Thesis Summary

^{57}Fe Mössbauer Studies of Ta/Nb-doped Fe_2O_3 and Application to Photocatalyst
(^{57}Fe メスバウアーによる Ta/Nb ドープ Fe_2O_3 の研究と光触媒への応用)

HABIBUR RAHMAN

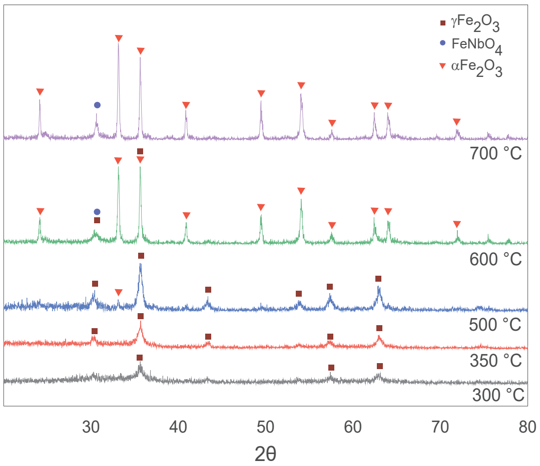

Figure 1. PXRD patterns of 9.1Nb.

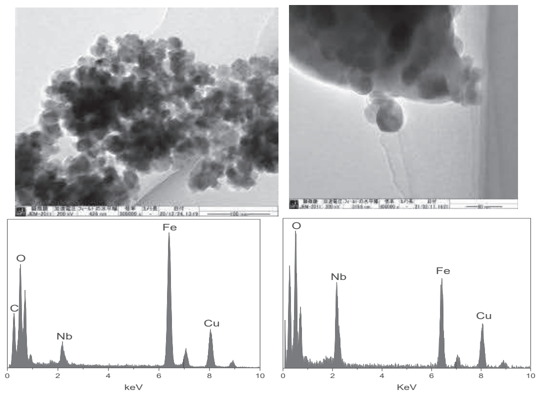

Figure 2. TEM-EDS of 9.1Nb samples calcined at 500 °C (left) and 700 °C (right).

Liquid nuclear waste remains as major problem in the industry. Recycling process frequently resulted in a large volume of secondary waste. γ-Fe_2O_3 and α-Fe_2O_3 have drawn attention for their wide range of application including magnetic separation and photo catalysis for liquid nuclear waste. The nature of γ-Fe_2O_3 is the easy transformation to α-Fe_2O_3, while α-Fe_2O_3 has low conductivity and slow catalytic activity. Several methods were used to overcome these drawbacks, one of the modifications is by doping with the other metal. Nb and Ta are group 5 elements with valence state of 5+, which have interesting characteristic such as high stability and corrosion resistance. In the present PhD Thesis, the research focused on characterization of Nb and Ta-doped Fe_2O_3 nanoparticle and its application to the photocatalyst. General introduction is shown in Chapter 1.

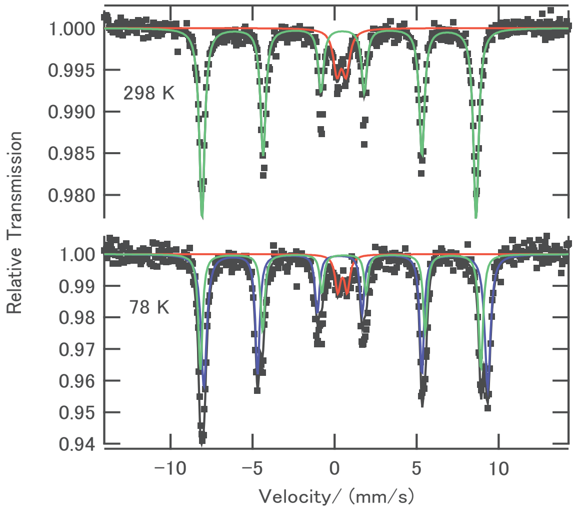

Figure 3. ^{57}Fe Mössbauer spectra at 298 and 78 K of 9.1Nb-Fe_2O_3 calcined at 700 °C.

In Chapter 2, niobium-doped Fe_2O_3 samples were prepared by epoxide sol-gel method at room temperature. Nb amount was changed (0, 1.9, 3.8, 5.7, 7.4 and 9.1 a.t. %). The samples were calcined at various temperatures. Sample characterization was carried out using PXRD, TEM EDS, and Mössbauer spectroscopy. Figure 1 shows PXRD patterns of 9.1Nb sample. Pure γ-Fe_2O_3 formed at 300 °C transforms completely to α-Fe_2O_3 at 500 °C, whereas 9.1Nb sample transformed to α-Fe_2O_3 at 600 °C. PXRD patterns show there is no other phase other than Fe_2O_3 up to 600 °C, and at 700 °C new diffraction ($FeNbO_4$) was observed. It was shown that the Nb doping to Fe_2O_3 suppressed the transformation of γ-Fe_2O_3 to α-Fe_2O_3. Scherrer's equation revealed 13.0 nm of particle size for the sample calcined at 500 °C, 31.6 nm for 600 °C, and 35.0 nm for 700 °C. TEM EDS measurement showed particle size of 14 nm for 9.1Nb500 sample with spherical shape as shown in Figure 2. EDS confirmed that Nb is present in the Fe_2O_3 lattice. The particle became bigger by calcination at 700 °C, and new small particle appeared. EDS, PXRD, and Mössbauer revealed that the small particle is $FeNbO_4$.

In Chapter 3, Mössbauer spectroscopic study on Nb-doped α-Fe_2O_3 was conducted. For the previous report on Nb-doped α-Fe_2O_3[1], Fe^{3+} changed to Fe^{2+} to compensate the charge giving Nb^{5+}-$2Fe^{2+}$. Mössbauer spectra for all Nb-doped samples in the present study did not show Fe^{2+} state. Instead, it was suggested that small amount of Fe^{3+} was expelled from the system to compensate Nb^{5+} charge. Pure α-Fe_2O_3 shows Morin transition (T_M) by the change of weak-ferromagnetism (WF) to anti-ferromagnetism (AF) at around 260 K which shows negative ΔEq value for WF, while positive ΔEq for AF in the Mössbauer spectrum. The 9.1Nb-doped α-Fe_2O_3 calcined at 600 ºC did not show T_M and it attracted to magnet. This is maybe due to ferrimagnetic-like interaction due to the existence of Nb^{5+} in the iron position. The Mössbauer parameters for the samples calcined at 700 ºC showed that the weak ferromagnetism partially exists even at lower temperature (78 K) by introducing Nb atom. One is AF iron, the other is WF iron (Fig. 3). It is thought that the Nb doping stabilizes the weak ferromagnetism even at low temperature. Figure 4 shows the area ratio of AF and WF depending on the amount of Nb. The higher the Nb doping the lower T_M. 7.4Nb700 sample shows T_M at 78K and does not attach to magnet as is typical hematite.

In Chapter 4, catalytic activity of the Nb-doped Fe_2O_3 was investigated. UV-Vis absorption spectra of α-Fe_2O_3 sample were measured. They show strong absorption at visible light region for both pure and Nb-doped α-Fe_2O_3. By using Tauc plot, band gap energy was calculated, ant it varied from 2.13 eV for 5.7Nb700 to 2.97 eV for 5.7Nb600. Catalytic properties were measured for degradation of Methylene Blue (MB) in the presence of H_2O_2 under visible light. Figure 5 shows that the rate of degradation of MB increases with an increase of doped Nb. This shows promising catalytic activity for environmental application.

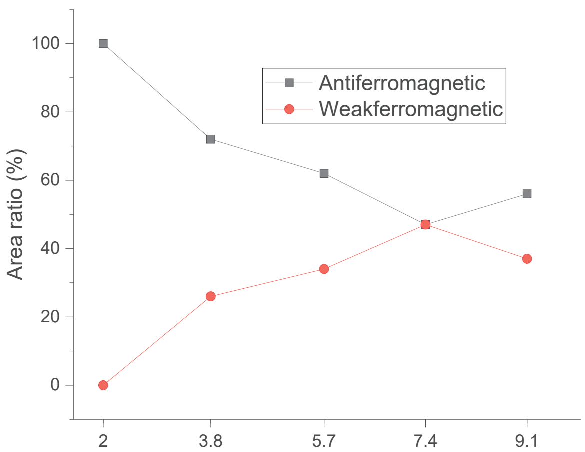

Figure 4. Area ratio of AF and WF for Nb-doped

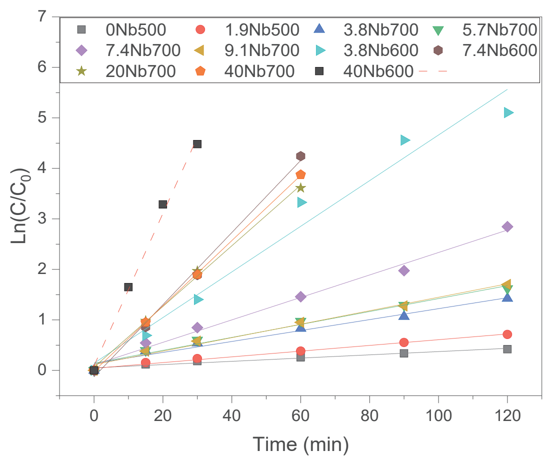

Figure 5. Photo-Fenton degradation of MB

Chapter 5 is the study for Ta-doped Fe_2O_3. Ta doping showed that the stability of γ–Fe_2O_3 increased, and the magnetic properties of hematite changed. For the 7.4Ta700 sample, the particle shows large size of 300nm but there is no T_M at 78K. Ionic radii of Ta^{5+} and Nb^{5+} are the same with 0.64Å, but the lattice constant of Ta is reported to be longer than Nb, which makes Ta have more influence on the lattice arrangement of hematite.

Chapter 6 shows general conclusions. Introduction of Nb and Ta to Fe_2O_3 suppresses the phase transformation from maghemite to hematite. Nb and Ta are incorporated to γ–Fe_2O_3 lattice by filling vacancy and replacing Fe position, stabilizing γ–Fe_2O_3. Nb/Ta atoms were expelled from lattice during transformation to α-Fe_2O_3. Nb/Ta also greatly affect the magnetic properties by lowering the Morin Transition temperature (T_M). The catalytic activity of sample is increased by the increase of Nb doping.

Reference

[1] Sanchez C et al., J Solid State Chem 61:47–55 (1986).