

Editor's choice paper

A DFT study of the effect of copper promotion upon iron oxide surface species

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ABSTRACT

Cluster models for sites on the {111} surface of Fe_3O_4 were used to study the strength of bonding of water-gas shift intermediates using density functional theory. Three site models were used, representing an unpromoted catalyst, a catalyst where copper cations substitute for iron cations below the surface and a catalyst where copper cations substitute in the surface. The strengths of bonding of oxygen, carbon dioxide, dissociated water and dissociated formic acid were all observed to decrease by less than 20 kJ mol^{-1} when copper substituted below the surface, but they decreased by $60\text{--}80 \text{ kJ mol}^{-1}$ when copper substituted in the surface of the catalyst. A minimum energy structure for molecularly adsorbed water was not identified because all attempts to do so resulted in dissociation.

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1. Introduction

Magnetite, Fe_3O_4 , is the active component of high temperature water-gas shift catalysts [1–3]. Copper is sometimes added to commercial catalysts as a promoter [4–16]. Promotion using copper is reported to improve the performance of the catalysts when the ratio of steam to carbon monoxide in the feed is below three [7,14], to improve activity [4–6,10,12,13,15], to improve stability [12,13], and to lessen product inhibition [15]. The role of copper has not been definitively established. One hypothesis is that copper cations substitute for iron cations in the oxide, and the associated changes in the electronic structure of the catalyst affect its catalytic behavior [10,11,14]. An alternative hypothesis is that under water-gas shift conditions, copper migrates to the surface of the catalyst and forms small metallic copper aggregates that are responsible for the modified catalytic properties [6,16]. More recently it has been suggested that copper within the oxide structure plays a role in catalyst stabilization while surface copper plays a separate role as an active site [12,13].

The mechanism of water-gas shift, and consequently its kinetics, might be affected quite differently by these two alternative views of the promotion process. If copper functions by substituting for iron cations within the oxide, the mechanistic steps would not necessarily change. The energetics associated with the steps would be modified due to the change in the electronic structure, but the sequence of molecular events could remain the same. In

the alternative model where metallic copper is formed, it seems more likely that the entire mechanism would be different on the metallic copper aggregates than it is on an iron oxide surface.

A comparison of the kinetics of water-gas shift over an unpromoted catalyst to the kinetics over a copper-promoted catalyst might help discriminate between the two models for promotion. That is, the substitutional promotion model would be favored if the same mechanistic kinetic model for water-gas shift (with only small changes in the energetic parameters) can accurately describe the kinetics for both an unpromoted catalyst and a copper-promoted catalyst. However, such a comparison will only differentiate the two promotional models if the energetic changes caused by copper substitution are relatively minor. The study described here was undertaken for the purpose of assessing the magnitude of such energetic changes. Specifically, cluster models of the active site were constructed with and without substitutional copper cations, and density functional theory was used to compute the structure and energy of suspected water-gas shift intermediates on those sites.

2. Experimental

In a previous study [17] DFT cluster models representing three different crystallographic surfaces of Fe_3O_4 were compared. The clusters were cut from the crystallographic structure of Fe_3O_4 , including the distortion at the tetrahedral cation sites. The model corresponding to a {111} surface provided the closest agreement with experimental kinetics results. Consequently, in the present work this same cluster model for the {111} surface has been used. Fig. 1 shows the cluster viewed (a) looking directly down on the {111} surface, (b) looking from the front with the [111] plane ori-

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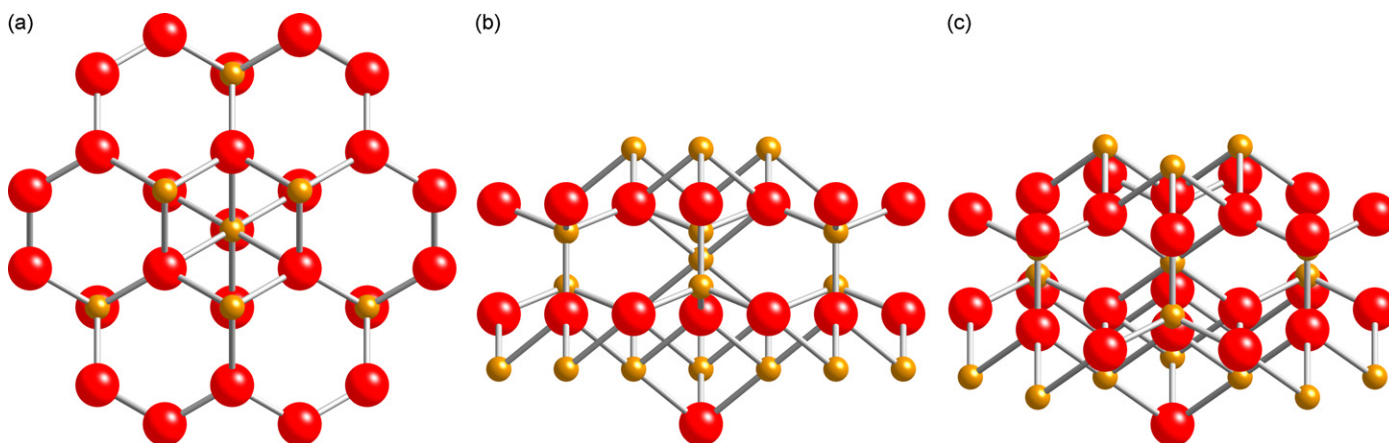


Fig. 1. Cluster representing the {111} surface of Fe_3O_4 as viewed (a) from above the surface, (b) from the front and (c) from the front and slightly above the surface. The smaller spheres represent iron cations and the larger spheres represent oxygen anions.

ented perpendicular to the page, and (c) looking slightly down and from the front. In all geometry optimizations reported here, the atoms shown in Fig. 1 were constrained to remain fixed in the positions shown; only the atoms in the species adsorbed on the surface were allowed to move.

Two different copper-substituted clusters were examined. In each of the two clusters studied, a single Cu^{2+} cation replaced an Fe^{2+} cation holding the geometry fixed. In one copper-substituted cluster, shown in Fig. 2a, the copper cation was located in an octahedral site just below the surface, directly below the three surface iron cations representing the active site. This copper cation is fully coordinated to six nearest neighbor oxygen anions. In the other copper-substituted cluster, shown in Fig. 2b, the copper cation replaced one of the three surface cations corresponding to the active site. Henceforth the site represented in Fig. 2a will be referred to as the sub-surface copper cluster, that in Fig. 2b will be referred to as the surface copper cluster, and the site represented in Fig. 1 will be referred to as the all iron cluster.

When cluster models are used to represent heterogeneous catalytic sites, bonds are broken as a result of cutting the cluster from the bulk structure. Often these broken bonds are capped, for example using a hydrogen atom so that the original valence is preserved. In the case of Fe_3O_4 , the broken bonds have a fractional valence associated to them, and consequently this is not possible. Here, instead, the clusters were selected so that they contained six Fe_3O_4 formula units plus (to prevent an asymmetric cluster) one additional Fe^{2+} and one additional O^{2-} . As a result, the clusters were uncharged, and the broken bonds were located some distance from the active sites so as to minimize their effect upon the bonding at the active site. (if, during geometry optimization, an adsorbed species ended up bonding to one of these atoms on the edge of the

cluster, the resulting geometry was discarded and the optimization was repeated.) This is the same approach as was used in the previous study [17] where it was found that energies calculated using the clusters were in reasonable agreement with energies derived from mechanistic kinetic studies.

Density functional theory was used to study the three sites as shown in Figs. 1 and 2 and also with different species adsorbed on their surface. The calculations were performed using version 7 of the Jaguar code [18]. B3LYP correlation and exchange functionals were employed along with a TZV** basis set. The calculations used fine grids, and no symmetry constraints were imposed during the optimization of geometries at the ultrafine level. The energies of the optimized structures are reported here without any basis set superposition corrections and without the calculation of the zero point energy. As in the previous study [17], the high spin state was assumed for the oxides, and initial guesses for the wavefunctions accounted for the ferromagnetic nature of Fe_3O_4 . In the clusters containing substitutional copper, the formal charge of the substituting copper was the same as the Fe^{2+} cation it replaced; in the initial guess the copper cation was assigned one unpaired electron with its spin in the same direction as the iron cation it replaced.

3. Results and discussion

Two mechanisms have been advocated for water-gas shift over Fe_3O_4 [3]. One mechanism, often referred to as the regenerative or redox mechanism, involves a sequence wherein sites are oxidized by H_2O generating H_2 , and then the resulting oxidized sites are reduced by CO , producing CO_2 and restoring the site to its original state. In its simplest form, this mechanism can be written as just two steps wherein the only surface species are a vacant site

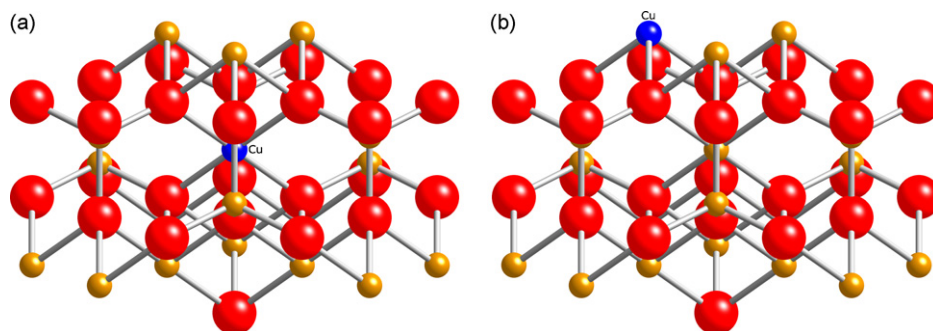


Fig. 2. Cluster representing the {111} surface of copper-promoted Fe_3O_4 wherein copper has substituted (a) within the oxide below the surface and (b) in the surface of the oxide. The copper atom is labeled; the other atoms are as in Fig. 1.

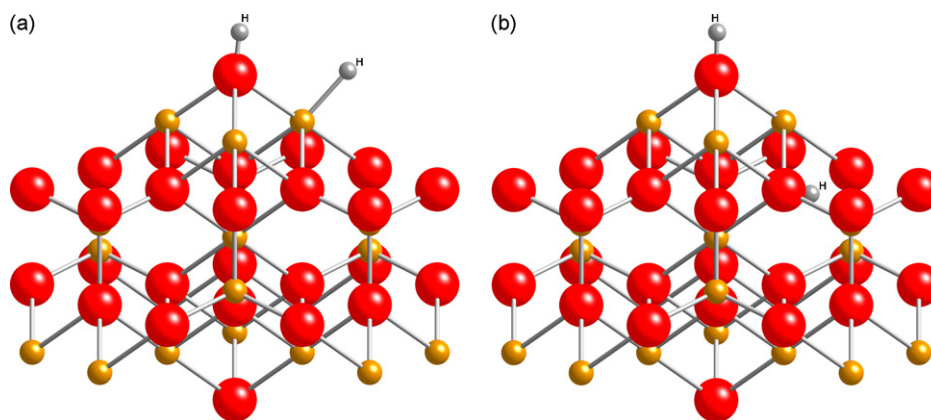
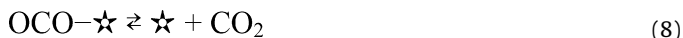
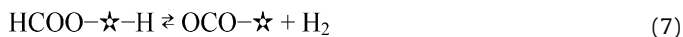
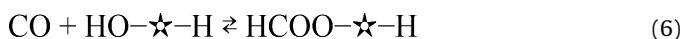


Fig. 3. Two low energy geometries for water dissociatively adsorbed on the site. The configuration shown in (a) is lower in energy by 14.5 kJ mol^{-1} than that shown in (b).

and an oxidized site [17]. It is more likely, however, that other surface intermediates are involved such as those indicated in reactions (1)–(5). In these reactions the site (\star) is taken to be an adjacent cation–anion pair so that $\text{HO}-\star-\text{H}$ actually represents two hydroxyl groups (one on the cation that includes the oxygen from the adsorbing water and one on the anion where only a hydrogen from the adsorbing water is involved). Indeed, there is spectroscopic evidence for the formation of hydroxyl groups, carbonates, carboxylates and other species on the surface of Fe_3O_4 [19–23].



While most investigators appear to favor the redox mechanism for shift over iron oxides, there is also evidence that supports an associative mechanism involving surface formates [3]. In that mechanism, reactions (3)–(5) are replaced by reactions (6)–(8).



The key difference is the insertion of CO into a hydroxyl group to produce a surface formate that subsequently reacts with an adjacent hydroxyl group yielding H_2 and a surface carbonate.

For present purposes it is not necessary to debate the merits of these two mechanisms; they simply serve to identify the surface species that have been studied here. Examining the mechanistic steps reveals five surface species in addition to the vacant site: molecularly adsorbed water ($\text{H}_2\text{O}-\star$), dissociatively adsorbed water ($\text{HO}-\star-\text{H}$), an oxidized site ($\text{O}-\star$), a carbonate ($\text{OCO}-\star$) and a formate ($\text{HCOO}-\star-\text{H}$). Density functional theory was used to identify minimum energy geometries for these species and to calculate the energy associated with their formation as discussed presently.

3.1. Geometry of the surface species

All attempts to minimize the energy of molecularly adsorbed water resulted either in dissociation of the water or its migration to the edges of the cluster where atoms had been cut away when forming the cluster. It is possible that molecularly adsorbed water might form on other Fe_3O_4 surfaces or sites, but it appears that water adsorbs dissociatively on the $\{111\}$ sites used here. In fact,

two geometries of nearly equal energy were found for dissociative adsorption of water. The lower energy structure is shown in Fig. 3a and the higher energy structure in Fig. 3b. In both cases a hydroxyl group formed from the adsorbing water is located in the three-fold site formed by the surface cations. The difference between the two structures is in the location of the other proton. In the lower energy structure (Fig. 3a) the proton is bound to one of the iron cations of the active site at a distance of 0.1529 nm . As shown in Fig. 3b, the proton can also form a hydroxyl group within the $\{111\}$ surface; this geometry is 14.5 kJ mol^{-1} higher in energy than that shown in Fig. 3a. The lower energy structure did not change appreciably when copper was substituted either sub-surface or on the surface. In the latter case, the proton was bonded to an iron cation in the final structure and not the copper cation. The present results are consistent with UPS and TDS studies of the adsorption of water on thin films of Fe_3O_4 where molecular water only underwent physisorption [21,22]. The only chemisorbed form of water was dissociated, forming a hydroxyl group on the cations and neighboring oxygen ions accepting the remaining proton.

The desorption of molecular hydrogen from either of the structures in Fig. 3 results in an oxidized site as shown in Fig. 4. The adsorbed oxygen atom is located in the three-fold site formed by the iron cations. The structure is essentially the same for the sub-surface and surface clusters. In all three cases the oxygen atom is slightly closer to one of the iron cations (0.1908 nm in the all iron cluster, 0.1919 nm in the sub-surface cluster and 0.1884 nm in the surface cluster) than to the other cations (0.2036 nm and 0.2031 nm in the all iron cluster, 0.2022 nm and 0.2034 nm in the sub-surface cluster, and 0.2020 nm (Fe cation) and 0.2032 nm (Cu cation) in the surface cluster).

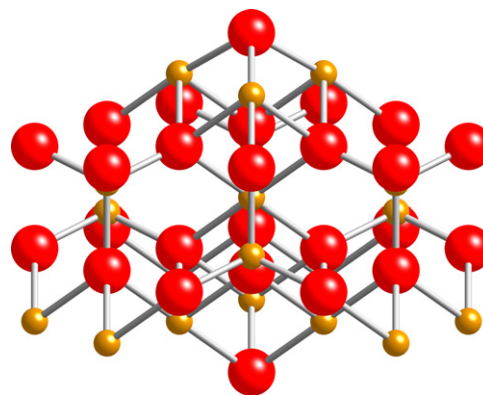


Fig. 4. Minimum energy geometry for an oxidized site. The unpromoted catalyst is shown, but the geometries on the promoted sites were nearly the same as discussed in the text.

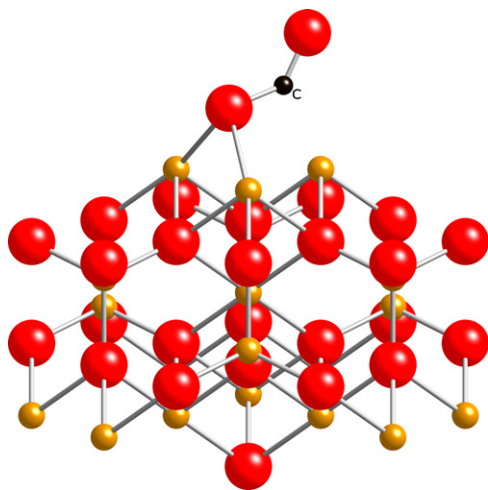


Fig. 5. Minimum energy geometry for carbon dioxide adsorbed on the active site. The unpromoted catalyst is shown, but the geometries on the promoted sites were similar as discussed in the text.

The adsorption of CO on the oxidized site, or, correspondingly, the adsorption of CO₂ on the vacant site, leads to the structure shown in Fig. 5. The surface carbonate is unidentate (bound through only one of its oxygen atoms), and it is located in a bridging position between two of the three surface cations. Geometry optimizations that began with a bidentate carbonate (both oxygen atoms bound to the site) transformed to the unidentate structure shown in Fig. 5. The structure is essentially the same for all three clusters studied. On the surface-substituted cluster, one of the two cations bridged by the carbonate was the copper cation. The difference between the two carbonate-cation bond lengths was 0.0026, 0.0024 and 0.0120 nm, respectively, for the all iron, sub-surface and surface clusters. The carbonate adsorbed on the surface cluster, where the bond length difference was the greatest, was closer by 0.0120 nm to the iron cation than to the copper cation.

The minimum energy structure for the formate species adsorbed on the all iron cluster is shown in Fig. 6. A very similar structure was found when the sub-surface cluster was used. The formate is bidentate with one oxygen atom bridging two iron cations and the other oxygen atom over the remaining cation. The other proton can be seen to form a hydroxyl group with a surface oxygen atom as was

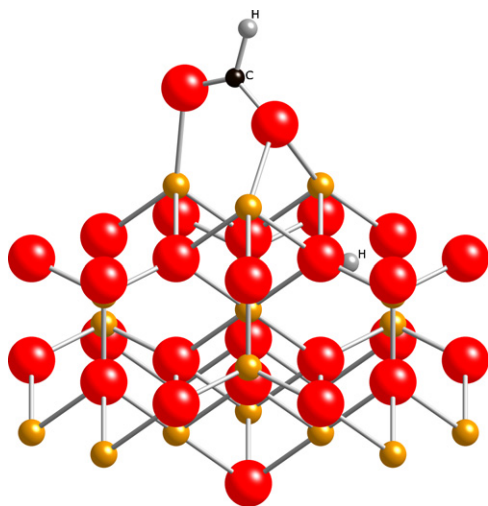


Fig. 6. Minimum energy geometry for formic acid adsorbed on an active site of unpromoted Fe₃O₄. The geometry was similar when for the promoted catalyst where the copper substituted below the surface within the oxide.

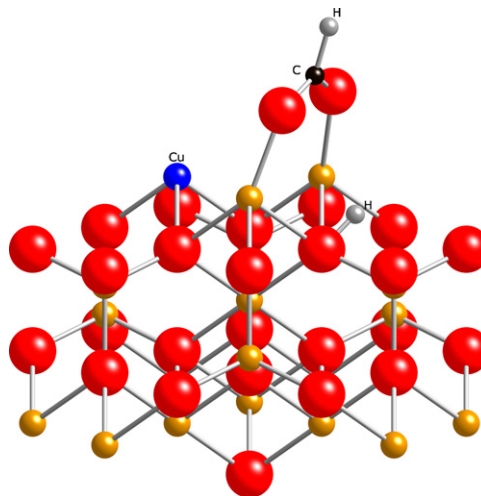


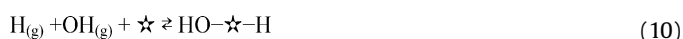
Fig. 7. Minimum energy geometry for formic acid adsorbed on an active site of the promoted catalyst where the copper substituted in the surface of the oxide.

found for the higher energy form of dissociated water. A very different structure was found, Fig. 7, when copper was present on the surface. As can be seen, the formate remains bidentate, but each of the oxygen atoms binds to a single iron cation and the copper cation does not participate. In addition, the second proton still forms a hydroxyl group with a surface oxygen anion, but it becomes positioned slightly above the plane of the oxygen anions instead of being slightly below that plane. STM results indicate that a bidentate, non-bridging formate does form on the {1 1 1} surface of magnetite, but the surface examined in that work was terminated by tetrahedral cations as opposed to the octahedral cation termination in the present work [19].

The geometric structure of each adsorbed species was very nearly the same for the all iron cluster and for the sub-surface cluster. When substitutional copper was present on the surface, there were more significant structural differences. In all cases, the surface copper cation was found to participate less in the formation of the adsorbed species than the iron cation it replaced. In the cases of dissociated water and the oxidized site the differences were small. When the adsorbed species contained carbon, however, the differences were greater. While the carbonate structure remained unidentate and bridged two cations in all cases, when one of the bridged cations was copper, the carbonate moved farther from it and closer to the iron cation. In the case of the formate, it remained bidentate in all cases, but when a copper cation replaced an iron cation on the surface, the formate changed from being coordinated to all three cations to being coordinated to only the two iron cations. The next section will show that significant energy differences accompany these structural variations.

3.2. Effect of copper substitution upon the energies of the surface species

The energy change associated with reactions (9)–(12) was calculated for each of the clusters studied. These particular reactions were selected because the corresponding enthalpies can be used as parameters when fitting mechanistic kinetic models to experimental data. As such, the values computed here can be compared directly with values obtained from mechanistic kinetic modeling. In essence, these reactions represent the energy of localizing the corresponding gas phase species on the surface.



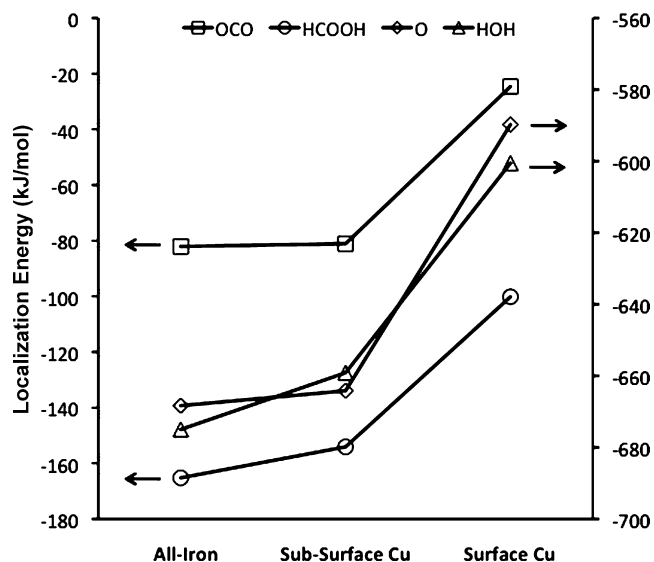


Fig. 8. Variation in the energy of localization of water-gas shift intermediates with the location of the promoting copper cation.



The resulting localization energies are plotted in Fig. 8. It can be seen that in all cases, the substitution of copper causes a weakening of the bond between the surface and the adsorbed species. When the copper substitution is sub-surface, the energy decreases for every species studied. However, the magnitude of the increase in the localization energy for the species on the sub-surface cluster ranged from 1.0 (for the carbonate) to 15.9 kJ mol⁻¹ (for dissociatively adsorbed water). This is smaller than expected uncertainty in calculated energies which is estimated to be 14–17 kJ mol⁻¹ [24]. Both of these results are consistent with the geometric findings: the structures of the adsorbed species were very nearly the same for the all iron and the sub-surface cluster, and the small differences that were revealed involved slightly longer bond distances on the sub-surface cluster.

The energy of localization decreased by a much greater amount (ranging from 57.4, for the carbonate, to 78.6 kJ mol⁻¹, for the oxygen adatom) when copper substituted in the surface. Again, this is consistent with the geometric findings. The structural differences in the species between the all iron cluster and the surface cluster were much greater than those between the all iron cluster and the sub-surface cluster. In some cases the degree of coordination to the surface decreased and in the other cases the surface bond lengths increased. Both of these effects are consistent with the result that the surface bonds were weaker for the species on the surface cluster.

3.3. Consequences of copper substitution upon the mechanism of water-gas shift

The most likely locations for copper atoms added as promoters to Fe₃O₄ are (i) substituted in place of iron cations within the bulk of the iron oxide, (ii) substituted in place of iron cations in the surface of the iron oxide, or (iii) on the surface of the iron oxide, perhaps in the form of small metallic aggregates. While only the localization energies, and not activation barriers, have been studied, the present results suggest that in case (i), the mechanism of water-gas shift probably would not differ from that on an unpromoted iron oxide. There would likely be small changes in the associated energetics, but the present results indicate that such changes would be small. In contrast, the present results suggest that for case (ii), there would

be substantial changes in the kinetics. The localization energies for the most likely surface intermediates are smaller than on an unpromoted iron oxide by ca. 60–80 kJ mol⁻¹. Changes of this magnitude should be experimentally measurable via mechanistic kinetic modeling, assuming the mechanistic pathway remains the same. If the mechanistic pathway changes, that too, should be apparent during mechanistic modeling of experimental kinetics data. Case (iii) has not been studied in the present work, but as already noted, it seems likely that if the copper forms small metallic aggregates that serve as the active sites, then the mechanistic kinetics will likely be quite different from an unpromoted iron oxide. This seems particularly likely given the substantial changes caused by substitution of copper cations in the surface of the iron oxide.

One goal of this study, as mentioned in the introduction, was to estimate the magnitude of the changes in the water-gas shift energetics due to copper substitution in order to determine whether detailed kinetic modeling might be useful in discriminating among the models proposed for copper promotion. The present results do suggest that comparing the mechanistic kinetics of a promoted catalyst to an unpromoted catalyst might be useful in this regard. Specifically, if the mechanistic kinetics of shift are only slightly different on the two catalysts, then the present results would support a promotional model involving substitution of copper within the bulk of the iron oxide. However, if the mechanistic kinetics for promoted and unpromoted catalysts were markedly different, the role of the copper would be less clear. The present results suggest that large differences could be due to copper substitution within the surface of the iron oxide (one model for promotion), but they do not rule out the alternative possibility that large changes could also be due to the formation of metallic copper aggregates. In light of these results, mechanistic kinetic studies are presently being performed.

4. Conclusions

On the basis of DFT calculations using cluster models for the active sites, the energy of localization of water-gas shift intermediates on iron oxide catalysts can be moderated by the substitution of copper cations in the iron oxide. If copper cations substitute for iron cations below the surface of the catalyst, the bonding of the intermediates to the surface is weakened only slightly (that is by less than 20 kJ mol⁻¹). In contrast, if copper cations substitute for iron cations in the surface of the catalyst, the bonding of the intermediates decreases by 60–80 kJ mol⁻¹. It should be possible to distinguish between these two possibilities by comparing the mechanistic kinetics for an unpromoted catalyst to the kinetics for a copper-promoted catalyst.

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