Influence of promoter and Fe$^{2+}$/Fe$^{3+}$ ratio on microstructure of fused iron catalysts for ammonia synthesis

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Fused iron catalysts have been prepared by melting a mixture of magnetite powder, reducing agent (iron) and promoters (K, Ca and Al). The effects of the Fe$^{2+}$/Fe$^{3+}$ ratio and addition of promoters on the microstructure of the catalysts have been investigated by X-ray diffraction, high-resolution scanning electron microscopy and energy disperse spectroscopy techniques. The XRD results indicate that the addition of the promoters restrains the occurrence of disproportionation reaction and favors the formation of wustite. SEM and EDS measurements show that the Fe$^{2+}$/Fe$^{3+}$ ratio significantly influences the microstructure of the catalyst as well as the distribution of the promoters K and Ca. The catalyst with high Fe$^{2+}$/Fe$^{3+}$ ratio is reduced more easily than that with low Fe$^{2+}$/Fe$^{3+}$ ratio. The promoter in the sample with high Fe$^{2+}$/Fe$^{3+}$ ratio is distributed homogeneously on the surface of particles as needle-like films. After being reduced, the sample with low Fe$^{2+}$/Fe$^{3+}$ ratio has a compact structure with the promoter being distributing heterogeneous on the catalyst surface in an amorphous state, while the sample with high Fe$^{2+}$/Fe$^{3+}$ ratio had a porous structure and on the surface of particles the promoter is crystalline.

Keywords: Catalysts, Fused iron catalysts, X-ray diffraction, Iron, Ammonia

The development of iron-based catalysts for ammonia synthesis has gone through three stages: Fe$_2$O$_3$-based catalysts, Fe-Co catalysts and Fe$_1$$_3$O$_4$-based catalysts. The oxides of potassium, aluminum and calcium are mainly used as the promoters with these catalysts, although their effects are different. The Al$_2$O$_3$ and CaO are structural promoters while K$_2$O is a typical electronic promoter$^{1-3}$. Nevertheless, for ammonia synthesis, the promoter and Fe$^{2+}$/Fe$^{3+}$ ratio were found to significantly influence the catalytic property$^{4-6}$. The effect of various promoters (e.g. Ba, Al and K) and different supports on ammonia synthesis was presented by investigating the chemisorption of nitrogen$^{7}$. Bridger et al.$^5$ have studied the fused iron catalysts consisting of Al$_2$O$_3$-K$_2$O promoters with low Fe$^{2+}$/Fe$^{3+}$ ratio and found that when the Fe$^{2+}$/Fe$^{3+}$ ratio of the catalyst is different from 0.5 (stoichiometric magnetite), either higher or lower, the activity decreases. Besides, Liu et al.$^{2,4,6}$ have systematically studied the relationship between iron oxide with different ranges of Fe$^{2+}$/Fe$^{3+}$ ratios and their catalytic activities and have successfully developed Fe$_1$$_3$O$_4$-based catalysts, ZA-5 (Fe$^{2+}$/Fe$^{3+}$ = 3.6) for industrial application. The ZA-5 catalyst has better catalytic activity than the other conventional Fe-Co catalysts such as ICI74-1$^9$ (a commercial catalyst produced by ICI, England) and has attracted extensive attention$^{10,11}$. We have earlier put forward several new points for catalysts preparation from the correlation of microstructure and catalytic activity such as single phase and uniformity principle$^{12}$, acid base synergy on the surface$^{13}$, rivalrousness mechanism$^{14}$, and hydrogenous strong adsorption$^{15}$. In addition, the reducibility and the microstructure difference of active phases were studied by in situ XRD and HRTEM$^{16}$. It is well known that the phase of catalysts and the promoter distribution are closely related to the catalytic activities and thermal resistance for ammonia synthesis catalysts. Thus, the microstructure as well as promoter distribution are key to making a better performance catalyst. However, the influence of Fe$^{2+}$/Fe$^{3+}$ ratio on the phase and microstructure of catalysts for ammonia synthesis has not been investigated systematically. Also, the effect of the promoter on the microstructure of the catalysts with different Fe$^{2+}$/Fe$^{3+}$ ratio has not been studied.
In this work, two series of fused iron catalysts (with and without promoter) with different Fe\(^{2+}/Fe^{3+}\) ratios have been prepared. The influence of promoter and Fe\(^{2+}/Fe^{3+}\) ratio on catalysts phase, lattice defect, microstructure and surface morphology have been investigated by XRD, HRSEM and EDS techniques. Based on these results, the relationship between the microstructure and the catalytic activity has also been discussed.

### Materials and Methods

#### Preparations and characterization of catalysts with different Fe\(^{2+}/Fe^{3+}\) ratios

Two series of catalysts (with and without promoter) with different Fe\(^{2+}/Fe^{3+}\) ratio were prepared by melting a mixture of magnetite, a certain amount of reducing agent, and promoters (Al\(_2\)O\(_3\), KNO\(_3\) and CaCO\(_3\)). The reducing agent was metallic iron except for low ratio (Fe\(^{2+}/Fe^{3+}\)) catalysts denoted as S1 and SP1, for which Fe\(_3\)O\(_4\) was used as reducing agent in order to decrease the Fe\(^{2+}/Fe^{3+}\) ratio lower than 0.5. The content of promoters Al\(_2\)O\(_3\) (AR), KNO\(_3\) (AR) and CaCO\(_3\) (AR) were 2.4 wt%, 1.3 wt% and 3.1 wt%, respectively. These materials were poured into a melt furnace after being ground homogeneously and the high temperature molten material was cooled down to room temperature in a cooling tank equipped with water jacket. During the preparation, the chemical composition and the Fe\(^{2+}/Fe^{3+}\) ratio, which was controlled by adjusting the ratio of magnetite and reducing agent, were determined by a chemical titration method according to HG1-1430-81 Standard of China\(^{12,13}\). The Fe\(^{2+}/Fe^{3+}\) ratio of the two series samples are listed in Table 1.

X-ray diffraction (XRD) patterns were collected on a Thermo ARL X’TRA powder diffractometer equipped with Si (Li) solid detector using Cu-K\(_\alpha\) radiation (\(\lambda = 0.1541\) nm). The energy range of the detector was 1.68–1.90 keV and the slits of 2, 5, 0.5 and 0.2 mm were used. The working voltage of the instrument was 40 kV, and the working current was 45 mA. The XRD data were collected at room temperature over a 20 range of 20°–80° with a step interval of 0.02° at a speed of 1° per second. The phase and microstructure analysis of the catalysts were determined by WinXRD software, which is supplied with the diffractometer.

Microstructures of the catalysts were obtained on Hitachi S-4700 II high-resolution scanning electron microscopy (HRSEM) operated at 15 kV. The EDX spectra were recorded on Thermo VANTAGE ESI instrument which was linked to the HRSEM.

Auger electron spectroscopy (AES) Analysis was performed with a Kratos AXIS Ultra DLD spectrometer equipped with Schottky field emission electron gun using an accelerating voltage of 10 keV and an extractor current of 276 \(\mu\)A.

### Results and Discussion

#### Effect of promoter and Fe\(^{2+}/Fe^{3+}\) ratio on the microstructure of the catalysts

Figure 1 shows the XRD patterns of the catalysts with and without promoter as a function of Fe\(^{2+}/Fe^{3+}\) ratio. It can be seen from Fig. 1(a) that the major phase is Fe\(_3\)O\(_4\) (JCPDS: 65-3107) when the Fe\(^{2+}/Fe^{3+}\) ratio is lower than 0.5. With increase in the Fe\(^{2+}/Fe^{3+}\) ratio, the intensity of the peaks ascribed to Fe\(_3\)O\(_4\) decreases and some new peaks attributed to wustite Fe\(_{1-x}\)O (JCPDS: 06-0615) appear. When the Fe\(^{2+}/Fe^{3+}\) ratio increases to 3.94, the dominant phase of the catalyst is wustite. Similar results can also be found in the catalysts with promoter (see Fig. 1(b)).

In order to further investigate the phase structure of the catalyst with different Fe\(^{2+}/Fe^{3+}\) ratios, we have performed a phase quantitative analysis of the refined XRD patterns. The Fe\(_3\)O\(_4\) and Fe\(_{1-x}\)O contents and the x value in Fe\(_{1-x}\)O are listed in

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### Table 1 – Phase quantitative analysis and \(x\) values in wustite for the catalyst with different Fe\(^{2+}/Fe^{3+}\) ratios

<table>
<thead>
<tr>
<th>Sample without promoter</th>
<th>(\text{Fe}^{2+}/\text{Fe}^{3+})</th>
<th>Content (wt%)</th>
<th>(x)</th>
<th>Sample with promoter</th>
<th>(\text{Fe}^{2+}/\text{Fe}^{3+})</th>
<th>Content (wt%)</th>
<th>(x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.409</td>
<td>98.54</td>
<td>1.46</td>
<td>SP1</td>
<td>0.405</td>
<td>99.04</td>
<td>0.96</td>
</tr>
<tr>
<td>S2</td>
<td>0.681</td>
<td>86.39</td>
<td>13.61</td>
<td>S2</td>
<td>0.546</td>
<td>93.75</td>
<td>6.25</td>
</tr>
<tr>
<td>S3</td>
<td>1.57</td>
<td>75.31</td>
<td>24.69</td>
<td>S3</td>
<td>1.24</td>
<td>56.45</td>
<td>43.54</td>
</tr>
<tr>
<td>S4</td>
<td>2.15</td>
<td>42.75</td>
<td>57.25</td>
<td>S4</td>
<td>2.05</td>
<td>41.98</td>
<td>58.02</td>
</tr>
<tr>
<td>S5</td>
<td>3.94</td>
<td>12.74</td>
<td>87.26</td>
<td>S5</td>
<td>3.47</td>
<td>5.53</td>
<td>94.47</td>
</tr>
<tr>
<td>S6</td>
<td>7.74</td>
<td>3.79</td>
<td>96.21</td>
<td>S6</td>
<td>5.74</td>
<td>2.59</td>
<td>97.41</td>
</tr>
<tr>
<td>S7</td>
<td>8.26</td>
<td>3.02</td>
<td>96.98</td>
<td>S7</td>
<td>7.04</td>
<td>100</td>
<td>0.0503</td>
</tr>
<tr>
<td>S8</td>
<td>12.38</td>
<td>100</td>
<td>0.0360</td>
<td>S8</td>
<td>8.43</td>
<td>100</td>
<td>0.0503</td>
</tr>
</tbody>
</table>

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Table 1. With increase in the Fe\(^{2+}\)/Fe\(^{3+}\) ratio, the content of Fe\(_3\)O\(_4\) in the catalyst decreases and the amount of wustite Fe\(_{1-x}\)O increases. In addition, the x value in wustite decreases when the Fe\(^{2+}\)/Fe\(^{3+}\) ratio increases. According to a previous report \(^6\), no Fe\(_3\)O\(_4\) was found when the value of Fe\(^{2+}\)/Fe\(^{3+}\) was higher than 3.15. In the present study, however, a minor Fe\(_3\)O\(_4\) phase still exists in the Fe\(^{2+}\)/Fe\(^{3+}\) range from 3.15–5.74 for the catalysts with promoter, which is inconsistent with the literature result \(^6\). This is probably because of the Si(Li) semiconductor detector used in our XRD analysis, which is much more effective than the detector used in earlier studies. The Si(Li) semiconductor detector can control the fluorescence interference of iron to copper target effectively by regulating the detector energy window and therefore possesses very high sensitivity and signal-noise ratio. Thus, the microcontent Fe\(_3\)O\(_4\) phase of the catalysts was detected effectively. A new phase, Ca\(_2\)Fe\(_{15.6}\)O\(_{25}\) crystals was also detected in the SP1 sample (discussed below), which further confirms this.

The effect of the promoter on the microstructure can also be observed from the above XRD measurements. Figure 2 shows the comparative XRD patterns of two samples (S1 and SP1) with nearly same Fe\(^{2+}\)/Fe\(^{3+}\) ratios. For the sample S1 without promoter, not only the diffraction peaks ascribed to magnetite (Fe\(_3\)O\(_4\)) but also those attributed to hematite (Fe\(_2\)O\(_3\)) and wustite (Fe\(_{1-x}\)O) can be observed. However, for the sample SP1 with promoter, the peaks ascribed to hematite almost disappear. Moreover, the diffraction peaks of Ca\(_2\)Fe\(_{15.6}\)O\(_{25}\) (JCPDS: 78-1184) are observed at 31.9 °, 33.3 ° and 34.2 °, indicating that the catalytic promoter, CaO, reacts with Fe\(_2\)O\(_3\) and forms a new phase Ca\(_2\)Fe\(_{15.6}\)O\(_{25}\) catalysts. In addition, the amount of wustite in SP1 was 0.96 %, lower than that in S1 (1.46 %) (see Table 1). This implies that the catalytic promoter inhibits the occurrence of the disproportionation reaction, which is in agreement with previous results \(^5\).

From Table 1, it is also seen that for the samples with almost same Fe\(^{2+}\)/Fe\(^{3+}\) ratio, addition of the promoter increases the x value in wustite (Fe\(_{1-x}\)O). Also, when the Fe\(^{2+}\)/Fe\(^{3+}\) ratio is higher than 3.47, the amount of Fe\(_3\)O\(_4\) in the catalyst decreases significantly when the promoters are added. These results indicate that with the addition of the promoters, Fe\(^{3+}\) tends to enter the lattice of wustite. Obviously, the high content of Fe\(^{3+}\) in wustite can lead to more lattice defects in the catalyst, thus favoring the reduction of the catalysts.
Influence of promoter and Fe$^{2+}$/Fe$^{3+}$ ratio on surface features

The HRSEM images of the six samples with or without promoters, S1, SP1, S3, SP3, S5 and SP5, are shown in Fig. 3. The dominant phase in the S1 and SP1 samples is magnetite, while in S5 and SP5 samples, the dominant phase is wustite. In the S3 and SP3 samples, magnetite and wustite coexist. The HRSEM images indicate that the surface of the samples without promoter is very compact, and boundaries of different phases are not observed. However, obvious crack is observed on the surface of the samples with catalytic promoter. In SP1, the promoter exists primarily as six-edge schistic crystals of about 2 μm diameter. According to the XRD results, the crystal may be Ca$_2$Fe$_{15.6}$O$_{25}$, classified to the hexagonal system. In the SP3, where magnetite and wustite coexist, both the particle size and the amount of Ca$_2$Fe$_{15.6}$O$_{25}$ decrease significantly, with appearance of many needle-like promoters. However, the Ca$_2$Fe$_{15.6}$O$_{25}$ phase appearing in SP3 sample could not be detected by XRD technique, which is probable due to the particle size of Ca$_2$Fe$_{15.6}$O$_{25}$ being too small for detection. The dispersiveness of promoter increases significantly comparing with SP1 catalyst. For SP5 sample, it can be observed from the SEM image that the dispersion of promoter is much more widespread and homogeneous than that in SP3, the promoter distribution is uniform and the distribution area is so lager that looks like a membrane covering on the surface of precursor. It is plausible that the uniform distribution of promoter was suitable for forming aperture structure for the catalysts precursor, and thus could promote the reduction reaction.

In order to further prove the promoter distribution on the surface layer, Auger electron analysis (AES) of the SP5 sample with high Fe$^{2+}$/Fe$^{3+}$ ratio has been carried out. AES is widely used to obtain information about the element and phase compositions of surface.
The AES spectra of SP5 catalyst (Fig. 4) shows the Auger emission line ascribed to K and Ca, although the Auger signal is very weak. This indicates that K and Ca promoters are enriched at the surface layer of the catalyst, which is in accordance to the HRSEM results.

**Effect of Fe$^{2+}$/Fe$^{3+}$ ratio on the promoter distribution**

In order to determine the distribution of promoter in the precursor particles, two samples with low Fe$^{2+}$/Fe$^{3+}$ ratio and high Fe$^{2+}$/Fe$^{3+}$ ratios, namely, SP1 and SP3, were studied by X-ray energy dispersion spectroscopy (EDS). The micro-distribution of the major constituent was analyzed by mapping of EDS. The element distribution of Fe, O and some representative promoter component (e.g. K and Ca) are shown in Fig. 5. It can be seen from these figures that K and Ca are distributed mainly in the cracks or scallops, complementing with the main element Fe. However, the distribution of O is almost the same as that of Fe. In SP1, the dispersion of K is higher than that of Ca. However, in SP3 with a higher Fe$^{2+}$/Fe$^{3+}$ ratio, the dispersion of Ca is much higher than that of K. This indicates that Ca and Fe react when the Fe$^{2+}$/Fe$^{3+}$ ratio increases, while K can not react with Fe. Therefore, it may be concluded that the effect of...
promoter K and Ca are different in the samples with varying Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio, and normally Ca takes the role of structural promoter when the ratio of Fe\textsuperscript{2+}/Fe\textsuperscript{3+} increases.

**Effect of Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio on the microstructure of reduced samples**

In order to study the influence of promoter on the microstructure of the catalyst after reduction, two samples, namely SP3 and SP5, were characterized by HRSEM after reduction under a mixed gas (N\textsubscript{2}:H\textsubscript{2}=1:3) condition by *in situ* XRD. The morphology of catalysts SP3 and SP5 after reduction are shown in Fig. 6. As can be seen from these figures, the promoter in the sample of SP3 appears mainly as amorphous material, and the interaction between promoter and particles is not evident. However, the structure of SP5 is more compact, and the promoter exists among the particles as bunches. High-resolution SEM of the two catalysts (Fig. 7) shows that in SP5 the particle

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**Fig. 6 – Morphology of the catalysts SP3 and SP5, after reduction.** [(a) SP3; (b) SP5 a’ and b’ are the respective enlarged view].

**Fig. 7 – HRSEM images showing the particle size and the porosity of SP3 and SP5 catalysts active phase.** [(a) SP3; (b) SP5].
size of the active phase is small and uniform, and the boundary of the active phase and pore structure are evident. However, in SP3 with low Fe$^{2+}$/Fe$^{3+}$ ratio, the active phase adheres together and thus the number of pores decreases significantly. It can be concluded from the above SEM results that the catalysts with high Fe$^{2+}$/Fe$^{3+}$ ratio are superior to those with low Fe$^{2+}$/Fe$^{3+}$ ratio samples, with respect to both promoter effect as well as the pore distribution among particles of active phase.

Conclusions
Two series of fused iron catalysts for ammonia synthesis with and without promoter were prepared and characterized by XRD, HRSEM and EDS techniques. It was found that the promoter had a significant influence on the phase and microstructure of the catalysts with different Fe$^{2+}$/Fe$^{3+}$ ratios. In the catalysts with high Fe$^{2+}$/Fe$^{3+}$ ratio, the promoter was present as needle-like films on the particle surface and the dispersion is much more widespread and uniform than that with low Fe$^{2+}$/Fe$^{3+}$ ratio. Moreover, the promoter could control the disproportionation reaction and favor the formation of wustite. With increase in Fe$^{2+}$/Fe$^{3+}$ ratio, the distribution of promoter K and Ca were opposite with Ca taking the role of structure promoter. The catalysts with high Fe$^{2+}$/Fe$^{3+}$ ratio were superior than low Fe$^{2+}$/Fe$^{3+}$ ratio samples in terms of both promoter effects as well as pore distribution. Therefore, high Fe$^{2+}$/Fe$^{3+}$ ratio and its microstructure may be the main factors for the high activity of catalysts.

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References