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Formation of brownmillerite type calcium ferrite ($Ca_2Fe_2O_5$) and catalytic properties in propylene combustion

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Several types of calcium ferrite base catalysts (Ca/Fe = 0.33–3) for propylene (C_3H_6) combustion were prepared. Calcium ferrite catalyst with brownmillerite crystal structure provided catalytic activity for C_3H_6 combustion in the temperature range of 250–450 °C. The brownmillerite phase ($Ca_2Fe_2O_5$) was responsible for the formation of oxygen adspecies (O_2^-) in the surface layer below 450 °C.

KEY WORDS: brownmillerite; calcium ferrites; superoxide.

1. Introduction

In recent years, the treatment of volatile organic compounds (VOCs) has attracted scientists' attention from various fields. In particular, catalytic combustion in the presence of oxidation catalysts has been shown to be a promising method for the destruction of the toxic chemicals [l, 2]. Noble metal based catalysts, such as platinum and palladium have been regarded as a desirable, due to high activity for the destruction of polluting materials [3–9]. The several transition-metal based catalysts (e.g. CoO, CuO) shows relatively high activity, but a large consumption of these metals would be desirable environmentally due to the toxicity.

Perovskite type oxides (figure 1(a)) are also candidates for VOCs combustion and are possible alternative oxidation catalysts and catalysts supports [10–13]. The structure permits accommodation of a wide variety of metal cations of different valences and has an unusual capacity to support a number of different types of defects. Depending on the composition, these structures provide important properties in the catalytic oxidation such as high electronic electron-hole and oxide-ion conductivity and the capacity of the conductive oxide ions. The oxide ions can be formed by the oxygen-exchange reaction between oxygen and the oxygen vacancies in the crystal lattice:

$$1/2O_2(g) + V_O^{\cdot\cdot} \Leftrightarrow O_x + 2h^{\cdot} \qquad (1)$$

where $V_O^{\cdot\cdot}$ represents oxygen vacancy included in the structure, O_x oxide ion at normal lattice site, $h^{\cdot}$ electron hole. Thus, it was considered that the defects in the perovskite structures strongly affect the formation of the conductive oxide ions as well as their catalytic activities. Catalytic combustion of C_3H_6 and other VOCs over perovskite-type oxides has been studied for decades, however there has been little attention on brownmillerite-type calcium ferrite for the same purpose. The brownmillerite structure ($Ca_2Fe_2O_5$, figure 1(b)) has an orthorhombic crystal, which is composed of a three-dimensional framework of corner-sharing FeO_6 octahedron and FeO_4 tetrahedron with two oxygen vacancies ($V_O^{\cdot\cdot}$). Accordingly, the brownmillerite structure should stabilize the oxygen defects which provide active sites for oxygen exchanging. The structure was investigated as a non-stoichiometric cubic perovskite which has originally includes anionic defects without doping other rare-earth metals. Several phases formulated $CaFe_{1-y}^{3+}Fe_y^{4+}O_{3-(1-y)}/2$ have been characterized depends on the way in which the compounds have been prepared (thermal treatment, nature of the starting materials, co-crystallization with other compounds) [14–16].

In this work, we examine the activity for C_3H_6 combustion over brownmillerite calcium ferrites ($Ca_2Fe_2O_5$) and related calcium ferrites without using toxic materials and costly noble metals. The formation of brownmillerite crystal structure at different Ca/Fe mixing ratio and the active species on the surface of the brownmillerite calcium ferrite for C_3H_6 combustion are discussed.

2. Experimental

Calcium ferrites powders were prepared by ceramic route by physically mixing an appropriate ratio of CaO

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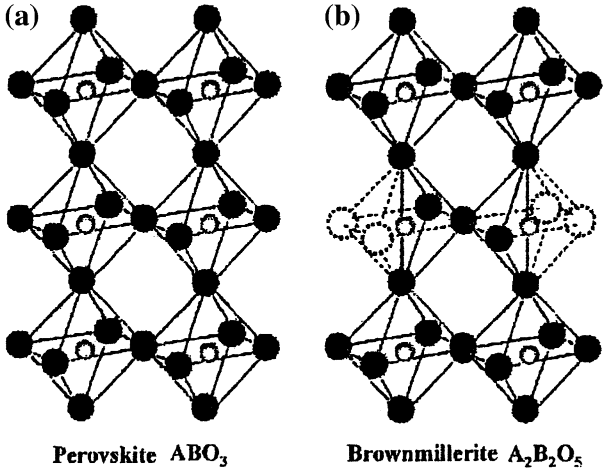

Figure 1. Perovskite ABO_3 and brownmillerite $A_2B_2O_5$ type structures (A = Ca, B = Fe for $Ca_2Fe_2O_5$). B cations are shown as yellow spheres in 6- or 4- coordinations with oxygen atoms (red spheres).

and Fe_2O_3 at different mixing ratios (Ca/Fe = 0.33–3) and calcining the mixture at 1000 °C for 3 h in air. The X-ray powder diffraction patterns were obtained with a diffractometer (RIGAKU, RINT-TTR) using CuK_α radiation (50 kV, 100 mA). ^{57}Fe-Mössbauer measurements were performed at 293 K in an ordinary mode, using spectrometers fabricated by Topologic Systems, Inc. The isomer shift and Doppler velocity scale were calibrated with respect to metallic iron at 293 K. The Raman spectroscopy experiments was carried out using a spectrometer with the 532 nm line of green laser for excitation (JASCO, NRS-1000), and about 100 mW of power was focused on the sample powders.

The combustion of C_3H_6 was performed using a conventional fixed-bed reactor of quartz glass in the temperature range from 100 to 900 °C. The concentration of C_3H_6 was 1000 ppmv. By mixing helium carrier with oxygen (90 vol % He, 10 vol % O_2), the flow rate was controlled to be 30 ml min^{-1} corresponding to a space velocity of ca. 9500 h^{-1}. The calcium ferrite powders were sieved to under 100 μm in particle size and put into the reactor between glass wools for packing and support. Analysis of the effluent gases was performed using an FID gas chromatograph (Shimazu, GC-8A). The specific surface area was measured using an N_2 adsorption–desorption equipment at 77 K (Bell Japan, BELSORP-28SP).

Temperature programmed reduction (H_2-TPR) and oxygen desorption/sorption measurements were carried out in a thermogravimetric analyzer (Shimazu, TGA-50). For H_2-TPR experiments, about 10 mg sample was loaded in a Pt cell in the TGA. The sample was first treated under flowing oxygen gas at 800 °C for 1 h, cooled down to 100 °C under the same atmosphere, and reduced (50 ml min^{-1}). The temperature increased from 100 to 1000 °C at a rate of 5 °C min^{-1}. For oxygen desorption/sorption measurements, the powders of calcium ferrites were reduced under 5 vol% H_2 at 450 °C and remained at this temperature during the analysis, followed by introduction of a pure O_2 (50 ml min^{-1}) to the powders (ca. 10 mg) dispersed on the Pt cell. The storage/release amount of oxygen [μmol/g] was calculated from the difference (gain/loss) between the initial and final weight balanced in each flows.

3. Results and discussion

3.1. X-ray diffraction patterns

Upon calcination of a mixture of CaO and Fe_2O_3 powders at 1000 °C, the mixture transforms to mainly

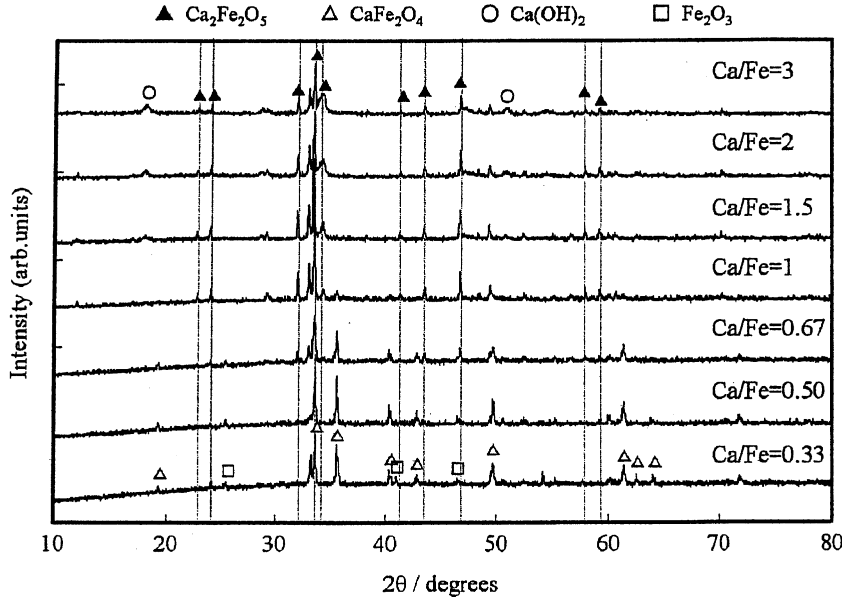

Figure 2. X-ray diffraction patterns of calcium ferrites prepared from the mixture of CaO and Fe_2O_3 with atomic Ca/Fe ratio between 0.33 and 3.

two calcium ferrites ($Ca_2Fe_2O_5$ and $CaFe_2O_4$) according to the following equations.

$$2CaO + Fe_2O_3 \rightarrow Ca_2Fe_2O_5 \text{ (Brownmillerite type)} \quad (2)$$

$$CaO + Fe_2O_3 \rightarrow CaFe_2O_4 \text{ (}CaV_2O_4\text{type)} \quad (3)$$

Figure 2 shows powder XRD patterns of the reaction products from the mixture of CaO and Fe_2O_3 with different Ca/Fe ratio. It was clearly found that there was a drastic change of crystal phases with decreasing Ca/Fe atomic ratio. The $Ca(OH)_2$ (formed from the CaO phase by hydration with atmospheric moisture after the reaction, marked by open circle) disappeared and then the brownmillerite-type $Ca_2Fe_2O_5$ phases (closed triangle) changed to the CaV_2O_4 type $CaFe_2O_4$ phase (open triangle). Here, the most clear peaks assigned to $Ca_2Fe_2O_5$ were observed at Ca/Fe = 1, although small peaks for $CaFe_2O_4$ and $Ca(OH)_2$ remain in the pattern. Similarly, the strongest peaks for $CaFe_2O_4$ were found at Ca/Fe = 0.5. In this case, clear peaks assigned to $Ca_2Fe_2O_5$ were not detected in the pattern.

3.2. ^{57}Fe-Mössbauer spectra

Typical ^{57}Fe-Mössbauer spectra measured at 293 K for calcium ferrites are shown in figure 3, where the mixing atomic ratios (Ca/Fe) in the starting mixtures are 0.33, 1, and 3. Analysis of the Mössbauer spectra revealed that a main product in the samples with Ca/Fe = 0.33 and 1.00 was brownmillerite type $Ca_2Fe_2O_5$ with two ferric ion (III) sites of tetrahedral and octahedral coordination (see figure 1(b)), however, the iron site containing ferric ion (IV) were not detected at room temperatures. Calcium ferrite (Ca/Fe = 1) appeared in the spectra of figure 3 as two sets of sextet with an almost identical intensity, although their absorptions were too weak for the Ca/Fe = 0.33 sample. The two sextets are indicated by the markers in the figure, where closed and open circles set for Fe^{3+} occupied at octahedral (FeO_6) and tetrahedral (FeO_4) sites, respectively. For the brownmillerite-type structure, the isomer shift, quadrupole splitting, internal field were evaluated to be 0.35 mm s^{-1}, -0.52 mm s^{-1}, and 50.7 T for the octahedral site and 0.18 mm s^{-1}, 0.72 mm s^{-1} and, 43.2 T for the tetrahedral site. Mössbauer parameters at 293 K agree with those at 300 K previously reported by Randhawa and Sweety [17]. These authors reported Mössbauer parameters of 0.37 mm s^{-1}, -0.52 mm s^{-1}, and 50.4 T for the octahedral site, and 0.18 mm s^{-1}, 0.72 mm s^{-1} and 42.9 T for the tetrahedral site of $Ca_2Fe_2O_5$.

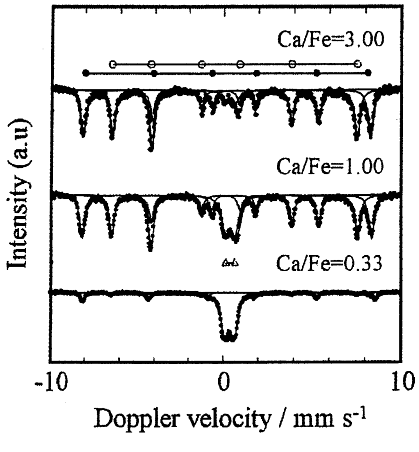

Figure 3. ^{57}Fe-Mössbauer spectra of calcium ferrites prepared from the mixture of CaO and Fe_2O_3 with atomic ratio Ca/Fe = 0.33 (bottom), 1 (middle) and 3 (top).

XRD (figure 2) and Fe-Mössbauer (figure 3) results suggest that the calcination of a CaO and Fe_2O_3 mixture in air at 1000 °C results in the formation of crystalline phases of $Ca_2Fe_2O_5$ and/or $CaFe_2O_4$. The brownmillerite-type $Ca_2Fe_2O_5$ phase was formed at Ca/Fe > 0.33. As the mixing atomic ratio was increased, the diffraction peaks became narrower and higher due to the crystal growth of $Ca_2Fe_2O_5$. In this case, the Mössbauer absorption area (which corresponded to the product yields of $Ca_2Fe_2O_5$) increased. The most pronounced change in the Mössbauer absorption spectra resulted from a mixing atomic ratio of 1, where the products yield of $Ca_2Fe_2O_5$ calculated from adsorption was about 75%.

3.3. Raman spectra

A very attractive feature of perovskite related compounds is the formation of active oxygen adspecies over the surface. Figure 4(a), (b) shows the Raman spectra of the powders after preparation at room temperature. The spectra were scanned in the range of 1200–850 cm^{-1} with a resolution of 2 cm^{-1}. According to Raman spectroscopic datum of the sample at Ca/Fe = 1; (b), an intense absorption at 1093 cm^{-1} is observed. This absorption has typically been assigned to the superoxide radical (O_2^-) in this region. Molecular O_2 species has

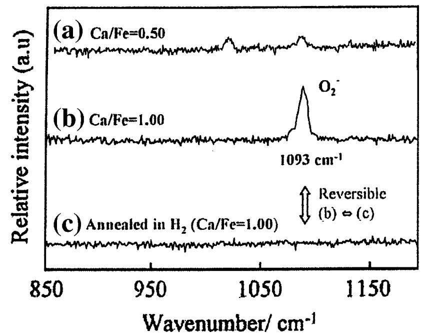

Figure 4. Raman spectra of calcium ferrites prepared from the mixture of CaO and Fe_2O_3 with atomic ratio Ca/Fe = 1; (b) and 0.5; (a), and spectrum (c) of calcium ferrite at Ca/Fe = 1 after annealing under H_2 flow at 500 °C.

been assigned to a band at ca. 1556 cm $^{-1}$; the superoxide radical (O_2^-) is observed to have a stretching vibration frequency at 1180 cm^{-1} on TiO_2 [18] and at 1160–1015 cm^{-1} on MgO–CoO [19, 20], mayenite type aluminum silicate [21–23] has been typically found an absorption in a broad range (640–970 cm^{-1}). Spectra at Ca/Fe = 0.50; (a) also exhibited two weak sifts at 1022 and 1092 cm^{-1}, however the former shift was less definitive. Figure 4(c) shows the Raman spectrum of calcium ferrite powders (Ca/Fe = 1) after annealing in H_2 flow at 500 °C. As can be seen, absorption due to superoxide radicals (O_2^-) almost disappeared after annealing. Moreover, the absorption at 1093 cm^{-1} appeared reversibly after the annealing in air flow for 6 h at 500 °C, although the intensity of the absorption was reduced. The above results suggest that the following adsorption equilibrium between O_2/O_2^- may exist on the surface of brownmillerite type $Ca_2Fe_2O_5$ under an air atmosphere.

$$O_2(g) \Leftrightarrow O_2(ads.) \Leftrightarrow O_2^-(ads.) \qquad (4)$$

3.4. Catalytic activity

We examined the catalytic activity of the prepared calcium ferrites. Figure 5 (the light-off curves) summarizes the results. For all the prepared catalysts, C_3H_6 conversion increased with the elevation of reaction temperature. The C_3H_6 combustion started around 150, 180, 200, 210, 300 and 320 °C, and completed around 180, 500, 600, 610, 700 and 720 °C for Pt/Al_2O_3, $Ca_2Fe_2O_5$, $CaFe_2O_4$ (Ca/Fe = 2), $Ca_2Fe_2O_5$ with CaO (Ca/Fe = 0.5), Fe_2O_3 and CaO, respectively. Pure CaO and Fe_2O_3 only showed low activities under the conditions of 10 vol% O_2 and GHSV = 9500 h^{-1}. After calcination of both pure oxides with different mixing ratio, the activities, especially for the calcium ferrites at Ca/Fe = 1 were found to be apparently improved resulting in a decrease in the reaction temperature (ca. 350 °C for Ca/Fe = 1) compared with the same conversion without catalyst. The promoting effect increased according to the sequence of CaO < Fe_2O_3 << $Ca_2Fe_2O_5$ with CaO (Ca/Fe = 0.5) < $CaFe_2O_4$ (Ca/Fe = 2) << $Ca_2Fe_2O_5$ (Ca/Fe = 1) << Pt/Al_2O_3, where the light-off temperatures defined as the temperature at 50% in conversion were ca. 540, 520, 450, 430, 340 and 190 °C, respectively. Accordingly, these results indicated that the existence of the brownmillerite type $Ca_2Fe_2O_5$ played significant promoting roles for C_3H_6 combustion as an oxidation catalyst. The above results also suggested that the catalytic activity of $Ca_2Fe_2O_5$ is correlated with the superoxide O_2^- formation on the surface of catalysts. The light-off curves also show a higher activation energy of Pt/Al_2O_3 than those of any other calcium ferrites. The conversion of Pt/Al_2O_3 was increased more quickly with the increase in temperature, indicates that the reaction pathway on the Pt/Al_2O_3 is different from that on calcium ferrites samples. The reaction rates on the calcium ferrite may be more strongly affected by diffusion process. A small amount of oxygen species formed on active ferric ion sites would slowly diffuse in the surface or the surface layer, and participated into the reaction.

3.5. Oxygen sorption/desorption property

Figure 6 shows the temperature programmed reduction (H_2-TPR) from calcium ferrite prepared with an atomic Ca/Fe ratio of 1 and 0.5, in which the ordinate (differential weight changes calculated from TG signal) corresponds to the rate of iron reduction accompanied with oxygen desorption from the calcium ferrites in a 5% H_2/N_2. For the calcium ferrite at Ca/Fe = 0.5, no peak was observed below 500 °C, and only a β-type peak (β') was observed at high temperature region (660 °C), indicates the direct reduction of Fe^{3+} to Fe^{2+}. Similar peak assigned to the reduction to FeO was observed in the bulk Fe_2O_3 [24]. For Ca/Fe = 1, the H2-TPR result shows a small peak (α) at 300 °C and a large peak (β) over 800 °C, indicated the presence of two types of the active site on $Ca_2Fe_2O_5$. Notably, the small peak (α) was observed at much lower temperature compared with that of the

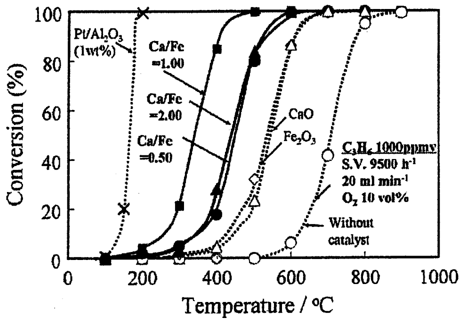

Figure 5. Catalytic activity of calcium ferrites prepared from a mixture of CaO and Fe_2O_3 with atomic ratio Ca/Fe = 0.5, 1 and 2.

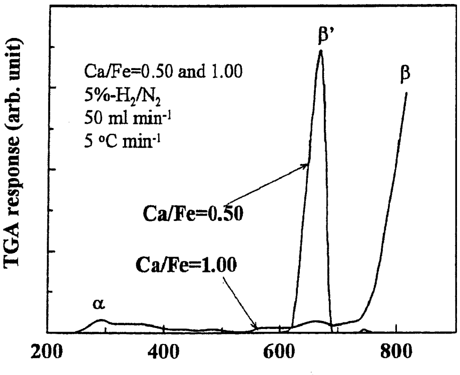

Figure 6. TPR-H_2 spectrum of calcium ferrite prepared from a mixture of CaO and Fe_2O_3 with atomic ratio Ca/Fe = 1 and 0.5.

iron reduction from Fe^{3+} to Fe^{2+} (β', 660 °C) and that of the reduction of pure Fe_2O_3 to Fe_3O_4 (430 °C in ref. [25]). The small peak (α) would be related to a reduction of a small amount of Fe^{4+} which releases oxygen species at lower temperature as observed for non-stoichiometric Fe-containing perovskites [26]. Fe^{4+} were observed in brownmillerite type oxide prepared in air, and always present even after annealing in Ar/N_2 atmosphere at 1000 °C [27]. It can be considered that the C_3H_6 oxidation proceeds at lower temperature on the abnormal valence iron, and that the abnormal valence site provides the oxygen adspecies such as superoxide (O_2^-, shown in figure 4) on the $Ca_2Fe_2O_5$ surface. The latter peaks at high temperature (β) can be assigned to the reduction of Fe^{3+} which corresponds to the release of lattice oxygen (O_x) from the perovskite type ferric iron site (FeO_6). The oxide ions seem to be formed by the oxygen exchange between oxygen and oxygen vacancies ($V_O^{\cdot\cdot}$) on the surface. These oxygen species may involve other higher temperature reaction. The peak areas in TPR spectra can be related to the density of the active sites. The results indicated that the density of Fe^{3+} site was much more than that of Fe^{4+} density in calcium ferrite at Ca/Fe = 1, indicated that the preparation under reducing or oxidizing condition results in significant difference in the catalytic activity. The peak area of Fe^{4+} was very small, and the molar concentration of Fe^{4+} was as lower as 2% of total amount of iron ideally included in stoichiometric brownmillerite crystals.

Figure 7 presents the oxygen sorption/desorption behavior of the calcium ferrites powder (Ca/Fe = 1) at 450 °C. The integrated sorption/desorption amount of oxygen estimated from the total weight change is also given in figure 7. It was observed that the amount of oxygen included in the calcium ferrites is decreased in a 5% H_2/N_2 flow, and then the amount was increased in the O_2 flow with time on stream. The sorption/desorption amount completely recovered to the initial value after saturation with O_2. The observed oxygen sorption/desorption amounts at 450 °C (83 μmol g^{-1}) corresponded to only ca. 6% of total oxygen contents calculated from the total amount of oxygen vacancies in the bulk $Ca_2Fe_2O_5$ crystal, however the value was larger than that calculated for monolayer sorption capacity of O_2 (40 μmol g^{-1}). In each steps, the oxygen sorption/desorption proceeded slowly on the surface layer. Namely, the active oxygen species over the $Ca_2Fe_2O_5$ crystals was slightly released, slowly consumed in the H_2/N_2 mixture flow, and then replenished by sorption onto the crystal surface in O_2 flow. These results indicated that not only adspecies but also a small amount of bulk oxygen in the surface layer could participate to the catalysis.

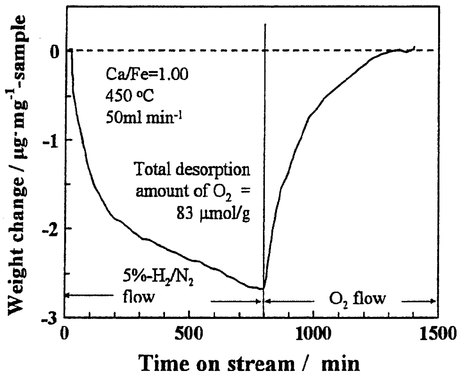

Figure 7. Oxygen desorption/sorption behavior of calcium ferrite prepared with atomic ratio Ca/Fe = 1.

In summary, the results shows that the redox cycles of brownmillerite phase with high oxygen deficiencies coming from the crystal structure can participate into the C_3H_6 oxidation due to a presence of easily reducible iron Fe^{4+} sites forming highly active oxygen species at lower temperature compared with a transition metal based catalyst such as Fe_2O_3. In the case of calcium ferrite samples synthesized at Ca/Fe = 1, such brownmillerite make it possible to promote combustion at temperatures above 180 °C, which may be significant interesting for applications to low-cost catalyst and catalyst supports. However, it should also be noted that further studies are necessary to improve the combustion activity of $Ca_2Fe_2O_5$, and to assess active sites in the brownmillerite type $Ca_2Fe_2O_5$ in detail. In addition, the formation of the oxygen species at the abnormal cation sites on the $Ca_2Fe_2O_5$ surface would significantly promote a catalytic activity of a very small amount of metal-based catalysts (~0.1% by weight) which was dispersed on the $Ca_2Fe_2O_5$ as a support. This attempt may be particularly useful and interesting.

4. Conclusions

In the current study, reasonable and environmentally friendly calcium ferrite based catalysts were synthesized by solid state reaction of the mixture of CaO and Fe_2O_3 powders with mixing atomic ratio from 0.33 to 3 at 1000 °C. The prepared calcium ferrite catalysts contained mainly two calcium ferrite phases (brownmillerite type $Ca_2Fe_2O_5$ and CaV_2O_4 type $CaFe_2O_4$). The brownmillerite type crystal phase grew at Ca/Fe > 1. The clear ^{57}Fe-Mössbauer absorption assigned to two ferric ion sites of octahedral (FeO_6) and tetrahedral (FeO_4 with oxygen vacancies) in brownmillerite structure were successfully observed in the spectra at Ca/Fe > 1, and the product yield of $Ca_2Fe_2O_5$ calculated from Mössbauer absorption was ~75% at Ca/Fe = 1. A highly active superoxide radical (O_2^-) could be formed on the surface of calcium ferrites and the atmospheric oxygen strongly affected the equilibrium formation of such oxygen adspecies. The formation of the brownmillerite type $Ca_2Fe_2O_5$ significantly promote the catalytic combustion of C_3H_6

in the temperature range between 250 and 450 °C. The light-off temperature of calcium ferrite at Ca/Fe = 1 ($Ca_2Fe_2O_5$) was 150 °C higher than that of Pt/Al_2O_3 and 180 °C lower than that of Fe_2O_3, and the combustion started at 90–140 °C lower temperature than those obtained using other calcium ferrites (Ca/Fe = 0.5, 2). The promoting effects of the combustion can be ascribed to the activation of oxygen adspecies (such as O_2^-), which was accompanied with the reduction of abnormal valence iron (Fe^{4+}) site in the surface layer (< 300 °C). The active oxygen species reversibly appeared and disappeared on the iron site due to the sorption of atmospheric oxygen at the same temperature range.

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