A Role for Induced Molecular Polarization in Catalytic Promotion: CO Coadsorbed with K on Co{$10\bar{1}0$}

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Abstract: The Fischer−Tropsch and higher oxygenate syntheses by hydrogenation of CO were two of the most intensively studied catalytic reactions of the last century, yet a complete understanding of their underlying mechanisms remains elusive. Promotion of the reactions by alkali metal coadsorption is often regarded as being due to enhanced CO dissociation, but a recent experimentally determined surface structure for Co-{$10\bar{1}0$}/(K + CO) indicates that more subtle processes may also be involved. This highly unusual structure, having no analogue in three-dimensional chemistry, is now reproduced using first-principles density functional theory. Our analysis of mixed-orbital bonding states demonstrates not only the importance of synergic processes in promoting CO dissociation, but also the existence of a remarkably strong alkali-induced polarization of the C−O bond itself. This polarized bond would be highly reactive in the presence of H_2. The implications for heterogeneous catalysis in general are profound, since the importance of promoter-induced molecular polarization has hitherto been largely ignored.

Introduction

The coadsorption of K and CO on Co{$10\bar{1}0$} is a subtle matter with profound implications for promoter action in heterogeneous catalysis. These implications are nowhere more important than in the industrially important Fischer−Tropsch process, whereby CO is hydrogenated and polymerized (in the presence of Fe, Co, or Ni) to form alkanes, and in higher oxygenate synthesis, through which synthesis gas is converted (over Cu, Cr, or Pd) to form alcohols.[1] It is widely believed that CO dissociation (promoted or otherwise) is the first step in the Fischer−Tropsch reaction, followed by hydrogenation of adsorbed C and O atoms. Alternative mechanisms, in which CO molecules are directly hydrogenated to form hydroxycarbyl groups, − CHOH, have been out of favor in recent years.

The Co{$10\bar{1}0$} surface considered here is notable in that CO dissociation does not occur, even in the presence of K, so that detailed experimental studies on the effect of coadsorption have been possible.[2−5] A wide variety of CO/alkali coadsorption models have previously been proposed in the literature, but most were comprehensively ruled out for Co{$10\bar{1}0$}/(K + CO) − $c(2 \times 2)$ by the quantitative low-energy electron diffraction (LEED) structure determination of Kaukasoina et al.[2] and the near edge X-ray absorption fine structure (NEXAFS) study of Gleeson et al.[3] Significantly, both LEED and NEXAFS analyses favored a nearly upright geometry for CO, with only a modest increase in bond length, precluding both the formation of polymeric $(CO)_y^{y-}$ anions,[6] *and* major re-hybridization of the CO molecular orbitals.[7−9]

A direct interaction between the K 4s/4p resonance and the CO 1π state[10,11] was also rejected on geometrical grounds, since analysis of the LEED data indicated the K atom was to be found *above* the level of the O atom, rather than straddling the C−O bond as might be expected if such a covalent hybrid were to be formed. The possibility of a kinetic explanation for the unusual raised location of K may be ruled out on the basis that the CO dosing was conducted at room temperature *after* the establishment of saturation K pre-coverage. The K atom in fact appeared to be lifted up and supported on a “tripod” of CO molecules and was found to lie a startling 0.4 Å above its position in the absence of CO (as determined by Barnes et al.[12]). The appearance of a K-induced peak in the NEXAFS spectrum was furthermore judged too high in energy to be related to a K/CO hybrid orbital.

The only bonding model consistent with both LEED and NEXAFS was a synergic, Blyholder-like[13] scheme, in which charge is ultimately transferred from the 4s/4p resonance of K to the 2π^* orbital of CO. Unfortunately, however, while such a model does not *preclude* the raised position of the K atom, neither does it actually *explain* it. The results of a reflection absorption infrared spectroscopy (RAIRS) study by Toomes and King,[4] in which a K-induced red-shift of 300 cm^{-1} was observed for the C−O stretch mode, were also not readily explicable in

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Table 1. Calculated and Experimental Atomic Separations

	C−O (Å)	3 × K−O (Å)			C−Co (Å)	K−Co (Å)	θ_{CO} (deg)
present	1.24	2.81	2.83	2.95	1.90	3.35	10.5
LEED[2]	1.20 ± 0.08	2.87	2.87	2.70	1.90	3.51 ± 0.11	4 ± 10
NEXAFS[5]	1.22 ± 0.04						

terms of this model. From earlier coadsorption studies, a much larger red-shift might have been expected.[8,14]

The motivation of the present theoretical study was therefore 3-fold: first, to confirm the highly unusual structure determined by LEED, second, to examine the red-shifted C−O stretch frequency revealed by RAIRS, and third, to analyze the bonding directly, through examination of charge density distributions, in an effort more fully to understand the above effects.

Methodology

Calculations for the K/CO coadsorbed system were performed within a primitive surface unit cell consistent with the experimentally observed $c(2 \times 2)$ symmetry. Periodic boundary conditions in the surface normal direction were satisfied by means of a slab geometry, with four $\{10\bar{1}0\}$ layers of Co (plus adsorbate layer) in a cell of length equivalent to 10 layers of Co. The absolute dimensions were fixed by our theoretically calculated[15] lattice parameters of $a = 2.52$ Å and $c = 3.97$ Å. No explicit corrections were attempted to remove spurious dipole interactions between slabs, but in line with other calculations of this type it is assumed that metallic screening within the slab should prevent this becoming problematic in such a strongly adsorbed system.

The $\{10\bar{1}0\}$ surfaces of hcp crystals may be terminated in one of two forms: the A form, in which the substrate terminates on a short interlayer spacing, and the B form, in which the terminal spacing is long. It is established, from LEED studies,[16] that the A form is uniquely preferred by Co, and thus we consider only this possibility here. In light of the firm LEED data for the coadsorption geometry,[2] we also considered only the structure in which near-upright CO molecules reside in sites of approximate 3-fold symmetry with respect to hollow site K atoms (Figure 1).

All atoms except the back two layers of the Co slab were then allowed to relax according to forces calculated within the density functional theory (DFT) of Hohenberg, Kohn, and Sham.[17,18] Initial atomic configurations in which K was positioned both above *and* below the level of O were tried, to lessen the chances of finding only a local energy minimum. In the event, the system relaxed to the same final geometry in each case.

Electronic exchange and correlation were included through the spin unpolarized local density approximation (LDA) of Kohn and Sham[18] and the correlation scheme of Ceperley and Alder.[19,20] Our previous experience with similar systems leads us to believe that inclusion of spin effects and gradient corrections in the exchange and correlation would have only a minor effect on the relative geometry.[15,21,22] In particular, we note that CO *remains* spin-unpolarized on the Ni$\{1\bar{1}0\}$ surface,[22] while K *becomes* spin-unpolarized on the Co$\{10\bar{1}0\}$ surface,[21] so that bonding interactions may be described without explicit reference to the spin. The electronic wave functions were expanded in a basis set of plane waves up to a 40 Ryd kinetic energy cutoff, with reciprocal space integration achieved by summation over a 3 × 3 × 2 mesh of Monkhorst−Pack[23] special **k**-points. These parameters have been found sufficient to produce numerically well-converged results, in good agreement with experiment, for the clean,[15] K-covered[21] and CO-covered[25] Co$\{10\bar{1}0\}$ surfaces.

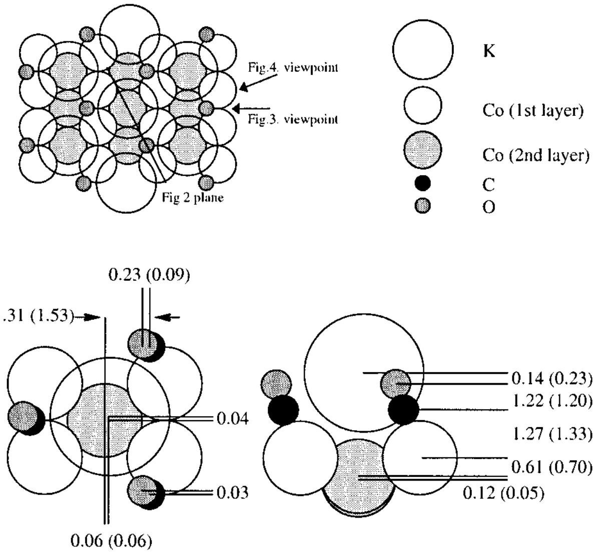

Figure 1. Schematic top and side views of the model for $c(2\times 2)$ half-monolayer K + CO coadsorption on the Co$\{10\bar{1}0\}$ − A surface. Calculated DFT structural parameters are noted in Å units, with LEED values from Kaukasoina et al.[2] given in parentheses where available. The slice plane for Figure 2 and the viewpoints for Figures 3 and 4 are also indicated.

Electron−ion interactions were accounted for through the use of Kleinman−Bylander ab initio pseudopotentials.[24] Such pseudopotentials are derived from first-principles and have no adjustable parameters other than the core radius yet are sufficiently transferable to allow reliable calculations of surface properties in slab calculations. The pseudopotential construction ensures that the valence band structure and charge density (beyond the core radius) are reproduced accurately, so that bonding and energetics are well-defined. Again we note that we have obtained structural, vibrational, and electronic results in good agreement with reliable experimental data and previous theoretical work using the same pseudopotentials for a variety of related systems.[15,21,25] Semicore 3s/3p and valence 4s electrons were explicitly relaxed for K (i.e., were *not* subsumed in the pseudopotential), as were 4s/3d electrons for Co. Core radii of 0.74 Å were used for the C and O pseudopotentials, with 1.06 Å used for K and Co (except for a radius of 1.27 Å used for the d channel of the Co potential).

Results and Discussion

Calculated structural parameters for the present coadsorption model are summarized in Table 1 and Figure 1. The CO molecules remain essentially upright but are tilted some 10.7°, nominally in the [0001] direction. A small component of this tilt (1.2°) is directed in the $[1\bar{2}10]$ direction, breaking the corresponding mirror symmetry. The K adatoms respond to their asymmetric environment by shifting 0.06 Å off the center-line of their trench and 0.04 Å *along* the trench direction. The result is that there are three distinct K−O distances in the fully relaxed model (2.81, 2.83, and 2.95 Å), instead of just two when mirror symmetry is imposed. Although the previous LEED study of Kaukasoina et al.[2] assumed the existence of the mirror plane,

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the present results are nevertheless in good agreement with their reported (symmetry restricted) lateral displacements. Our calculated tilt angle of 10.7° also falls comfortably within the error bars of the LEED result.[2] Concerning the NEXAFS tilt angle of 0 ± 10° reported by Gleeson et al,[3] and the estimate of ≤8.9° quoted in a very recent NEXAFS study by Wang et al,[5] it is necessary to realize that those experiments were carried out in the $[1\bar{2}10]$ azimuth, and thus were only sensitive to the component of tilt in that direction, where we also find a small tilt of just 1.2°.

More importantly, regardless of the initial height before relaxation, we confirm the experimental observation that the *stable site* for K in the coadsorbed geometry lies *above* the level of the three neighboring O atoms, by some 0.14 Å as compared to 0.23 ± 0.11 Å determined by LEED.[2] As was discussed in that earlier study, this geometry argues somewhat against the direct interaction of the K 4s/4p resonance with the 1π orbital of CO, since this would be maximized if K straddled the C−O bond. The preferred explanation at that time was a local electrostatic field induced enhancement of the Blyholder[13] back-donation of electrons into the CO $2\pi^*$ orbital, which has the added bonus of also explaining their observation of an increased C−O bond length of 1.20 ± 0.08 Å. This, in effect, is the standard model of promoter action in the Fischer−Tropsch reaction, as outlined by Nørskov, Holloway, and Lang[26,27] on the basis of model calculations in the 1980s.

We too find that the C−O bond is rather stretched, at 1.24 Å, compared to 1.17 Å calculated in a $c(2 \times 2)$ array on short bridge sites in the absence of K (cf. 1.138 Å calculated in the gas phase[28]). This is again in good quantitative agreement with the NEXAFS study of Gleeson et al.,[3] which revealed a K-induced C−O bond length increase of 0.11 ± 0.04 Å, and that of Wang et al.[5] which confirms this finding with a deduced C−O bond length of 1.22 ± 0.04 Å.

One further notable indicator of the weakened C−O bond is the influence of the local environment on the CO stretch frequency. The accepted value for the gas-phase frequency is 2143 cm^{-1} (cf. 2200 cm^{-1} calculated by DFT[28]), but adsorption on Co$\{10\bar{1}0\}$ causes the frequency (as measured by RAIRS[29,30]) to drop into the range 1933−2020 cm^{-1}, dependent on coverage. Coadsorption with K, however, causes an *additional* red-shift down to a frequency measured by RAIRS[4] at 1732 cm^{-1}. Our present calculations yield a frequency of 1568 cm^{-1}, some 9% too small. Although this suggests that our CO molecule may be a little over-stretched, it is more or less in line with the stretch frequencies measured for coadsorption with K on Ru$\{0001\}$[8] (1625 cm^{-1}) and on Pt$\{111\}$[14] (1510−1610 cm^{-1}). It should also be noted that our result was calculated simply by stretching the C−O bond while keeping the K adatom and the substrate frozen. Although the molecular adsorbate is much lighter than the other system components, it should be recognized that dynamic coupling between CO, K, and Co may lead to a somewhat higher value of the actual normal mode. The present level of agreement is in fact rather pleasing in such a complex system, and it is clear that the structure calculated in the current work accounts, at least qualitatively, for the observed red-shift.

The structural and vibrational properties of the surface may give us broad hints as to the nature of the bonding in the coadsorbed system, but it is to the electronic structure that we must turn if we are to understand what is really going on. In determining the rearrangement of charge that ultimately leads to the formation of chemical bonds upon coadsorption, one of the most useful forms of evidence is the charge density difference plot (Figures 2a and 3a). Here, the charge densities of an isolated raft of K atoms, $\rho_K^{\text{isol.}}$, and of a half-monolayer of CO molecules adsorbed in their coadsorbed geometry on the relaxed substrate, $\rho_{CO}^{\text{subs.}}$, are subtracted from the total charge density of the coadsorbed system. The resulting charge density difference $\Delta\rho$, therefore, reveals the *changes* in the charge density of the Co$\{10\bar{1}0\}$/CO system upon coadsorption of K, subject to the caveat that changes due to the displacement of atoms are not included:

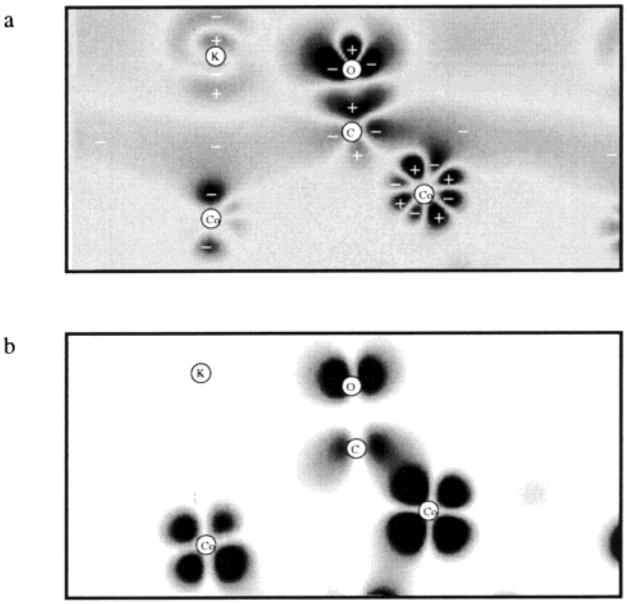

Figure 2. Vertical slice through the plane marked in Figure 1, showing (a) charge density difference (see text), and (b) the $2\pi^*$d orbital at the Brillouin zone center. Annotation in (a) refers to the change in the charge, so that "−" indicates an *increase* in electron density, and "+" indicates a *decrease* in electron density, with the maximum depth of shading corresponding to a density change of ±0.15 electrons/Å^3. In (b), the maximum depth of shading corresponds to 0.05 electrons/Å^3.

$$\Delta\rho = \rho^{\text{subs.}}_{\text{K/CO}} - \rho^{\text{isol.}}_{\text{K}} - \rho^{\text{subs.}}_{\text{CO}} \qquad (1)$$

A number of features in the charge density difference plot are familiar from our previous investigation of Co$\{10\bar{1}0\}$/K.[15] Once again, we observe a broad, delocalized feature situated between the K adatoms and the substrate, together with a marked counterpolarization of the K semicore electrons. The effects of K upon CO, however, are quite different.

Clearly, electrons are depleted from the σ-bonding region of the CO molecule and accumulate in its $2\pi^*$-antibonding region, accounting for the increase in C−O bond length. This much is similar to results of early model calculations by Wimmer et al.[31] for K/CO coadsorption on Ni$\{100\}$, even though the details of their geometry differ markedly from ours (e.g., their K atoms were fixed below the level of the O atoms). Indeed, as mentioned earlier, such synergic bonding has long been suspected of promoting CO dissociation, as the first step in Fischer−Tropsch catalysis.[1,26,27] Nevertheless, we would stress the importance of a number of evident departures from the standard model. These challenge the tacit assumption that ionic bonding at surfaces is

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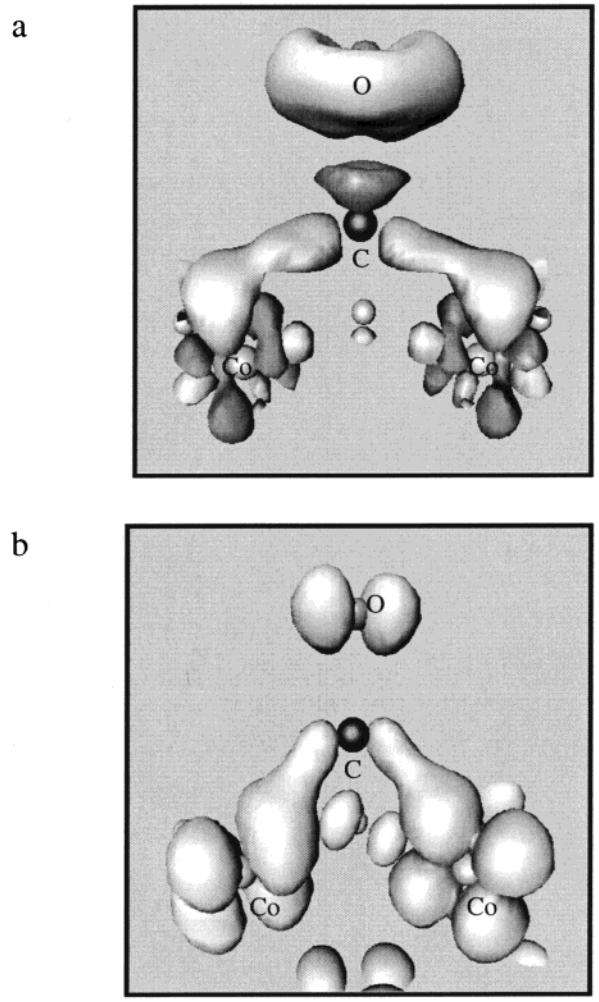

Figure 3. Adsorbed CO molecule as seen from the direction marked in Figure 1: (a) charge density difference isosurfaces for +0.025 electrons/Å^3 (light) and −0.025 electrons/Å^3 (dark); (b) isosurface plot, at 0.025 electrons/Å^3, for the $2\pi^*$d orbital at the Brillouin zone center.

dominated by charge exchange between essentially “pure” unmixed molecular and substrate orbitals.

To understand the nature of the K−CO interaction in more detail, it is necessary first to isolate the $2\pi^*$ eigenstate from the total charge density. A systematic band-by-band search through the partial charge densities of the slab eigenvalues revealed just such a state some 1.51 eV below the Fermi level at the Brillouin zone center (Figures 2b and 3b), although a number of important differences from the corresponding orbital in the free molecule are apparent. Most obvious initially is the fact that significant mixing with substrate d states has occurred. Accordingly, the synergic charge transfer process is more properly represented by $5\sigma \rightarrow 5\sigma$d, d $\rightarrow 2\pi^*$d (where 5σd and $2\pi^*$d indicate covalent mixed orbitals formed between metal d states and the adsorbate $5\sigma/2\pi^*$ states respectively). Furthermore, the molecular component has become substantially polarized, and ionic bonding is seen to be primarily due to the attractive electrostatic interaction of $K^{\delta+}$ with $O^{\delta-}$, rather than simply with the $CO^{\delta-}$ molecule as a whole. Thus, the polarization of the $2\pi^*$d orbital at last explains the preference for a high-lying K adlayer.

Bader’s theory of the topology of the total charge density field[32] allows a physically appealing approach to quantify this polarization effect. By considering the zero-flux surfaces that

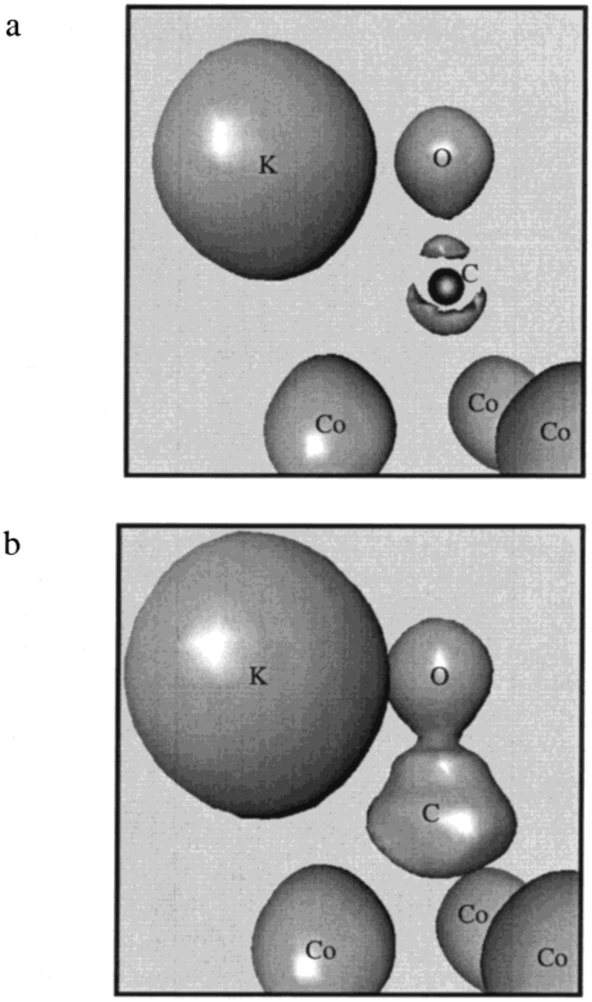

Figure 4. Adsorbed CO molecule as seen from the direction marked in Figure 1: (a) electronic charge accumulation regions with $\nabla\rho^2 <$ 25 electrons/Å;[5] (b) $\nabla\rho^2 = 0$ surface.

exist in the total charge density gradient between ion cores it is possible to describe the “basin of attraction” which uniquely defines each atom. Integrating charge density within these volumes, we find that the CO molecule, in the absence of K, gains a net charge of −0.34e (coadsorbed geometry). Enhanced back-donation due to the presence of K increases the net negative charge of CO to −0.71e per molecule. Furthermore, if we model the mean charge distribution within the CO basin with a monopole of appropriate magnitude located at the center of charge, we can evaluate the dipole moment of the neutral remainder without ambiguity. The gas-phase CO molecule has a dipole moment of 0.11 D, with negative C and positive O. Upon adsorption without K, the polarization is reversed, with a surface normal component of 0.37 D. Coadsorption with K sees this polarization further enhanced, yielding a surface normal component of 0.90 D.

Conclusions

In summary then, our study of the structural, vibrational and electronic properties of the K/CO coadsorbed phase on Co-$\{10\bar{1}0\}$ has revealed a wealth of information regarding the nature of the underlying bonding scheme. We confirm experimental evidence that the K adlayer lies higher than the level of the O atoms, and that the C−O bond is apparently weakened (at least stretched) by the presence of the alkali metal. Through examination of the charge density changes upon coadsorption, we have

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conclusively demonstrated that enhanced Blyholder-like charge transfer between *mixed* orbitals is responsible for these effects.

In addition, however, the marked charge transfer along the C−O bond now suggests that the promoter effect of K in Fischer−Tropsch hydrogenation is in part due to the strong polarization of CO molecules which thus become susceptible to electrophilic/nucleophilic attack. In particular, it is plausible to speculate that H_2 molecules in the presence of the surface dipole may become polarized to $H^{\delta+}H^{\delta-}$ and would constitute an effective reactant for the activated CO; equally, one might also suppose that adsorbed H atoms might become reactive to polarized CO due to their charge transfer with the surface. These suppositions may be strengthened by examining the topology of the Laplacian of the charge density, in the manner originally proposed by Bader.[32] The charge accumulation zone in the vicinity of the O atom (Figure 4a) highlights a reactive surface for electrophilic attack, while the exposed C atom is susceptible to nucleophilic attack. Furthermore, the existence of an extremely narrow "neck" in the $\nabla^2\rho = 0$ surface (Figure 4b) is indicative of an additional highly reactive site for nucleophilic attack close to the midpoint of the C−O bond.

Indeed, it is a widely applicable chemical principle that polar bonds are usually significantly more reactive than nonpolar bonds. Furthermore, it has recently been demonstrated that polarization of the substrate in homogeneous catalysis can profoundly alter the mode of reaction in the hydrogenation of alkenes.[33] Thus, while the presence of K may simply promote the dissociation of CO in certain circumstances, the alternative non-dissociative hydrogenation pathway via the formation of hydroxycarbyl groups, −CHOH, is *also* suggested by the present analysis. The implications, for Fischer−Tropsch studies in particular and heterogeneous catalysis in general, are significant, as the role of induced molecular polarization in promoted catalysis may turn out to have been crucially underestimated.

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