

Surface Science 350 (1996) 113-122



Highly sintered nickel oxide: surface morphology and FTIR investigation of CO adsorbed at low temperature

Estrella Escalona Platero^a, Domenica Scarano^b, Adriano Zecchina^{b,*}, Giancarlo Meneghini^c, Roberto De Franceschi^c

^a Departamento de Química, Universidad de las Islas Baleares, 07071 Palma de Mallorca, Spain
^b Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Via Pietro Giuria 7, 10125 Torino, Italy
^c CSELT, Centro Studi e Laboratorio Telecomunicazioni, Via Reiss Romoli 274, 10148 Torino, Italy

Received 3 August 1995; accepted for publication 17 November 1995

Abstract

The monolayer of CO molecules adsorbed at low temperature on highly sintered nickel oxide, gives rise to a very symmetric IR absorption band at 2136 cm⁻¹ (θ_{max}) with a full-width at half-maximum (FWHM) of 3.7 cm⁻¹. This band shifts to higher frequency upon decreasing the coverage, reaching the 2152 cm⁻¹ value for $\theta \rightarrow 0$. The observed shift is due to changes in the lateral interactions (dynamic and static) among the adsorbed molecules. The observed spectral simplicity implies that most of the adsorbed CO molecules occupy crystallographically identical sites with a similar environment. Moreover, the remarkably small half-width indicates that inhomogeneous broadening effects, due to surface defects, are very small and that NiO microcrystals behave as single crystals. The morphology of microcrystals has been studied by SEM, AFM and HRTEM techniques: it was concluded that the surface termination of the sample is mainly represented by the (100) and (111) faces.

Keywords: Atomic force microscopy; Carbon monoxide; Chemisorption; Electron microscopy; Infrared absorption spectroscopy; Nickel oxides; Surface structure; Vibrations of adsorbed molecules

1. Introduction

The polycrystalline materials used in heterogeneous catalysis consist of random oriented particles showing several crystallographic faces on which the catalytic processes take place. Chemisorption is the first step in the catalytic process and the understanding of this step is fundamental to elucidate the corresponding reaction mechanisms. To this end, chemisorption of probe molecules is a very important technique of catalysts characterization and, in this context, vibrational spectroscopy is a powerful tool for the study of and species adsorbed on them. surfaces Polycrystalline materials are normally very heterogeneous and the corresponding vibrational spectra of adsorbed molecules are complex and difficult to interpret. The problem can be simplified if well defined homogeneous surfaces, such as those of selected single crystal faces, can be studied. Alternatively, highly sintered polycrystalline materials can be also appropriate, when single crystals are not available.

In line with the above paragraph, ten years ago we began to study the surface properties of polycrystalline nickel oxide progressively sintered. To

^{*} Corresponding author. Fax: 39 11 6707855.

^{0039-6028/96/\$15.00 © 1996} Elsevier Science B.V. All rights reserved PII 0039-6028(95)01076-9

this scope, we basically employed infrared spectroscopy of adsorbed probe molecules (CO, NO, O_2), by using a dispersive Perkin Elmer 580B spectrometer at a resolution of 5 cm⁻¹, equipped with a data station. Moreover, NiO characterization was completed by means of transmission electron microscopy, UV-vis spectroscopy and adsorption calorimetry [1–8].

In order to obtain microcrystals with increasing dimensions and perfection and decreasing surface area and defects concentration, nickel oxide was calcined at increasing temperature. Infrared spectroscopy of adsorbed probe molecules allowed us to follow the surface changes occurring as a function of temperature treatment. After the first step of thermal treatment the infrared spectra of adsorbed CO and NO, used as probe molecules, showed several bands in the 2150-2000 cm⁻¹ and in the 1900–1700 cm^{-1} intervals, in general very broad, due to both reversible and irreversible adsorbed carbonvlic and nitrosylic species [1,2,4,5]. These spectra were found to become simpler and simpler by increasing the calcination temperature. We obtained the most simplified spectra by heating the nickel oxide sample in O_2 atmosphere (50 Torr) at 1073 K for several hours (in order to favour the sintering process). In this case, the IR spectrum of adsorbed CO at low temperature gave only one prominent band at 2136 cm^{-1} with a full-width at half-maximum (FWHM) of 9 cm⁻¹ and two minor components at higher and lower frequency respectively [4]. In view of the evolution observed before, we thought that these shoulders could be eliminated only by using more drastic sintering procedure. However, such process produced a material scarcely transparent to IR radiation and so we were not able to study it with the spectrometer available at that time. According to these results, and on the basis of gravimetric measurements, the main band at 2136 cm⁻¹ was assigned to CO molecules linearly adsorbed through the carbon atom onto half of the Ni²⁺ ions emerging on the cubic faces of the NiO crystals; the minor components were assigned to CO adsorbed on defects still present in low proportion at the surface of NiO [4]. Recently, King et al. [9] have studied the IR spectra of CO adsorbed on NiO thin films grown

on (110) Ni single crystals: the observed band is very similar to that described here and was similarly assigned to CO adsorbed on Ni^{2+} ions.

In spite of the residual surface inhomogeneity still present on the most sintered NiO sample, the 2136 cm⁻¹ band was observed to shift gradually with CO coverage as a consequence of progressive building up of lateral interactions among the adsorbed molecules [10-15]. This behaviour, typical of adlayers adsorbed on extended flat surfaces, was considered as a proof that the solid was exposing a high fraction of extended and regular faces. The shift of the peak upon coverage changes is well known on metal single crystals, but less studied on metal oxides. Using the method of the diluted isotopic mixture [16], we were able to evaluate the dynamic and the static contributions to the total adsorbate-adsorbate interaction [3-5].

As some of the problems arising from scarcely IR transparent samples can be overcome nowadays by using FTIR instruments, we decided to repeat the study of the CO adsorption on a NiO sample even more sintered. In this article we show the FTIR spectra of CO adsorbed at low temperature on highly sintered nickel oxide. SEM, AFM and HRTEM micrographs are also shown to illustrate the morphology of the sample. The main aim of this paper is to show that spectra of high quality can be obtained even on a polycrystalline material when it has been sintered in the appropriate way. In fact, the FTIR spectra showed in this paper are closer to those expected for single crystals surfaces than to those typical of polycrystalline materials.

2. Experimental procedure

Nickel hydroxide was used as a precursor of nickel oxide. $Ni(OH)_2$ was prepared by adding a nickel nitrate solution onto diluted ammonium hydroxide (Aldrich, analytical grade reagents). The gel thus obtained was thoroughly washed, and airdried in a furnace at 400 K for 24 h. In order to obtain highly sintered and stoichiometric nickel oxide, we proceeded as follows:

Nickel hydroxide, in the form of a self-supported pellet, was dehydrated at 525 K for 15 h and

subsequently calcined at 1175 K for a further 15 h. These thermal treatments were carried out in an electric furnace, the sample being exposed to the atmosphere. Then the nickel oxide pellet was placed inside a suitable cell for IR measurements (similar to that described by Marchese et al. [17]) which allowed in situ activation and gas dosification. For activation the sample was heated for 30 min at 775 K under a dynamic vacuum (final residual pressure $\sim 10^{-5}$ Torr). In order to obtain a stoichiometric sample, the nickel oxide was heated in O_2 (30 Torr) for 2 h at 975 K. The sample was then cooled in the oxygen atmosphere and after it had reached 575 K it was outgassed for 2 h at the same temperature under vacuo. After this thermal treatment the sample is pale green, implying a high degree of stoichiometry, (in fact, a small proportion of Ni^{3+} or Ni^{0} makes the sample dark).

Infrared spectra were recorded in situ in transmission mode at 2 cm^{-1} resolution using a Bruker IFS 48 spectrometer equipped with a cryogenic detector. All of the spectra shown were taken with the cell cooled with liquid nitrogen. High purity CO and O₂ were from Matheson.

The surface characterization, both morphological and microstructural, was carried out by using different techniques:

(i) Secondary electron images (SEM) were obtained on a Jeol JSM 6301 F field emission scanning electron microscope, operating at low accelerating voltage (5 kV) with resolutions ranging from 1.5 to 2 nm.

(ii) Atomic force microscopy (AFM) images were obtained on a Park Scientific Instruments AutoProbe LS, equipped with a high aspect ratio Silicon conical tip and operating in the constant force mode, with a scanning frequency of 1 Hz. The resolution obtained was in the range of 1.5–3 nm. All measurements were performed in air at room temperature.

(iii) High resolution transmission (HRTEM) images were obtained on a Jeol JEM 2000 EX electron microscope equipped with a top entry stage.

3. Results and discussion

3.1. Electron microscopy data

3.1.1. SEM images

From a set of SEM micrographs, like those reported in Figs. 1a and 1b, an overall view of a complex NiO agglomerate with dimensions ranging from 2000 to 5000 Å can be directly observed. In more detail these structures are constituted by many cubic or prismatic microcrystals which, being grown along a few preferential directions, expose the more stable faces so minimizing the surface energy. It is very interesting to notice that, besides the most thermodynamically stable and neutral (100) square faces, also largely predominant on NiO sintered in vacuo [4], (111) triangular surfaces are developed as well, when NiO is sintered in a free atmosphere (Figs. 1a and 1b). These triangular surfaces, developing with variable extension and at different levels on the image (as it results from the thickness contours on Fig. 1b) are (111) faces, which although polar and therefore unstable, are stabilized by either the presence of adsorbates or by reconstruction and/or relaxation phenomena (which are reducing the surface potential). Recently Cappus et al. [18] have pointed out that the presence of OH groups leads to a reduction of the surface charge, while Langell and Nassir in a more recent paper have experimentally found that hydroxylation is the most powerful agent for stabilization of (111) faces [19]. This hypothesis is the correct one and it will be confirmed in the following by means of IR results.

3.1.2. AFM images

From AFM micrographs a direct imaging of the surface morphology was also obtained (Fig. 1c). On this figure a large flat area is selected, where an extended planar (100) surface of the order of $(1730 \times 1730 \text{ Å}^2)$ is observed to intersect a smaller triangular (111) face having an extension of the order of $(800 \times 800 \text{ Å}^2)$. On this latter face a few triangular terraces are observed, very similar to those illustrated in Fig. 1b. The height of these triangular terraces was evaluated to be of the order of 100 Å, as it results from the direction drawn in the figure.



Fig. 1. (a), (b) Secondary electron microscopy (SEM) images of highly sintered NiO crystallites. (c) Atomic force microscopy (AFM) three dimensional image obtained by selecting an extended flat surface of NiO single microcrystal, where the (100) and (111) faces are also shown. Along the direction drawn in the figure (with a doted line) the height profile was evaluated as ~ 100 Å. (d) High resolution electron transmission image (HRTEM) of highly sintered NiO microcrystals. In the inset: diffraction pattern corresponding to the selected area in the figure.

Although these results are quite comparable with those obtained from SEM observations, the relevance of AFM analysis is due to the fact that it adds further evidences about the flat character of the exposed faces and shows its applicability to powdered samples which, as far as we know, are not numerous and certainly absent for polycrystalline NiO.

3.1.3. HRTEM images

From the high resolution transmission images, like that shown in Fig. 1d, it comes out that the individual crystallites (with cubic habit) have dimensions prevalently in the range of 500-2000 Å(as already seen from SEM). As these crystals are too thick to give interference fringes, we have performed diffraction patterns on selected areas (see inset in figure). From this analysis it was concluded that the most frequent observed orientations are the [100] and [111] ones and therefore the corresponding (100) and (111) planes are the most largely exposed.

3.2. FT-IR data

3.2.1. The IR spectra of CO adsorbed on (100) faces

Fig. 2 shows the FTIR spectra of decreasing amounts of ¹²CO (¹²CO: ¹³CO; 99:1) at low temperature on the highly sintered nickel oxide obtained following the procedure illustrated before. The most intense spectrum exhibits a very symmetric band at 2136 cm⁻¹ with FWHM = 3.7 cm⁻¹. The presence of such a narrow, single band at high coverage (θ_{max}), when half of the Ni²⁺ ions are saturated with coordinated CO molecules, implies that adsorbed molecules occupy crystallographically identical sites of a single face and have similar environment. This spectrum is not very common on polycrystalline materials, because the inherent



Fig. 2. FTIR spectra of decreasing amounts of CO (at low temperature) on highly sintered nickel oxide. The inset shows the OH stretching frequency region of the NiO sample after evacuation at 975 K.

surface heterogeneity of these materials often gives rise to more complex spectra, with several bands and larger FWHM [2] (inhomogeneous broadening effect); for this reason the spectra in Fig. 2 are more similar to those of CO adsorbed on single crystals faces [12,20-22]. As far as oxides are concerned, this spectrum can be considered as quite exceptional.

In view of the well ascertained morphology of the NiO microcrystals, where the (100) faces are predominant, and in agreement with Ref. [4], the narrow band at 2136 cm⁻¹ is assigned to CO adsorbed through the carbon end on Ni²⁺ sites at the (100) faces. The absence of a second peak implies that on (111) faces no CO adsorption is occurring because they are still covered by OH groups after evacuation at 975 K. In agreement with this hypothesis, it is noteworthy that after the thermal treatment, carried out on these highly sintered NiO, a residual O–H stretching band is still present at 3618 cm⁻¹ (see inset in Fig. 2), and it is not modified by CO adsorption at low temperature.

3.2.2. The FWHM of the 2136 cm^{-1} band

If we compare the most intense spectrum in Fig. 2 with those described in the Introduction for less sintered nickel oxide samples (Fig. 3), we can fully appreciate the value of the progressive sintering procedure in gradually simplifying the spectroscopic manifestations of adsorbed CO. In fact, we can easily see that, as the morphology of crystallites becomes closer to that of perfect cubes, all the components around the 2136 cm^{-1} band disappear, and more important that the FWHM of the single 2136 cm^{-1} band has considerably decreased (from 25 (spectrum 3) to 9 (spectrum 4) to 3.7 cm^{-1} (spectrum 5)). These differences are primarily due to the larger and larger surface homogeneity of the progressively sintered NiO and (to a smaller extent) to the higher resolution (2 cm⁻¹) obtained with the FTIR spectrometer (spectrum 5).

It is known that the FWHM of an IR absorption depends primarily on the surface homogeneity, and to a smaller extent on the interaction energy between the adsorbent and the adsorbate [21,22]. For instance, as thoroughly reported in Ref. [22],



Fig. 3. FTIR spectra of CO adsorbed at low temperature and at maximum coverage on progressively sintered nickel oxide. Spectra 1-4: adapted from Ref. [6].

CO adsorbed on single crystal Cu faces has a FWHM ≈ 13 cm⁻¹, while CO adsorbed on polycrystalline Cu films has a FWHM ≈ 17 cm⁻¹. The same holds for CO adsorbed on single crystal faces of Pt as compared with CO on supported platinum [22]. As far as the second effect is concerned, it is known that the FWHM increases with increasing interaction energy because the lifetime of vibrationally excited molecules is smaller. This explains why the FWHM of the corresponding band of CO adsorbed onto metal single crystals is 10-30 cm^{-1} [12,13], when obtained with dispersive spectrometers, and becomes 4-6 cm⁻¹ using FT-RAIRS [22-24]. It was reported that the increased resolution (up to 0.5 cm^{-1}) does not give rise to sharper bands, so apparently showing that the $4-6 \text{ cm}^{-1}$ figure represents the intrinsic halfwidth of the $v_{(CO)}$ stretching mode of CO on metals. This high half-width is in agreement with the large interaction energies evaluated for the adsorption of CO on metal single crystal faces [23-25],

characterized by strong charge transfer effects from the CO molecule to the metal surface and vice versa. Accordingly, the spectra of CO adsorbed on some sintered oxides like ZnO [26,27] and α -Cr₂O₃ [28] where the interaction is much weaker and primarily electrostatic in nature (and the contribution of charge donation is consequently less important), show the presence of unusually narrow peaks (with FWHM \approx 1.5 cm⁻¹ at ~100 K [26] and ~0.3 cm⁻¹ at 4 K, for the CO–ZnO system [27]).

However, as those oxides were in a microcrystalline form, it was difficult to estimate the relative role of the inhomogeneous broadening in determining the FWHM of the CO peak. To solve this problem, it should be interesting to know which is the FWHM of CO molecules polarized through the carbon end by a cationic site (and so experiencing only electrostatic effects) on a perfect and infinite face. In absence of extensive data on oxide single crystals, it is useful to recall that the FWHM of CO adsorbed on (100) faces of NaCl single crystals (where interaction energies are very weak, as a consequence of the purely electrostatic nature of the bond [20]) is very small. In particular the temperature dependence of the fundamental vibrational transition of CO on NaCl single crystal surfaces [20] on passing from 4 to 55 K, shows that the FWHM increases from 0.11-0.17 to 0.39 cm^{-1} . Similarly Disselkamp et al. [29] found a value of 0.07-0.09 cm⁻¹ at 4 K for the same CO-NaCl (100) system. In conclusion, the FWHM of CO adsorbed at 77 K on well defined NaCl and ZnO faces should not be larger than 1 cm^{-1} .

On the basis of previous considerations concerning the comparison of the FWHM of CO on metals on one side and ionic solids on the other side, it is reasonable to conclude that CO bonded to surface cations via chemical bonds with small $d-\pi$ contribution (as on some transition metal oxides) should be characterized by intrinsic halfwidths larger than that observed on NaCl and ZnO but lower than that observed on metals. The FWHM=3.7 cm⁻¹ found in this study is in line with this expectation. In fact, in a system like CO/NiO, although dominated by the electrostatic and sigma contributions (as found on the basis of HF calculations) [30], the contribution of $d-\pi$ overlap effect also plays a small role, in agreement with LCGTO-LDF results [31]. However, in view of the weakness of the interaction (vide infra), the relatively large value (3.7 cm^{-1}) of the FHWM of CO adsorbed on NiO, as compared to that on NaCl and ZnO (<0.5 cm⁻¹), cannot find explanation solely in the presence of very small d- π effects. We think that inhomogeneous broadening effects are still contributing according to the fact that this study is carried out on a polycrystalline material and not on a single crystal.

3.2.3. Adsorbate-adsorbate interactions on (100) faces and the shift of v_{CO} with the coverage

By lowering the CO pressure in the IR cell we observe the following modifications of the v_{CO} band (Fig. 2):

The peak shifts from 2136 $(\theta \rightarrow \theta_{max})$ to 2152 cm⁻¹ $(\theta \rightarrow 0)$.

The peak intensity decreases gradually up to the total disappearance. This implies the total reversibility of the CO adsorbed at low temperature on highly sintered nickel oxide samples.

The FWHM increases from 3.7 $(\theta \rightarrow \theta_{max})$ to 7.5 cm⁻¹ $(\theta \rightarrow 0)$.

The peak becomes slightly asymmetric, showing a tail on the low frequency side.

(1) The progressive frequency shift of the absorption band with θ is caused by modifications of two types of lateral interactions among the adsorbed molecules: *dynamic* and *static*. The *dynamic contribution* is due to the coupling among the vibrating dipoles of the adsorbed molecules; each molecule experiences an oscillatory electric field which is the sum of the incident optical field and that due to the surrounding vibrating dipoles [11]. Coupling among identical molecules, as in this case, gives rise to a single infrared-active mode (Fig. 2), having a vibrational frequency higher than that of the isolated molecule (singleton) and shifting with θ .

The static contribution to the frequency shift arises from two separate effects: through space, and through solid. The through space effect is associated with dipole-dipole interactions of static dipoles and is similar to solvent effect. The functional dependence of this effect upon coverage is similar to that found for the dynamic dipole-dipole interactions [20]. The through solid effect (which can be reasonably considered as the real "chemical" part of the total static effect) is due to the influence transmitted by the solid at a given site because of the adsorption occurring at another site. Two interconnected transmission mechanisms can be hypothesized: i.e. one associated with purely inductive effects (without substantial change in surface atoms positions), the second associated with surface relaxation effects (where surface geometry is mainly altered). The inductive effect can be defined as the effect induced at a given site by electron donation or withdrawing at another site. This effect is very common in homogeneous complexes. When no overlap forces are involved, the inductive effect is missing. The surface relaxation effect is the effect induced at a given site by structural modifications caused by adsorption at another site. To illustrate this, let us consider that in vacuo, positive and negative ions are relaxed inwards and outwards in different extent, with the anions usually remaining outer than the cations [32]. Adsorption at a given cationic site induces a small outward movement of the cation towards its "normal" bulk position, while an opposite effect is expected (to a first approximation) on the surrounding anions. The relaxation effect dies away in a few spacings (how far this influence is transmitted is not known). This through solid effect can also occur even in absence of formation of a real bond between the molecule and the cation centre [33].

The two situations illustrated so far can be considered as limit cases: in the majority of real cases the two static effects (through space and through solid) will be simultaneously operating and their separation will be consequently troublesome or impossible.

The estimation of the relative contribution of static and dynamic effects was carried out by using the (12 CO : 13 CO; 12 : 88) diluted isotopic mixture [16] and the corresponding FTIR spectra are shown in Fig. 4. each spectrum exhibits two bands shifting towards lower frequencies in different way as the coverage increases from 0 to θ_{max} . The peak due to the diluted isotope (12 CO) is not affected by dynamic effects and hence it can be used to evaluate experimentally the $\Delta v_{\text{static}} = -43 \text{ cm}^{-1}$ (no coupling with surrounding 13 CO molecules is possible because their infrared-active modes are



Fig. 4. FTIR spectra of decreasing amounts of the isotopic mixture (${}^{12}CO : {}^{13}CO/12 : 88$) at low temperature on highly sintered nickel oxide. The inset shows the ${}^{12}CO$ -peak intensity as a function of the ${}^{13}CO$ -peak intensity for the above mixture.

47 cm⁻¹ apart). The peak due to the concentrated isotope (¹³CO) is affected by both static and dynamic effects, in the same way as does the pure ¹²CO shown in Fig. 2.

The difference between Δv_{static} and Δv_{total} (obtained from the shift of the pure ¹²CO) gives the $\Delta v_{\text{dyn}} = +27 \text{ cm}^{-1}$, as reported in the scheme, where the frequencies of the ¹²CO component, at $\theta \rightarrow 0$ and $\theta \rightarrow \theta_{max}$, in the isotopic mixtures employed are also indicated.



In Fig. 4 (see also inset) we can also see that there is a characteristic transfer of intensity from the low frequency mode to the higher frequency counterpart [12]. In fact, at the highest coverage the intensity of the high frequency band associated with the diluted species is considerably greater than expected from the composition of the isotopic mixture (inset Fig. 4). This effect is observed only at high coverages, whereas at low coverages the two bands (separated by 50 cm⁻¹) have intensity ratios reflecting the isotopic composition. This clearly indicates that for $\theta \rightarrow 0$ dynamic and static effects are absent: this in turn implies that for $\theta \rightarrow 0$ admolecules show a negligible tendency to group into islands.

(2) As far as the reversible character of the CO band is concerned, the following can be commented:

(a) The weakness of CO adsorption implies a very weak interaction enthalpy in agreement with the theoretical expectations based on purely polarization forces with no or small $d-\pi$ contribution [30,31].

(b) This result is in apparent contradiction with the ascertained presence of enormously large dynamic and static contributions, which definitely differentiates NiO from the isostructural MgO [3] and, in general, cations with or without d electrons. These effects are certainly associated with $d-\pi$ interactions forces.

A way to solve this contradiction is to admit that, although the interaction is primarily electrostatic, a very small $d-\pi$ contribution is however present which while not having a great influence on the adsorption enthalpy is distinctly influencing the dynamic and static contributions. This conclusion agrees with the theoretical results of Neyman and Rösch [31] obtained with the density functional method.

(3), (4) As we have discussed in a previous paragraph, the band half-width is mainly determined by inhomogeneous broadening effects. These effects derive from inhomogeneities in the adsorbed layer and in the adsorbent solid. At full coverage the first effect is minimized and consequently the half-width is minimum. In fact, when the CO pressure is not the saturation one, the adsorbed layer becomes disordered, because different variants of the surrounding of the CO molecules are occurring and therefore molecules having different neighbours experience different dipole fields and hence have different stretching frequencies. This factor causes an increase of half-width with respect to an infinite ordered adlayer, which has only a single active mode (in which all molecules vibrate in phase). Another equivalent way to describe this effect is to say that a disordered distribution, due to non-equivalent adsorbed molecules, causes also modes associated with anti-phase vibrations to achieve small but finite intensity [15]. The presence of these modes explains the observed asymmetry (inhomogeneous broadening) and the corresponding FWHM increase of the CO band upon decrease of coverage (Fig. 2).

At $\theta \rightarrow 0$, all the CO–CO lateral interactions are absent. The observed band has no more collective character: it is simply the $v_{(CO)}$ of a single isolated oscillator (singleton). Its half-width will so entirely depend on the inhomogeneity in the adsorbing solid. As the NiO is highly ionic, the role of long range (Madelung) forces deriving from distant inhomogeneities (like surface terminations, steps, kinks, etc.) and relaxation effects will be relatively large.

4. Conclusions

The surface morphology of highly sintered NiO samples was accurately determined by means of different electron microscopy techniques: SEM, AFM and HRTEM. On the basis of the gained

knowledge on the exposed faces [(100) and (111)], we have evidentiated the effect of decreasing the defect concentration and of progressively increasing the perfection of the crystal on the IR spectra of adsorbed CO. The utility of sintered specimens, as model solids for surface vibrational studies, is testified by the remarkably small half-width ($\Delta v =$ 3.7 cm⁻¹) of the stretching band of CO adsorbed on (100) faces, as a consequence of the regularity of the exposed faces. The (111) faces do not give origin to distinct absorption peaks of adsorbed CO.

Acknowledgements

This research has been partially supported by the Spanish DGICYT: PB93-0425 and partially by CNR, Progetto Strategico Tecnologie Chimiche Innovative and MURST.

References

- E. Escalona Platero, G. Spoto and A. Zecchina, J. Chem. Soc., Faraday Trans. I 81 (1985) 1283.
- [2] E. Escalona Platero, S. Coluccia and A. Zecchina, Langmuir 1 (1985) 407.
- [3] E. Escalona Platero, D. Scarano, G. Spoto and A. Zecchina, Faraday Disc. Chem. Soc. 80 (1985) 183.
- [4] E. Escalona Platero, S. Coluccia and A. Zecchina, Surf. Sci. 171 (1986) 465.
- [5] E. Escalona Platero, B. Fubini and A. Zecchina, Surf. Sci. 179 (1987) 404.
- [6] E. Escalona Platero, G. Spoto, S. Coluccia and A. Zecchina, Langmuir 3 (1987) 291.
- [7] E. Garrone, B. Fubini, E. Escalona Platero and A. Zecchina, Langmuir 5 (1989) 240.
- [8] E. Escalona Platero, E. Garrone, G. Spoto and A. Zecchina, in: Studies of Surface Science and Catalysis, Vol. 48, Eds. C. Morterra, A. Zecchina and G. Costa (Elsevier, Amsterdam, 1989) p. 395.
- [9] H.E. Sanders, P. Gardner, D.A. King and M.A. Morris, Surf. Sci. 304 (1994) 159.

- [10] R.A. Hammaker, S.A. Francis and R.P. Eischens, Spectrochim. Acta 21 (1965) 1295.
- [11] G.D. Mahan and A.A. Lucas, J. Chem. Phys. 68 (1978) 1344.
- [12] B.N.J. Persson and R. Ryberg, Phys. Rev. B 24 (1981) 6954.
- [13] R.F. Willis, A.A. Lucas and G.D. Mahan, in: The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 2, Eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982) pp. 59–163 (and references therein).
- [14] F.M. Hoffmann, Surf. Sci. Rept. 3 (1983) 107.
- [15] V.M. Browne, S.G. Fox and P. Hollins, Catal. Today 9 (1991) 1.
- [16] A. Crossley and D.A. King, Surf. Sci. 68 (1977) 528.
- [17] L. Marchese, S. Bordiga, S. Coluccia, G. Martra and A. Zecchina, J. Chem. Soc. Faraday Trans. 89 (1993) 3483.
- [18] D. Cappus, C. Xu, D. Ehrlich, B. Dillmann, C.A. Ventrice, Jr., K. Al Shamery, H. Kuhlenbeck and H.-J. Freund, Chem. Phys. 177 (1993) 533.
- [19] M.A. Langell and M.H. Nassir, J. Phys. Chem. 99 (1995) 4162.
- [20] (a) C. Noda, H.H. Richardson and G.E. Ewing, J. Chem. Phys. 92 (1990) 2099; (b) D.J. Dai and G.E. Ewing, Surf. Sci. 312 (1994) 239.
- [21] J.W. Gadzuk, in: Vibrational Spectroscopy of Molecules on Surfaces, Eds. J.T. Yates, Jr and T.E. Madey (Plenum, New York, 1987) pp. 49-103.
- [22] P. Hollins, Surf. Sci. Rept. 16 (1992) 251.
- [23] M.A. Chesters, S.F. Parker and R. Raval, Surf. Sci. 165 (1986) 179.
- [24] R. Raval, S.F. Parker, M.E. Pemble, P. Hollins, J. Pritchard and M.A. Chesters, Surf. Sci. 203 (1988) 353.
- [25] R.P.H. Gasser, An Introduction to Chemisorption and Catalysis by Metals (Clarendon, Oxford, 1985).
- [26] D. Scarano, G. Spoto, S. Bordiga, A. Zecchina and C. Lamberti, Surf. Sci. 276 (1992) 281.
- [27] A.A. Tsyganenko, L.A. Denisenko, S.M. Zverev and V.N. Filimonov, J. Catal. 94 (1985) 10.
- [28] D. Scarano, A. Zecchina, S. Bordiga, G. Ricchiardi and G. Spoto, Chem. Phys. 177 (1993) 547.
- [29] R. Disselkamp, H.C. Chang and G.E. Ewing, Surf. Sci. 240 (1990) 193.
- [30] G. Pacchioni, G. Cogliandro and P.S. Bagus, Surf. Sci. 255 (1991) 344.
- [31] K.M. Neyman and N. Rösch, Chem. Phys. 177 (1993) 561.
- [32] H.H. Kung, Transition Metal Oxides: Surface Chemistry and Catalysis (Elsevier, Amsterdam, 1989).
- [33] A.A. Tsyganenko and S.M. Zverev, React. Kinet. Catal. Lett. 36 (1988) 269.