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Segregation of Fischer-Tropsch Reactants on Cobalt Nanoparticle Surfaces

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Using scanning tunnelling microscopy, we have visualized the segregation of carbon monoxide and hydrogen, the two reactants in Fischer-Tropsch synthesis, on cobalt nanoparticles at catalytically relevant coverages. Density functional theory was used to interrogate the relevant energetics.

Fischer-Tropsch synthesis (FTS), the reaction of carbon monoxide and hydrogen to form aliphatic hydrocarbons, is a widely-used industrial process that has recently gained much attention for its ability to produce fuels with lower environmental impact.[1-4] Cobalt has recently become the favoured catalyst for FTS due to its low water-gas shift activity, higher chain growth probability, and reduced operating temperature. While the exact mechanism of FTS is unknown, it is thought that the dissociation of CO is a kinetically relevant step that could affect the overall FTS reaction rate.[3,5-7] There are two dominant mechanisms that are debated for the dissociation of CO: direct and indirect.[3,5-12] Direct dissociation involves the dissociative adsorption of CO molecules on the Co surface, where the resulting C monomers combine with adsorbed atomic H on the surface to form CH_x intermediates.[7-9] The indirect mechanism involves the addition of H to molecularly adsorbed CO, followed by the breaking of the C-O bond.[5,6,10-13]

Due to the uncertainty in the CO dissociation mechanism and its importance to the overall FTS rate, an atomic-scale understanding of the interaction of CO and H on Co surfaces is essential. Surface analysis techniques offer the best means for determining information on this scale, as the dynamic state of adsorbates during catalysis is difficult to measure. To this end, previous surface science studies have detailed the adsorption behaviour of CO and H_2 on Co(0001).[14-22] Hydrogen was shown to dissociatively adsorb on the Co(0001) surface, forming two coverage-dependent phases: a 2H-(2x2) where coverage (θ) = 0.5 monolayers (ML), and a 6H-(3x3) with θ = 0.67.[17,18] Using Co nanoparticles deposited on Cu, we demonstrated that a high-coverage H-(1x1) phase can also be formed with θ ~ 1 ML.[18] CO

adsorbs molecularly on Co(0001) surfaces and forms a number of coverage-dependent phases, where a $(\sqrt{3}x\sqrt{3})R30°$ phase dominates at low coverage (θ = 0.33 ML) and a $7CO\text{-}(2\sqrt{3}x2\sqrt{3})R30°$ phase dominates at high coverage (θ = 0.58 ML).[19-22]

Studies of the coadsorption of H and CO on Co(0001) have been relatively limited despite their importance in FTS. Early work by Lambert and co-workers examined the coadsorption of CO and H_2 on Co(0001) with temperature programmed desorption (TPD) and demonstrated that CO partially displaces H on the surface with limited interaction between the coadsorbed species.[15] Another TPD study by Lahtinen and co-workers found that post-dosing CO on a deuterium-covered surface resulted in the reduction of the D_2 desorption temperature.[16] Low energy electron diffraction (LEED) was used to examine the adsorbates after co-dosing and showed that CO was present in its most dense $(2\sqrt{3}x2\sqrt{3})R30°$ phase. No mention was made of the D adsorption structure after co-dosing; however the authors postulated that there was a repulsive interaction between the CO and D due to the unperturbed CO structure. Recently using scanning tunnelling microscopy (STM), we demonstrated that CO exerts a two-dimensional pressure on pre-adsorbed H on Co nanoparticles, which leads to the initial compression of H to its most dense, and previously unreported, H-(1x1) phase. This compression eventually destabilizes H and forces it to spill over onto the Cu support.[23]

Here we extend our previous work by using STM to further study the co-adsorption of CO and H on Co nanoparticles grown on Cu(111). This chemically novel Co system allows us to examine a more catalytically relevant form of Co while still maintaining a well-defined surface geometry (Figure 1E). We demonstrate that CO and H remain segregated on the Co nanoparticles, regardless of preparation procedure or surface coverage. Thus by using a scanning probe technique, we have elucidated a long-standing question about the interaction of H and CO on Co surfaces that has previously only been postulated by other surface-averaged methods. We justify our interpretation using density functional theory (DFT) calculations,

which confirm that the segregation of the two adsorbates is energetically preferred. Given that the segregation is apparent even at high, catalytically relevant coverages, these results indicate that the reaction between CO and H might be kinetically limited by the length of the interface between the species.

Fig. 1 illustrates the segregation that occurs between CO and H at a range of surface coverages. Fig. 1A and B show the high coverage co-adsorbed system, where H exists in its high-coverage H-(1x1) structure and CO is in a high-density disordered structure. CO appears as a bright protrusion and preferentially adsorbs around the outside edges of the nanoparticles. The adsorbed H is not well-resolved in Fig. 1A, but its presence is confirmed by the appearance of dark triangles in the centre of the nanoparticles; previously we have established that these triangles are defects in the H-(1x1) overlayer,[18] as detailed in Fig. 1B. The same segregation effect is observed at lower coverages of CO and H, in their ($\sqrt{3}$x$\sqrt{3}$)R30° and 2H-(2x2) phases, respectively (Fig. 1C and D).
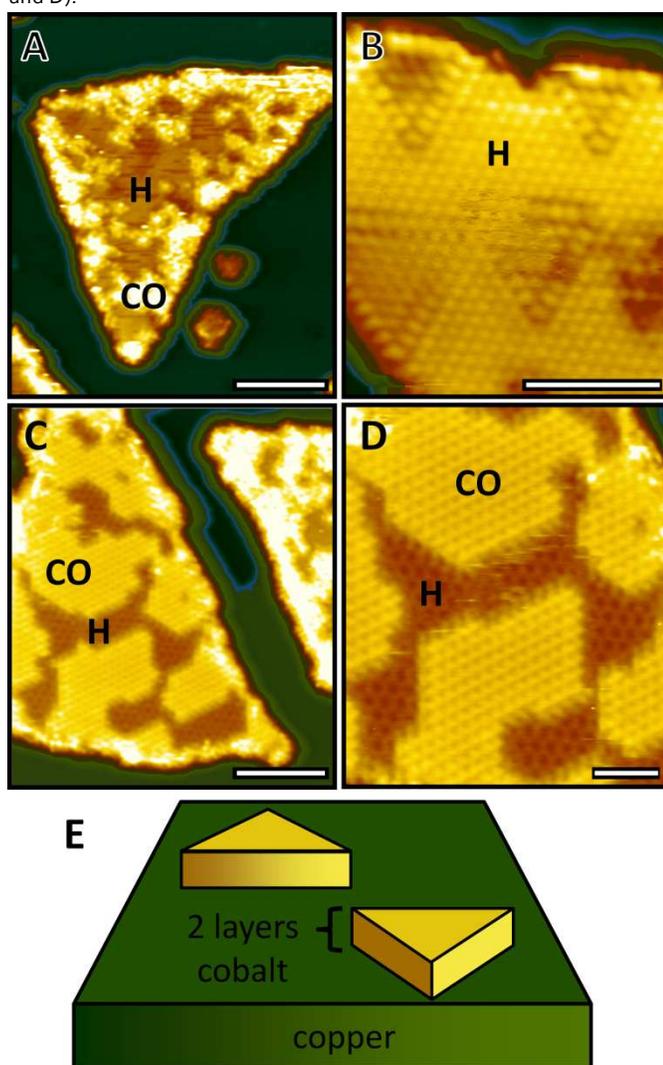
Fig. 1 STM images of segregated H and CO on cobalt nanoparticles on Cu(111). A.) Image of the high-density, compressed state of the CO/H-Co system. CO is completely disordered, and H exists in its high density H-(1x1) phase, as indicated by the dark triangles on the nanoparticle. Scale bar = 5 nm. B.) High resolution image showing the high density H-(1x1) phase with triangular H layer defects. Scale bar = 2 nm. C.) STM image of the low density phases of CO and H: CO-($\sqrt{3}$x$\sqrt{3}$)R30° structure and 2H-(2x2). Scale bar = 5 nm D.) High resolution image showing the interface between the CO-($\sqrt{3}$x$\sqrt{3}$)R30° (yellow) and the 2H-(2x2) (brown). Scale bar = 2 nm. E.) Schematic of Co islands grown on Cu(111).

To confirm that segregation is energetically preferred, we took time-lapse STM movies, created by recording sequential STM images, in the low coverage regime (movie in ESI†). We found that CO and H diffuse freely on the Co nanoparticle surfaces at 80 K, with each adsorbate domain shifting in response to movement of the other. Throughout this mass transport, the two species remain segregated, which indicates that mixing between them is not energetically favourable. While the high coverage phases of CO and H are always segregated as well, we are not able to observe them diffusing because they are locked in place due to the absence of vacant Co sites.

To further examine this segregation, we performed DFT calculations of the binding energies of the known phases of H and CO on Co(0001), as well as an array of mixed CO-H phases (Fig. 2). While it is impossible to model every type of mixed CO and H phase on the Co surface, we chose phases that maintained similar H and CO structures to the pure phases, while conserving the coverage of molecules on the surface. To examine the mixing of the low coverage CO and H, two mixed phases were examined: a 2CO, 3H-(2$\sqrt{3}$x2$\sqrt{3}$)R30° structure with θ = 0.42 ML (Fig. 2A), and a 1CO, 1H-(2x2) structure with θ = 0.50 ML (Fig. 2B). A phase similar to the latter was previously observed for CO and H on Ni(111).[24] To model the mixing of the high coverage CO and H phases, a 1CO, 2H-(2x2) structure (Fig. 2C) was used with θ = 0.75 ML. Other details of computational parameters and settings can be found in our previous work.[23] The binding energy, which is the sum of the adsorption energy of each molecule in the unit cell, was calculated for each of the mixed phases (Table I).
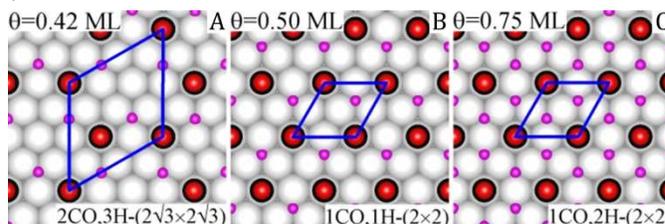
Fig. 2 The three mixed phases of CO and H on Co(0001) that were calculated with DFT (pink circles represent H, and red/black circles denote CO). A.) 2CO, 3H-(2$\sqrt{3}$x2$\sqrt{3}$); Θ = 0.42 ML. The ratio of H:CO = 3:2. We postulate that this phase could result from the mixing of the low coverage 2H-(2x2) and CO-($\sqrt{3}$x$\sqrt{3}$)R30°. B.) 1CO, 1H-(2x2); Θ = 0.50 ML. The ratio of H:CO = 1:1. This phase is an alternative possibility for the mixing of low coverage CO and H, as a similar phase was observed on Ni(111).[24] C.) 1CO, 2H-(2x2); Θ = 0.75 ML. The ratio of H:CO = 2:1. This phase is a likely result from the mixing of the high coverage H-(1x1) and 7CO-(2$\sqrt{3}$x2$\sqrt{3}$) phases.

To determine whether the mixed or segregated phases were preferred energetically, the adsorption energy (E$_{ads}$) of each molecule of CO or atom of H was calculated in the pure phase (Table I), where the 7CO-(2$\sqrt{3}$x2$\sqrt{3}$)R30° was used to model high CO coverage. This E$_{ads}$ value was then scaled to account for the stoichiometry of the species in the resulting mixed phase to obtain the comparable binding energy of the pure phases. For example, to compare the preference of formation for the mixed 2CO, 3H-(2$\sqrt{3}$x2$\sqrt{3}$)R30° structure with that of the segregated low coverage CO-($\sqrt{3}$x$\sqrt{3}$)R30° and 2H-(2x2) phases, we used the difference in binding energy between them as defined in the following:

$$\Delta E_{seg} = E_{bind[2CO, 3H-(2\sqrt{3}x2\sqrt{3})]} - \{2E_{ads[CO-(\sqrt{3}x\sqrt{3})]} + 3E_{ads[2H-(2x2)]}\}$$

where E_{bind} is the binding energy of the overlayer unit cell. The resulting ΔE_{seg} for this example is -0.44 eV. For the comparison of the mixed 1CO, 1H-(2x2) with the segregated CO-($\sqrt{3}$x$\sqrt{3}$)R30° and 2H-(2x2), the corresponding ΔE_{seg} is -0.44 eV; for the comparison of the mixed 1CO, 1H-(2x2) with the segregated 7CO-(2$\sqrt{3}$x2$\sqrt{3}$)R30° and 2H-(2x2), the corresponding ΔE_{seg} is -0.17 eV; and for the comparison of the 1CO, 2H-(2x2) mixed phase with the 7CO-(2$\sqrt{3}$x2$\sqrt{3}$)R30° and H-(1x1) segregated phases, the corresponding ΔE_{seg} is -0.12 eV.

Table I Adsorption energy per molecule and binding energy of the overlayer unit cell

Overlayer unit cell	E_{ads} (eV)*	E_{bind} (eV)†
CO		
CO-($\sqrt{3}$x$\sqrt{3}$)R30°	1.29	1.29
7CO-(2$\sqrt{3}$x2$\sqrt{3}$)R30°	1.02	7.14
H		
2H-(2x2)	0.54	1.08
H-(1x1)	0.42	0.42
Mixed CO & H		
2CO, 3H-(2$\sqrt{3}$x2$\sqrt{3}$)R30°	-	3.76
1CO, 1H-(2x2)	-	1.39
1CO, 2H-(2x2)	-	1.74

*E_{ads} values are calculated per atom of H or molecule of CO
†E_{bind} values are the sum of the E_{ads} values for each species in the overlayer unit cell

By comparing the binding energies of the segregated and mixed phases in this way, it can be seen that segregation is always preferred (negative ΔE_{seg}) if the surface packing density remains roughly equivalent in the mixed and segregated phases. Since the area of the Co nanoparticles is fixed, the coverage cannot decrease upon mixing as desorption is not possible at the temperatures examined, consistent with the fact that mixing is never observed experimentally. This conclusion holds for all our considered mixed phases.

Using a scanning probe approach, we have elucidated the segregation of CO and H on Co with atomic-scale resolution. Where previous surface-averaged studies have only been able to postulate the segregation between these species, we have been able to show that segregation is energetically preferred over a wide-range of catalytically relevant (high) coverages on Co nanoparticles. While we consistently observe these segregation effects, it is somewhat unexpected considering other CO-H coadsorbed systems. On Ni(111) and Fe(100), which are chemically close relatives of Co(0001), CO and H form well-ordered mixed phases.[24,25] Segregation has previously been observed for coadsorbed CO and H on Pd(111), but this metal shares fewer catalytic similarities with Co.[26,27] The observed segregation may provide further insight into the FTS mechanism on catalytic Co nanoparticles, demonstrating the value of scanning probe studies in understanding surface catalysed reactions.

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