



Identifying the active sites for CO dissociation on Fe–BCC nanoclusters



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ABSTRACT

CO dissociation rate is fundamental for determining selectivity and yield for growing carbon chains on iron catalysts in, e.g., Fischer–Tropsch and carbon nanotube syntheses. CO dissociation is a highly structure sensitive reaction; on crystal surfaces and large particles CO dissociation is facile only at step sites. However, small (<3 nm) nanoparticles cannot contain steps and even in macroscopic clusters step concentration is small. Here, density functional theory is used systematically to map several CO dissociation pathways to find and explain the nature of active sites in small BCC iron nanoclusters. It is shown that BCC(100–110) edges of the particle are responsible for the reactivity of small Fe–BCC clusters and that low CO dissociation barrier is achievable even without stepped surfaces. Careful analysis proves the essential role of local geometry at the active site leading to strong interaction between the metal and $2\pi^*$ orbitals and accessible, empty states. Furthermore, CO dissociation on Fe–BCC particles is more facile than on smooth crystal surfaces and icosahedral and amorphous iron particles exemplifying the importance of nanoparticle geometry on reactivity. Providing suitable particle geometry is used, CO dissociation on Fe–BCC nanoparticles occurs even under mild conditions, enabling controlled synthesis of carbon structures from CO.

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1. Introduction

Transition metals are known for their catalytic activity towards various chemical transformations. As most heterogeneous catalysis takes place on nanoparticles it is of primary importance to understand and explain how size and geometry of particle affect its catalytic activity. The reactivity of conventional, noble metal nanoparticles (Au, Pd, Pt, Ag) has been extensively studied and the observed increase in reactivity of smaller particles is mainly due to presence of edge/step sites and high-energy *d*-states at these low-coordinated sites [1–4]. Unfortunately, studies on nanoeffects on reactivity remain quite scarce for a large fraction of the periodic table. Apart from explaining size–structure–reactivity relationships, there is also need for replacing expensive noble metal catalysts by cheaper, more abundant metals or even non-metal catalysts. Understanding the reactivity of non-noble metal nanoparticles allows rational design of cheaper catalyst. Here we focus on the capability of iron nanoparticles to dissociate CO. Understanding changes in reactivity of iron as function of size and geometry is important from both fundamental and application-driven point of

views. Industrially important and traditional uses of heterogeneous iron catalysts are Fischer–Tropsch synthesis (FTS) of hydrocarbons from CO and H₂ as well as water–gas shift reaction to produce H₂ and CO₂ from a mixture of H₂O and CO. A more modern application relying on CO dissociation on iron nanoparticles is the growth of carbon nanotubes (CNT).

CO dissociation is a highly structure sensitive reaction [4]. As such, CO dissociation is effective only at special sites of the catalyst; a step–edge site with high-coordination through the carbon atom is required for facile CO dissociation. The high activity of such high coordination sites is rationalized by the strong back-bonding from metal to CO resulting from large overlap between metal $d_{yz/xz}$ and CO $2\pi^*$ orbital leading to weakening and elongation of the C–O bond [3,5–7]. Presence of steps allows further increase in back-bonding, earlier transition state (less C–O stretching) and reducing repulsive interactions between C and O since they do not share the same atoms at the step [3]. On crystal surfaces, only stepped surfaces provide such step–edge sites. In nanoparticles, these sites emerge only after a certain particle size (around 3–4 nm [3]) is reached which explains the increasing of CO dissociation as particle size is increased [8]. However, the relative amount of step–edges decreases quickly when particle size increases.

Knowing the size, shape, and state of catalyst particle are crucial for understanding and controlling both the FTS and CNT syntheses. As discussed above, particle geometry and the presence of spe-

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Table 1

Dissociation barriers of CO on various iron surfaces and nanoparticles. E^\ddagger (eV) stands for the height of the dissociation barrier, ΔE (eV) is the energy difference between initial and final stages. $\{H\}$ and $\{T\}$ indicate that the dissociation pathway starts from hollow or top site, respectively.

Surface	E^\ddagger	ΔE	Reference
BCC (1 0 0) $\{H\}$	1.06	-0.43	[18]
BCC (1 0 0) $\{H\}$	1.07	-0.45	[18]
BCC (1 1 0) $\{T\}$	1.52	0.50	[19]
BCC (1 1 1) $\{H\}$	1.53	-0.36	[21]
BCC (1 1 1) $\{H\}$	1.05	-0.28	[18]
BCC (2 1 1) $\{H\}$	0.78	-0.27	[22]
BCC (2 1 1) $\{H\}$	1.02	-0.24	[18]
BCC (7 1 0) $\{H\}$	0.67	-1.19	[18]
BCC (3 1 0) $\{H\}$	0.72	-0.89	[18]
BCC (3 1 0) $\{H\}$	0.94	-0.19	[23]
Fe ₁₃ (ico) $\{T\}$	2.12	0.40	[5]
Fe ₅₅ (ico) $\{T\}$	1.63	-0.37	[5]
Fe ₁₄₇ (ico) $\{H\}$	1.1	-0.41	[5]
Fe ₇₈ (amorphous) $\{T\}$	1.12	0.03	[5]
Fe ₁₄₅ (BCC) $\{H\}$	0.89	-0.21	This work

cial sites is essential for efficient catalysis. When a particle exhibits large nanoeffects, even small changes in the number of atoms may cause large changes in geometric, physical, and chemical properties allowing tailoring. Small, gas-phase iron particles with few tens of atoms favor icosahedral I_h or Mackay transformed icosahedral structures whereas larger particles have BCC structure. The I_h -to-BCC transformation has been proposed to take place between 59 and 140 atoms (1–1.5 nm) [9]. All particles beyond 140 atoms are expected have BCC structure, even though icosahedral particles up-to 13 nm have been synthesized [10] and FCC iron particles may be formed at high temperatures. Depending on the conditions for CNT growth, the Fe particle may adopt BCC [11,12], FCC [13,14] or liquid-like [15] geometries. Furthermore, BCC-Fe particles have been shown to deform dynamically with refaceting during CNT growth due to changes carbon adsorption and formation of graphitic carbon [12]. Also surface coverage of adatoms and -molecules depends on reaction conditions [16] which leads to changes in surface energies and (Wulff) equilibrium shape of the particle.

Even though geometry of iron nanoparticles is sensitive to particle size and conditions, only few studies have focused on catalyzing CO chemistry on iron particles. From CO activation energies on different heterogeneous iron catalysts collected in Table 1, it is seen that CO dissociation is a strongly structure- and size-dependent reaction. Size-dependent reactivity of icosahedral iron nanoparticles towards CO dissociation showed that their reactivity increases as particle size is increased. It was also shown that “realistic”, rugged particles are more reactive than small, ideally symmetric icosahedral particles but not as reactive as larger icosahedral clusters [5]. Another systematic study [17] on CO dissociation on 1–65 atomic iron nanoclusters shows that dissociation becomes easier as cluster size is increased. However, of all studied heterogeneous iron catalysts, stepped BCC iron crystal surfaces, such as (710), (310), or (211), show smallest activation energies for CO dissociation. Of the low-index surfaces, open BCC(100) with 4-fold hollow sites exhibits smaller activation energies for CO dissociation than the compact BCC(110/111) surfaces. Furthermore, low-index BCC-surfaces are more active than the dense Fe-FCC(111) surface [5]. In [5], it has been proposed that increasing particle size, presence of loosely bound atoms at steps, corners, or kinks, and increased Fe-Fe distances at surfaces contribute to increase in reactivity towards CO dissociation in iron nanoparticles.

Studies on reactivity of crystal surfaces give invaluable information about the basic mechanisms and understanding of heterogeneous reactions. However, small enough particles cannot be modeled or understood using crystal surfaces; geometries,

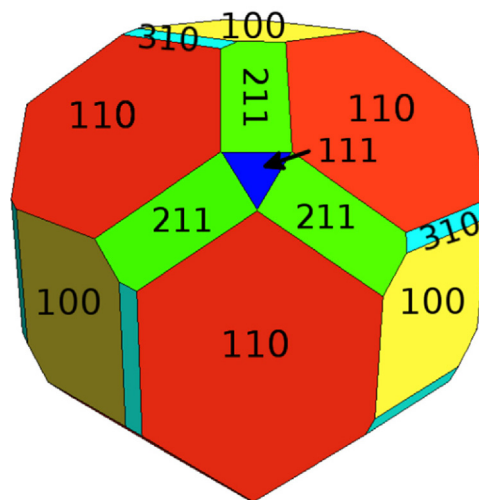


Fig. 1. Wulff construction of a BCC iron cluster based on the surface energies from Ref. [41]. Particle generated with the Wulffmaker software [42].

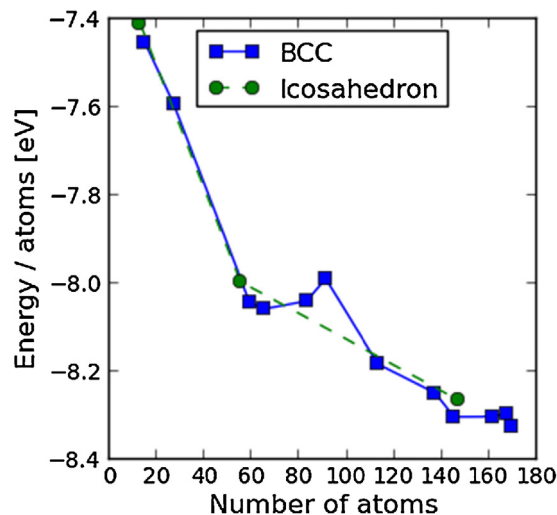


Fig. 2. Energies of I_h and BCC cluster as a function of their size.

bond lengths, electronic structures etc. of small particles may differ significantly from crystal surfaces. Nanoparticles have structures not found in crystal surfaces such as icosahedral packing of small iron particles as well as various corner- and edge-sites between nanoparticle facets (see Figs. 1 and 2). In nanoparticles the bond lengths are shorter than in bulk values to minimize their surface energy. Nanoparticles are also more flexible than their crystal counterparts which affect adsorption, reaction, activation energies, and even dynamic evolution and re-faceting of the catalyst particle under reaction conditions [12]. As a result, nanoparticles provide reaction sites not found on common crystal surfaces. The effect of these different factors on reactivity is at the heart of modifying and developing nanoparticle catalysts.

How catalyst size, structure and composition affect the selectivity and activity of FTS is still an open question. Kinetic studies of van Santen et al. have shown how the relative rates of CO dissociation and chain growth affect the growth and activity in FTS [24–26]. It appears that maximum CO consumption (and activity of FTS) is achieved when chain growth is the limiting step and fast CO dissociation provides a constant carbon feedstock. To achieve high activity and selectivity in producing long hydrocarbon chains, CO dissociation should have low dissociation barrier without poisoning the active site. As CO dissociation is a highly structure sensitive reac-

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