at low temperature [9,11–13,24]. In fact, H_2CO on Ni(110) decomposes at 300 K [22]. The adsorbed formic acid on Ni(110) may be only one exceptional case [25], that is, the formic acid undergoes bimolecular dehydration reaction on Ni(110) to form HCOO and HCO at 310 K, and the

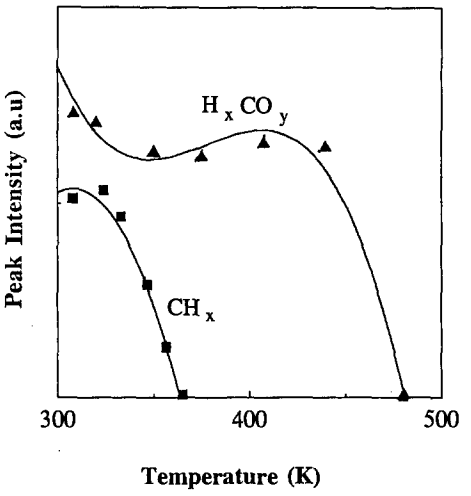
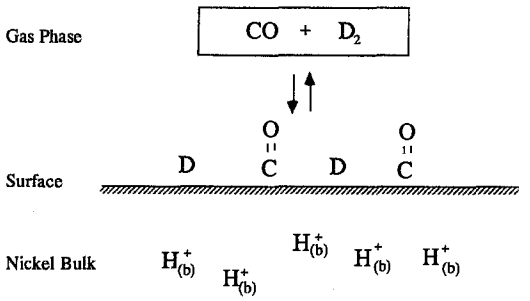


Fig. 5. Contrast in intensity of C–H stretching for (a) CH_x on carbided Ni(100) and (b) H_xCO_y on Ni(100) hex-OH as sample is annealed (10 K s^{-1}) in UHV.

HCO and/or HCOO gives a large CO desorption peak at around 400 K. However, the methoxy (CH_3O) intermediates on the sulphided Ni(100) surface undergo dehydrogenation to yield H_2CO [14], and the desorption temperature of H_2CO increases from 430 to 520 K with increasing sulfur coverage on Ni(100). In our experiments, the H_xCO_y species might be stabilized by the hexagonal OH overlayer, and the mechanism for the formation of H_xCO_y species is an interesting subject which should be addressed.

It is accepted that adsorbed CO on nickel does not react with hydrogen, and the same is true on p(2 × 2)-O Ni(100). When a clean Ni(100) surface is exposed to H_2 containing 10 ppm of O_2, and then CO was postdosed to it, the hex-OH overlayer was formed on the Ni(100) surface, but no detectable C–H vibration was formed. It is also confirmed that when the hex-OH Ni(100) surface is exposed to CO, no reaction occurs at room temperature. It was also confirmed that when a trace amount of O_2 was premixed in CO, the direct hydrogenation of CO occurred on the Ni(100). It should be pointed out that the results shown in fig. 3 were obtained on Ni(100) pretreated with D_2 at high temperature. When the H atoms in the Ni bulk were not replaced with D atoms, neither D_xCO_y (a) nor OD (a) were appreciably formed although the surface was exposed to $D_2 + CO + O_2$. This is very similar to the formation of the OH overlayer when Ni(100) containing H atoms in the bulk is exposed to D_2 with a trace amount of O_2, that is, H in the bulk of Ni is more liable to form OH(a) than gas-phase D_2 [16,17]. Therefore, we suppose that H(b), H atoms absorbed in the bulk, are abstracted by the adsorbed oxygen, and these bulk hydrogens undergo the reaction with O(a) and CO(a) to yield OH(a) and H_xCO_y species. These phenomena suggest that the adsorbed H atoms from H_2, H(a), are distinctive from the hydrogen extracted from the bulk, H(b). That is, H(b) under-



Scheme 1.

goes selective hydrogenation of O and/or CO. The differences of $CO + D_2$ and $CO + D_2 + O_2$ are shown in schemes 1 and 2, respectively.

The reactions in scheme 2 may be expressed as follows:

$$H_2 \text{ or } D_2 \rightleftharpoons H(a) \text{ or } D(a)$$

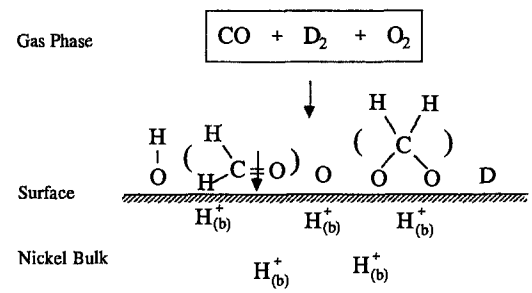
$$O_2 \rightarrow O(a)$$

$$O(a) + H(b) \text{ or } D(b) \rightarrow OH(a) \text{ or } OD(a)$$

$$CO(a) + H(b) \text{ or } D(b) \rightarrow H_xCO_y(a) \text{ or } D_xCO_y(a).$$

These facts are quite interesting to relate to the phenomena observed on some metal oxides and oxide-supported metals [26–28].

As we can see in figs. 2 and 4, the desorption of CO_2 gives two peaks between 400 and 520 K. The CO_2 peak at 410 K may be formed by the decomposition of HCOO(a) but the CO_2 peak at 490–520 K is probably produced by the oxidative decomposition of H_xCO. Therefore, the possibility of the water–gas shift reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$, which occurs via the HCOO intermediates, should be confirmed [29]. In order to know whether the CO_2 peak at 410 K corresponds to the



Scheme 2.

water–gas shift reaction or not, the p(2 × 2)-O or the C(2 × 2)-O of Ni(100) surface was exposed to CO and H_2O at 300 K, but neither OH(a) nor the C–H species were detected on the surface.

Therefore, we conclude that a trace amount of O_2 in CO + H_2 gas extracts the ionic hydrogen dissolved in the bulk to the surface, and the ionic hydrogen undergoes preferential reaction with O and CO to yield the hexagonal OH overlayer and H_xCO_y species on the Ni(100) surface. The H_xCO_y species are stabilized by the hex-OH overlayer, so that they have a rather high decomposition temperature. This fact suggests that the formation of oxygen containing compounds by the hydrogenation of CO depends on the ionic character of the hydrogen which is supplied onto the catalyst surface.

References

[1] R. Zenobi, J. Xu and T. Yates Jr., Surf. Sci. 276 (1992) 241.
[2] L. Westerlund, L. Jönsson and S. Andersson, Surf. Sci. 199 (1988) 109.
[3] G. Rangelov, U. Bischler, N. Memmel, E. Bertel, V. Dose, M. Pabst and N. Rösch, Surf. Sci. 273 (1992) 61.
[4] S. Shen, F. Zeara, D.A. Fischer and J.L. Gland, J. Chem. Phys. 89 (1) (1988).
[5] J.L. Gland, S. Shen, F. Zeara and D.A. Fischer, J. Vac. Sci. Technol. A 6 (4) (1988).
[6] A. Takeuchi and J.R. Katzer, J. Phys. Chem. 85 (1981) 937.
[7] A. Deluzarche, J.P. Hindermann, R. Kieffer, A. Kiennemann, Rev. Chem. Inter. 6 (1985) 255.
[8] T. Matsuzaki, K. Takeuchi and H. Arakawa, Shokubai (Catalyst) 32 (1990) 2, 71.
[9] B.A. Gurney and W. Ho, J. Chem. Phys. 87 (2) (1987) 15.
[10] T. Morl, H. Masuda, H. Imai, A. Miyamoto, S. Baba and Y. Murkami, J. Phys. Chem. 86 (1982) 2753.
[11] S.R. Bare, J.A. Stroscio and W. Ho, Surf. Sci. 150 (1985) 399.
[12] J.J. Vajo, J.H. Campbell and C.H. Becker, J. Phys. Chem. 95 (1991) 9457.
[13] S.R. Bare, J.A. Stroscio and W. Ho, Surf. Sci. 155 (1985) L281.
[14] R.J. Madix, S.B. Lee and M. Thornburg, J. Vac. Sci. Technol. A 1 (1983) 1254.
[15] T. Yamada, K. Tanaka and Y. Murata, J. Vac. Sci. Technol. A 7 (1989) 2808.
[16] T. Yamada, J. Nakamura, S. Kawamura and K. Tanaka, J. Electron Spectry. Rel. Phenom. 44 (1987) 79.
[17] T. Yamada, J. Nakamura, I. Matsuo, I. Toyoshima and K. Tanaka, Surf. Sci. 207 (1989) 323.
[18] B.A. Sexton, A.E. Hughes and N.R. Avery, Surf. Sci. 155 (1985) 366.
[19] E.M. Stuve, R.J. Madix and B.A. Sexton, Surf. Sci. 119 (1982) 279.
[20] J.B. Benziger and G.R. Schoofs, J. Phys. Chem. 88 (1984) 4439.
[21] S. Andersson, Solid State Commun. 24 (1977) 183.
[22] L.J. Richter and W. Ho, J. Chem. Phys. 83 (5) (1985) 2165.
[23] H. He, J. Nakamura and K. Tanaka, Surf. Sci. 283 (1993) 117.
[24] T.S. Jones, M.R. Ashton and N.V. Richardson, J. Chem. Phys. 90 (12) (1989) 15, 7564.
[25] R.J. Madix, J.L. Gland and G.E. Mitchell, Surf. Sci. 125 (1983) 481.
[26] P.R. Watson and G.A. Somorjai, J. Catal. 72 (1981) 347.
[27] M. Ichikawa, CHEMTECH 12 (1982) 674.
[28] J.M. Driessen, E.K. Poels, J.P. Hindermann and V. Ponec, J. Catal. 82 (1982) 26.
[29] T.H. Ellis, E.J. Kruus and H. Wang, Surf. Sci. 273 (1992) 73.