CO Dissociation Site on Fe

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Comparison of potential energies along a variety of pathways calculated for CO dissociation on various sites of the Fe(100) surface indicates that a four-fold site provides the lowest energy pathway and suggests the generalizations that multicentre bonding is favoured and that pathways which have the C and O atoms bonded to the same surface atoms are unfavourable because they are high energy pathways.

There is great interest in CO dissociation on metal surfaces because one mechanism which has been demonstrated to occur in CO hydrogenation[1] proceeds *via* CO dissociation. This mechanism is reasonably well established for hydrocarbon production over Ru[2] and for the methanation reaction on Ni.[3] Because CO has been shown to readily dissociate on most transition metals in the temperature range from 100 to 300 °C where CO hydrogenation is usually carried out, the CO dissociation mechanism is presumed to contribute to reaction on other transition metals as well.[4]

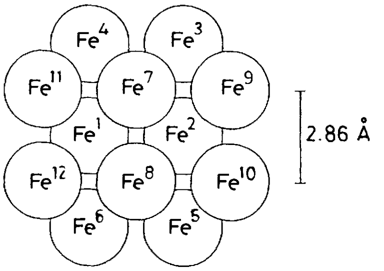
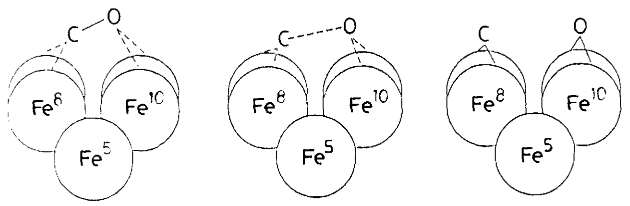


Figure 1. Fe_{12} cluster.



R(C-O) = 1.29 R(C-O) = 2.22 R(C-O) = 2.87

Figure 2. Structure for the starting point, activated complex, and ending point for CO dissociation on a four-fold site.

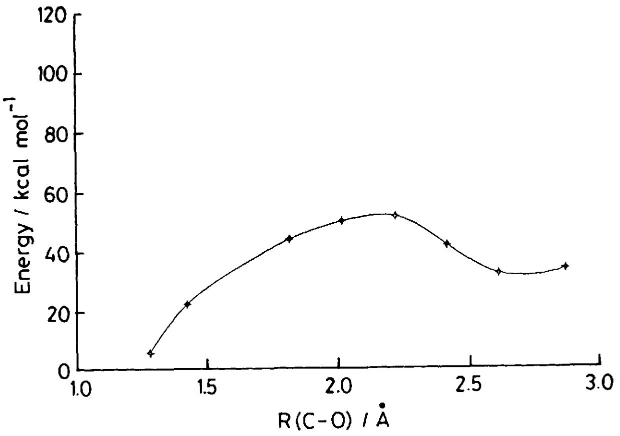


Figure 3. Potential energy along pathway of dissociation on the four-fold site.

The precise atomic motions and surface atom interactions which lead to CO dissociation are not determinable from available experimental methods. This communication presents for the first time a comparison of potential energies along a variety of reaction paths for different sites on an iron surface. These calculations give a four-fold site on the Fe(100) surface as the site providing the lowest energy dissociation path. A comparison of the various paths and sites reveals some general principles about which sites and pathways produce the lowest energy reaction paths. These principles can guide future thinking about surface reaction mechanisms. A knowledge of the most appropriate reaction sites provides goals for catalyst design to maximize the number of these sites and to test the validity of the theoretical results.

The CO dissociation pathways are on various sites of the (100) surface of the Fe_{12} cluster shown in Figure 1. This cluster is large enough to give several different types of surface sites but small enough that calculations could be done in a reasonable length of time. The calculations were done, using the MINDO/SR method, with the Fe atoms fixed in the bulk positions with the top layer atoms 2.86 Å apart and a nearest neighbour distance to atoms in the next layer of 2.48 Å. The details of the method as well as its ability to handle a wide variety of compounds including large metal clusters have been reported previously.[5—9] The MINDO/SR procedure explicitly includes electron–electron repulsions and is parameterized to give bond energies and lengths for selected reference compounds in agreement with experimental values. The most stable site calculated for an adsorbed CO molecule has the carbon atom in a four-fold site bonding equally to Fe-7, 8, 9, and 10 with a binding energy of 27 kcal mol^{-1} (1 cal = 4.184 J), which is in good agreement with experimental values.

Calculated CO dissociation pathways include the following. (i) From CO in a four-fold site the oxygen atom passes over an Fe–Fe bond to an adjacent four-fold site; (ii) with the CO axis over the Fe-7–Fe-8 axis, the C atom moves to a position over Fe-8 while the O atom moves over Fe-7; (iii) with the CO axis approximately parallel to the surface and perpendicular to the Fe-7–Fe-8 axis, the C and O atoms move to the adjacent four-fold sites on either side of the Fe-7–Fe-8 atom pair; (iv) starting with CO upright in a two-fold site between Fe-7 and Fe-8, the O atom moves to the adjacent two-fold site between Fe-9 and Fe-10; (v) with the CO axis approximately parallel to the surface and centred over a four-fold site, the C and O atoms separate to adjacent two-fold sites.

The lowest energy path was (v)5 and is illustrated in Figure 2. The potential energy along this path is given in Figure 3. The potential energies for the points along the path were calculated by constraining the C and O atoms to remain on a vertical line and separating the lines to produce a particular direction of separation. At each point the energy was minimized by allowing the C and O atoms freedom of vertical motion. Thus the path energies represent minima along a path of changing horizontal C–O separation.

While experimental data does not give the site for CO dissociation during reactions, one adsorbed state of CO on the Fe(100) surface has been found to have a strained C–O bond indicated by an unusually low stretching frequency.[10] It has been suggested that this state which occurs only on the Fe(100) face and not on other Fe faces is a precursor to dissociation. The site for this strained CO has been said to be a four-fold site with the CO tilted with respect to a surface normal.[11,12] The lowest energy CO dissociation path and site calculated here is consistent with these experimental findings.

Comparison of the potential energies calculated along the various pathways leads to the following general principles for reactions at an iron surface. (i) The larger the number of surface metal atoms bonding to an adsorbate, the greater the adsorption energy is (*i.e.*, multicentre bonding is favoured); (ii) the dissociating atoms should be bonded to different surface atoms. In all pathways examined here, when the C and O atoms were bonded to the same surface atom a high energy pathway was obtained. For the particular case of CO dissociating on the Fe(100) surface these generalizations lead to the lowest energy pathway being dissociation over a four-fold site as shown in Figure 2.

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