

Coadsorption of barium and oxygen on nickel—effect on oxide nucleation: Photoelectron spectroscopic studies

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Adsorption studies of oxygen on barium-promoted Nickel surface by x-ray photoelectron spectroscopy show that the presence of submonolayer coverages of barium has a profound effect on the nucleation of the oxide on the Ni surface. The Ni surface, in addition to oxidic oxygen, stabilizes a second oxygen species O' which was earlier thought to be $OH(ad)$. Barium coverages less than 6×10^{19} atoms/cm² make the oxidation of Ni more facile. For barium coverages higher than 6×10^{19} atoms/cm², the nucleation of the oxide is greatly suppressed resulting in the stabilization of more reactive, coordinatively unsaturated chemisorbed oxygen. By monitoring the barium coverage, it is possible to control the relative proportions of the oxidic O' species and the surface-stabilized chemisorbed oxygen $O'(ad)$ on the surface. The presence of predosed barium enhances the intensity of reactive chemisorbed oxygen which cannot coalesce to form the passive, oxidic overlayer even after excess oxygen dosage. Thermal stability of chemisorbed oxygen shows interesting trends. Both charge transfer from Ba to Ni and site occupation play crucial roles.

1. INTRODUCTION

The interaction of oxygen with the Ni surface is one of the most studied surface reactions. Investigations of the kinetics have shown three distinct stages; dissociative oxygen adsorption followed by oxide nucleation and lateral growth finally leading to coalescence to form passive NiO film.¹⁻³ Although extensively studied, there have been varying opinions about the various core level shifts. This is particularly true of the $O(1s)$ emission where as many as three different oxygen species have been assigned. It is generally agreed upon that the 529.7 ± 0.2 eV peak is due to the oxidic oxygen of stoichiometric NiO with $Ni(2p_{3/2})$ binding energy at 854.5 ± 0.2 eV. The other $O(1s)$ peak at 531.5 eV has been a point of debate; it has been differently ascribed to $OH(ad)$, $O(ad)$, and to oxygen of the defect oxide $Ni_{0.3-0.5}O$. In our earlier paper, we have assigned the 531.5 eV $O(1s)$ peak to a second oxygen species $O'(ad)$. The He I spectra show characteristic peaks at 6 eV due to O'^{-} ion and 9.7 , and 12 eV assignable to final states $'P'$, $'D'$, and $'S'$ of $O(ad)$ on photoionization of $O'(ad)$.⁴ The presence of O' has also been confirmed in a recent paper.⁵

In the present study, the Ni-O₂ system has been investigated on a comparative basis with the Ni/alkali/O₂ system to throw more light on the nature of oxygen adspecies on clean as well as the modified surface and the effect of alkali adatoms, on the kinetics of oxide growth as these have relevance not only as a source of surface activation in heterogeneous catalysis but also have implications in the chemistry occurring at electrode surfaces.

II. EXPERIMENT

Al K α x-ray photoelectron spectroscopy (XPS) and He II ultraviolet photoemission spectroscopy (UPS) experiments

have been carried out in ESCA3 Mark11 spectrometer of V.G. Scientific Ltd. (UK). The base vacuum was 2×10^{-10} Torr in the preparation as well as the spectrometer cham-

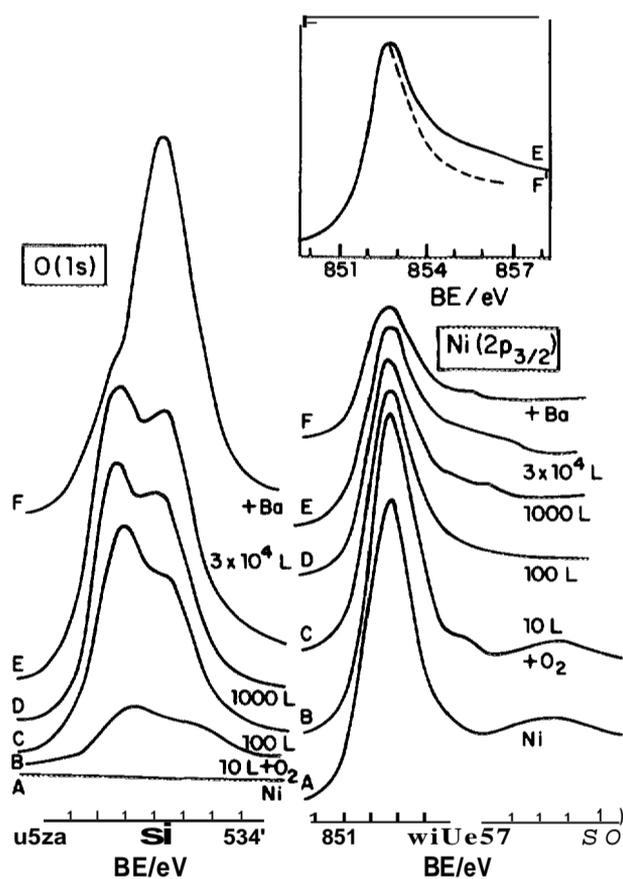


Fig. 1. $O(1s)$ and $Ni(2p_{3/2})$ spectra as a function of O_2 dosage and subsequent Ba dosage. Inset: see text.

bers. Pure polycrystalline Ni foil has been used in the study. The metal surface was cleaned by repeated heating and argon ion etching. Barium was dosed from a barium getter. The spectrometer was operated at 20 eV pass energy for XPS. The gas handling line was fully baked at 200 °C to reduce any contamination. The purity of the oxygen was checked with a quadrupole mass spectrometer fitted in the preparation chamber. There was no detectable impurity of H₂O, CO, and CO₂, when O₂ was leaked in the preparation chamber at 10⁻⁶ Torr.

III. RESULTS

The O(1s) spectra on oxygen exposure to the clean Ni surface at 300 K show two characteristic peaks at 529.7 and 531.3 eV. The O(1s) spectra with increasing O₂ exposure to the clean Ni surface are shown in Fig. 1. As is clear from the figure, near saturation of surface chemisorbed oxygen occurs by 100 L O₂ exposure. The Ni(2p_{3/2}) region shows a depletion in the intensity of the Ni 2p band with an increase in the emission at 854.5 eV.

On this oxygen predosed surface, barium was deposited ($\theta_{Ba} \approx 8 \times 10^{14}$ atoms/cm² - 0.5 monolayer). A major decrease in the 529.5 eV O(1s) peak was observed [see curve F, Fig. 1(a)]. This was accompanied by a large increase in the peak at 531.3 eV. Further oxygen exposure to this surface did not show any change in the peak shape or intensity in the O(1s) region. There was some decrease in the intensities of the peaks in the Ni(2p_{3/2}) region also. To see the relative decrease, the peaks on Ni + O₂ and Ni + O₂ + Ba (curves E and F) were normalized (see inset) and it is clearly seen that there is a significant reduction in the emission at 855 eV, after barium dosage.

Oxygen adsorption was done on barium predosed Ni; typical O(1s) and Ni(2p_{3/2}) spectra are shown in Fig. 2 for a barium coverage of 8×10^{14} atoms/cm² (about 0.5 monolayer). Curves show O(1s) and Ni(2p_{3/2}) regions on clean Ni. On barium dosage, there is no change in the nickel core level spectrum. The O(1s) region shows a small pick-up of oxygen impurity. To this barium predosed surface, oxygen was exposed. Curves C show the O(1s) and Ni(2p_{3/2}) regions after 100 L O₂ exposure. As is clear from the figure, the O(1s) region again shows two peaks at 529.7 and 531.3

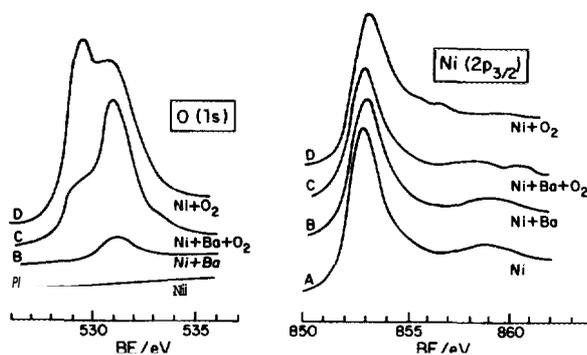


FIG. 2. O(1s) and Ni(2p_{3/2}) spectra on Ni, Ni + Ba ($\theta_{Ba} = 8 \times 10^{14}$ atoms/cm²); Ni + Ba + O₂ (100 L) and Ni + O₂ (100 L).

TABLE I. Core level and valence-band energies in Ni/Ba/O₂ system (eV).

System	Ni(2p _{3/2})	Ba(3d _{5/2})	O(1s)	O(2p)
Ni (clean)	852.8
Ni + O ₂ (100 L, 300 K)	852.8	...	229.7	5.7, 10.2
	854.6	...	531.5	12.2
Ni + O ₂ (1 WL, 5 WK)	852.8	...	529.7	5.7
	854.6
Ni + Ba + O ₂ (100 L, 300 K, $\theta_{Ba} = 3 \times 10^{14}$ atoms/cm ²)	852.8	780.2	529.7	5.6, 10.0
	854.6	...	531.3	12.0
Ni + Ba + O ₂ (100 L, 300 K, $\theta_{Ba} = 1 \times 10^{14}$ atoms/cm ²)	852.8	780.2	529.7	5.6, 9.8
	531.3	11.9

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eV. It is noteworthy that appreciable intensity of the peak at around 529.7 eV is still seen. But the Ni(2p_{3/2}) region does not show any growth in the peak at 855 eV. For comparison, the Ni(2p_{3/2}) signal seen after 100 L O₂ exposure to the clean Ni surface is also shown in the figure. The core level binding energies are summarized in Table I.

It was of interest to examine the variation in the oxygen adsorption behavior as a function of barium coverage. To study this, the same O₂ exposure of 100 L was given after each dosage of barium to clean Ni. The Ba(3d_{5/2}) and O(1s) spectra are given in Fig. 3 for three representative barium precoverages: 3.5, 8.3, and 12.3 $\times 10^{14}$ atoms/cm². It is evident from the figure that for low values of θ_{Ba} , there is little change in the nature of the composite O(1s) peak, but the intensity of the low binding energy peak is found to increase (compare with curve D, Fig. 2) for a barium coverage of 3.5×10^{14} atoms/cm²; this increase is about 40%. As θ_{Ba} is further increased, there is a drastic fall in the intensity of the low binding energy peak. This is clearly shown by curve B ($\theta_{Ba} = 8.3 \times 10^{14}$ atoms/cm²). For higher values of θ_{Ba} , there is a selective increase in the intensity of the peak at 531 eV (curve C, $\theta_{Ba} = 1.2 \times 10^{14}$ atoms/cm²). The variation in the intensity of the 529.5 eV peak with respect to barium coverage is quantitatively shown in the inset (Fig. 3).

It was of interest to examine thermal stability of the oxygen associated with the low binding energy O(1s) peak. Figure 4 shows the surface concentration of this oxygen on Ni + Ba + O₂ (100 L at 300 K) for two different initial barium coverages (3.5 and 8.3 $\times 10^{14}$ atoms/cm²). Here all values have been normalized to unity with respect to the surface oxygen concentration seen at 300 K. The corresponding concentrations seen in the absence of barium, i.e., on Ni + O₂ (100 L) have also been plotted. It is to be seen that the variation even for a low θ_{Ba} value (3.5×10^{14} atoms/cm²) is not the same as that in the absence of barium. The depletion temperature of surface oxygen is shifted by about 70–80 K to higher values. When the θ_{Ba} value is about 8×10^{14} atoms/cm², it is seen that after an initial decrease.

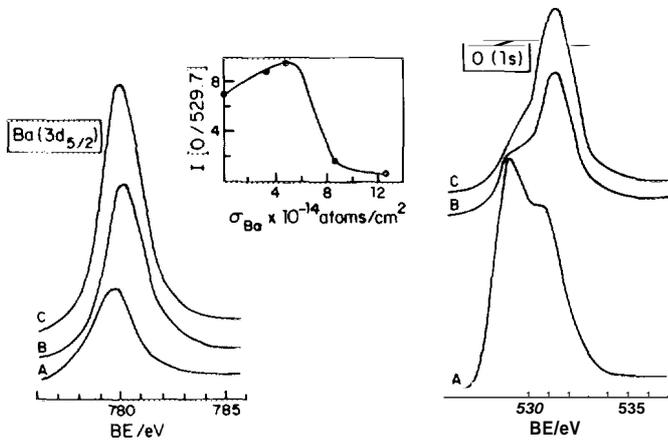


FIG. 3. Ba(3d_{5/2}) and O(1s) spectra as a function of Ba precoverage (σ_{Ba} , for curves A, B, and C = 3.5, 8.3, and 12.3 $\times 10^{14}$ atoms/cm²). Inset shows the variation in the intensity of the O(1s) peak at 529.7 eV with barium coverage on Ni + Ba + O₂ (1000 L).

the concentration of the 529.5 eV O(1s) peak still continues to remain about half of the initial concentration.

IV. DISCUSSION

The adsorbed oxygen on clean Ni is manifested in the form of two peaks in the O(1s) region with binding energies 529.7 and 531.3 eV. These have been discussed in our earlier paper.¹ The low binding energy O(1s) peak and the O(2p) peak at 5.7 eV in the UPS can be ascribed to O⁻ anions¹¹

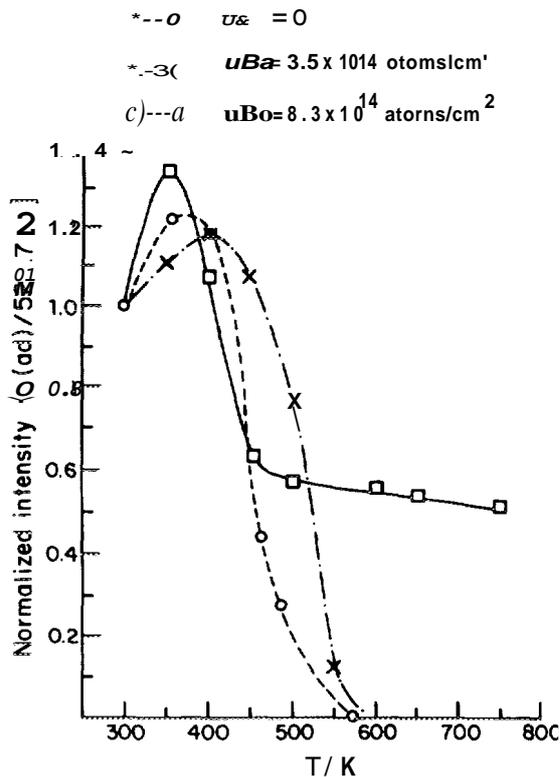


FIG. 4. Surface depletion of O(ad) at 529.7 eV binding energy with temperature on Ni + Ba + O₂ (1000 L).

which lead to oxide nucleation and growth of surface oxide at higher oxygen coverages. The Ni(2p_{1/2}) peak intensity shows a depletion with growth in a shifted peak around 854.5 eV. This peak with a satellite 6.3 eV away is indicative of surface oxide NiO. The 2.5 eV feature in the He11 UPS can be assigned to the 3d band of nickel oxide, NiO, whereas that at 0.6 eV due to the 3d band of metallic Ni.

Unlike the O(1s) spectra on other oxygen dosed metals like Cu, Ag, and Au, a 531.5 eV peak in the O(1s) region is present on oxygen-dosed Ni even when the surface is not pre-dosed with barium. This peak is accompanied by two peaks at 10.2 and 12.2 eV in the He11 UPS. These have been assigned in our earlier paper¹ to the final ¹P and ¹D states produced by the photoionization of O⁻ (ad). The relative proportion of O₂⁻ and O⁻ can be varied depending upon the barium concentration. What is even more interesting is that conversion of O⁻ to O⁻ is also possible on dosing barium upon oxidized Ni surface as is evident from Fig. 1 (curve F).

Decreased intensity of O⁻ is also observed on the barium precovered surfaces also. This can be seen from the comparison made in Fig. 2. But it is important to emphasize that the decrease in O₂⁻ intensity is observed only for barium coverages higher than 5 $\times 10^{14}$ atoms/cm². For smaller coverages, interestingly, the intensity of O⁻ is enhanced as compared with the clean Ni surface (Fig. 3). This, therefore, means that small coverages of barium make the oxidation of nickel more facile but beyond a certain critical value (6 $\times 10^{14}$ atoms/cm²), the oxidation propensity of Ni falls off drastically. The charge transfer from the surface alkali metal to the substrate Ni₁₀₀ seems to make charge transfer from Ni to oxygen easier at low σ_{Ba} values. Direct charge transfer from Ba to O₂ also cannot be ruled out. But as the barium precoverage is increased, oxide nucleation gets hindered. Nickel is one of those metals which show sharp dependence of the surface coverage on the onset of oxide nucleation.¹² The restriction of oxide nucleation and coalescence seems to explain the drastic fall in O₂⁻ intensity. On a well ordered Ni(100) lattice, oxide nucleation has been shown to be very slow; the onset of oxide nucleation is believed to occur with a local coverage of O₂ > 0.5.¹³

However, it is important that at a barium precoverage of, say, 8 $\times 10^{14}$ atoms/cm², one can still see appreciable intensity of adsorbed oxygen associated with Ni, with a binding energy of 529.7 eV. This is not to be considered as the oxidic overlayer. This is reactive chemisorbed oxygen which cannot coalesce to form the passive oxidic layer in presence of coadsorbed barium. That there exists a subtle difference in reactivity between the oxidic oxygen and the chemisorbed oxygen has been shown conclusively in the study of oxidation of CO, for example.¹⁴ It is in this context that the surface oxygen on Ni in presence of dosed barium is to be seen. With a regulated amount of surface barium concentration, it is possible to selectively enhance or deplete the oxidic oxygen vis-a-vis oxygen in coordinatively unsaturated chemisorbed state.

Besides the preferential presence of dissociatively chemisorbed oxygen, its thermal stability also shows an interesting

trend. For $\theta_{\text{Ba}} = 8 \times 10^{-2}$ atoms/cm², $\theta_{\text{O}}(700\text{K})/\theta_{\text{O}}(300\text{K})$ continues to remain as high as 0.5. In the case of clean Ni, Holloway and Outlaw¹¹ have noticed that for $T > 550\text{K}$, while NiO disappeared from the surface due to dissolution, chemisorbed oxygen phase was stable until $T > 1100\text{K}$.

As is clear from Fig. 4, a major portion of surface oxygen is removed at 450 K due to oxygen dissolution and at 550 K, the surface is oxygen free. In contrast to this, the surface stability of oxygen to temperature is considerably enhanced in presence of barium. The presence of the oxygen associated with Ni on the surface even at 800 K on Ni + Ba + O, further confirms the view that this oxygen is in a chemisorbed phase and not oxidic. Based on these facts, we conclude that the presence of coadsorbed barium on the surface may provide an important step in activating adsorbed molecules in their interaction with oxygen on the nickel surface. Besides, the extent of barium dosage can be used to prevent the formation of the passive oxidic overlayer in the surface oxidation of nickel itself.

ACKNOWLEDGMENT

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- ¹ D. F. Mitchell and M. J. Graham, Surf. Sci. **114**, 546 (1982).
- ² T. Fleisch, N. Winograd, and W. N. Delgass, Surf. Sci. **78**, 141 (1978).
- ³ P. R. Norton, R. L. Tapping, and J. W. Goodale, Surf. Sci. **65**, 13 (1977).
- ⁴ A. F. Carley, S. Rassias, and M. W. Roberts, Surf. Sci. **135**, 35 (1983).
- ⁵ A. F. Carley, P. R. Chalker, and M. W. Roberts, Proc. R. Soc. London **A 399**, 167 (1985).
- ⁶ M. S. Hegde and M. Ayyoob, Surf. Sci. **173**, L635 (1986).
- ⁷ P. S. Badyal, X. Zhang, and R. M. Lambert, Surf. Sci. Lett. **225**, L15 (1990).
- ⁸ M. Ayyoob and M. S. Hegde, Surf. Sci. **147**, 361 (1984).
- ⁹ C. R. Brundle and H. Hopster, J. Vac. Sci. Technol. **18**, 663 (1981).
- ¹⁰ F. Labohm, O. L. J. Gijzen, and J. W. Geus, Surf. Sci. **135**, 409 (1983).
- ¹¹ P. H. Holloway and R. A. Outlaw, Surf. Sci. **111**, 300 (1981).