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Promoting the cleavage of C-O bonds at the interface between a metal oxide cluster and a Co(0001) support

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Abstract

As a first step toward the rational design of Co-based catalysts with a higher activity and selectivity, we determine how one can activate a C-O bond at the interface between a metal oxide cluster and a Co(0001) support. The hypothesis here is that the metal ions in metal oxide clusters on a Co(0001) support enhance the adsorption of CO and weaken the C-O bond strength, which can then facilitate the dissociation of the CO reactant. To test this hypothesis, we developed three computational models of Ti₄O₈/Co(0001), Zr₄O₈/Co(0001), and Mn₈O₈/Co(0001). We quantify the CO adsorption behavior at the interface sites between an oxide cluster and the Co(0001) support as well as the corresponding IR spectra. We correlate the computed CO stretch frequencies with their CO adsorption energies, as well as the CO stretch frequency with the C-O bond length. The interface is the most favorable site for CO adsorption. Adsorption results in an increase of the C-O bond length and a decrease in its vibrational frequency.

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From a chemical bonding analysis, the bond order in CO at this site drops from 3 to 1. This is helpful for CO dissociation. The experimental measurements of the corresponding FTIR spectra support this point. The favorability of CO adsorption at the interface sites is due to an electron transfer from the metal ion in the metal oxide cluster to the O atom in CO. We establish a linear relationship between C-O bond length and CO frequency and is found to be independent of support, type of metal oxide cluster, or the adsorption site.

Introduction

Recent efforts to enlarge the feedstock portfolio generated by the Fischer-Tropsch (FT) process have focused on designing complex catalyst compositions and tuning them under reactive synthesis conditions. As a result of these efforts, metal-oxide supports with distinct metal valence fluxionality have been identified to shift the product selectivity from paraffins to olefins and oxygenates. For example, studies with Co/MnO_x catalysts, possibly alkali-promoted, have demonstrated their capacity to produce olefins¹⁻⁷ or alcohols/aldehydes.⁷⁻¹⁰ Interestingly, such Co/MnO_x catalysts undergo a significant chemical reconstruction involving a Co to Co₂C phase transition during CO hydrogenation, as simultaneously demonstrated by Zhong et al.¹ and Xiang⁷ and further investigated by others.²⁻⁵ Different from earlier investigations stating detrimental effects on the catalytic performance when using alumina-supported Co catalysts,⁷ the reaction-induced Co-Co₂C phase transformation clearly proved beneficial when choosing reducible metal oxides, including also LaO_x, NbO_x and others, rather than just MnO_x, in conjunction with Co metal¹¹ or CoCu bimetallic phases.¹²⁻¹³ The above (and apparently contradicting) findings suggest the Co₂C phase to be a necessary yet not sufficient prerequisite for directing the FT selectivity towards terminal olefins/oxygenates. The simultaneous presence of a reducible metal-oxide support/promotor and, therefore, the occurrence of

favorable metal/metal-oxide interfaces seems to give rise to a synergy effect and has therefore to be regarded key to understanding functionalized product formation in FT synthesis.

With regard to oxygen functionalization, early efforts in the 1970's have shown that CoCu bimetallic phases on various oxide support materials can promote "higher alcohols" production.¹⁴ Long-chain terminal alcohols favoring C₈ to C₁₄ slates became accessible by realizing the need for atomic-scale mixing of the relevant metal compounds. However, there are thermodynamic limitations to the miscibility Co and Cu in 3D bulk phases, one of the consequences being the occurrence of Co@Cu core-shell structures.^{8, 15} The experimental strategy chosen to prepare such core@shell structures included the co-precipitation as polymeric oxalates of Co and Cu before activation.⁸ The interaction of these catalysts with CO (and H₂) under Fischer-Tropsch conditions was shown to cause major reconstruction¹⁶⁻¹⁸ and mobility effects.¹⁹ This was verified in model calculations for both the basal and stepped facets of Co@Cu catalysts by performing density functional theory calculations. Roughly 1/4 of the basal, Cu-terminated, facet can be enriched with Co, while only 1/6 of the stepped facet is being enriched similarly. This is due to the formation of multiply bonded CO molecules coordinating to single Co atoms—the steps themselves enrich up to 50% Co, leaving the terrace sites predominantly Cu-terminated.¹⁹ Somewhat differently, while oxalate co-precipitation of Co and Mn^{6-7, 17} turned out to be likewise possible, thermal activation of such co-precipitates led to Mn-oxide (Mn₅O₈, containing both Mn²⁺ and Mn⁴⁺ states) besides metallic Co particles. Interestingly, from the viewpoint of selective long-chain oxygenates production,^{7, 10} the most efficient Mn-oxide amounts (on an atomic weight basis) were always considerably below parity in 'CoMn' catalysts. Johnson et al.²⁰⁻²¹ developed a decoration model, in which small aggregates of MnO_x populate the surface of Co nanoparticles so

as to maximize the Co-MnO_x interface. The same authors proposed Lewis acid–base interactions between Mn²⁺ and adsorbed CO to weaken the triple bond in C≡O and thereby promote its dissociation.

In order to develop a mechanistic model describing the reduction of the bond order in C≡O as a precursor step to dissociation, we suggest investigating the CO adsorption on a Co(0001) surface next to co-adsorbed metal oxide clusters (TiO₂, ZrO₂ and MnO) of well-defined morphology. This way we determine a clear relationship between the adsorption energy of CO and its corresponding IR vibrational modes and thus bond strength.

Computational Details

All calculations were carried out in the Vienna *Ab-initio* Simulation Package (VASP),²²⁻²⁴ which uses Projector Augmented Wave (PAW) method²⁵ using the datasets released in 2015 to solve the Kohn-Sham Equations.²⁶⁻²⁷ For all the calculations, we utilized the Perdew-Burke-Enzerhof (PBE) Generalized Gradient Approximation (GGA) functional²⁸⁻²⁹ to describe the exchange-correlation. We determined that a plane wave basis set expanded to a 450 eV energy cutoff and the first Brillouin zone of the *p*(5×5) Co(0001) supercell sampled with a Monkhorst-Pack k-point mesh of 1 × 1 × 1 accurately described the underlying energetics of the adsorbate system. The optimized lattice constants of bulk Co are *a*= 2.494 Å and *c*= 4.070 Å, where a k-point mesh of 12 × 12 × 12 was used in this bulk calculation. Spin polarization was incorporated to account for the presence of ferromagnetic Co and dipole corrections were included to eliminate the fictitious dipole created by the asymmetric finite metal slab. Self-consistent field (SCF) and geometric optimization criteria were set at 1.0 × 10⁻⁴ eV and 3.0 × 10⁻² eV/Å, respectively. To eliminate z-direction interaction between slabs, a ~15 Å vacuum layer was imposed. It is clear that metal oxide clusters represent a formidable challenge for

electronic structure calculations, as they certainly have massive amount of static and dynamic electron correlation. While the much needed multireference calculations are currently not possible for periodic systems, DFT can provide the needed qualitative insight, since we are not so much concerned with the clusters themselves, but with their effect on CO and the comparison between its binding modes, benefitting from an additional error-cancellation.

The adsorption of CO on top, hollow, and bridge sites (as shown in Figure S1 of the Supporting Information) on the Co(0001) surface was investigated first and the adsorption energy results and the corresponding C-O frequencies are displayed in Figure S2 of the Supporting Information. These results will be compared with the CO adsorption results when adsorbed on sites that are in the vicinity of metal oxide cluster that is supported on a Co(0001) surface as will be presented in the Discussion section.

The models used here were constructed by adsorbing a Ti_4O_8 , Zr_4O_8 , and Mn_8O_8 metal oxide cluster on $p(5\times 5)$ Co(0001) surface, respectively. Ti_4O_8 , Zr_4O_8 , and Mn_8O_8 are chosen so that a similar cluster size is achieved for comparison. The supporting $p(5\times 5)$ Co(0001) surface has a unit size of 12.47 Å in the surface plane dimension. This results in a distance of about 7 Å between the metal cluster and its image induced by periodic boundary conditions—enough to eliminate the interaction between the metal clusters. This is displayed in Figure S3 of the Supporting Information.

The chemical bonding analysis was done with the Natural Bonding Orbitals (NBO) analysis performed on the optimized $\text{Ti}_4\text{O}_8/\text{Co}(0001)$, $\text{Zr}_4\text{O}_8/\text{Co}(0001)$, and $\text{Mn}_8\text{O}_8/\text{Co}(0001)$ structures, with CO adsorbed on the interface site, and on the FCC hollow site on Co(0001). For each structure, plane-wave wave functions obtained from VASP calculations were projected onto the Def2-SVP basis set³⁰ and analyzed with the Periodic NBO Software.³¹⁻³² NBO performs a

unitary transformation on the delocalized valence multi-electron wave function while preserving electron pairs onto 1 center -2 electron bonds (lone pairs, LPs), 2 center - 2 electron (2c-2e) bonds, and multi center - 2 electron bonds. The electron occupancy cutoffs of 1.65 (out of 2) for LPs and 1.70 for 2c-2e bonds were used. Special attention was paid to the CO molecule, its bond order at different sites, and its interaction with the metal oxide cluster.

Experimental Details

Three different cobalt based catalysts (CoTi, CoZr, and CoMn) were prepared using the oxalate co-precipitation method.³³ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, and $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ co-precipitated in the presence of oxalic acid using tetrahydrofuran (THF) as the solvent. Relative metal atomic amounts in oxalate co-precipitation can be easily varied to design catalysts with well-defined composition. IR experiments were performed on a Bruker Vertex 70 spectrometer using a DRIFT cell Praying Mantis, Harrick. The passivated catalysts were mixed with KBr powder (mechanically) and each catalyst was reactivated at 450 °C in H_2 (10% in Ar) flow followed by cooling to 220 °C. After collecting the background spectra under H_2/Ar flow, the gas flow was then switched to CO (10% in Ar) at 220 °C and the DRIFT signals were recorded after 10 min with the resolution of 4 cm^{-1} , 32 total scans. The DRIFT spectra are presented using the inverse reflectance (1/R) function. Comparing pseudo-absorbance with Kubelka-Munk transformations (as the commonly used functions) has shown that the absorbance function better represent the band intensity against surface coverage.³⁴

Results and Discussions

The structure of the Ti_4O_8 cluster was obtained from the literature,³⁵ and four different configurations were calculated, as shown in Figure S4 of the Supporting Information. The most favorable configuration of the $\text{Ti}_4\text{O}_8/\text{Co}(0001)$ structure is displayed in Figure 1. The difference between this configuration and the other three configurations is that in this configuration, the top Ti atom in the Ti_4O_8 cluster has a coordination number of 4 instead of 3, as shown in Figure 1b. We then proceeded to test the adsorption of a CO molecule on various adsorption sites on this surface.

Figure 1. (a) top and (b) side view of the $\text{Ti}_4\text{O}_8/\text{Co}(0001)$ structure.

The adsorption site of CO on the $\text{Ti}_4\text{O}_8/\text{Co}(0001)$ surface can be broken down into three categories: 1) sites at the interface between the Ti_4O_8 cluster and $\text{Co}(0001)$ surface; 2) sites on the $\text{Co}(0001)$ surface (far from the oxide cluster); and 3) sites on the Ti_4O_8 cluster

itself. Figure 2 shows the corresponding most favorable configuration for each category. The CO adsorption energies are -2.43, -1.94 and -0.60 eV for structure (a), (b) and (c) in Figure 2, respectively. It is found that the interface sites are the most favorable site for CO adsorption while the sites on the Ti_4O_8 cluster are the least favorable. The stronger adsorption energy (Figure 2a) results in a lower C-O wavenumber of 1345 cm^{-1} and a longer C-O bond length of $1.285\text{ \AA}$, as compared with the corresponding values of 1709 cm^{-1} and $1.201\text{ \AA}$ for the configuration shown in Figure 2b. Additionally, the weakest adsorption energy (Figure 2c) has the highest C-O stretch frequency of 2162 cm^{-1} and a shorter C-O bond length of $1.136\text{ \AA}$. It is concluded that a stronger adsorption of CO comes with a weaker C-O bond strength. This conclusion supports the experimental result of the $\text{MnO}_x/\text{Co}(0001)$ system, where Mn promotion increases the abundance of adsorbed CO and weakens C-O bonds wherein a peak is observed with a lower CO wavenumber in the *in situ* IR spectra.²¹ In addition, concerning the most favorable site for CO adsorption, as shown in Figure 2a, CO bonds to the surface by forming C-Co and O-Ti bonds. This is direct evidence for the model proposed by Johnson et al.²¹ We can now understand how the formation of O-Ti bond weakens the C-O bond strength at the electronic level by analyzing its charge density difference.

Figure 2. Top and side views of structures for CO adsorption on (a) a site at the interface between the Ti₄O₈ cluster and the Co(0001) surface, (b) a fcc hollow site on the Co(0001) surface and (c) site the Ti₄O₈ cluster. The location of CO is labeled by a dashed yellow circle.

Here, we focus on the Ti₄O₈/Co(0001) surface to investigate the different CO adsorption behaviors on the interface site (Figure 2a) and the fcc hollow site of the Co(0001) surface (Figure 2b) via charge density differences. The charge density difference, $\Delta\rho$, can be derived by considering: $\Delta\rho = \rho^{\text{sys}} - \rho^{\text{slab}} - \rho^{\text{CO}}$, where ρ^{sys} , ρ^{slab} , and ρ^{CO} are the charge densities of CO adsorbed on Ti₄O₈/Co(0001), the Ti₄O₈/Co(0001) slab and the CO molecule in the gas phase. In calculation of the latter two quantities, the atomic positions are fixed as they are in the system of CO adsorbed on Ti₄O₈/Co(0001). Figure 3 displays the charge density difference for two structures with CO adsorbed on the interface site and the fcc hollow site on Co(0001). From these redistributions, it is found that CO gains more electron density from the support when at the interface site than when at the fcc hollow site on Co(0001). As shown in Figure 3a, the depletion (blue) of the electron density for the Ti atom in the Ti₄O₈ cluster and a significant accumulation (yellow) around CO shows that the Ti atom transfers electrons to CO upon

adsorption. The electron transfer can weaken the C-O bond, which results in a longer C-O bond length and a lower wavenumber in the IR spectra. This is expected to promote the cleavage of the C-O bond.

Figure 3. Top and side view of charge density difference for two structures with CO adsorbed on (a) the interface site and (b) the fcc hollow site on Co(0001). The isosurface value is set at 0.002 electrons/ $\text{\AA}^3$. Yellow and blue distribution represent electron gain and loss, respectively.

In order to examine if the previous conclusion is consistent on other metal oxide clusters supported on Co(0001), models of $\text{Zr}_4\text{O}_8/\text{Co}(0001)$ and $\text{Mn}_8\text{O}_8/\text{Co}(0001)$ are also studied. These systems are shown in Figure 4. The $\text{Zr}_4\text{O}_8/\text{Co}(0001)$ structure was built similarly to that of $\text{Ti}_4\text{O}_8/\text{Co}(0001)$ because Zr and Ti are in the same group in the periodic table of the elements. As mentioned before, the $\text{Mn}_8\text{O}_8/\text{Co}(0001)$ structure was built by choosing a similar cluster size as the $\text{Ti}_4\text{O}_8/\text{Co}(0001)$ and $\text{Zr}_4\text{O}_8/\text{Co}(0001)$ models. Here, for these different models, we summarize the relationship between the adsorption energy of CO and its corresponding IR vibrational modes, and thus bond strength, as shown in Figure 5a and 5b. The stretch frequency for CO decreases with increasing adsorption energy while the C-O bond length increases. The CO frequency has a linear

relationship with the CO adsorption energy and C-O bond length, independent of the environment around CO, whether CO be in the gas phase or adsorbed on Co(0001), $\text{Ti}_4\text{O}_8/\text{Co}(0001)$, $\text{Zr}_4\text{O}_8/\text{Co}(0001)$ and $\text{Mn}_8\text{O}_8/\text{Co}(0001)$. Thus far, we have found that stronger adsorption of CO indeed weakens the C-O bond and promotes CO dissociation. These results can be understood by the amount of electron transfer to CO, as obtained through a Bader charge analysis (see Table S1), which weakens the C-O bond and promotes CO dissociation. As shown in Figure 5c, the more electron density that is transferred to CO, the lower the CO stretch frequency, and correspondingly the stronger the adsorption energy and the longer the C-O bond length.

Figure 4. Top and side views for a Zr_4O_8 and a Mn_8O_8 cluster adsorbed on a Co(0001) surface.

Figure 5. The linear relationship between the (a) adsorption energy, (b) the C-O bond length and (c) the electron transferred to CO and the CO frequency. The structures and corresponding data are listed in Figure S5 to S7 and Table S1 to S3 of the Supporting Information.

Electron transfer to the CO manifests itself in the change of the chemical bonding within the bound CO in an important way. Using a Natural Bond Orbital (NBO) analysis, we found that in all structures with CO adsorbed on FCC hollow site on Co(0001) far away from the cluster, the C-O bond is of the third order, comprised of three two-center bonds. One of these bonds has a hybrid 40% *s* and 60% *p* character on both C and O, while the other two have nearly 99% *p* character. In other words, NBO recovers the familiar single σ -bond and two π -bonds in the CO bound to this site. This calculated bonding behavior shows no signs of the interaction between CO molecule and metal oxide cluster. On the other hand, in all structures with the CO molecule adsorbed on the cluster-surface interface, the C-O bond is of the first order, formed by 35% *s* and 65% *p* hybrids on the C and O atoms. For the $\text{Ti}_4\text{O}_8/\text{Co}(0001)$ and $\text{Mn}_8\text{O}_8/\text{Co}(0001)$ structures with CO adsorbed on the interface site, we found an additional 2c-2e bond between CO's oxygen atom and a metal atom from the oxide cluster. This bond is formed by a hybrid of mostly *d* character on the metal and a hybrid of mostly *p* character on the O. In the case of $\text{Zr}_4\text{O}_8/\text{Co}(0001)$, for the structure with the CO molecule adsorbed on the interface site, we find that no such polar covalent bond was present. Instead, our NBO analysis sees a largely ionic interaction, with a large positive charge (+1.61) on the Zr atom involved in the bonding with CO, and a relatively large negative charge (-0.61) on O atom of the CO molecule, as can be seen in the Figure S11, which provides information about the electron occupancies and charge on different atoms. The electron occupancy (number of electrons, or natural population) of an atom is the number of valence electrons (subject to the used pseudopotentials), occupying Natural Atomic Orbitals (NAOs). NAOs are constructed from plane-wave wavefunctions by projecting onto the Def2-SVP basis set, while fulfilling the requirements of orthonormality and maximal electron occupancy. In general, NAOs mostly retain single

center character and, therefore, are suited to qualitatively describe the molecular electron density around each atom. Thus, the charge of an atom is simply the difference between the occupancy and the number of valence electrons taken with the minus sign. Ultimately, structures with the CO molecule adsorbed on the interface site show a significant interaction between CO and the metal oxide cluster, through the formation of either covalent, or ionic bonds, resulting in C-O bond weakening.

Figure 6. FTIR measurements of CO adsorption over different cobalt-based catalysts measured at 220 °C. The DRIFT spectra are collected after 10 min of CO adsorption for all the catalysts.

The above findings and correlations call for a rigorous experimental analysis by IR spectroscopy. Unfortunately, as will be shown below on account of DRIFTS, the relevant spectral region below 2000 cm^{-1} contains a number of features that overlap with those that come into consideration for weakened C-O binding in adsorbed CO. In particular, surface formate, carboxylate and carbonate structures are known to show a variety of vibrational transitions down to $\sim 1000 \text{ cm}^{-1}$.

It is noteworthy that DRIFTS with MnO_x , in the absence of supported Co particles, showed an entirely flat spectrum between 1000 and 2000 cm^{-1} . While we recognize that the fairly dark color of the samples is unfavorable for recording DRIFTS spectra, it is clear from Figure 6 that CO-induced surface complex structures are formed for Co/MnO_x as well as Co/ZrO_x . We conclude that these features are to be related to the metal-metal oxide interface since a metallic Co surface is unlikely to form any of the above complex structures during CO adsorption. We also note with regard to Figure 6 and in relation to the theoretical calculations of the present paper that DRIFTS with Co/TiO_x showed, similar to MnO_x -only, an essentially flat spectrum within the 1000 to 2000 cm^{-1} spectral region. This measurement has therefore not been included in Figure 6.

In an attempt to provide an assignment for the various peaks in Figure 6, we proceed as follows. The feature at 1782 cm^{-1} , seen to occur for all samples except Co_1Mn_1 , may be attributed to bridge-bonded CO on Co.²⁰⁻²¹ The absence of this feature for Co_1Mn_1 seems to be in agreement with the decoration model developed by Johnson²⁰⁻²¹ according to which MnO_x clusters tend to spread over the surface of Co particles and therefore decrease the number density of Co adsorption sites.

Peaks at 1486 cm^{-1} and 1346 cm^{-1} are similar to those reported previously in kinetic studies of the CO hydrogenation.⁶ It appears, however, that these peaks are rather broad and closer to each other in the present study (as compared to 1530 cm^{-1} and 1430 cm^{-1} in ref. 6). Assuming asymmetric and symmetric vibrations of O-C-O in adsorbed formate/carboxylate to be responsible for these features, the question arises for whether bidentate, monodentate or a mixture of both types of species are to be considered here. This question cannot be solved with the data presently at hand. Furthermore, in relation to the theoretical calculations, see Figure 5, we can also not exclude the

occurrence of adsorbed CO in close vicinity to metal-oxide entities of MnO_x and ZrO_x contributing to the low frequency modes in Figure 6. In this regard it is interesting to note that Sachtler et al.,³⁶ on account of work by Ichikawa et al.³⁷, mentioned Mn^{2+} promoted Rh catalysts to exhibit a band around 1530 cm^{-1} for adsorbed CO, suggesting simultaneous C- and O-bonding to metal and metal oxide.

The lowest absorption frequency observed in DRIFTS occurs at $\sim 1047\text{ cm}^{-1}$. Once again, a similar band was previously observed in CO hydrogenation studies and tentatively attributed to the O-C bond in adsorbed alkoxy.⁶ The occurrence of such species in the present study seems to be unlikely, though. Instead, one may speculate about a model-specific adsorption mode in which CO binds to two O^{2-} of the $\text{Me}_4\text{O}_8/\text{Co}(0001)$ conformation. The calculated corresponding frequency for $\text{Zr}_4\text{O}_8/\text{Co}(0001)$, see earlier, would be 1073 cm^{-1} for this “pseudo-carbonate” adsorption mode. Alternatively, as shown in Figure S10 of the Supporting Information, the insertion of CO into a hydroxyl terminated $\text{Zr}_4\text{O}_8/\text{Co}(0001)$ surface would generate absorption frequencies of 1070 and 1024 cm^{-1} , similar to the experimental finding of $\sim 1047\text{ cm}^{-1}$ in the present DRIFTS study. We refrain from further speculations but recognize the importance of extending our DRIFTS/DFT combined efforts to further develop a foundational understanding of the rich variety of CO-induced adsorption features over Co/MeO_x catalyst surfaces.

Conclusions

We studied the effect of the interface site on the adsorption behavior of CO. The adsorption energy of CO away from and at the interface site between the metal oxide cluster and the Co support is -1.94 and -2.43 eV , respectively. The calculated stronger adsorption energy results in a lower wavenumber of 1345 cm^{-1} and a longer C-O bond length of $1.285\text{ \AA}$, as compared with the corresponding values of

1709 cm^{-1} and 1.201 Å when CO is adsorbed away from the interface site. The charge density difference shows that the metal ion in the metal oxide cluster transfers more electron density to CO to weaken the C-O bond, which is expected to promote the cleavage of CO. Furthermore, models of metal oxide clusters (TiO_2 , ZrO_2 and MnO) supported on a Co surface are used to determine the relationship between the adsorption energy of CO and its corresponding IR vibrational modes, and thus bond strength. The CO stretch frequency decreases as its adsorption energy increases and its C-O bond length increases. Thus far, we have found that a stronger adsorption of CO indeed weakens the C-O bond strength and promotes CO dissociation. The experimental measurement of FTIR seem to support this conclusion, despite an obvious overlap of low-frequency modes in adsorbed CO with the possible occurrence of more complex adsorbate species like formate/carboxylate and carbonate. Our results are also similar to those of Metiu and coworkers, where a similar decrease of the CO stretch frequency was obtained for CO adsorbing in the vicinity of a potassium atom that was coadsorbed on a Ni(111) surface.³⁸ Since the presence of potassium generates a high positive local electric field,³⁹⁻⁴² we further postulate that a large local electric field will be present at the interface between the metal oxide cluster and the Co(0001) surface, which can assist in the weakening of the C-O bond strength. These conclusions have clear implications for the metal-oxide doped Co FT catalyst design since an established linear relationship between CO stretch frequency and CO activity will provide a simple yet powerful tool for tuning CO dissociation and controlling the CO/ H_2 reaction selectivity.

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