Mechanism of Metastable Wüstite Formation in the Reduction Process of Iron Oxide below 570°C

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The possibility of metastable wüstite below 570°C during the reduction of iron oxides was discussed. There was uncertainty regarding the formation of metastable wüstite in the reduction of hematite below 570°C. Planar disregistry (1/δ) was employed to predict the probability of metastable wüstite formation during the reduction process. The calculated results showed that the δ of wüstite/magnetite is similar to that of iron/magnetite with plain and normal structures, but less than flake and finger structures. The difference in disregistry of different geometries of interfaces was suggested to be the principal driving force for the formation of metastable wüstite. This implies that the formation of metastable wüstite always accompanies the nucleation of iron structures with high δ relative to magnetite. The latter structures form easily in supported iron, leading to the relatively common observation of metastable wüstite in an iron catalyst. The analysis showed that the temperature range for metastable wüstite formation, 400°C~500°C, was most likely to occur where it created a predominance of flake and finger structures.

Introduction

An increased understanding of phase transformation in the reduction of iron oxides is beneficial to the study of catalyst characterization and the reduction processes of iron oxide. Wüstite (Fe1−δO), magnetite and hematite are the three important phases of iron oxide, with each compound having a different oxygen content.1,2 From a thermodynamic viewpoint, wüstite decomposition occurs through a disproportionation below 570°C. There are, however, reports regarding the formation of metastable FeO below 570°C. Metastable wüstite was reported by Romanov et al.3) during the reduction process of pure hematite. The Mössbauer technique was used to probe the powder sample as they were reduced from pure hematite in a hydrogen atmosphere. The spectra of the samples showed an absorption line of wüstite at a velocity of about 0.9 mm/s, which indicated the presence of stoichiometric wüstite after more than 10 min reduction at 450−570°C. The non-equilibrium process was suggested to be:

\[ \alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{wüstite} \rightarrow \alpha\text{-Fe}. \]  

Significantly different results were later reported by Graham and his partners4) in a similar experiment. Rau et al.5) also reported that they did not find any metastable wüstite in their experiment. In fact, the majority of related reports regarding pure hematite reduction in hydrogen did not mention metastable wüstite in the experimental results. A limited number of experiments6,7) report metastable wüstite following the reduction of pure hematite (refer Table 1). The temperature at which metastable wüstite forms was reported to be around 400−570°C. The experimental research of Pineau et al.8) indicated that the reduction of magnetite should be as follows:

\[ \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}_1\text{−}\delta\text{O} + \alpha\text{-Fe} \rightarrow \alpha\text{-Fe}. \]  

Although there are limited reports regarding the formation of metastable wüstite in the reduction of pure hematite by reducing gas, many researchers in the field of mechanical alloying and catalyst preparation report observing metastable wüstite in experiments. The studies of mechanical alloying used pure ferritic oxides as principal raw materials. Wüstite could be formed in the mechanical alloying processes of iron oxides/iron or hematite/carbon mixtures at low temperatures9−13, as well as in the milling of Ni/Fe2O3 mixture14). In such investigations, wüstite was proposed to be the product of the reaction in a non-equilibrium state, promoted by the energy storing in the form of structural disorder and grain boundary15). This energy could also affect the defect structure of wüstite product15). Whilst no models were proposed by these studies regarding the effect of energy on phase transformation, they did, however, suggest a line of enquiry for the formation of metastable wüstite in terms of energy.

A study of iron oxide-based catalysts was undertaken. Iron catalysts are widely used in Fischer-Tropsch synthesis15,16), ammonia production17,18), hydrotreatment19,20) and tar breakdown21) and many other chemical processes22). The presence of metastable wüstite phase was reported in the reduction of iron oxides loading catalysts such as Fe/MgO, Fe/γ-Al2O323), iron-manganese oxides24), implanted and annealed Fe/α-Al2O325), Fe/ZrO2, Fe/Ce/ZrO2, Fe/La/ZrO226) and Fe/SiO227).

Table 1  Evidences of metastable wüstite in the reduction of pure hematite.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temp./°C</th>
<th>Evidences</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>425−520</td>
<td>Mossbauer spectra of powder sample</td>
<td>3)</td>
</tr>
<tr>
<td>Experiment</td>
<td>&lt;570</td>
<td>Thermomagnetic analysis in ammonia synthesis</td>
<td>6)</td>
</tr>
<tr>
<td>Experiment</td>
<td>400</td>
<td>XRD and mass gain</td>
<td>7)</td>
</tr>
<tr>
<td>Experiment</td>
<td>450−570</td>
<td>△E calculation and X-ray furnace test in H2-N2 mixtures</td>
<td>8)</td>
</tr>
<tr>
<td>Inference</td>
<td>300</td>
<td>Higher selectivity to oxygenates in CO conversion</td>
<td>9)</td>
</tr>
</tbody>
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in a hydrogen-containing atmosphere. Wüstite as an intermediate phase in the reduction of catalysts is more common than in the case of pure hematite. Schlögl suggested that some of the wüstite could be crystallized from the amorphous wüstite-containing industrial catalysts. It was generally implied, however, that a certain interaction of the support and loading could stabilize the metastable wüstite phase, thus inhibiting the reduction of iron oxide. The strong interaction between the catalyst supports and iron oxides could result in the formation of new oxides as an intermediate species, or it could modify the lattice parameters of the iron oxides. In such an interaction, an observable amount of ions moves from catalyst support into the lattice of wüstite and incorporate with it, enhancing the stabilizing of the wüstite phase. No explanation was given concerning how changing the iron oxide lattice parameters affects wüstite stability.

It could be surmise that if there are traces of impurities in the raw materials that interact strongly with iron oxides, metastable wüstite could form in the reduction process of pure hematite at low temperature. An alternate and quantitative explanation relating to the interface energy was carried out in this work, which can be a more reasonable explanation for this non-equilibrium reaction. In order to investigate metastable wüstite, the theoretical possibility of metastable wüstite formation was investigated via a quantitative analysis. Such an investigation would be helpful for understanding the non-equilibrium phase transformation in the reduction of both iron catalyst and unsupported pure iron oxides.

2. Theoretical Analysis

The energy of wüstite nucleation includes the energy functions of chemical reaction and topographic transformation. As Kock et al. suggested, the wüstite phase could be stabilized by lowering the Gibbs free energy function of wüstite with respect to that of other phases. The nucleation energy, including the interfacial energy between parent and product phases, could also affect the transition phenomenon of oxides in the reduction. An estimation of the formation energy of different interface geometries could therefore be helpful in exploring this issue. Equation (2) indicates that the competitive couples to investigate should be Fe₃O₄/α-Fe and Fe₂O₃/ wüstite.

In Turnbull and Vonnegut’s theory of nucleation catalysis, the free energy required for the nucleation of a new phase is a function of the disregistry (1/δ), where the increase of disregistry between two phases at the interface will result in a depression of the nucleation energy barrier. Thus, the new phase will nucleate more readily on the support phase when there is a large disregistry (low lattice mismatch, δ) of the two phases at the interface. The disregistry of Fe₂O₃/Fe and Fe₂O₃/wüstite could therefore be employed to predict whether the metastable wüstite phase rather than α-Fe could nucleate on magnetite phase.

Based on the chosen orientation of the two phases, the planar disregistry 1/δ of the new phase nucleated on the base is defined to be:

\[
\delta^{(hkl)} = \frac{1}{3} \sum_{i=1}^{3} \left| \frac{h_1 + n_1 \cos \theta - d_{(hkl)}^{(i)}}{d_{(hkl)}^{(i)}} \right| \times 100\%
\]

where, \((hkl)^{(i)}\) and \((hkl)^{(n)}\) are a low-index plane of the substrate and the nucleated phase, respectively; \([uvw]^{(i)}\) and \([uvw]^{(n)}\) are a low-index direction in \((hkl)^{(i)}\) and \((hkl)^{(n)}\), respectively; \(d_{(hkl)}^{(i)}\) and \(d_{(hkl)}^{(n)}\) are the interatomic spacing along \([uvw]^{(i)}\) and \([uvw]^{(n)}\), respectively; and \(\theta\) is the angle between the \([uvw]^{(i)}\) and \([uvw]^{(n)}\).

The wüstite/magnetite orientation in the reduction is [001] to [001], with (220) to (220) and (200) to (440). It should be noted that θ of magnetite and wüstite is zero, which implies that eq. (4) can be used for the lattice mismatch calculation. It has been suggested that the wüstite lattice formed is based on the oxygen atoms in the magnetite lattice with a similar structure. The distance of oxygen atoms in such a structure is 0.4122 nm. The calculated δ of wüstite formed on magnetite was 2(α₁ - α₃)/(α₃ + 0.4122), which varies from 0.32% to 4.61% according to the ICDD PDF2 data. An early reference suggested, however, that the misfit is within 3%. Similarly, the report of Condon suggested that the mismatch in their experimental should be 2.33%, which corresponds to Fe₂₋₄O₄(111) paralleling to Fe₃O₄(111) (accorded distances of iron atoms are 0.304 nm, 0.297 nm, respectively). These calculated values were listed in Table 2.

The experimental study of Holme concluded that there were several types of metallic iron structures with different orientations to the magnetite crystal in the reduction of iron crystal, which included normal structure, finger structure, plain structure, and flake structure. These structures have a different orientation to magnetite. Based on this classification, the δ values of the four structures were calculated and are listed in Table 3. Besides Holme’s research results, we developed some other similar sub-structures within the four base structures.
sic structures using as many different ion arrangements at the interface as possible. The potential lattice mismatch of iron/magnetite could also be estimated. Holme\textsuperscript{45}) found that the projection [110\textsubscript{Fe}] of iron rotated 35° to [110\textsubscript{m}] of magnetite, whilst we calculated a similar sub-structure, which is listed below the item of finger structure in Table 3. The values in Table 3 highlight the available ions for matching at the Fe\textsubscript{3}O\textsubscript{4}/Fe interface. The geometries of these possible interfaces are shown in Fig. 1.

It can be found that the $\delta$ of wüstite to magnetite is small in general, whilst the $\delta$ of iron to magnetite varies over a relatively large range according to the different possible structures. The data in Table 3 indicates that the lattice mismatch of some iron structures, particularly the finger structure and flake structure, are significantly greater than that of the wüstite/magnetite interface. The plain-2 structure and normal-O structure also have a larger lattice mismatch than the wüstite/magnetite interface, and so it is possible that wüstite may form preferentially with them. If a finger structure or flake structure was to form during the reduction of magnetite, there is a high probability that wüstite would nucleate in preference to the finger or flake structures. Furthermore, it is noted that the probability of nucleation could be poor if the lattice mismatch is larger than 12\%\textsuperscript{35}). It would therefore be unlikely for a new phase to nucleate on magnetite if the value of lattice mismatch is too high. Thus, it is surmised that an iron structure with large $\delta$ would be unlikely to form, resulting in a limited proportion of new structures with large $\delta$ being present in the reduced iron oxides. The nucleation of such structures should really only be possible if there is some natural distortion, disorder or defect of the magnetite structure. Since the formation of wüstite is associated with these low proportion iron structures, it should be unlikely to find metastable wüstite in the reduced samples. This could explain why there are relatively few reports that found metastable wüstite in the low temperature reduction of unsupported iron oxides. The interaction between substrate and iron oxides could change the lattice parameters of iron oxides. Lattice distortion is likely to promote the matching of structures that would usually have a low probability of forming. This explains why there is such a considerable quantity of reports of metastable wüstite being observed in the field of iron catalyst preparation.

3. Application to the Practical System

Based on his statistical results on a large number of samples, Holme\textsuperscript{42}) suggested that the most common iron structure in reduced iron catalyst was the plain structure. The normal structure could be the predominant structure when there was almost no plain structure detected. Holme and Taftø\textsuperscript{47}) indicated that the interface energy in the normal structure could be higher than that in the plain structure, possibly explaining the reason for more frequent observation of the plain structure in reduced samples. Their results imply that our analysis in terms of the comparison of lattice mismatch is valid. Their results showed that flake structure and finger structure are rarely found, and it is noted that wüstite in the reduced sample was always observed in samples with relatively high proportions of finger structure. This is in good agreement with the theoretical analysis based on lattice mismatch.

An additional experimental result of Holme and his partners\textsuperscript{48}) indicated that the volume fractions of finger structure

\begin{table}[h]
\centering
\caption{Lattice mismatch of Fe\textsubscript{3}O\textsubscript{4}/Fe.}
\begin{tabular}{lcccccccc}
\hline
\textbf{Structures} & \textbf{Plain} & & \textbf{Normal} & & \textbf{Finger} & & \textbf{Flake} & \\
\hline
\hline
$\delta$ & 1 & 2 & Fe & O & Fe-O & 1 & Fe-O & 2 & Fe & O & 35° & Fe & 1 & Fe & 2 & O & 1 & O & 2 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Schematic geometries of magnetite/iron interfaces with different possible structures (balls with the largest size correspond to O\textsuperscript{2−}, those with an intermediate sizes are Fe\textsuperscript{3+} and Fe\textsuperscript{2+}, and the smallest balls correspond to Fe; the white line marks the boundary of the crystal cell of metallic iron).}
\end{figure}
and flute structure increased with the increasing alumina content in reduced alumina promoted magnetite. The sum of volume fractions of finger structure and flute structure was sufficient in the constant reduction temperature range from 350°C to 500°C, especially 400°C to 500°C. Based on our analysis of lattice mismatch, the first results suggested that metastable wüstite could form in magnetite with support, which has been proved in many investigations, as mentioned in the introduction. Their second results implied that metastable wüstite could have a relatively high probability of forming in the temperature range of 400°C to 500°C, which corresponded to the reported temperature ranges of metastable wüstite formation in Table 1. The calculated results are consistent with these experimental results, which implies that lattice mismatch is a suitable explanation of metastable wüstite formation.

4. Conclusions

The mechanism of metastable wüstite formation in the reduction of iron oxides was studied.

(1) Lattice mismatch ($\delta$) of the wüstite/magnetite interface and iron/magnetite interfaces with varying structures, was calculated using the method of planar disregistry, which considered the angle between two low-index directions of substrate and the nucleated phase. The $\delta$ of wüstite/magnetite ranges from 2.32% to 4.61%, and is usually lower than that of iron/magnetite, especially those of the finger structure (14.14%–28.44%) and flute structure (6.89%–21.27%).

(2) The possibility of metastable wüstite formation was discussed using the lattice mismatch parameter as a criterion. The phase with larger $\delta$ compared to magnetite will be harder to nucleate. It is suggested that the larger $\delta$ of the iron in the finger structure and the flute structure compared to magnetite could result in the co-nucleation of metastable wüstite clusters in the reduction. The relatively low proportion of the finger and flute structures in reduced iron oxides is suggested to be the reason for the low probability of metastable wüstite formation.

(3) According to the above mentioned theory, thanks to the relatively high proportion of finger and flute structures formed in the reduction, allows metastable wüstite to form easily within the temperature range of 400°C to 500°C or within the iron oxides with support.

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REFERENCES