Atomic Exchange between CO Molecules Coadsorbed with Potassium on Ni(111)

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It is shown that the presence of potassium on a Ni(111) surface induces atom exchange between adsorbed CO molecules. The temperature dependence of the metastable quenching spectrum indicates that the exchange process might be concerted rather than a dissociation followed by atom recombination with CO desorption.

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Recent high-pressure studies[1] of the methanation reaction have shown that the catalytic activity of Ni single-crystal surfaces is comparable to that of supported Ni catalysts. The kinetic studies suggest[1b] that CO dissociation is the first reaction step. Therefore one would like to be able to study this simple step on a well characterized single-crystal surface under UHV conditions of cleanliness. Unfortunately, in an UHV environment, CO desorbs from all single-crystal[2] Ni surfaces before the surface becomes hot enough to cause dissociation. In this Letter we report the first direct experimental evidence that CO can be thermally dissociated in UHV, if it is adsorbed on a Ni(111) surface covered with moderate amounts of K. This suggests that the main role of potassium as a methanation promoter[3] might be to increase the CO binding energy to the surface and facilitate its dissociation.

The observations reported here add to the mounting evidence that the presence of small amounts of potassium on a transition-metal surface can have substantial effects on the properties of chemisorbed CO: It causes a substantial increase of its desorption energy[4]; it induces a dramatic downward shift of the CO stretch frequency[5]; it causes a shift in the 4σ binding energy and a splitting of the $1\pi+5\sigma$ ultraviolet photoelectron spectroscopy (UPS) peak for CO adsorbed on K/Fe(110)[6] and some changes for CO adsorbed on K/Pt(111).[7]

The only suggestion that CO might be dissociated on a potassium covered Ni(100) surface has been made by Kiskinova[4b] who noticed a potassium-induced change in the carbon Auger line shape. She interpreted this as an indication that atomic carbon is present on the surface. Here we present direct evidence for CO dissociation. By monitoring the CO thermal desorption spectrum of a mixture of chemisorbed $^{13}C^{16}O$ and $^{12}C^{18}O$ we find that the exchange products $^{13}C^{18}O$ and $^{12}C^{16}O$ appear if the Ni(111) surface is precovered with potassium and the coverage is in the range $0.13 \lesssim \theta_K \lesssim 0.36$ potassium atom per surface Ni atom. At lower potassium coverages the binding energy of CO to the surface is increased but the CO molecule desorbs upon heating, before it dissociates. At higher coverages potassium blocks CO adsorption sites. The metastable quenching spectrum (MQS) of the surface (CO+K)/Ni(111) at various temperatures shows that the spectrum of the molecular CO is observable until all the CO molecules are removed from the surface; there is no evidence for the existence of the atomic C and O on the surface. This suggests that the exchange process might be concerted, rather than a two-step process in which CO dissociates at some temperature, and the atoms recombine and desorb at a higher temperature.

The apparatus used in the present work has been described previously.[8c] Potassium was deposited on Ni(111) at 300 K by heating a getter wire impregnated with K. The getter emits, besides potassium, small amounts of H_2 and CO. For typical potassium deposition times of about two minutes, the emission of H_2 and CO by the getter causes the pressure in the chamber to increase to about 3×10^{-10} Torr. These small amounts of CO and H_2 do not affect the results reported here. Potassium surface coverage was calibrated by separate low-energy electron diffraction (LEED), Auger-electron spectroscopy (AES), and thermal-desorption (TD) measurements.[9] We found that a monolayer of K on Ni(111) corresponds to an atom density of $\sigma_K=6.3\times10^{14}$ atoms/cm^2. This gives a coverage $\theta_K=0.34$ potassium atom per surface Ni atom.

Metastable quenching spectroscopy has been described in detail in earlier work.[8] The surface is exposed to a low-kinetic-energy beam containing He atoms in the ground state and in the excited, metastable 2^1S state. When the excited atoms collide with the surface, their excitation energy (20.6 eV) is transferred to the adsorbate, causing electron emission from it. We measure the number of electrons $N(E_K)$ ejected with a given kinetic energy E_K. The plot of $N(E_K)$ versus E_K is the metastable quenching spectrum of the surface. As in ultraviolet photoelectron spectroscopy, the peaks in the spectrum permit the determination of the binding energies of the electron to the adsorbate. A potential advantage of MQS over UPS is its higher surface specificity since the primary electrons in MQS originate from the adsorbate only.

In Fig. 1(a) we show the thermal desorption spectrum of CO from a clean Ni(111) surface (dashed lines) and a Ni(111) surface having a low potassium coverage $\theta_K = 0.1$ K atom per surface Ni atom [corresponding to a K(252)/Ni(848) Auger peak ratio of $\gamma = 0.12$] (full lines). Both surfaces were exposed to 3.2 L [1 L (langmuir) $= 10^{-6}$ Torr sec] of a CO isotopic mixture (49% $^{13}C^{16}O$ and 51% $^{12}C^{18}O$) at a surface temperature of 90 K. In both cases there is very little desorption of $^{13}C^{18}O$ (corresponding to isotopic impurities present in the mixture used to dose the surface), which indicates that no atom exchange takes place between the adsorbed CO molecules. Since such exchange has been observed on stepped surfaces^2 we conclude that our Ni(111) surface has a low step density. The presence of a small amount of potassium increases the CO desorption activation energy, as observed in other studies.^{4}

In Fig. 1(b) we present the thermal-desorption (TD) spectrum of the same isotopic mixture for a potassium coverage $\theta_K = 0.28$ ($\gamma = 0.36$). The dashed lines represent desorption from the back of the Ni sample; if we cover the back of the sample with a thin potassium film, these peaks disappear because potassium does not absorb CO. The full lines represent the CO TD spectrum from the potassium-covered surface ($\theta_K = 0.28$, $\gamma = 0.36$) after the CO emission from the back of the sample (the dashed lines) has been removed.

The spectrum shows that at $\theta_K = 0.28$ the isotopic exchange takes place and that the CO desorption temperature goes up with θ_K [Fig. 1(a)]. A further increase of θ_K results in site blocking and CO adsorption is prevented. We also find that the presence of CO increases the surface

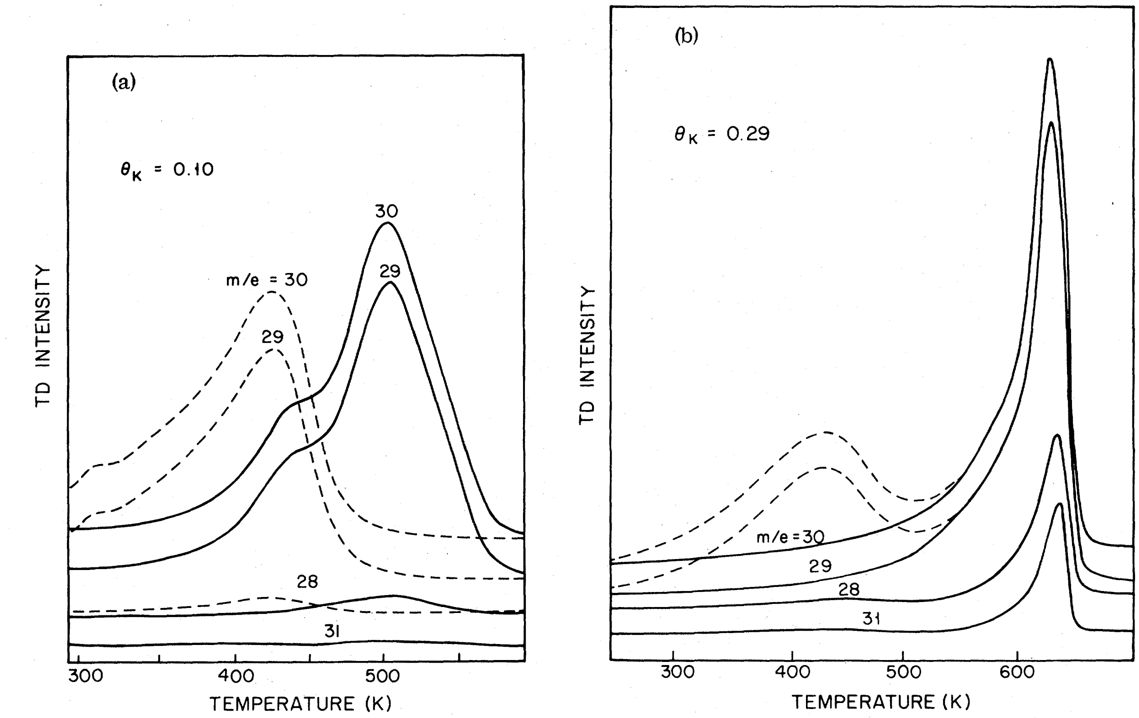

FIG. 1. CO thermal desorption spectra. (a) Broken lines: Thermal desorption spectra of CO iostopes from a clean Ni(111) surface. The surface was held at 90 K and was exposed to 3.2 L of a CO isotope mixture containing 51% $^{12}C^{18}O$ and 49% $^{13}C^{16}O$. Full lines: Thermal desorption spectra of CO from a K/Ni(111) surface having a potassium coverage of $\theta_K = 0.1$ potassium atom per surface Ni atom. (b) Full lines: Thermal desorption spectra of CO isotopes from a K/Ni(111) surface with $\theta_K = 0.29$. The initial exposure was the same as in (a). Broken lines: CO desorption from the back of the sample (clean Ni), which was discarded from the full-line spectrum.

binding energy of potassium and narrows the potassium desorption peak.[10] The desorption temperature of potassium is slightly above that of CO,[10] namely $T_K \simeq 650$ K.[10]

While the desorption spectra of the isotopic mixture show clearly the existence of atom exchange between the adsorbed molecules, they do not indicate whether CO decomposes on the surface and the atoms recombine to desorb, or whether the exchange is a one-step, concerted process; nor do they indicate at what temperature these changes take place. To answer these questions, we have monitored the temperature dependence of the metastable quenching spectrum of the surface. This was done by exposing the surface, at 90 K, to 3.2 L of CO; then the surface was heated to the temperature indicated on the graphs; that temperature was maintained for five seconds and the surface was cooled back to 90 K. The metastable quenching spectrum was taken after this thermal treatment was completed. At 90 K the spectrum shows a sharp peak (17 eV) due to emission from potassium, a small, broad peak (15 eV) associated with the $2\pi^*$ orbital of CO,[11] the ($1\pi + 5\sigma$) and the 4σ CO peaks (8 and 5 eV, respectively), and a low-energy shoulder due to secondary electrons and possibly to metastable ionization followed by ion neutralization.[8a]

A joint reading of the thermal desorption and metastable quenching spectra gives the following information concerning the changes caused by heating the (K+CO)/Ni(111) system. Thermal desorption gives no signal below 500 K. Throughout the 90–500-K temperature range, the molecular emission from the 4σ and the $1\pi + 5\sigma$ orbitals of CO is practically unchanged. The $2\pi^*$ is slightly affected, but the change is too small to warrant an interpretation. We conclude that the great majority of the adsorbed CO molecules are not dissociated in this temperature range during the five seconds of exposure to high temperature. The TD spectrum of Fig. 1(b) indicates that the CO isotopes originally deposited on the surface (masses 30 and 29) start desorbing at ~500 K, while the isotopes 28 and 31, corresponding to CO molecules formed by atomic exchange, start desorbing at ~580 K. The MQ spectra in this temperature range show well defined peaks corresponding to the 4σ and $1\pi + 5\sigma$ molecular emission. The potassium emission is much more intense and a shoulder corresponding to the ion neutralization spectrum (INS) of the bare Ni surface appears at 11 eV [the spectrum of the clean Ni surface is shown as the highest curve in Fig. 2 ($T = 1100$ K)]. These observations show that MQS is sensitive enough to detect the removal of a few CO molecules from the surface. Furthermore, the spectra show that even though some atomic exchange takes place, as shown by TDS, the majority of the CO molecules are not dissociated.

In the temperature range from 620 to 640 the TDS spectra show [Fig. 1(b)] a substantial desorption of $^{13}C^{18}O$ and $^{12}C^{16}O$, formed as a result of atomic exchange between absorbed $^{12}C^{18}O$ and $^{13}C^{16}O$. The MQ spectrum at 620 K shows a trip-

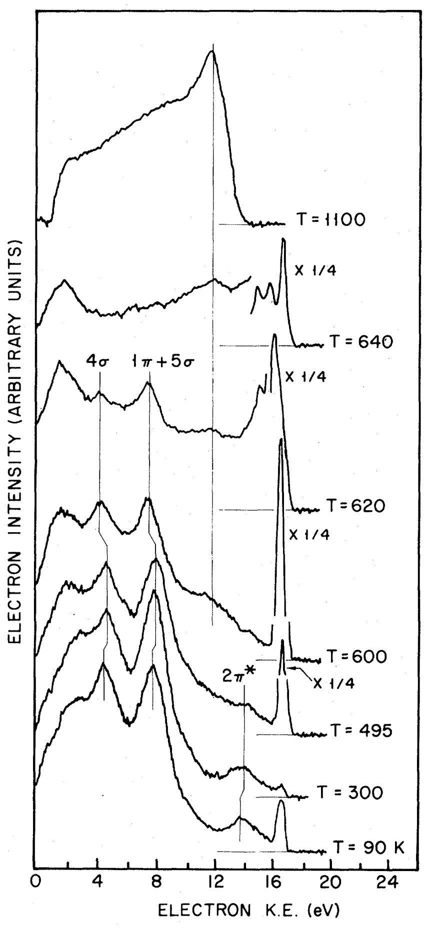

FIG. 2. He*(2^1S) metastable quenching spectra of CO adsorbed on a K/Ni(111) surface with a potassium coverage $\theta_K = 0.24$ K atom per surface Ni atom. The surface was kept at $T = 90$ K and then exposed to 3.2-L CO. The MQ spectra were taken after the following treatment was performed: The surface temperature was raised to one of the values specified on the figure; was held there for five seconds; then it was lowered to 90 K; then the MQ spectrum was taken. The energy scale in these spectra has not been corrected for changes in the work function.

let (at about 14 eV) corresponding to potassium emission,[10] a very small shoulder (at 11 eV) corresponding to emission from Ni patches, and the 4σ and $1\pi+5\sigma$ peaks characteristic of molecular CO; if the features characteristic to the molecular CO are removed, the remaining spectrum is very similar to that of the K/Ni(111) system.[10] They are very different from the MQ spectrum of Ni(111) covered with C, O, and K.[9] At 640 K there is no emission from molecular CO and the spectrum is that of the K/Ni(111) surface. At higher temperature, potassium desorbs and the spectrum becomes that of clean Ni(111) surface (upper curve in Fig. 2, labeled $T=1100$).

We emphasize the fact that we have not observed, at any of these temperatures, spectral features that can be associated with adsorbed C and O atoms. It is also possible that no C and O signals are observed in the MQ spectra because the method lacks sensitivity. However, in the case of NO on Ni(111) or on K/Ni(111), the decomposition of NO has been unambiguously detected by MQS and a spectrum characteristic of adsorbed N and O is clearly observed.[10]

We have shown that the coadsorption of CO and potassium on a Ni(111) surface has dramatic effects: The surface binding energy of both K[9] and CO is increased, adsorbed CO molecules exchange atoms at high temperature for $0.13 \leqslant \theta_K \leqslant 0.36$, and site blocking (for CO) occurs if $\theta_K \geqslant 0.36$. Even though the exchange of atoms between the adsorbed CO molecules takes place at 580 K, the great majority of the CO molecules are undissociated at 600 K and some survive at 620 K. The desorption of all CO isotopes stops at 640 K and potassium desorbs at 650 K. While the existence of the atom exchange is generally considered a proof of the dissociation of the molecule, we find no evidence in the metastable quenching spectra for the presence of dissociation products on the surface. Therefore we cannot rule out the possibility that the atomic exchange between adsorbed molecules is a concerted process. The exchange process is induced by the presence of potassium which weakens the CO bond; no exchange takes place on clean Ni(111).

These observations are consistent with the idea[12] that K causes an electron abundance at the Ni surface which facilitates back-donation to the $2\pi^*$ orbital of the chemisorbed CO. This results in a decrease in CO stretch frequency, an increase in surface binding energy, a decrease in the CO bond strength, and an increase in the $2\pi^*$ emission intensity in the metastable quenching spectrum.[11]

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