University of Wollongong

Research Online

Faculty of Science, Medicine and Health -
Papers: part A

Faculty of Science, Medicine and Health

1-1-2017

Tunability of the CO adsorption energy on a Ni/Cu surface: site change and coverage effects

Erik Vesselli

University of Trieste, IOM-CNR Laboratorio TASC

Michele Rizzi

University of Trieste

Sara Furlan

University of Trieste

Xiangmei Duan

Ningbo University

Enrico Monachino

University of Trieste, em805@uowmail.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/smhpapers>

Part of the [Medicine and Health Sciences Commons](#), and the [Social and Behavioral Sciences Commons](#)

Recommended Citation

Vesselli, Erik; Rizzi, Michele; Furlan, Sara; Duan, Xiangmei; Monachino, Enrico; Dri, Carlo; Peronio, Angelo; Africh, Cristina; Lacovig, Paolo; Baldereschi, Alfonso; Comelli, Giovanni; and Peressi, Maria, "Tunability of the CO adsorption energy on a Ni/Cu surface: site change and coverage effects" (2017). *Faculty of Science, Medicine and Health - Papers: part A*. 4782.
<https://ro.uow.edu.au/smhpapers/4782>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Tunability of the CO adsorption energy on a Ni/Cu surface: site change and coverage effects

Abstract

The adsorption energy of carbon monoxide on Ni ad-islands and ultra-thin films grown on the Cu(110) surface can be finely tuned via a complex interplay among diffusion, site change mechanisms, and coverage effects. The observed features of CO desorption can be explained in terms of migration of CO molecules from Cu to Ni islands, competition between bridge and on-top adsorption sites, and repulsive lateral adsorbate-adsorbate interactions. While the CO adsorption energy on clean Cu(110) is of the order of 0.5 eV, Ni-alloying allows for its controlled, continuous tunability in the 0.98-1.15 eV range with Ni coverage. Since CO is a fundamental reactant and intermediate in many heterogeneous catalytic (electro)-conversion reactions, insight into these aspects with atomic level detail provides useful information to potentially drive applicative developments. The tunability range of the CO adsorption energy that we measure is compatible with the already observed tuning of conversion rates by Ni doping of Cu single crystal catalysts for methanol synthesis from a CO₂, CO, and H₂ stream under ambient pressure conditions.

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

Publication Details

Vesselli, E., Rizzi, M., Furlan, S., Duan, X., Monachino, E., Dri, C., Peronio, A., Africh, C., Lacovig, P., Baldereschi, A., Comelli, G. & Peressi, M. (2017). Tunability of the CO adsorption energy on a Ni/Cu surface: site change and coverage effects. *Journal of Chemical Physics*, 146 (22), 224707-1-224707-8.

Authors

Erik Vesselli, Michele Rizzi, Sara Furlan, Xiangmei Duan, Enrico Monachino, Carlo Dri, Angelo Peronio, Cristina Africh, Paolo Lacovig, Alfonso Baldereschi, Giovanni Comelli, and Maria Peressi

Tunability of the CO adsorption energy on a Ni/Cu surface: Site change and coverage effects

Erik Vesselli,^{1,2,a)} Michele Rizzi,^{3,b)} Sara Furlan,^{3,b)} Xiangmei Duan,⁴ Enrico Monachino,^{1,b)} Carlo Dri,^{1,2,b)} Angelo Peronio,^{1,2,b)} Cristina Africh,² Paolo Lacovig,⁵ Alfonso Baldereschi,^{3,6} Giovanni Comelli,^{1,2} and Maria Peressi^{3,7}

¹Physics Department and CENMAT, University of Trieste, via Valerio 2, I-34127 Trieste, Italy

²IOM-CNR Laboratorio TASC, Area Science Park, S.S. 14 km 163.5, Trieste I-34149, Basovizza, Italy

³Physics Department, University of Trieste, Strada Costiera 11, I-34151 Trieste, Italy

⁴Department of Physics, Ningbo University, 818 Fenghua Road, Jiangbei District, 315211 Ningbo, People's Republic of China

⁵Elettra-Sincrotrone Trieste S.C.p.A., Area Science Park, S.S. 14 km 163.5, I-34149 Trieste, Italy

⁶Institute of Theoretical Physics, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

⁷IOM-CNR DEMOCRITOS, Trieste, Italy and Italian Consortium on Materials Science and Technology (INSTM), Trieste, Italy

(Received 12 April 2017; accepted 24 May 2017; published online 14 June 2017)

The adsorption energy of carbon monoxide on Ni ad-islands and ultra-thin films grown on the Cu(110) surface can be finely tuned via a complex interplay among diffusion, site change mechanisms, and coverage effects. The observed features of CO desorption can be explained in terms of migration of CO molecules from Cu to Ni islands, competition between bridge and on-top adsorption sites, and repulsive lateral adsorbate-adsorbate interactions. While the CO adsorption energy on clean Cu(110) is of the order of 0.5 eV, Ni-alloying allows for its controlled, continuous tunability in the 0.98–1.15 eV range with Ni coverage. Since CO is a fundamental reactant and intermediate in many heterogeneous catalytic (electro)-conversion reactions, insight into these aspects with atomic level detail provides useful information to potentially drive applicative developments. The tunability range of the CO adsorption energy that we measure is compatible with the already observed tuning of conversion rates by Ni doping of Cu single crystal catalysts for methanol synthesis from a CO₂, CO, and H₂ stream under ambient pressure conditions. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4985657>]

I. INTRODUCTION

At present, the practical conversion of CO₂ in industrial processes is still limited to few cases like the synthesis of urea, salicylic acid, and polycarbonates for plastics. However, the catalytic hydrogenation of carbon dioxide is currently attracting growing attention for the clean synthesis of energy vectors and chemicals.^{1–3} Both heterogeneous catalytic conversion and electrochemical reduction are considered as promising processes.⁴ In the former case, progress toward high efficiency and selectivity is a technological quest. In particular, NiCu alloys show higher conversion rates, with respect to conventional Cu-based catalysts,⁵ for the methanol synthesis starting from CO₂.^{6–9} Limitations relate to

stability issues associated with surface segregation processes. The reaction involves direct hydrogenation of the carbon and oxygen atoms of the CO₂ molecule, but the co-presence of carbon monoxide in the gas phase is essential. Both the atomic-level mechanism involved in the hydrogenation of carbon dioxide^{9–16} and the role of Ni segregation induced by carbon monoxide^{17,18} have been recently tackled and investigated with great detail. However, a thorough description of the interaction of CO (adsorption, diffusion, and desorption processes) with the surface alloy is still missing. Concerning the reduction of carbon dioxide by means of electrochemical processes, no electrode catalyst has yet been developed that can perform this transformation with an overpotential low enough to make this reaction of applicative interest.^{4,19,20} In a recent study,⁴ it was found that protonation of adsorbed CO is the most important reaction step dictating the overpotential, thus fostering further investigation of the CO chemistry at the surface electrodes. In particular, within a volcano plot model scenario,²¹ and on the basis of a predictive theoretical approach based on Density Functional Theory (DFT),²² NiCu surfaces are found to be more active for CO reduction than other metal surfaces. In any case, it has to be mentioned that an accurate and detailed investigation of the chemistry of NiCu alloy surfaces is of particular complexity due to the role of segregation mechanisms regulating the effective Ni

^{a)} Author to whom correspondence should be addressed: vesselli@iom.cnr.it. Telephone: +39 040 375 6442. Fax: +39 040 226767.

^{b)} Present addresses: M.R.–Axpo Group, Zurich, Switzerland; S.F.–Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy; E.M.–Zernike Institute for Advanced Materials, University of Groningen, Nijenborg 4, 9747AG Groningen, The Netherlands; School of Chemistry, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia; C.D.–Elettra Sincrotrone Trieste ScpA, SS 14 km 163.5, 34149 Basovizza (Trieste), Italy; A.P.–Institute of Experimental and Applied Physics, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany.

surface concentration as a function of temperature and chemical potential. It has been recently found that kinetics plays a major role,¹⁸ together with coverage,¹⁷ geometric, and electronic effects.²³

Within the framework of this complex scenario, the present work aims at describing specific fundamental mechanisms characterizing carbon monoxide adsorption, diffusion, and desorption at a model NiCu alloy surface: an ultra-thin Ni film deposited in ultra-high vacuum (UHV) on the (110) surface of a copper single crystal. We performed temperature programmed desorption (TPD) spectroscopy and time-resolved core-level photoelectron spectroscopy (XPS) measurements, complemented by DFT *ab initio* calculations, providing atomic-level insight into the elementary CO reaction steps by means of a combined experimental and computational approach.

Adsorption of CO on the clean Cu(110) termination was thoroughly investigated in the past, finding a coverage-dependent sticking coefficient, related to the presence of a hot precursor species, as for Ni.^{24,25} Saturation is reached at a surface coverage of 0.8 ML,²⁶ with CO molecules adsorbed at on-top sites.²⁷ Two distinct (2×1) ordered structures and a compression structure form depending on the CO surface density.^{27,28} Adsorbed CO is found to be stable up to about 200 K,²⁸ while at higher temperature, desorption without dissociation occurs in UHV conditions.

On Ni(110), a stronger molecule-metal bond is established, thus yielding stable adsorption phases up to 400–450 K in UHV, again without CO decomposition.^{29,30} At saturation (1 ML), a (2×1) ordered structure is formed, with CO adsorbed in short bridge positions, the molecular axis being slightly tilted from the normal to the surface.³¹ At lower coverage, a peculiar site competition is observed, depending on both the adsorbate surface density and temperature, yielding occupation of both on-top and bridge sites, the latter being the most stable.¹¹ Interestingly, at room temperature, no significant differences are observed for CO adsorption on Ni(110) from UHV up to ambient pressure, while above room temperature, high pressure CO induces restructuring of the Ni substrate, where strained (111) microfacets are formed.^{15,16,32}

The interaction of carbon monoxide with the bimetallic Ni/Cu(110) surface was already investigated by means of a combined experimental and theoretical approach based on TPD spectroscopy and DFT *ab initio* calculations.^{33–35} Distinct desorption peaks (β_i with $i = 1, 2, 3$) were identified at intermediate temperature between the features corresponding to CO desorption from pure Cu (α_1 —200 K) and from pure Ni (α —450 K).^{33,34} The β_i states were associated with CO adsorption geometries in which the molecule is bound to “mixed” sites, where both Ni and Cu atoms are present in the surface and/or subsurface layers. The presence of these configurations was related to the Ni layer preparation recipes, which resulted in Ni–Cu intermixing.

In the present study, we adopted a Ni deposition recipe that prevents Cu segregation to the top layer,¹⁸ allowing for the growth of pure Ni ad-islands in the sub-monolayer coverage regime, followed by a layer-by-layer growth process at higher coverage. In this way, we show that the CO adsorption energy can be continuously tuned by controlling the Ni adlayer

thickness and explain this behavior on the basis of a complex interplay among surface diffusion, site change mechanisms, and coverage effects.

II. METHODS

A. Experimental methods

The Cu(110) sample was cleaned under UHV by standard sputtering and annealing recipes.¹⁸ Ni was evaporated on the substrate kept at 170 K from a pure, resistively heated Ni filament. Subsequent annealing of the surface up to 270 K yielded good (1×1) ad-layer ordering without inducing Ni–Cu mixing (see discussion of TPD data in Sec. III). The deposition rate was calibrated by means of a quartz crystal microbalance, adopting a flux of 0.5 ML/min. TPD measurements were performed with a heating rate of 1.5 K/s in a multipurpose UHV setup with a base pressure of 5×10^{-11} mbar. Desorption energies, ΔE , were obtained from TPD data by the numerical solution of first-order desorption rate equations at $T = T_{\text{max}}$, assuming a standard pre-exponential factor of 10^{13} s^{-1} .³⁶ The latter crude approximation may bias the quantitative results but not the trends. Core-level photoelectron spectroscopy experiments were performed at the SuperESCA beamline of Elettra, the 3rd generation synchrotron radiation source in Trieste (Italy).³⁷ A Phoibos (SPECS GmbH) hemispherical electron energy analyzer equipped with an in-house-developed detector was used to collect the spectra at normal emission, yielding an overall energy resolution of 50 meV³⁸ and a time resolution of about 10 s in the time resolved experiments. A heating rate of 0.15 K/s was used for the time resolved desorption experiments. C and O 1s spectral regions were routinely checked to ensure sample cleanliness before and after Ni evaporation. C and O 1s intensities were obtained from the experimental spectra by evaluating the areas of the adiabatic peak and its corresponding satellites for each non-equivalent CO species. Photon energies of 650, 410, and 200 eV were used to excite O, C 1s, and Cu and Ni 3p core levels, respectively. After subtraction of a Shirley background,^{39,40} spectra were best-fitted using a Doniach-Sunjic function⁴¹ and convoluted with a Gaussian envelope in order to account for experimental resolution, inhomogeneity, and temperature induced broadening. All core level binding energies were calibrated with respect to the Fermi level. The CO surface coverage was calibrated assuming saturation values on Ni(110) and Cu(110) equal to $\vartheta_{\text{CO}}^{\text{sat}}(\text{Ni}) = 1.0 \text{ ML}$ and $\vartheta_{\text{CO}}^{\text{sat}}(\text{Cu}) = 0.8 \text{ ML}$, respectively, in agreement with the literature.^{24,27}

B. Theoretical methods

Calculations were performed within the framework of DFT in the spin-polarized generalized gradient approximation using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.⁴² Dispersive forces with the DFT-D approach are included,⁴³ keeping the same computational scheme of our previous work.¹⁸ We used the plane-wave-based PWSCF codes of the QUANTUM-ESPRESSO (QE) distribution,⁴⁴ with publicly available ultrasoft pseudopotentials. Slab geometries with a seven layer metallic slab plus a vacuum space of about 15 Å, i.e., about twice the slab

thickness, were used to simulate the Ni/Cu surface. The in-plane dimension of the simulation cells depends on the CO coverage: in some cases, it corresponds to (3×2) Ni(110) surface unit cells, which allows us to describe a CO coverage as low as 0.17 ML or higher and in other cases to (2×2) . Other technical details (energy cutoff, thresholds, smearing, and k-point set for Brillouin-zone sampling) are similar to those previously described.^{17,18} In general, a simulation cell contains n CO adsorbed molecules and we calculate the adsorption energy E_{ads} of the first desorbing CO molecule, defined as the total energy difference between the cell with n CO molecules and the cell with $(n - 1)$ CO molecules plus the total energy of the free CO molecule.³⁴ Thus, the adsorption energy can vary according to the specific site, apart from the case of $\theta_{\text{CO}} = 0.25$ ML, where we use simulation cells containing only one adsorbed CO molecule. With this definition, the adsorption energy is negative for stable adsorption configurations. In the case of non-activated adsorption and desorption processes, as for CO, the absolute values of adsorption (calculated by DFT) and desorption (as obtained from TPD) energies coincide.

III. RESULTS AND DISCUSSION

As a first approach, we performed TPD experiments after exposure of the Ni/Cu(110) termination at liquid nitrogen (LN_2) temperature to different CO doses for different initial Ni coverage values. In Fig. 1, the TPD spectra ($m/e = 28$ signal) are reported as a function of the CO exposure (bottom panel) and the Ni layer thickness (top panel). In agreement with the literature,^{33,34} a single sharp desorption peak (α_1) is observed at about 190 K for CO desorption from the pure Cu(110) surface (top panel, 0 ML). By increasing the thickness of the Ni adlayer up to 4 ML and still in agreement with previous work,³⁴ we observe a continuous shift of the desorption peak (α) toward higher temperatures. The discrete intermediate desorption peaks in the 200–350 K range (β_i), reported in previous works,^{33,34} are not observed, thus excluding surface alloying between Ni and Cu. Instead, a large shoulder is observed at lower temperature with respect to the main desorption peak, in analogy to TPD spectra of CO from the Ni(110) surface.⁴⁵ In the bottom panel of Fig. 1, the TPD spectra show a dependence of the CO desorption energy also on the CO coverage.

In order to extract the CO desorption energies from the position of the TPD peak maxima, we differentiated the rate equation describing first order desorption (1) and solved numerically for ΔE at $T = T_{\text{max}}$ and $\frac{d^2\theta_{\text{CO}}}{dt^2} = 0$ with $\beta = \frac{dT}{dt} = 1.5 \text{ K/s}$ and $\nu_0 = 10^{13} \text{ s}^{-1}$,

$$\frac{d\theta_{\text{CO}}}{dt} = -\nu_0\theta_{\text{CO}}e^{-\frac{\Delta E}{kT}}. \quad (1)$$

In Fig. 2, we report the resulting CO desorption energies as a function of the Ni layer thickness for low and high initial CO coverage values. The corresponding, raw TPD spectra are reported in the [supplementary material](#). A monotone behavior is clearly observed, showing the possibility to tune the average CO bond strength to the surface with continuity in the 0.98–1.15 eV range. The actual consequences of this effect will be discussed later in this section.

FIG. 1. TPD spectra of the Cu(110) sample with different Ni coverages at LN_2 temperature following exposure to different doses of carbon monoxide; bottom panel: different CO doses on 1 ML Ni/Cu(110); top panel: 4 L CO on different Ni coverages on Cu(110). Dashed lines are drawn to guide the eye in order to highlight the peak displacement as a function of the CO (bottom panel) and Ni (top panel) coverage.

FIG. 2. Desorption energy of CO to the Ni/Cu(110) surface as a function of the Ni coverage from 0 to 16 ML. CO was dosed at LN_2 temperature. Values are obtained from the TPD spectra upon numerical solution of the first order rate equation for desorption at the TPD peak maximum. Two sets of experiments are reported, corresponding to a CO initial coverage of 0.1 (grey curve) and 1.0 (black curve) ML, respectively. Dashed lines are drawn to guide the eye.

We will now focus on the atomic-level mechanisms. To investigate this issue, we performed a series of high energy resolution XPS measurements with synchrotron light, following in real time the evolution of the carbon and oxygen 1s, and of the Ni and Cu 3p core levels in separate uptake and annealing experiments. After exposing the clean or the Ni-covered Cu(110) surface to CO at LN₂ temperature up to saturation (Fig. 3), the sample was heated at a constant rate in order to induce CO desorption (Fig. 4). For both Figs. 3 and 4, the 2D maps report the XPS signal (color scale) as a function of the binding energy (horizontal axis) for the measured core levels and as a function of the CO dose (vertical axis, Fig. 3) or the annealing temperature (vertical axis,

FIG. 3. In the top panels [(a)-(c)], selected XPS spectra are reported (c), together with the best fit and deconvolution for the O (a) and C (b) 1s core levels; adiabatic peaks are color filled, while satellites' contributions are represented by the black line. In the bottom part of the figure, images obtained from XPS spectra of O 1s, C 1s, Ni and Cu 3p core levels (columns) are reported: the signal intensity (color scale) is plotted as a function of the binding energy (horizontal axis) and the exposure (vertical axis) during the CO uptake at LN₂. The same color scale is adopted as in (c). The experiments were repeated for each panel (the initial Ni coverage values are indicated for each sequence on the right).

FIG. 4. Images obtained from XPS spectra of O 1s, C 1s, Ni and Cu 3p core levels (columns): the signal intensity (color scale) is plotted as a function of the binding energy (horizontal axis) and the temperature (left axis) during the linear annealing. The experiments were repeated for each panel (the initial Ni coverage values are indicated for each sequence on the right).

Fig. 4). Each sequence corresponds to a different sample preparation.

Concerning the Cu and Ni 3p signals, it has to be observed that no surface core level shifted component could be resolved due to the large intrinsic linewidth of the core levels. During the CO uptake, a shift of the Ni 3p peaks towards higher binding energies was observed (Fig. 3), accompanied by a decrease of the signal intensity. The same trend was observed also for the Cu 3p components for Ni coverage lower than 1 ML. Selected Ni and Cu core level spectra are reported in the top panel of Fig. 3. Upon annealing and thus desorbing CO (Fig. 4), both binding energy positions and intensities of the Cu and Ni features were restored to the initial values of the as-prepared surface prior to the CO uptake, thus indicating that no segregation occurred during the process.^{17,18}

The analysis of the C and O 1s regions deserves a dedicated discussion. Indeed, the spectroscopic lineshape of C and O 1s core levels of CO adsorbed on Ni and Cu surfaces is quite complex, as reported in the literature.^{17,46,47} For adsorbed CO, when a core electron is ionized, a previously unoccupied valence orbital in the molecule is pulled down below the Fermi energy by the attractive core-hole potential.^{46,47} The different time scales of the photo-ionization and relaxation phenomena make the wave function of the remaining electrons not an eigenstate of the final-state Hamiltonian, and the filling of this level increases the relaxation energy, thus giving origin

to distinct satellites.⁴⁶ To the purpose of the present discussion, we clarify that the evolution of the coverage of the different CO species was obtained by integrating the area under the whole associated XPS features, thus considering both the adiabatic and satellite peaks, whose shape was extracted by analyzing the spectra obtained upon CO adsorption on Ni multilayers and the bare Cu sample, respectively. For CO adsorption on Cu, two main satellite components were identified for the C (O) 1s core levels, shifted by about +2.5 and +8.5 eV (+3.0 and +7.5 eV) towards higher binding energies with respect to the adiabatic feature. On Ni, a single satellite was observed for the O 1s component at +6.5 eV from the main peak, while two features were observed in the C 1s spectra at +2.5 and +5.5 eV, respectively, in agreement with the literature.⁴⁶ Selected core level spectra are reported in the top panels of Fig. 3, together with the best fit and deconvolution for the C and O 1s signals. The spectra in the intermediate Ni coverage range (between 0 and 1 ML) could be properly fitted by a linear combination of the two profiles, allowing for variation of the relative intensities and a shift of the satellite components. Further details about the data analysis can be found in our previous work.¹⁷

From the C and O 1s regions, monitored upon CO adsorption and desorption for different Ni surface coverage values, three non-equivalent CO adsorbed species could be unambiguously identified in the XPS spectra. According to the observed core level binding energies, we could distinguish C and O 1s components originating from CO molecules adsorbed at on-top Cu sites (285.9 and 532.8 eV), at on-top Ni sites (285.8 and 532.4 eV), and at short-bridge Ni sites (285.4 and 531.0 eV).¹⁷ An interesting insight into the behavior of this system can be obtained by plotting the distinct core level intensities as a function of the CO dose and sample temperature. This analysis is shown in Fig. 5, where data from the O 1s signal are considered since the larger binding energy separation between adjacent non-equivalent components minimizes the cross talk in the peak-fitting procedure. In the top half of the figure, the coverage of CO adsorbed on Ni [panels (a) and (c)] and Cu [panels (b) and (d)] is plotted as a function of the CO exposure [(a) and (b)] and of the subsequent annealing temperature [(c) and (d)]. The local CO coverage was calculated on Ni and Cu islands separately, by normalizing the corresponding CO coverage to the relative Ni and Cu surface densities, and taking into account the CO saturation coverage values for the corresponding bare surfaces, i.e., 1.0 and 0.8 ML for Ni and Cu(110), respectively.¹⁷ Different colors correspond to different initial Ni coverage values from 0.2 to 1.8 ML. In the uptake part of the figure (left), it is evident that a complex mechanism governs CO adsorption on the bimetallic surface. Convex and concave initial uptake profiles are indeed observed for CO adsorption on the Ni [panel (a)] and Cu [panel (b)] islands, respectively. Recently,¹⁷ this behavior was attributed to the interplay between two phenomena governing CO adsorption: indeed, on both Ni and Cu surfaces, the presence of a hot precursor introduces a peculiar coverage dependence of the CO sticking coefficient, which can be modeled according to King and Wells.^{25,48,49} In addition, the concavity of the initial CO uptake profile for Cu [panel (b)] can only be explained by considering a strong contribution of CO diffusion from Cu

FIG. 5. Exposure (left panels) and temperature (right panels) evolution of the concentration of CO species at the Ni/Cu(110) surface for different Ni loadings (colors). Data are obtained from areas below O 1s features associated with the different adspecies. In the top part of the figure, data of the CO uptake are shown, indicating CO coverage at Ni [panel (a)] and Cu [panel (b)] sites, followed by surface annealing [panels (c) and (d), respectively]. In the bottom part of the figure, the relative abundance of CO species adsorbed at on-top Ni sites is reported for both uptake [panel (e)] and annealing experiments [panel (f)].

to Ni ad-islands,¹⁷ where a larger molecule-surface adsorption energy can be achieved. With concern to the dependence of the coverage of CO species on the annealing temperature (right part of Fig. 5), CO desorption from Cu sites in the 150–200 K range [panel (d)] competes with CO migration to Ni ad-islands, where the local CO coverage increases up to 230 K [panel (c)] yielding saturation (locally 1 ML CO) for small Ni ad-islands (Ni coverage <1 ML). Above 340 K, CO desorbs also from the Ni-covered parts of the surface [panel (c)]. Interestingly, in analogy to TPD data corresponding to Ni coverage values above 1 ML (Figs. 1 and 2), a continuous shift [black arrow in panel (c)] of the temperature corresponding to the maximum desorption rate is observed for increasing Ni coverage also in the sub-monolayer regime. At this point, we can further drill into the information contained in the core level spectra by separating the contributions from CO molecules adsorbed in on-top or bridge sites at the Ni ad-islands [bottom part of Fig. 5, panels (e) and (f)]. It is found that during the uptake, the two non-equivalent adsorption sites are both populated [panel (e)], with increasing preference for the bridge site for growing Ni coverage. However, another interesting behavior is observed when heating the surface: in parallel with the progressive migration of CO towards Ni ad-islands [panel (c)], a competing site change process takes place between on-top and bridge Ni configurations above 200 K [panel (f)], yielding oscillations in the relative population of the two sites. The dashed line depicted in panel (f) of Fig. 5 indicates the temperature of the maximum CO desorption rate. For low Ni coverage (yellow and red lines), CO mainly populates on-top sites upon desorption, while for increasing thickness of the Ni film up to 1.8 ML, progressive population of the bridge sites occurs

FIG. 6. Relative abundance of CO bridge species as a function of the initial Ni coverage at the end of the uptake at LN_2 temperature (dashed lines) and at the maximum of the desorption rate (continuous lines).

at high temperatures. This provides a clear explanation for the continuous temperature shift observed in the TPD peaks, which can be ascribed to a progressive increase in the CO adsorption energy: indeed, the relative population of the energetically non-equivalent on-top and bridge sites changes with Ni coverage and consequently their contribution to the desorption peak. This occurs since both local Ni concentration and CO surface coverage affect the relative stability of bridge and on-top sites, yielding consequent Boltzmann-dependent populations if equilibrium is assumed throughout the process.

The relative population of the two sites is better highlighted in Fig. 6, where the population of the bridge sites is plotted as a function of Ni coverage at the end of the CO uptake at LN_2 temperature (dashed line) and at the maximum of the desorption rate (continuous line). These results confirm and further explain the observations reported by means of high-resolution electron energy loss spectroscopy on the CO/Ni/Cu(100) system.⁵⁰ Indeed, a progressive shift of the C–O stretching frequency and a variation of the relative

TABLE I. Calculated CO adsorption energies for on-top and short bridge sites for the three systems of interest, using a (3×2) unit cell with one adsorbed CO molecule (CO coverage: 0.17 ML).

Site	Cu(110)	1 ML Ni/Cu(110)	Ni(110)
Short bridge	–1.04	–2.41	–2.05
On-top	–1.02	–1.96	–1.90

population of on-top and bridge sites were found as a function of the Ni layer thickness and were ascribed to strain effects.

On the basis of the results obtained from the experiments, we have shown that the CO average adsorption energy can be continuously tuned by varying the Ni coverage. The effect is associated with the competition between energetically similar adsorption sites and ascribed to the contribution of coverage effects.

To better unravel the origin of the experimental observations, we performed an extensive set of DFT *ab initio* calculations. The results are reported in Tables I and II and in Fig. 7. Remarkably, at low CO coverage (0.17 ML), strong over-binding to the 1 ML Ni/Cu(110) is expected for both CO adsorption sites (on-top and short bridge) as evident from Table I and panel (b) of Fig. 7, in analogy to the case of carbon dioxide adsorption on the same system.¹⁷ However, this is not observed experimentally in the TPD data [Fig. 7, panel (a)]. Indeed, at higher CO coverage, the effect is canceled by the lateral repulsion between the adsorbed CO molecules [Fig. 7, panel (c)]. In panel (d), the dependence of the CO adsorption energy on the CO coverage is reported. For $\theta_{\text{CO}} \leq 0.25$ ML, only the on-top adsorption site is considered. Multiple markers for $\theta_{\text{CO}} = 0.50$ and 0.75 ML correspond to different possible sites for the desorption of the first molecule contained in the cell. An example is reported in the inset for $\theta_{\text{CO}} = 0.75$ ML. The lines connect average values. The most relevant result is the crossing of the black (1 ML Ni/Cu) and cyan (Ni) lines, indicating that over-binding occurs only for CO coverage values below 0.5 ML. DFT systematically overestimates the CO adsorption energy by about 0.3 eV. Nevertheless,

TABLE II. Calculated coverage dependence of the CO adsorption energy at the on-top site using a (2×2) unit cell; for $\theta_{\text{CO}} = 0.25$ ML, the cell contains only one molecule; for $\theta_{\text{CO}} = 0.50$ and 0.75 ML, the cell contains 2 and 3 CO molecules, respectively, and adsorption energies are reported for different possible initial configurations and first desorption sites. For instance, with reference to the inset of Fig. 7, for $\theta_{\text{CO}} = 0.50$ ML, the possible initial configurations are $t1 + t2$, $t1 + t3$, or $t2 + t3$, where first desorption can occur from one of the two (equivalent) occupied sites; for $\theta_{\text{CO}} = 0.75$ ML, the only possible initial configuration is $t1 + t2 + t3$, and first desorption can occur from $t1$, $t2$, or $t3$ non-equivalent sites.

	0.25 ML	0.50 ML			0.75 ML			1.00 ML
		$t2 + t3$	$t1 + t3$	$t1 + t2$	$t1$	$t2$	$t3$	
Cu(110)	–1.07	–0.86	–1.07	–1.01	–1.02	–0.81	–0.87	–0.82
1 ML Ni/Cu(110)	–2.03	–1.73	–1.97	–1.94	–1.30	–1.06	–1.09	^a
Ni(110)	–1.80	–1.59	–1.97	–1.95	–1.87	–1.49	–1.50	–1.45

^aIn this case, the on-top configuration is unstable and the equilibrium configuration corresponds to CO molecules adsorbed at short-bridge sites.

FIG. 7. Experimental (a) and computational results [(b)-(d)] for the CO adsorption energy at Cu(110), 1 ML Ni/Cu(110), and Ni(110) surfaces: (a) experimental desorption energies obtained from TPD data; (b) site dependence of the DFT CO adsorption energy at small CO coverage (1/6 ML) where over-binding is observed for both on-top (diamonds) and short bridge (circles) adsorption sites; (c) DFT CO adsorption energy at high CO coverage (2/3 ML) for the on-top site, which is the most populated at the maximum of the observed desorption rate; (d) DFT coverage dependence of the CO adsorption energy for on-top sites where the CO adsorption energy suffers a strong coverage influence, yielding over-binding for 1 ML Ni/Cu(110) with respect to the Ni(110) surface below 0.5 ML CO; the lines indicate average values among multiple possible desorption configurations (dots); the ball model (top view) shows the 3 distinct on-top sites in the (2×2) simulation cell for a CO coverage of 0.50 and 0.75 ML [here for 1 ML Ni/Cu(110)], but analogous models have been considered for Ni(110) and Cu(110): the spreading of the calculated adsorption energy is due to its dependence on the specific site. See also the caption of Table II.

relative values are in the correct order: for instance, at 1 ML coverage, the values predicted by DFT are -0.82 and -1.45 eV for bare Cu(110) and Ni(110), respectively (Table II), compared with the corresponding experimental values of -0.52 and -1.12 eV.

We have therefore shown experimentally and explained by means of *ab initio* methods that it is possible to tune the

CO bond strength to the model electrode surface with continuity in the 0.98 – 1.15 eV range (i.e., in a $\pm 10\%$ span) by varying the Ni content from 1 to 15 ML. By combining the results obtained from *in situ* time resolved XPS measurements with the quantitative output of DFT calculations, we have shown that the observed behavior is related to a complex interplay among diffusion, site change, and coverage effects. As already observed in the previous literature, where a first attempt to tune the CO adsorption energy on this surface was performed,³⁴ this is of paramount importance for tailoring the surface catalytic activity and selectivity. As mentioned above, carbon monoxide is both a fundamental reactant and intermediate in the (electro-)reduction reaction for the synthesis of fuels and valuable chemicals starting from carbon dioxide. In some cases, CO has been demonstrated to be the key molecule, its hydrogenation barrier being the rate limiting step of the reaction.⁴ Conversely, CO is the main carbon dioxide decomposition product at the NiCu surface.¹⁷ The reactivity and selectivity depend therefore on the CO and CO₂ reaction barriers, which are linearly dependent on the molecules' adsorption energy to the surface in a Brønsted-Evans-Polanyi scenario,^{22,51} which has been observed to hold also in the case of a NiCu adsorption system.²² Within the framework of this scenario, the capability of tuning the carbon monoxide adsorption energy automatically translates into the possibility of controlling the energy of the transition state, i.e., the reaction barrier, thus putting in evidence the relevance of this result. Moreover, in a Boltzmann picture, energies appear inside the exponential terms of the rate equations that describe the surface reactions. Therefore, the ability to control the CO adsorption energy in the 0.98 – 1.15 eV range yields potential tuning capability of the expected rates within a range of more than two orders of magnitude (340 times) at 350 K and more than one order of magnitude (40 times) at 550 K. This estimate is in remarkable agreement with previous observations about the carbon dioxide reduction to methanol ($\text{CO}_2 + \text{CO} + \text{H}_2$ stream) on a model Ni/Cu(100) catalyst at ambient pressure conditions at 543 K, where Ni doping in the 0–1 ML range was found to account for an increase in the CO₂ turnover frequency.^{6–8}

IV. CONCLUSIONS

The adsorption, diffusion, and desorption behavior of carbon monoxide on the bimetallic Ni/Cu(110) surface was studied by means of a combination of experimental and theoretical techniques. It was found that tuning of the CO adsorption energy and consequently the molecule's reactivity is possible with continuity. This is achieved by means of a fine control of the Ni concentration and growth at the Cu surface. The CO adsorption energy was controlled within a $\pm 10\%$ range, corresponding to expected changes in the reaction rates, up to more than two orders of magnitude, in agreement with previous observations under realistic reaction conditions.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the full set of raw TPD data.

ACKNOWLEDGMENTS

The work was supported by the Italian MIUR through the project Futuro in Ricerca FIRB 2010 No. RBFR10J4H7. E.V. also acknowledges financial support from Fondazione Kathleen Foreman Casali, Beneficentia Stiftung, and Consorzio per l'Incremento degli Studi e delle Ricerche dei Dipartimenti di Fisica dell'Università degli Studi di Trieste. E.V., C.D., and G.C. acknowledge support from Università degli Studi di Trieste through the Project No. FRA 2012. C.A. and C.D. acknowledge support from Italian MIUR through Project PRIN 2010-2011 No. 2010N3T9M4 and Futuro in Ricerca FIRB 2010 No. RBFR10FQBL, respectively. Computational resources have been obtained partly through Italian SuperComputing Resource Allocation (ISCR) grants of the Consorzio Interuniversitario CINECA, partly within the agreement between the University of Trieste and CINECA and partly under the HPC-EUROPA2 project (Project No. 583) with the support of the European Commission Capacities Area—Research Infrastructures Initiative. We are grateful to S. Lizzit and A. Baraldi for their contribution to the experiments.

- ¹W. Wang, S. Wang, X. Ma, and J. Gong, *Chem. Soc. Rev.* **40**, 3703 (2011).
- ²G. Centi and S. Perathoner, *Catal. Today* **148**, 191 (2009).
- ³C. Song, *Catal. Today* **115**, 2 (2006).
- ⁴A. A. Peterson and J. K. Nørskov, *J. Phys. Chem. Lett.* **3**, 251 (2012).
- ⁵M. Behrens, F. Studt, I. Kasatkin, S. Kühn, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Knip, M. Tovar, R. W. Fischer, J. K. Nørskov, and R. Schlögl, *Science* **336**, 893 (2012).
- ⁶J. Nerlov, S. Sckerl, J. Wambach, and I. Chorkendorff, *Appl. Catal., A* **191**, 97 (2000).
- ⁷J. Nerlov and I. Chorkendorff, *Catal. Lett.* **54**, 171 (1998).
- ⁸J. Nerlov and I. Chorkendorff, *J. Catal.* **181**, 271 (1999).
- ⁹Y. Yang, M. G. White, and P. Liu, *J. Phys. Chem. C* **116**, 248 (2012).
- ¹⁰E. Vesselli, L. De Rogatis, X. Ding, A. Baraldi, L. Savio, L. Vattuone, M. Rocca, P. Fornasiero, M. Peressi, A. Baldereschi, R. Rosei, and G. Comelli, *J. Am. Chem. Soc.* **130**, 11417 (2008).
- ¹¹X. Ding, L. De Rogatis, E. Vesselli, A. Baraldi, G. Comelli, R. Rosei, L. Savio, L. Vattuone, M. Rocca, P. Fornasiero, F. Ancilotto, A. Baldereschi, and M. Peressi, *Phys. Rev. B* **76**, 195425 (2007).
- ¹²C. Dri, A. Peronio, E. Vesselli, C. Africh, M. Rizzi, A. Baldereschi, M. Peressi, and G. Comelli, *Phys. Rev. B* **82**, 165403 (2010).
- ¹³E. Vesselli, M. Rizzi, L. De Rogatis, X. Ding, A. Baraldi, G. Comelli, L. Savio, L. Vattuone, M. Rocca, P. Fornasiero, A. Baldereschi, and M. Peressi, *J. Phys. Chem. Lett.* **1**, 402 (2010).
- ¹⁴C. Liu, T. R. Cundari, and A. K. Wilson, *J. Phys. Chem. C* **116**, 5681 (2012).
- ¹⁵E. Monachino, M. Greiner, A. Knop-Gericke, R. Schlögl, C. Dri, E. Vesselli, and G. Comelli, *J. Phys. Chem. Lett.* **5**, 1929 (2014).
- ¹⁶M. Roiaz, E. Monachino, C. Dri, M. Greiner, A. Knop-Gericke, R. Schlögl, G. Comelli, and E. Vesselli, *J. Am. Chem. Soc.* **138**, 4146 (2016).
- ¹⁷E. Vesselli, E. Monachino, M. Rizzi, S. Furlan, X. Duan, C. Dri, A. Peronio, C. Africh, P. Lacovig, A. Baldereschi, G. Comelli, and M. Peressi, *ACS Catal.* **3**, 1555 (2013).
- ¹⁸M. Rizzi, S. Furlan, M. Peressi, A. Baldereschi, C. Dri, A. Peronio, C. Africh, P. Lacovig, E. Vesselli, and G. Comelli, *J. Am. Chem. Soc.* **134**, 16827 (2012).
- ¹⁹X. Nie, M. R. Esopi, M. J. Janik, and A. Asthagiri, *Angew. Chem., Int. Ed.* **52**, 2459 (2013).
- ²⁰M. Bevilacqua, J. Filippi, A. Lavacchi, A. Marchionni, H. A. Miller, W. Oberhauser, E. Vesselli, and F. Vizza, *Energy Technol.* **2**, 522 (2014).
- ²¹F. Studt, F. Abild-Pedersen, Q. Wu, A. D. Jensen, B. Temel, J. D. Grunwaldt, and J. K. Nørskov, *J. Catal.* **293**, 51 (2012).
- ²²L. Gan, R. Tian, X. Yang, H. Lu, and Y. Zhao, *J. Phys. Chem. C* **116**, 745 (2012).
- ²³G. Held, *Appl. Phys. A: Mater. Sci. Process.* **76**, 689 (2003).
- ²⁴M. Kunat, C. Boas, T. Becker, U. Burghaus, and C. Wöll, *Surf. Sci.* **474**, 114 (2001).
- ²⁵S. Kneitz, J. Gemeinhardt, and H.-P. Steinrück, *Surf. Sci.* **440**, 307 (1999).
- ²⁶M. Christiansen, E. V. Thomsen, and J. Onsgaard, *Surf. Sci.* **261**, 179 (1992).
- ²⁷P. Hofmann, K.-M. Schindler, S. Bao, V. Fritzsche, a. M. Bradshaw, and D. P. Woodruff, *Surf. Sci.* **337**, 169 (1995).
- ²⁸C. Harendt, J. Goschnick, and W. Hirschwald, *Surf. Sci.* **152–153**, 453 (1985).
- ²⁹R. J. Behm, G. Ertl, and V. Penka, *Surf. Sci.* **160**, 387 (1985).
- ³⁰B. A. Gurney and W. Ho, *J. Vac. Sci. Technol., A* **3**, 1541 (1985).
- ³¹D. Woodruff, *Surf. Sci. Rep.* **62**, 1 (2007).
- ³²K. Peters, C. Walker, P. Steadman, O. Robach, H. Isern, and S. Ferrer, *Phys. Rev. Lett.* **86**, 5325 (2001).
- ³³E. Demirci and A. Winkler, *Surf. Sci.* **604**, 609 (2010).
- ³⁴E. Demirci, C. Carbogno, A. Groß, and A. Winkler, *Phys. Rev. B* **80**, 85421 (2009).
- ³⁵X. Cui and X.-M. Duan, *Comput. Mater. Sci.* **104**, 40 (2015).
- ³⁶P. A. Redhead, *Vacuum* **12**, 203 (1962).
- ³⁷A. Baraldi, G. Comelli, S. Lizzit, M. Kiskinova, and G. Paolucci, *Surf. Sci. Rep.* **49**, 169 (2003).
- ³⁸J. Li, Y. Wang, D. Curcio, S. Lizzit, A. Baraldi, L. Kantorovich, and A. Floris, *J. Phys. Chem. C* **121**, 7967 (2017).
- ³⁹D. Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- ⁴⁰A. Proctor and P. M. A. Sherwood, *Anal. Chem.* **54**, 13 (1982).
- ⁴¹S. Doniach and M. Sunjic, *J. Phys. C* **3**, 285 (1970).
- ⁴²J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁴³S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- ⁴⁴P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Mater.* **21**, 395502 (2009).
- ⁴⁵C. S. Feigerle, S. R. Desai, and S. H. Overbury, *J. Chem. Phys.* **93**, 787 (1990).
- ⁴⁶A. Nilsson and N. Mårtensson, *Phys. Rev. B* **40**, 10249 (1989).
- ⁴⁷W. Wurth, D. Coulman, A. Puschmann, D. Menzel, and E. Umbach, *Phys. Rev. B* **41**, 12933 (1990).
- ⁴⁸D. A. King and M. G. Wells, *Surf. Sci.* **29**, 454 (1972).
- ⁴⁹K. Christmann, O. Schöber, and G. Ertl, *J. Chem. Phys.* **60**, 4719 (1974).
- ⁵⁰E.-K. Whang, J. Oh, S.-K. Kim, J.-S. Kim, and G. Lee, *Phys. Rev. B* **63**, 075401 (2001).
- ⁵¹D. Loffreda, F. Delbecq, F. Vigné, and P. Sautet, *Angew. Chem. Int. Ed.* **48**, 8978 (2009).