

Effects of Potassium on the Chemisorption of CO on the Mo₂C/Mo(100) Surface

L. Bugyi and F. Solymosi*

Institute of Solid State and Radiochemistry, University of Szeged, Reaction Kinetics Research Group of the Hungarian Academy of Sciences,[†] P.O. Box 168, H-6701 Szeged, Hungary

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The interaction of CO with K-free and K-covered Mo₂C/Mo(100) surfaces has been investigated by HREELS, AES, and TPD. CO adsorbed molecularly on the clean Mo₂C/Mo(100) surface at 140 K. A part of the adsorbed CO desorbed from the saturated adlayer with $T_p = 330$ K, which was accompanied by dissociation of the molecule at 300–350 K. The C and O adatoms formed recombined at higher temperatures, giving a CO desorption peak at 960 K. Preadsorbed potassium at intermediate coverages ($\Theta_K = 0.5$ – 0.8 ML) led to a considerable weakening of the C–O bond even at 140 K, as evidenced by the HREELS feature at 1320 – 1375 cm⁻¹. The appearance of this loss suggested a short-range interaction, while the development of losses at 1670 – 1685 and 1860 cm⁻¹ is attributed to long-range interaction in the coadsorbed layer. Potassium adatoms decreased the amount of CO desorbed and converted it into a more reactive form, which—instead of desorption—underwent dissociation at 350–550 K. The recombinative desorption of CO occurred at 970 K; its amount was 3 times higher than that measured for K-free Mo₂C. Potassium was stabilized in the adsorbed layer mainly by O adatoms arising from the decomposition of CO.

1. Introduction

Mo₂C is a promising catalyst because it shows catalytic activity similar to that of platinum metals in several reactions, accompanied by less sensitivity to sulfur impurity.^{1,2} Recently, it was found that Mo₂C supported by ZSM-5 is an active catalyst in the conversion of CH₄,^{2–5} ethane,⁶ and propane⁷ into benzene with high selectivity. Mo₂C is also an effective catalyst in the hydrogenation of CO and CO₂.^{9–11} The product distribution is sensitively influenced by adding potassium salts to Mo₂C catalyst, which markedly enhances synthesis of light olefins from syngas.^{12,13}

The interaction of CO with clean Mo single-crystal surfaces is well documented. The clean Mo(100) surface is rather active in the dissociation of a chemisorbed CO molecule; it decomposes to C and O atoms at 170 K and desorbs recombinatively with $T_p = 1030$ and 1290 K.¹⁴ From this it is obvious that an initially clean Mo sample may turn quickly to a carbon- and O-covered surface even under the conditions of a hydrogenation reaction of CO. Potassium adatoms on Mo(110) definitely increased the adsorption probability of CO, but it was not considered as an effective promotor, as the dissociation of CO preceded the desorption even in the absence of potassium.¹⁵

The bonding of CO to carbon-modified Mo surfaces and to Mo₂C was studied both theoretically¹⁶ and experimentally.^{17–26} It was established that on the Mo(110) surface even a thicker carbide layer with an estimated C/Mo atomic ratio of 0.8 remained reactive toward dissociation.²⁶

The possibility of altering the catalytic behavior of Mo₂C in CO hydrogenation by potassium salts^{12,13} motivated our study concerning the adsorption of CO on clean and K-modified Mo₂C under UHV conditions. Apart from some exploratory measure-

ments in connection with the adsorption of CO,^{2,27} the effect of potassium on the chemistry of CO on Mo₂C has not been explored, yet. The present work is a continuation of our study of the interaction of small molecules with the Mo₂C/Mo(100) surface.^{28–30}

2. Experimental Section

The experiments were performed in an UHV chamber with a routine base pressure of 5×10^{-10} mbar produced by turbomolecular, ion-getter, and titanium sublimation pumps. The chamber was equipped with facilities for AES, HREELS, and TPD. The HREEL spectrometer (VSW, type HA-50) is situated in the lower level of the chamber and has a resolution of 70 – 100 cm⁻¹. All spectra reported were recorded with a primary energy of 5.0 eV and at an incident angle of 45°. The Mo(100) crystal was mounted between two tantalum wires which were connected via a copper block directly to a liquid nitrogen reservoir. The sample was heated resistively from 140 to 1275 K; its temperature was monitored by a chromel–alumel thermocouple spot-welded to the edge of the crystal and was controlled with a feedback circuit to provide a linear heating rate of ca. 10 K/s. CO was dosed through a 0.1 mm diameter capillary that terminated 2 cm from the sample. The local pressure at the sample was about 10^{-7} mbar during dosing. The dosing temperature was 140 K unless otherwise noted.

The Mo(100) crystal used in this work was a product of Materials Research Corp., purity 99.99%. Initially the sample was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1–2 kV, 1×10^{-7} mbar Ar, 1000 K, 10 μ A for 10–30 min), and annealing at 1270 K for several minutes. Mo₂C over a Mo(100) surface was prepared by the method of Schöberl.³¹ The Mo(100) surface was exposed to 200 L of ethylene at 900 K and then flashed to 1200 K in UHV. The partial pressure of ethylene near the sample was about 10^{-7} mbar. The resulting surface as checked by AES turned out to be carbidic, showing the characteristic three-lobe

* To whom correspondence should be addressed. Fax: + 36 62 420 678. E-mail: fsolym@chem.u-szeged.hu.

[†] These laboratories are part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

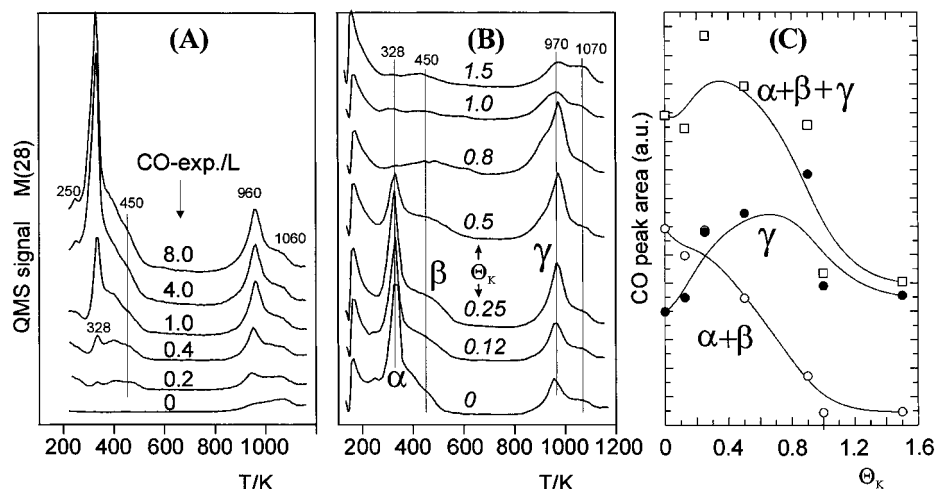


Figure 1. TPD spectra taken at $m/e = 28$ (A) for K-free $\text{Mo}_2\text{C}/\text{Mo}(100)$ surfaces as a function of CO exposure and (B) for a K-covered sample at different K coverages ($T_a = 140$ K, CO exposure 4 L). (C) Amounts of CO desorbed in different states as a function of potassium coverage. The curves were fitted by spline interpolation.

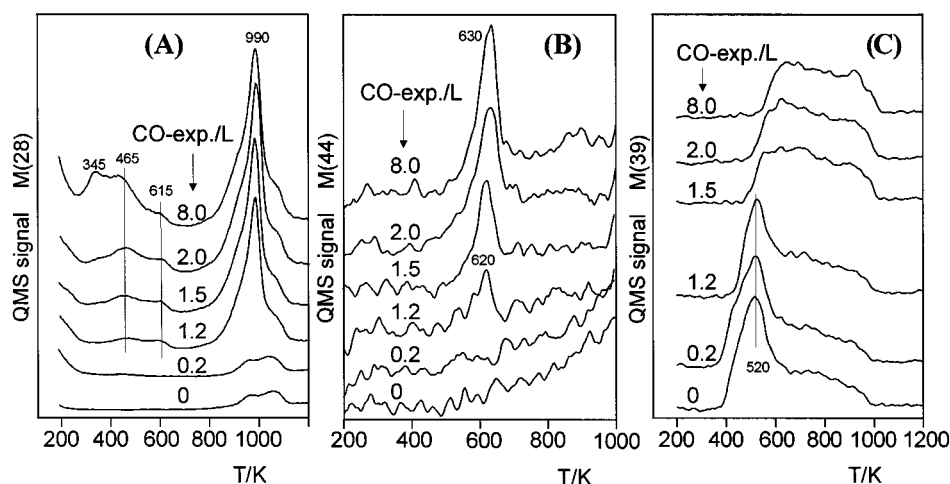


Figure 2. TPD spectra for a K-promoted ($\Theta_K = 0.8$ ML) sample as a function of CO exposure at (A) $m/e = 28$, (B) $m/e = 44$, and (C) $m/e = 39$ ($T_a = 140$ K).

line shape of carbidic carbon in AES at 255.6, 262.1, and 272.7 eV.³² CO was a product of Linde, 99.99%. A commercial SAES getter source situated 3 cm from the sample was used to deposit potassium metal onto the Mo_2C surface. The getter was resistively heated. The deposition of the potassium was done at 250–300 K. The onset of potassium desorption from the second adlayer ($T_p = 355$ K) was accepted as an indication of the completion of a monolayer denoted by $\Theta_K = 1.0$ ML. The potassium coverage related to the underlying unit cell can be estimated to be ~ 0.33 on the basis of similar thermal desorption and depolarization behavior of K on Pt metals³³ and on the $\text{Mo}_2\text{C}/\text{Mo}(100)$ surface.²⁸

3. Results

3.1. TPD Measurements. The adsorption of CO on the clean $\text{Mo}_2\text{C}/\text{Mo}(100)$ surface was followed by TPD after different CO exposures performed at 140 K (Figure 1A). A small amount of CO was desorbed from the unexposed surface, which can be partly attributed to a slight CO uptake from the rest gas during cooling of the sample (~ 8 min), and partly to the recombinative reaction of C and O atoms present in the bulk. An interesting feature of this adsorption system is that the desorption peaks of CO could be recorded at high ($T_p = 960$ K) and at low temperatures ($T_p = 328, 450$ K) even at the lowest CO exposure

(0.05 L, not shown). With the increasing gas exposures, these desorption features were intensified practically without changing their position. Above 1 L of CO exposure the 320 K peak dominated the spectrum. The small peak at 1060 K increased only slightly with the gas exposure.

The TPD spectra in Figure 1B reveal that the preadsorbed potassium exerts a dramatic influence on the adsorption of CO on the $\text{Mo}_2\text{C}/\text{Mo}(100)$ surface. As a result of increasing K coverage, the peaks below 600 K (α - and β -states) were suppressed, whereas the HT peak at 960 K (γ -state) gained intensity up to 0.8 ML of potassium coverage, accompanied by a slight shift to 970–980 K. In addition, a very small peak appeared at 615 K. Above this alkali-metal concentration the CO uptake of the surface was strongly suppressed. The areas of the α -CO, β -CO, and γ -CO peaks as a function of K coverage are shown in Figure 1C.

The effect of CO exposure on the CO desorption at a K coverage of 0.8 ML is presented in Figure 2A. It shows that the γ -state is the dominant feature in the whole exposure range. CO_2 is also released from the surface (Figure 2B), indicating the disproportionation of CO at this alkali-metal coverage. The production of the CO_2 peak, however, requires higher gas exposure; it can only be detected at and above 1 L of CO exposure. The amount of CO_2 is only 0.2% of the total amount

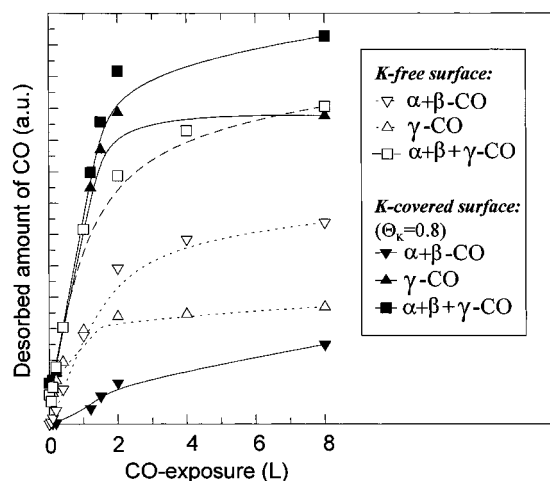


Figure 3. Amounts of CO desorbed in different states as a function of CO exposure.

TABLE 1: Characteristic Data for CO Thermal Desorption from Clean and K-Modified Mo₂C/Mo(100) Surfaces

T_p/K	state	$E_a^a/kJ\ mol^{-1}$	T_p/K	state	$E_a^a/kJ\ mol^{-1}$
$\Theta_K = 0\ ML$					
328	α	81	970	γ	240
450	β	111	1070	γ'	265
$\Theta_K = 0.8\ ML$					
345	α	85	990	γ	245
465	β	115	1070	γ'	265
615	β'	152			

^a E_a was calculated by assuming first-order kinetics with a preexponential factor of $1 \times 10^{13}\ s^{-1}$.

of CO adsorbed. The desorption of potassium from the coadsorbed layer is presented in Figure 2C. An interesting feature is the elimination of the low-temperature desorption peak of potassium at higher CO exposures. Potassium desorbed from the coadsorbed layer between 550 and 1000 K.

The quantitative relations of CO uptake calculated from CO desorption curves on the K-free and K-covered surfaces are presented in Figure 3. The promotional effect of preadsorbed potassium is reflected in the extent of recombinative CO desorption (γ -state), which is enhanced by a factor of ~ 3 . Characteristic data for the thermal desorption of CO are summarized in Table 1, assuming first-order desorption kinetics and a preexperimental factor of $1 \times 10^{13}\ s^{-1}$.

3.2. HREELS Measurements. **3.2.1. CO Adsorption on the Clean Mo₂C/Mo(100) Surface.** The effect of different CO exposures on the HREEL spectra at 140 K is shown in Figure 4A. Two peaks developed with the increasing CO exposure, at 380 and 2060–2100 cm^{-1} , attributable to molecularly adsorbed CO. When the adsorption temperature was 320 K, no sign of molecularly adsorbed CO was detectable; only one intense loss appeared at 568–539 cm^{-1} , corresponding to the vibration of Mo–O. This suggests the complete dissociation of CO. The adlayers formed by saturation of Mo₂C/Mo(100) at 140 K and heated to different temperatures are characterized by the HREEL spectra presented in Figure 4B. At 300 K losses developed at 500 and 800 cm^{-1} . The 380 and 2090 cm^{-1} losses are completely eliminated between 300 and 355, accompanied by the intensification of losses at 500, 800, and 1000 cm^{-1} . The latter peaks exhibited high thermal stability; they were eliminated only between 800 and 1000 K, suggesting that they belong to some form of adsorbed oxygen.

3.2.2. CO Adsorption on a K-Modified Mo₂C/Mo(100) Surface. The effect of potassium on the HREEL spectra of

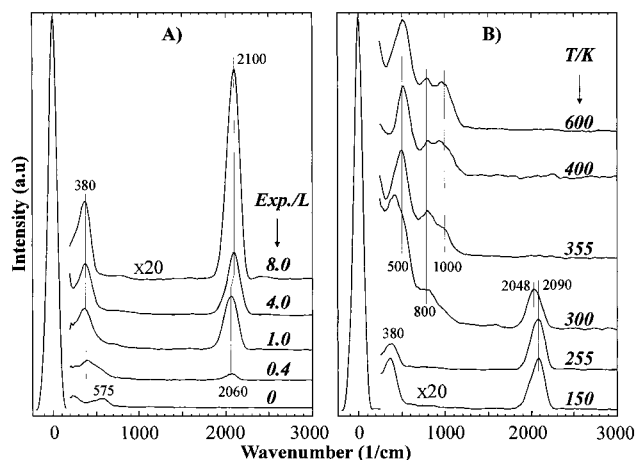


Figure 4. HREEL spectra taken (A) following different CO exposures onto the Mo₂C/Mo(100) surface at 140 K and (B) after stepwise heating of the CO-saturated adlayer (CO exposure 6 L).

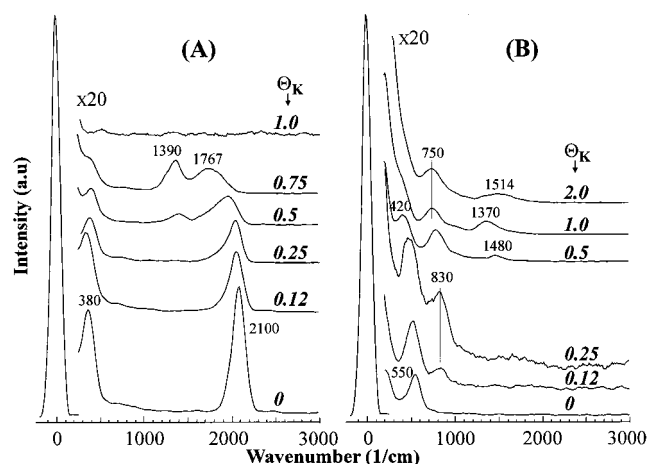


Figure 5. Effect of preadsorbed potassium on the HREEL spectra of CO adsorbed (A) at 140 K and (B) at 300 K (CO exposure 4 L).

adsorbed CO at 140 K is illustrated in Figure 5A. The 2100 cm^{-1} loss observed for a K-free surface gradually shifted to lower frequencies with increasing potassium coverage up to $\Theta_K \approx 0.75\ ML$. At 0.5–0.75 ML of potassium coverage a new loss developed at 1420–1390 cm^{-1} . The vibration at 380 cm^{-1} was slightly shifted toward higher frequencies and attenuated at higher K coverages. At monolayer alkali-metal coverage only a weak HREELS feature could be detected at 520 cm^{-1} .

A different behavior was observed when the adsorption temperature was 300 K (Figure 5B). In the potassium coverage range of 0.12–1.0 ML, intense losses were detected at 420–500, 750–830, and 1370–1480 cm^{-1} . It is remarkable that CO adsorbed on the sample covered by 2 ML of potassium resulted in loss features at 750 and $\sim 1550\ cm^{-1}$.

To establish the surface intermediates formed prior to decomposition of CO on the K-modified surface, we followed the development of HREELS peaks at 140 K as a function of CO exposure at a K coverage of 0.8 ML. As can be seen in Figure 6A, even the lowest gas exposure yielded a discrete HREELS feature with a vibration frequency of 1305 cm^{-1} . After 1 L of CO exposure, the loss at 1305 cm^{-1} is shifted to 1360 cm^{-1} and enhanced with the appearance of a new one at $\sim 1600\ cm^{-1}$. At and above CO exposure of 2.0 L, the positions of losses were at 400, 1375, 1683, and 1860 cm^{-1} .

HREEL spectra following the stepwise heating of a coadsorbed layer formed by exposing 0.4 L of CO to the K-covered

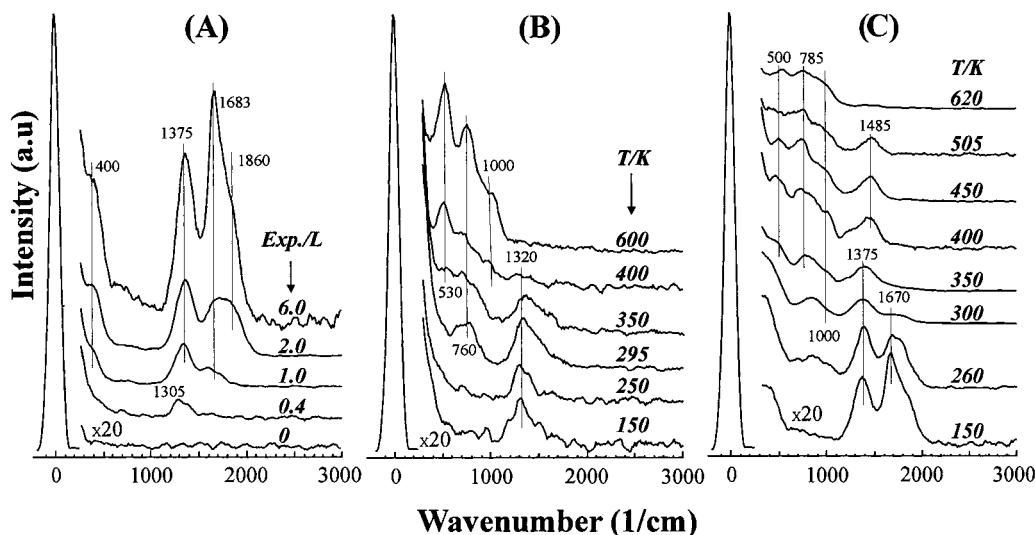


Figure 6. (A) Effect of CO exposure on the HREEL spectra of a K-covered Mo₂C/Mo(100) surface. Effect of stepwise heating on the HREEL spectra of a Mo₂C/Mo(100) surface exposed (B) to 0.4 L of CO and (C) to 6 L of CO. $\Theta_K = 0.8$ ML. $T_a = 140$ K.

surface ($\Theta_K = 0.8$) are shown in Figure 6B. At 295 K new vibration losses appeared at 670 and 770 cm^{-1} , while the loss at 1305 cm^{-1} was slightly broadened at the high-frequency side. Further heating to 350–400 K caused the development of an intense vibration at 530 cm^{-1} and the formation of a faint loss at 980–1000 cm^{-1} accompanied by the attenuation of the 1320 cm^{-1} feature. At 600 K losses could be observed at 530, 760, and 1000 cm^{-1} .

Divergent behavior was experienced when the coadsorbed layer was produced by saturation of a K-dosed (0.8 ML) surface with CO (Figure 6C). The losses at 1670 and 1860 cm^{-1} were nearly eliminated by heating the sample to 300 K. The 500 cm^{-1} loss became discernible at 350–400 K in the company of 785 and 1000 cm^{-1} losses, while the 1375 cm^{-1} peak shifted to 1485 cm^{-1} and remained the single feature at 450–500 K above 1000 cm^{-1} . It was eliminated only by heating the sample to 620 K.

4. Discussion

4.1. Interaction of CO with Clean Mo Single-Crystal Surfaces. To interpret the observed vibrational and thermal desorption features on the C-modified Mo(100) surface, first we survey the adsorption forms of CO obtained on clean Mo single crystals. It was established that CO interacts strongly even with the most closely packed Mo(110) surface at 120 K.¹⁷ Besides the losses ascribed to terminally bonded (2010–2055 cm^{-1}) and bridge-bonded (1920–1975 cm^{-1}) adsorption forms, peaks were observed at 1130, 1345, and ~ 1500 cm^{-1} .¹⁷ The interesting feature of the species giving the 1345 cm^{-1} peak is that it can be completely either dissociated or converted to terminally bonded CO. Dissociation of CO starts at 200–250 K, and at low initial CO coverage, it is completed at around 300 K on this surface.

The adsorption of CO on a Mo(100) surface led to losses at 1065 and 1235 cm^{-1} at low CO exposures and to the population of terminal CO (2090 cm^{-1}) at saturation CO coverages. The adsorption form characterized by a 1235 cm^{-1} $\nu(\text{CO})$ frequency was assigned to the presence of CO adsorbed in the 4-fold hollow site.²⁰ The formation of an adlayer consisting of the dissociation products of CO leads to less ability of the surface for dissociation, and to an enhanced probability to bind and release CO in molecular form, as was proved by a readsorption experiment on a Mo(100) sample.²¹

4.2. Interaction of CO with a Clean Mo₂C/Mo(100) Surface. In an earlier study it was established that the presence of carbon severely hindered the ability of Mo(100) to dissociatively adsorb carbon monoxide.²² A similar observation was reported for the C-modified Mo(110) surface.²³ A carbonaceous layer formed on Mo(100) by decomposition of propane prevented the adsorption of CO under UHV conditions, but at higher pressures CO adsorbed reversibly in a form characterized by a $\nu(\text{C}-\text{O})$ of 1867 cm^{-1} .²⁴ In contrast, the p(4 \times 4)-C/Mo(110) surface even with a thicker carbide layer, C/Mo ratio of 0.8, behaved reactively toward CO dissociation.²⁵ From the divergent results it was inferred that the reactivity of carbon-modified Mo(110) surfaces strongly depends on whether carbon atoms are located on the surface or in the interstitial/subsurface sites.²⁶

In our sample the C/Mo atomic ratio was 0.5, which corresponds to the formation of an interstitial Mo₂C compound. A remarkable phenomenon observed for the Mo₂C/Mo(100) surface is that CO desorbs from the sample in several states with $T_p = 328, 460, 960$, and 1060 K even after the smallest CO exposures, which indicates the heterogeneity of the surface. The two desorption states at 328 and 460 K (Figure 1A) may belong to differently coordinated CO molecules. The heterogeneity of the surface is increased further by the dissociation of CO molecules, which starts at around 300 K (Figure 4B). The recombination of C and O proceeds at rather high temperature characterized by $T_p = 960$ K. The amount of CO desorbed from the molecularly adsorbed state at saturation coverage is ~ 2 times higher on this surface than the amount arising from the recombinative reaction (Figure 3). It is remarkable that the positions of CO TPD peaks are practically unaltered at different gas exposures (Figure 1A). For the low-temperature peaks ($T_p < 600$ K), this suggests a molecular desorption in first order, which is in harmony with earlier observations.¹⁸ The apparent first order of the high-temperature desorption of CO ($T_p = 960$ K) hints to the participation of the carbidic carbon of the Mo₂C surface in the C + O reaction. This idea is supported by our observation that CO is released from the O-covered Mo₂C/Mo(100) surface at 926 K. The CO peak at 1060 K can be attributed to the oxidation of carbidic carbon diffusing from the bulk to the surface. A similar picture emerged from the study of the O₂/WC system.³²

As on the p(4×4)-C/Mo(110) surface a “side-on”-bonded CO characterized by 1130 cm⁻¹ loss was detected even at 80 K,²⁶ we conclude that the carbided Mo(100) surface is less active in rupturing the C–O bond than the carbided Mo(110) plane.

The thermally activated decomposition process of CO on the Mo₂C/Mo(100) surface is also suggested by HREELS. While there was no sign of dissociation at 140 K on the HREEL spectra (Figure 4A), the appearance of an intense loss at 510 cm⁻¹ ascribed to M–O vibration clearly indicates the occurrence of the dissociation of CO. This process proceeds between 300 and 355 K (Figure 4B). Note that this temperature is higher by 100 K than that observed for the carbon-free Mo(100) surface, which reflects that C atoms decrease the reactivity of the Mo(100) crystal. Interestingly, the side-on-bonded or highly coordinated forms of CO characterized by C–O frequencies between 1000 and 1500 cm⁻¹ could not be observed during the heating process, probably due to the too narrow temperature range in which these forms exist.

4.3. Interaction of CO with the K-Modified Mo₂C/Mo(100) Surface. The characteristics of the adsorption of potassium on the clean Mo₂C/Mo(100) surface are the subject of our previous paper.²⁸ We observed the same features as on platinum metals. Work function changes suggested a considerable charge transfer from potassium to Mo₂C at lower coverages, and a gradual neutralization at and above monolayer coverage. As a consequence of this, at low coverages potassium is bonded in ionic form, while at high concentrations potassium is in a metallic state.²⁸ At low K coverage, potassium desorbed with a $T_p = 850$ K. This peak shifted to 525 K for monolayer coverage and to 325 K for multilayer coverage. The linearity of desorbed amounts of potassium as a function of exposure and the onset of a line for K uptake at zero coverage indicate that the adatoms do not dissolve in the bulk during TPD measurements.

The behavior of the CO + K system on the Mo₂C/Mo(100) surface resembles, in many respects, that observed for platinum metals.^{33–35} There are, however, features which were registered only for more reactive metals (Re³⁶, Fe³⁷), on which the extent of CO dissociation is remarkable even on the clean surfaces. TPD measurements showed that the low-temperature TPD peaks at 328 and 450 K were almost completely eliminated by potassium at coverages of 0.8–1.0 ML. At the same time the amount of CO desorbed in the high-temperature peak, $T_p = 970$ K, is 3 times higher than that measured for the K-free surface (Figure 3). As this peak is attributed to the recombinative desorption of CO, we can conclude that potassium greatly promotes the dissociation of CO on Mo₂C.

In contrast to Pt metals, we could not detect the state of stabilized CO by TPD, which desorbed simultaneously with potassium, suggesting the existence of a surface compound between CO and K.³⁴ The peak temperature for this kind of desorption, 650–690 K, was only slightly affected by the nature of the host metal.³⁴ The possible reason is that the large majority of adsorbed CO is activated by potassium to such an extent that it dissociates far below the above temperature. As the TPD spectra in Figure 2A show, only a very small fraction of CO, desorbing at 615 K, escapes the dissociation. The quantity of CO released at this temperature is 0.7% of the total amount of CO desorbed. Nevertheless, the stabilization of K in the coadsorbed layer occurs, particularly at higher CO exposures, when most of the potassium desorbs in a high-temperature range, 550–1000 K (Figure 2C). We assume that, in addition to the effect of CO, the increased desorption temperature of potassium is due to its strong interaction with adsorbed O formed in the dissociation of CO (Figure 2C).

At higher K coverages ($\Theta_K > 0.8$ ML) we experienced the inhibition of CO uptake, which is in harmony with the former finding that CO reacts only reluctantly with alkali metals under UHV conditions.^{33–35} At 0.8 ML of potassium coverage there was a sign of disproportionation of CO; a small amount of CO₂ was released into the gas phase with $T_p = 630$ K. Calculation showed that only about 0.2% of the adsorbed CO was converted into CO₂ (Figure 2B).

Analysis of the HREEL spectra discloses further details on the unique behavior of the CO + K adsorbed layer over Mo₂C. The strong influence of potassium was exhibited by the spectra taken at 140 K. Whereas on the K-free surface only terminally bonded CO could be observed (Figure 4A), with the increasing potassium coverage a gradual shift of the C–O vibration frequency to lower values, 1683–1767 cm⁻¹, was experienced (Figures 5A and 6A). In addition, a low-frequency loss at 1375–1390 cm⁻¹ also developed. At higher exposures, a shoulder at 1860 cm⁻¹ can also be identified (Figure 6A). The 1683–1767 cm⁻¹ loss may belong to CO bonded to the adsorption sites strongly influenced by the presence of K, while the 1860 cm⁻¹ feature may belong to CO molecules bridge-bonded to adsorption sites having a much weaker influence of potassium. The low-frequency loss at 1390 cm⁻¹ at $\Theta_K = 0.5$ –0.75 ML suggests the formation of either an inclined CO species¹⁷ or a CO species bound to a 4-fold hollow site.²⁰ The formation of an adsorption state with such a low $\nu(\text{C–O})$ vibration frequency implies either an enhanced electron back-donation toward the molecule due to a change in the density of metal states at the Fermi level of the substrate by potassium³⁸ or an electrostatic interaction among CO and the nearest potassium ion neighbors.^{39,40} Different adsorption states of CO were also identified by vibration spectroscopic methods for various K-dosed metals.^{33,35,41} The observation of the adsorption states with a considerably weakened C–O bond suggests a short-range interaction, while the detection of CO_(a) with a less perturbed C–O bond supports the operation of long-range interaction.

Upon heating the CO adsorbed layer, vibration losses at high frequencies disappeared around 300 K, whereas the 1375 cm⁻¹ loss moved to 1485 cm⁻¹, and remained there up to 505 K. The appearance of this single peak suggests a uniform alkali-metal–CO configuration, that is, the formation of domains with fixed local K/CO stoichiometry. The formation of well-defined alkali-metal coadsorption structures characterized by discrete C–O vibration frequencies was observed, for example, on Pt, Ru, and Co single-crystal surfaces.^{41–43} The Mo–O vibration at 500 cm⁻¹ was detected first at 350 K accompanied by losses at ~800 and ~1000 cm⁻¹, which were ascribed to adsorbed oxygen.⁴⁴ The intensity of these features slightly increased at elevated temperatures (Figure 5C). Annealing the adsorbed layer prepared by low CO exposure, which is characterized by the loss at 1320 cm⁻¹ (Figure 6B), showed that this CO decomposed at lower temperature, slightly above 400 K. This is consistent with the expectation that on this surface compared to the CO-saturated sample there are more free adsorption centers necessary for the dissociation of CO.

5. Conclusions

CO adsorbs molecularly on the clean Mo₂C/Mo(100) surface at 140 K, characterized by a $\nu(\text{C–O})$ mode of 2100 cm⁻¹. No sign of inclined or bridge-bonded CO could be detected on this surface. Annealing the CO-saturated surface led to molecular CO desorption and to complete dissociation of CO at 300–350 K. Recombinative desorption of atomic C and O occurred at high temperatures with $T_p = 960$ and 1060 K.

Preadsorbed potassium at $\Theta_K = 0.8$ considerably weakened the C–O bond even at 140 K, which was manifested in the appearance of a $\nu(\text{C–O})$ mode at as low a frequency as 1320–1375 cm^{-1} (short-range interaction). The generation of other adsorption forms of CO with $\nu(\text{C–O})$ frequencies at 1670–1683 and 1860 cm^{-1} suggests a long-range interaction. The appearance of the single loss at 1485 cm^{-1} at higher temperatures may indicate a fixed K/CO stoichiometry, very likely the formation of a $\text{K}^{\delta+} + \text{CO}^{\delta-}$ surface compound. Potassium adatoms stabilized and activated the adsorbed CO to such an extent that most of the CO underwent dissociation at 350–550 K instead of desorption.

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