

K-promoted oxidation of CO on Ni(111)

A. Cupolillo, G. Chiarello,* V. Formoso, D. Pacilè, M. Papagno, F. Veltri, E. Colavita, and L. Papagno
*Istituto Nazionale di Fisica della Materia, Unità della Calabria Dipartimento di Fisica, Università della Calabria,
 I-87036 Rende (CS), Italy*

(Received 30 May 2002; published 19 December 2002)

The oxidation of CO promoted by K atoms is observed on Ni(111) for temperatures ranging from room temperature down to 160 K. The catalytic reaction at 160 K gives rise to the formation of adsorbed CO₂ molecules which are stable up to 180 K, above that temperature they completely desorb. The reaction follows the Langmuir-Hinshelwood mechanism and the uptake order of the involved species seems to be of minor importance.

DOI: 10.1103/PhysRevB.66.233407

PACS number(s): 68.43.Pq, 71.20.Dg, 82.65.+r

The oxidation of carbon monoxide on metal surfaces has been intensively studied in the last few years.¹⁻⁵ From the fundamental point of view, the reaction of CO with oxygen on transition-metal surfaces is regarded as a model system in order to understand the nature of surface chemical bonds. On the other hand, this reaction is of extreme practical importance in the reduction of CO in car exhaust-catalytic converters.

On many transition metals such as Pt, Ru, Rh, and Pd, the oxidation of CO takes place spontaneously. In an ultrahigh vacuum (UHV) the reaction is based on the Langmuir-Hinshelwood mechanism: CO molecules adsorb first on the metal surface and then react with chemisorbed oxygen atoms forming CO₂ molecules, which remain adsorbed on the surface or desorb depending on the sample temperature. On Pt(111), the oxidation reaction was investigated⁵ by scanning tunneling microscope, and was stated that the reaction takes place at the boundaries between O-*p*(2×2) and CO-*c*(4×2) islands. Density-functional theory calculations for CO oxidation on Pt(111),³ Rh(111),⁶ and Ru(0001) (Ref. 7) surfaces showed that the dominant energetic barrier for turning on the reaction is the strength of the O-metal bond, and, moreover, that oxygen and CO react only when oxygen atoms migrate from hollow to bridge sites where they are characterized by a weaker O-metal bond. On Ni(111), oxygen and CO bind so strongly to the surface that the reaction producing CO₂, does not occur, at least in UHV conditions.⁸

In this paper, we present experimental evidence of the K promoted oxidation of CO on Ni(111). By using high resolution electron energy loss spectroscopy (HREELS) we observe the formation of adsorbed CO₂ when K is dosed at 160 K on a preadsorbed (O+CO) layer. Moreover, we find that the adsorption uptake order of the reagent species (CO, O, and K) is not important and CO oxidation occurs also when oxygen atoms are added onto a preadsorbed (CO+K) layer.

The geometrical structures of potassium, oxygen, and carbon monoxide adsorbed separately on Ni(111) were extensively investigated, and by now the results are well established. Potassium atoms form an ordered *p*(2×2) structure and adsorb at on top sites;⁹ oxygen molecules adsorb dissociatively at threefold hollow sites and may form ordered *p*(2×2) and ($\sqrt{3}\times\sqrt{3}$)R30° structures;¹⁰ CO adsorption gives rise to a *c*(4×2) low-energy electron-diffraction (LEED) pattern with molecules adsorbed in threefold sites.¹¹

Coadsorption of oxygen and potassium on the Ni(111) surface produces a number of ordered structures.¹² Also CO/O and CO/K coadsorption phases^{9,13} on the same surface were accurately investigated, and the results showed no change in the adsorption sites of each species. Interestingly, it was shown⁸ that in the CO/O coadsorbed phase, CO molecules move almost freely on the Ni(111) surface.

Present experiments were performed by an electron energy loss spectrometer (Delta 0.5 by SPECS) operating routinely at a base pressure of 6×10^{-11} Torr. Loss spectra were recorded in specular geometry with an incident angle of 55° with respect to the surface normal, using an electron beam energy of 4 eV and an energy resolution of 3–4 meV. The Ni(111) crystal was cleaned in a preparation chamber (base pressure 2×10^{-10} Torr) by repeated cycles of ion sputtering and annealing at 900 K. Surface cleanliness and order were checked by the same LEED Auger apparatus. Potassium was evaporated from a well out gassed SAES getter source. CO contamination due to the K evaporation was reduced to the minimum maintaining the evaporation pressure accurately below 6×10^{-10} Torr.

We started by preparing an O-*p*(2×2)/Ni(111) structure at the temperature of 250 K for which the adsorption is dissociative; then, we dosed 3 L (1 L = 1×10^{-6} Torr s) of CO on the oxygen layer at the same temperature. Soon after, we cooled the sample down to 160 K and we did not observe any change in the LEED O-*p*(2×2) pattern. The loss spectrum of the (O+CO) phase is shown in Fig. 1. The loss at 71 meV is due to oxygen atoms vibrating perpendicular to the Ni(111) surface and the losses at 230 and 258 meV are due to the intramolecular C-O stretching modes.¹⁴ In particular, the low-energy loss at 230 meV is indicative of the existence of CO molecules not influenced by oxygen coadsorption. Their C-O stretching energy, in fact, is the same as that on the clean Ni(111) surface. Conversely, the feature at 258 meV is a sign of the interaction between oxygen atoms and the rest of the CO molecules, in excellent agreement with previous infrared reflection absorption spectroscopy measurements.¹⁴

This result on the (O+CO) coadsorbed phase shows that, while the presence of O atoms may modify the bonding strength of CO molecules and, consequently, of the CO-Ni bond, on the contrary, the presence of CO does not seem to cause any shift of the O-Ni vibration energy. As is well known, increasing the C-O vibration means a weakening of

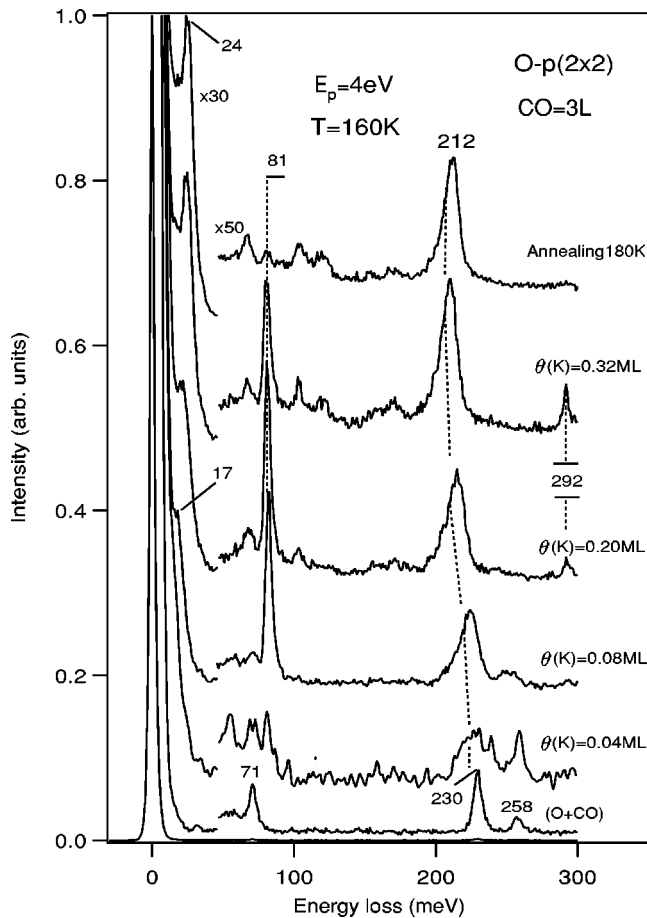


FIG. 1. HREEL spectra obtained by adsorbing potassium at 160 K on a $O-p(2 \times 2) + CO$ layer deposited on the Ni(111) surface. The upper spectrum is taken after an annealing of the sample at 180 K. All spectra were recorded in the specular geometry. The K full coverage corresponds to 0.32 ML.

the CO-metal bond due to direct O-CO lateral interactions or to a reduced back-donation into $2\pi^*$ antibonding orbitals of CO. Thus CO molecules in this state should diffuse rather free on the surface and approach oxygen atoms closely; nevertheless, no evidence of a chemical reaction between CO and oxygen atoms is observed so far.

On the (O+CO) layer, we deposited different amounts of potassium up to the full coverage (Fig. 1). The final potassium coverage (0.32 ML) was estimated by measuring the $K-L_{2,3}VV$ Auger line after a calibration against the $K-p(2 \times 2)$ coverage (0.25 ML), and intermediate K coverages were estimated by deposition time. The loss spectrum obtained after a K coverage of 0.04 ML shows several features in the regions of O and CO vibrations. They are not easily interpretable, although they are a clear sign of the occurrence of a chemical reaction on the surface. Moreover, the deposition of K causes a disordering of the surface being the $O-p(2 \times 2)$ pattern no more visible. By increasing potassium coverage up to 0.08 ML, the loss spectrum substantially modifies since intense features develop at 17 and 81 meV. Further K deposition causes a continuous shift of the CO vibration from 230 meV toward lower vibration energies as well as the rise of new features at 24 and 292 meV.

Losses at 17 and 24 meV are due to K-Ni (Refs. 15 and 16) and O-K (Ref. 17) vibrations, respectively, while the losses at 81 and 292 meV are a clear sign of an innovative and unexpected process, i.e. the oxidation of CO, and are assigned to the product of this chemical reaction. Such losses are interpreted as CO_2 normal vibrations for several reasons: (a) their energy¹⁸ corresponds to the ν_2 (81 meV) and ν_3 (292 meV) vibration modes of CO_2 molecules; (b) the same vibrations were observed for CO_2 adsorbed at 100 K on the Fe(111) surface;¹⁹ (c) upon a mild annealing of the surface from 160 K up to 180 K, these two losses disappear completely as it would occur for CO_2 molecules weakly bound to the surface; (d) no losses that may be assigned to O, CO, or to the interaction of CO with K and O with K, are expected at these energies.

These CO_2 features grow at the expense of oxygen and of those CO molecules which are mostly influenced by the presence of oxygen atoms, i.e., of the CO molecules whose intramolecular vibration is at 258 meV. The reaction, however, does not consume all the carbon monoxide present on the surface and thus, one CO vibration is still observed. If we assume that CO and oxygen on Ni(111) are localized in separate domains, as observed⁵ on Pt(111), then CO molecules belonging to the body of the CO island are unlikely to participate to the oxidation process because too far away from oxygen atoms; very likely, only those molecules lying on the border line of CO and oxygen domains are expected to interact strongly.

Present interpretation was further tested by changing the procedure of the experiment. We prepared a (K+CO) layer at 160 K, and we adsorbed increased amounts of oxygen on the precovered surface. The loss results are shown in Fig. 2. Particularly, we deposited 0.04 ML of K at 250 K, and then we exposed the surface layer at 3 L of CO at the same temperature. The peak at 14 meV is the K-Ni vibration and that at 215 meV is the internal CO vibration energy, strongly influenced by K atoms. Adsorption of oxygen at 160 K on the (K+CO) surface gives rise to the features at 81 and 292 meV, indicating that the oxidation process is promoted by K atoms regardless of the initial surface conditions. We note that the feature at 292 meV is weaker with respect to the peak at 81 meV. Interestingly, any step of the oxygen exposition gives rise to an increase of the peak at 81 meV and a decrease of that at 215 meV.

The K-promoted effect on CO oxidation was verified also at room temperature for which we did not expect to observe adsorbed CO_2 , but only to reveal the sign of the occurred reaction. In Fig. 3 we show the results of this experiment for two different K coverages: i.e., 0.08 and 0.20 ML, exposed to different amounts of oxygen. Particularly, in Fig. 3(a), a (CO+K) preadsorbed layer was exposed to 300 L of oxygen. A clear decreasing of the intensity of the CO loss and a strong oxidation of the Ni surface were observed. The high consumption of CO adsorbed on the surface is clear evidence that the reaction occurred. Actually, two O-Ni vibrations at 69 and 58 meV and the K-Ni vibration (14 and 16 meV) were observed. Changing the initial K coverage to 0.20 ML and the exposition of oxygen to 100 L, as indicated in Fig. 3(b), we deduced that the strength of the reaction depends on

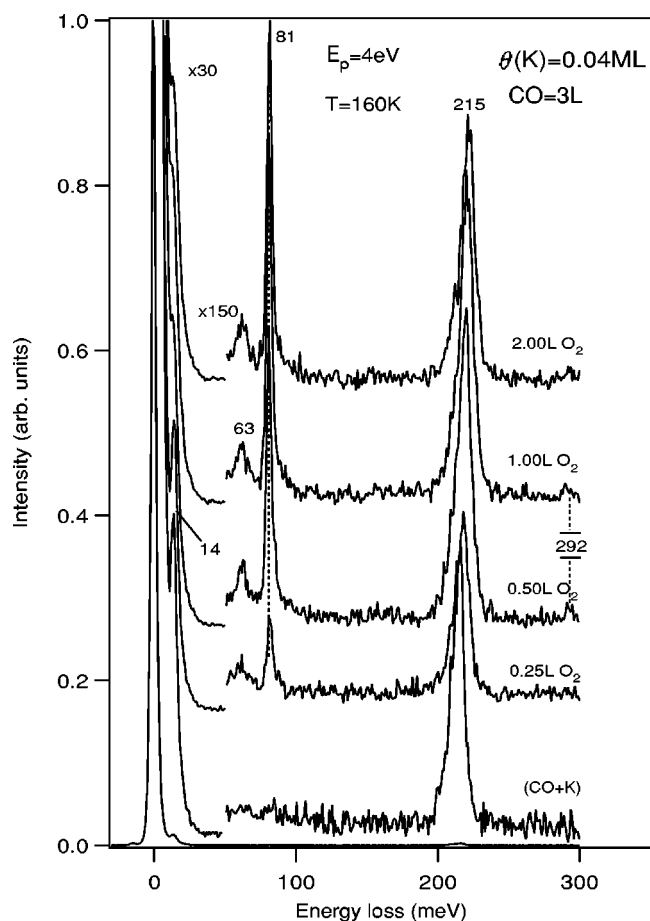


FIG. 2. HREEL spectra taken after adsorbing oxygen at 160 K on a (K+CO) layer preadsorbed on the Ni(111) surface.

the initial K coverage. In fact, the CO oxidation gives rise to an almost complete disappearance of CO molecules from the surface, as further confirmed by the absence of the C-KVV Auger peak. Thus we did not find any carbon atom on the surface after the reaction: no carbon belonging to CO molecules eventually lying in a flat geometry on the surface, and no carbon eventually due to some CO dissociation. Moreover the potassium coverage in Figs. 3(a) and 3(b), estimated by time deposition is the almost the same of that obtained by measuring the K- $L_{2,3}VV$ Auger line after the HREELS experiments. In other words, the above results show that the original (CO+K)-Ni(111) surface was almost cleaned up from CO molecules, while O and K atoms were still lying on the surface.

The present study has demonstrated that the addition of K atoms on the Ni(111) surface promotes the CO oxidation for temperature as low as 160 K. To our knowledge this is the first time that a similar effect is reported. The CO_2 molecule is formed through a Langmuir-Hinshelwood process and is weakly bound to the Ni(111) surface, as suggested from the desorption temperature (180 K) and by the vibration frequencies which are nearly similar to those measured for CO_2 in the gas phase.¹⁸ The presence of the asymmetric stretching vibration (ν_3 mode) at 292 meV of O-C-O, and its weak intensity, strongly suggests that CO_2 molecules are adsorbed

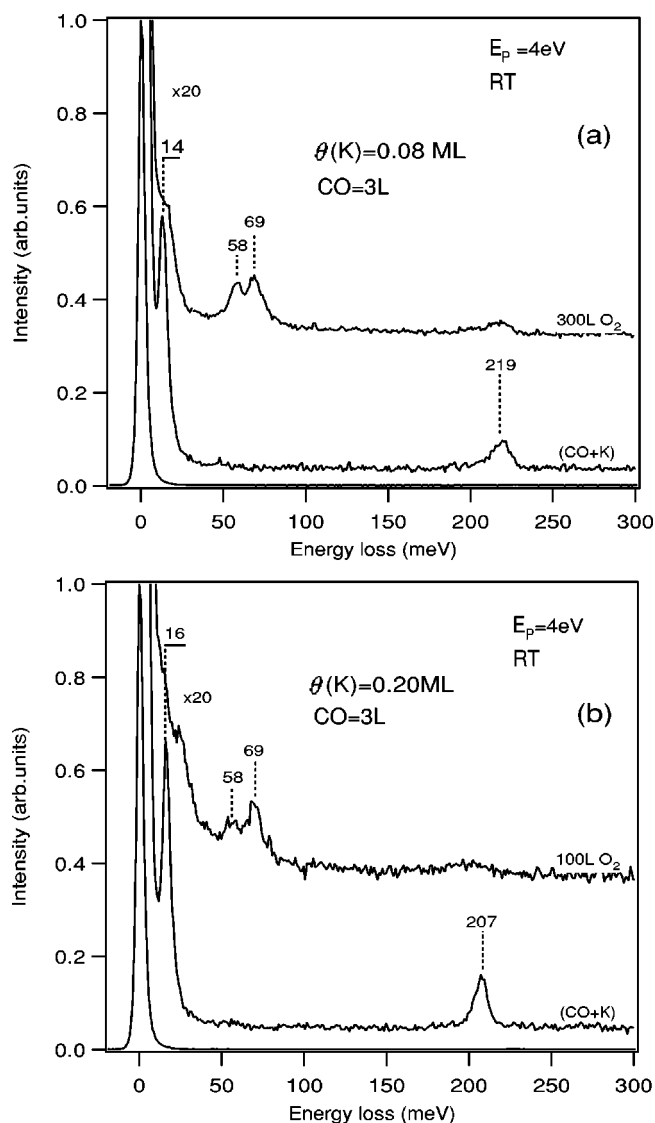


FIG. 3. HREEL spectra taken after adsorbing oxygen at room temperature on a (K+CO) layer preadsorbed on the Ni(111) surface. The two panels differ for the potassium coverage and for the oxygen dose.

in a nearly linear configuration with the molecular axis parallel to the surface. On the other hand, a similar configuration was suggested for CO_2 on Pt(111). In fact, calculations³ showed that chemisorbed CO_2 obtained by CO oxidation on Pt(111) exhibits a bond angle of 131° .

We can image two mechanisms that may activate the CO oxidation promoted by potassium atoms: (a) alkali K atoms cause a modification of the electronic properties of the substrate, thus lowering the activation barrier; and (b) the mobility of the reactants is greatly increased by K atoms, allowing oxygen and carbon monoxide species to approach each other. In principle, the effect may be chemical or electrostatic;²⁰ however, the net effect is very likely the result of a cooperative interaction between co-adsorbates species (O, K, and CO) and between them and the Ni substrate.

In summary, our measurements show that K atoms pro-

mote CO oxidation on Ni(111) for temperatures as low as 160 K. The reaction takes place by adsorbing K on a preadsorbed (CO+O) layer or equally, by adsorbing oxygen on a (K+CO) preadsorbed layer. We hope that the present findings may stimulate detailed theoretical investigations, shed-

ding light on the fundamental mechanisms at the base of this important catalytic phenomenon.

This work was funded by the MIUR - Programmi di rilevante interesse nazionale (COFIN 2001).

*Author for correspondence: G. Chiarello. Email address: chiarello@fis.unical.it, Tel. ++39-984-496157, Fax: ++39-984-494401.

¹J.R. Hahn and W. Ho, Phys. Rev. Lett. **87**, 166102 (2001).

²C.C. Cudia, S.W. Hla, G. Comelli, Z. Sljivancanin, B. Hammer, A. Baraldi, K.C. Prince, and R. Rosei, Phys. Rev. Lett. **87**, 196104 (2001).

³A. Alavi, P. Hu, T. Deutsch, P.L. Silvestrelli, and J. Hutter, Phys. Rev. Lett. **80**, 3650 (1998).

⁴C. Stampfl and M. Scheffler, Phys. Rev. Lett. **78**, 1500 (1997).

⁵J. Winterlin, S. Volkening, T.V.W. Janssens, T. Zambelli, and G. Ertl, Science **278**, 1931 (1997).

⁶C.J. Zhang and P. Hu, J. Am. Chem. Soc. **122**, 2134 (2000).

⁷C. Zhang, P. Hu, and A. Alavi, J. Am. Chem. Soc. **121**, 7931 (1999).

⁸V. Fernandez, K.M. Schindler, O. Schaff, Ph. Hofmann, A. Theobald, A.M. Bradshaw, V. Fritzsche, R. Davis, and D.P. Woodruff, Surf. Sci. **351**, 1 (1996).

⁹D. Fisher, S. Chandavarkar, I.R. Collins, R.D. Diehl, P. Kaukasoina, and M. Lindroos, Phys. Rev. Lett. **68**, 2786 (1992).

¹⁰H. Ibach and D. Bruchmann, Phys. Rev. Lett. **44**, 36 (1980).

¹¹M.E. Davilla, M.C. Asensio, D.P. Woodruff, K.M. Schindler, P.

Hofmann, K.U. Weis, R. Dippel, P. Gardner, V. Fritzsche, A.M. Bradshaw, J.C. Conesa, and A.R. Gonzales-Felipe, Surf. Sci. **311**, 337 (1994).

¹²Z.Y. Li and D. Diehl, J. Phys.: Condens. Matter **9**, 3701 (1997).

¹³R. Davis, D.P. Woodruff, O. Schaff, V. Fernandez, K.M. Schindler, P. Hofmann, K.U. Weiss, R. Dippel, V. Fritzsche, and A.M. Bradshaw, Phys. Rev. Lett. **74**, 1621 (1995).

¹⁴Z. Xu, L. Surney, K. Uram, and J.T. Yates, Jr., Surf. Sci. **292**, 235 (1993).

¹⁵J.R. Hannon, M. Giesen, C. Clunker, G. Shoulze Icking-Konert, D. Stapel, H. Ibach, and J.E. Muller, Phys. Rev. Lett. **78**, 1094 (1997).

¹⁶K. Jacobi, H. Shi, M. Gruyters, and G. Hertel, Phys. Rev. B **74**, 5733 (1994).

¹⁷R.A. De Paola, F.M. Hoffmann, D. Heskett, and E.W. Plummer, J. Chem. Phys. **87**, 1361 (1987).

¹⁸G. Herzberg, *Infrared and Raman Spectra* (Wiley, New York, 1945).

¹⁹G. Hess, H. Froitzheim, and Ch. Baumgartner, Surf. Sci. **331**, 138 (1995).

²⁰J.J. Mortensen, B. Hammer, and J.K. Norskov, Phys. Rev. Lett. **80**, 4333 (1998).