Journal of Solid State Chemistry **156,** 225–229 (2001)
doi:10.1006/jssc.2000.8992, available online at http://www.idealibrary.com on IDEAL®

In Situ XRD and *In Situ* IR Spectroscopic Analyses of Structural Change of Goethite in Methane Oxidation

Masahiro Katoh,* Masanao Orihara,† Toshihiro Moriga,* Ichiro Nakabayashi,*,[1]
Shigeru Sugiyama,* and Suminori Tanaka†

**Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, 2-1 Minami-Josanjima, Tokushima 770-8506; and*
†Okura Industrial Co., Ltd., 1515 Nakatsu, Marugame, Kagawa 763-8508, Japan

Received April 17, 2000; in revised form September 14, 2000; accepted October 6, 2000; published online December 21, 2000

This paper examines the methane oxidation activity of iron oxides from goethite synthesized from different types of iron compounds. The variation of crystal structure caused by heat treatment of goethite under methane and oxygen gas mixtures was investigated by *in situ* X-ray diffractometry and *in situ* infrared spectroscopy. Methane oxidation commenced at a low temperature of 573 K when goethite was used as a catalyst, after the goethite had changed into hematite by dehydration at approximately 493 K. It was found that the active species in methane oxidation was hematite. © 2001 Academic Press

Key Words: **goethite; hematite; methane oxidation; *in situ* XRD; *in situ* IR.**

INTRODUCTION

The catalytic activity of iron oxides in the oxidation of H_2, CO, CH_4, and olefins is never vigorous enough in comparison with precious metals, transition metals such as nickel, cobalt, etc., and the oxides of the metals. However, iron oxides, which are widely available in a natural state, are inexpensive and seldom affect human beings. For this reason, the oxides are widely used as combustion catalysts. For example, a report has been released suggestions that addition of the oxides to incinerators helps restrict dioxin, carbon monoxide, and nitrogen oxides in the exhaust fumes (1). Thus garbage bags or resin bags for daily procurement into which goethite (α-FeOOH) is impregnated are in production (2).

Dioxin discharged from incineration plants is produced by reactions of unburned granular carbon particles, reacting with dioxin precursors through *de novo* synthesis with materials such as inorganic chlorine, air, and moisture (3). It is also produced by decomposition or synthetic reactions of chlorobenzenes or chlorophenols. Accordingly it is believed that reduction of unburned granular carbon particles, together with the accomplishment of complete combustion in the incinerators, makes it possible to restrict dioxin generation.

This study examines the catalytic activity of iron oxide obtained from goethite synthesized from different types of iron compounds. As a model experiment, an investigation was made with the oxidation of methane, which is the least reactive of the hydrocarbons. Structural change caused by heat treatment of goethite in the gas mixture of methane and oxygen was followed by *in situ* X-ray diffractometry and *in situ* infrared spectroscopy.

MATERIALS

As starting substances, three types of goethite were used (4). Type 401 was obtained by air-oxidizing an alkali-suspension liquid brought about by mixing $FeSO_4 \cdot 7H_2O$ aqueous solution with Na_2CO_3 in N_2. Type 402 was obtained by dispersing the 401 into distilled water with the addition of $Na_2O \cdot nSiO_2$ and H_3PO_4 as a sintering retardant after dehydration at 392 K. Type 403 was obtained by air-oxidizing an alkali suspension liquid brought about by mixing $FeSO_4 \cdot 7H_2O$ and NaOH. From TEM photographs shown in Fig. 1, we can see that the three types of goethite are all spindle- or needle-shaped. The needle-shaped crystals of the goethite are characteristic of those published in the literatures (5–9). It is also found that the particle diameter of 401 and 402 is approximately 0.25 μm, which is approximately $\frac{1}{3}$ of that of 403. The surface areas of the three specimens were measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700). The BET surface areas of 401, 402, and 403 pretreated at 473 K were 82, 74, and 18 m^2/g, respectively.

MEASUREMENTS

The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric

---

[1] To whom correspondence should be addressed. Fax: + 81-88-655-7025. E-mail: ichiro@chem.tokushima-u.ac.jp.

0022-4596/01 $35.00

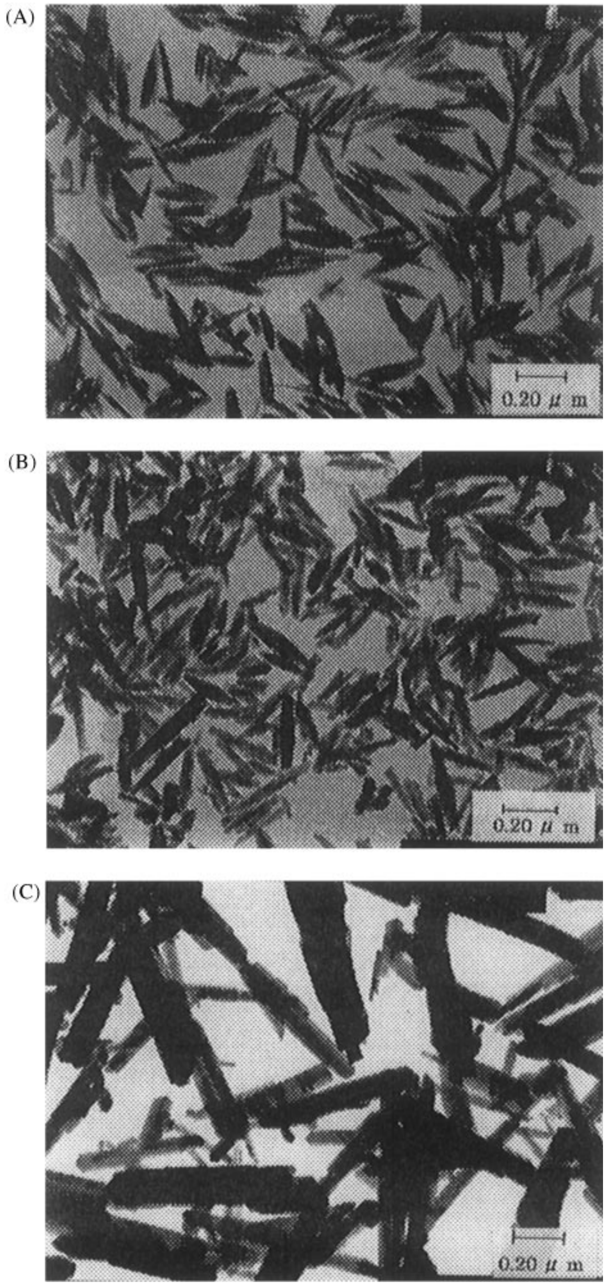

FIG. 1. TEM photographs of the three types of goethite: (A) 401, (B) 402, and (C) 403.

pressure. Details of the reactor design have been described elsewhere (10). Prior to reaction, the catalyst was calcined *in situ* in a helium flow ($F = 25$ ml/min) at a given reaction temperature for 20 min. A half-gram of the catalyst was loaded ($W = 0.5$ g). The gas used was diluted with helium so that the pressures of methane and oxygen would be kept at 3.4 and 20.3 kPa, respectively ($P(CH_4) = 3.4$ kPa and $P(O_2) = 20.3$ kPa). The reactants and products were analyzed with an on-stream gas chromatograph (Shimadzu GC-8APT) equipped with a TC detector and integrator (Shimadzu C-R6A). TG–DTA was done by using a Shimadzu DTG-40 Thermoanalyzer with a heating rate of 10 K/min from room temperature to 1073 K under airflow (10 ml/min). Powder X-ray diffraction data were collected using a high-performance diffractometer (Rigaku RINT200VHF$^+$) with monochromatized Cu$K\alpha$ radiation with a source power of 40 kV–150 mA for phase identification of the specimens and for *in situ* measurement in methane/oxygen mixed gas at higher temperature. The sample was mounted on a platinum holder. The same gas mixture as that used in the catalytic experiments was introduced to the reaction chamber at a rate of 50 ml/min. The heating rate to the given temperatures was 10 K/min, and the temperature was held for 1 min prior to the *in situ* measurement. The scanning rates were 2°/min for phase identification and 10°/min for the *in situ* measurement, respectively. Transmission infrared spectra of the samples under reaction were recorded on an FT-IR spectrometer (Shimadzu 8200PC) with 4 cm^{-1} resolution. The sample pellets were prepared by pressing powdered 401 mixed with or without KBr as a diluent. Details of the sample holder for the IR measurements are described elsewhere (11). The KRS-5 window was used for high transmittance in the low wave number region.

RESULTS AND DISCUSSION

Catalytic Activity

It was found that no methane oxidation occurred even at 873 K in the absence of the catalyst. The reaction was started at as low temperature as 573 K on goethite (12). Under the present conditions, carbon dioxide and water exclusively were produced. This result that neither carbon monoxide nor C_2 compounds (such as ethane) were found is consistent with the previous papers (6, 7). Figure 2 shows the conversion of methane (C_M) and oxygen (C_O) on goethite. The C_M and C_O were calculated by the following formulas, respectively,

$$C_M(\%) = \left\{1 - \frac{CH_4(P)}{CH_4(P) + CO_2(P)}\right\} \times 100, \qquad [1]$$

$$C_o(\%) = \left\{1 - \frac{O_2(P)}{O_2(R)}\right\} \times 100 \qquad [2]$$

where $O_2(R)$ represents the mole number of oxygen in the gas introduced, and $CH_4(P)$, $CO_2(P)$, and $O_2(P)$ represent the mole numbers of methane, carbon dioxide, and oxygen in the product stream. The carbon mass balances were 101 ± 5%, based on our 98 runs. The conversions of both methane and oxygen, for which catalytic activities were in the order 401 > 403 > 402, increased with increasing reaction temperature. With 401, a decrease was seen in the rate

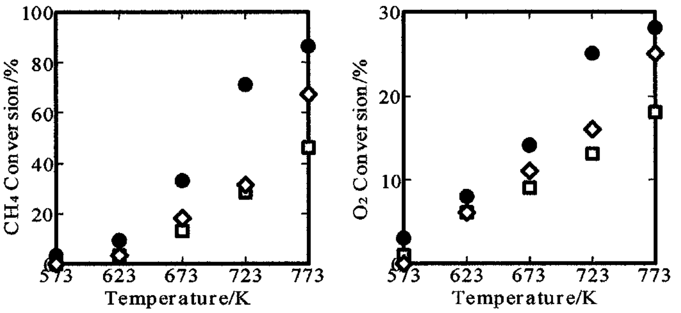

FIG. 2. CH_4 and O_2 conversion as a function of temperature over the three types of goethite: 401 (●), 402 (□), and 403 (◇). Conditions: $W = 0.5$ g, $F = 25$ ml/min, $P(CH_4) = 3.4$ kPa, $P(O_2) = 20.3$ kPa diluted with He.

of the increment of the conversion above 773 K, exhibited as an S shape in the graph. This might derive from contact between methane and oxygen with the catalyst becoming restricted due to the decrease in the partial pressure of the methane caused by the consumption of a large amount of methane. Especially, 401 showed a conversion ratio as high as nearly 80% at 723 K. The larger number of covered active sites for methane conversion with substances and/or reactants would lead to the lower number of attacks to fresh active sites by substrates. This causes the decrease of the increment of the conversion.

The particle diameter, obtained from TEM photography, of 401 (0.25 μm) was smaller than that of 403 (0.7 ∼ 0.8 μm). The BET surface area of 401 is larger than that for 403 (82 and 18 m^2/g, respectively), which results in higher conversion. Comparing 402 (particle diameter 0.25 μm, specific surface area 74 m^2/g) with 401, we see that the methane conversion was extremely small, despite the fact that their particle diameters and specific surface areas were almost the same. This would suggest that the sintering-restricting agents, $Na_2O \cdot nSiO_2$ and H_3PO_4 (the existence of P on the 402 surface was confirmed by XPS), covered the goethite particles in 402. It should be noted that the specific activity (i.e., surface-area normalized conversion of both methane and oxygen) was in the order 403 > 401 > 402. It is generally accepted that the activity for the oxidation of methane is strongly influenced by Na-containing species on the catalyst surface (13), indicating that the nature of the Na-containing species on 403 may be rather different from that on 401 and 402. In the following, we describe *in situ* high-temperature XRD and *in situ* IR analyses of 401, on which the oxidation activity of the methane was the highest and the sintering effects seemed to be negligible.

In Situ High-Temperature XRD Analysis

TG–DTA measurement for goethite in air showed that an endothermic reaction accompanied by weight loss occurred from 473 to 523 K, as shown in Fig. 3. This reaction temperature determined by TGA is in good agreement with that reported in the literature (8). Little change was seen up to 1073 K. High-temperature XRD measurement in air was performed for 401, as seen in Fig. 4. All the diffraction peaks at 473 K could be assigned to goethite, whereas those at 503 K could be assigned to hematite (α-Fe_2O_3). Diffraction profiles at 483 and 493 K showed mixed phases of these materials. These results show that structural change accompanied by dehydration from goethite to hematite occurs from 473 to 503 K. From the fact that the goethite becomes catalytically active above 573 K, it is suggested that the active species of the reaction is hematite. It is notable that in Fig. 4, a pronounced reflection width anisotropy is apparent in the XRD pattern of hematite. It has been reported that the (012), (014), (024), and (214) peaks of hematite are preferentially broadened with respect to the others (5, 9).

To examine the structure variation of the hematite in the course of methane oxidation, *in situ* high-temperature XRD measurements were conducted for the catalysts in the gas mixture, as shown in Fig. 5. Above 753 K, diffraction peaks assigned to magnetite appeared beside those assigned to hematite and increased in intensity as the temperature was raised. When the reaction temperature exceeded 753 K, methane oxidation occurred, resulting in a shortage of oxygen in the system. The hematite would be unable to fully supplement the shortage of oxygen with the oxygen contained in the gas, so that hematite partially changed into magnetite. The temperature when the magnetite appeared was in a good agreement with that at which there was a decrease in the rate of the increment of the methane conversion.

In Situ IR Analysis

In situ IR measurement was performed using goethite (401) pretreated at room temperature *in vacuo* (1.0×10^{-2} Pa) for 2 h in an *in situ* IR cell. The spectra in Fig. 6 were obtained in methane and oxygen mixed gas. At room temperature, in addition to bands assigned to the

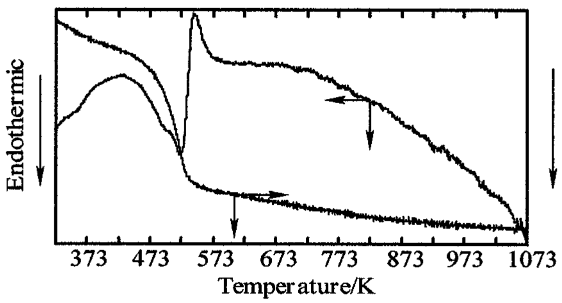

FIG. 3. TG–DTA curves of goethite (401). Conditions: $W = \sim 0.06$ g, heating rate = 10 K/min, under airflow.

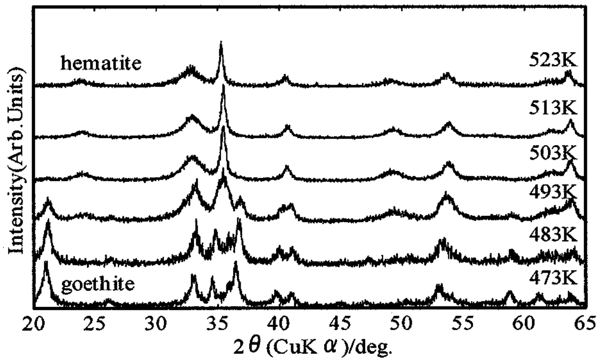

FIG. 4. High-temperature XRD profiles for goethite (401) in air at various temperatures. Conditions: $W = \sim 0.5$ g, heating rate = 10 K/min, holding duration prior to the measurement = 1 min, under methane/oxygen mixed gas flow diluted by He.

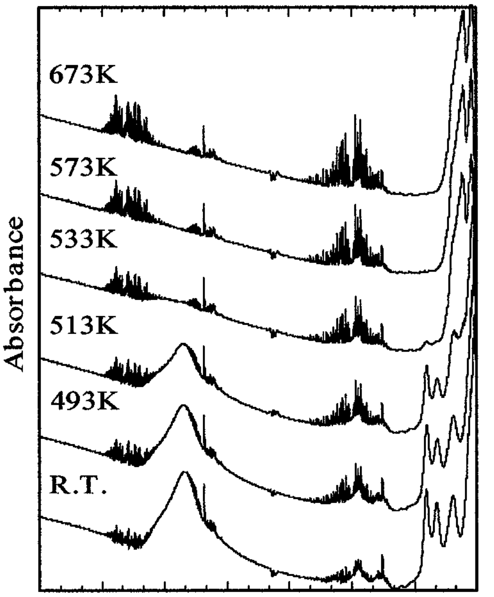

FIG. 6. *In situ* infrared spectra of goethite (401) diluted with KBr in methane and oxygen mixed gas at various temperatures.

gaseous methane (about 3020 and 1300 cm^{-1}) (14), free water (about 3700 and 1600 cm^{-1}) (14), and carbon dioxide (about 2350 cm^{-1}) (14) in air which exists in the circumference of the cell, bands assigned to the goethite (about 900, 800, 600 and 450 cm^{-1}) (5, 15) were observed. The broad band (about 3200 cm^{-1}) assigned to the OH groups of goethite (α-FeOOH) was also observed. Little change in the spectrum was seen from room temperature to 513 K. From 513 to 533 K, however, there were considerable changes. The bands assigned to goethite disappeared and were replaced by bands assigned to the hematite (550 and 450 cm^{-1}) (5, 15). In particular, since the bands assigned to the OH groups disappeared while the intensities of the bands for water increased, the proposal of a dehydration reaction from goethite to hematite is supported. Structural change from goethite to hematite at 513–533 K was confirmed with IR measurement in the gas mixture of methane and oxygen, which was almost in coincidence with the high-temperature XRD measurement. Since little change of the band was seen from 533 to 673 K, it is confirmed that there was no effect of the IR emission that is generated with an increase in the sample temperature (16) on the spectrum in the measured temperature region.

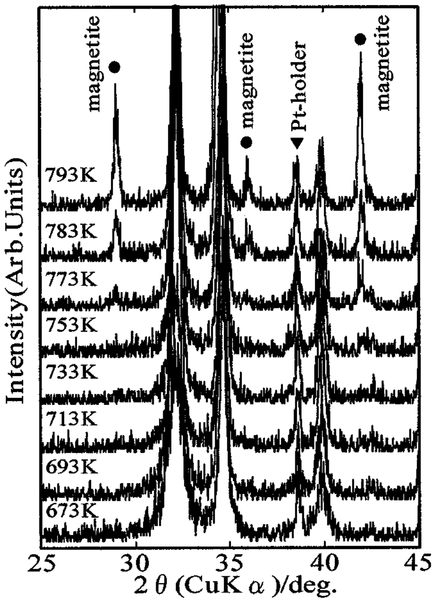

FIG. 5. *In situ* high-temperature XRD profiles for hematite in methane and oxygen mixed gas at various temperatures.

However, no change was observed in the spectrum corresponding to the oxidation of methane, which is believed to occur at temperatures above 573 K. This might result from the use of KBr as a diluent, preventing the iron catalyst from coming into contact with the methane. With such a situation in mind, pure 401 (6.3 mg) was molded into a pellet having a diameter of 13 mm and thickness of 57 μm. The pellet was pretreated at 623 K *in vacuo* (4.0×10^{-3} Pa) for 10 h and the goethite was converted to hematite, in order to confirm the activity of hematite to methane oxidation. For the self-supported pellet, an excellent IR spectrum was obtained over 4000–800 cm^{-1} although the spectrum was saturated at a wave number below 800 cm^{-1}. The results of the measurements are shown in Fig. 7. From room temperature to 573 K, only the bands assigned to gaseous methane, free water, and carbon dioxide in air were observed. The differences between the intensities of the methane peaks obtained at all measurement temperatures could not be recognized, because of the small catalyst quantity in the IR

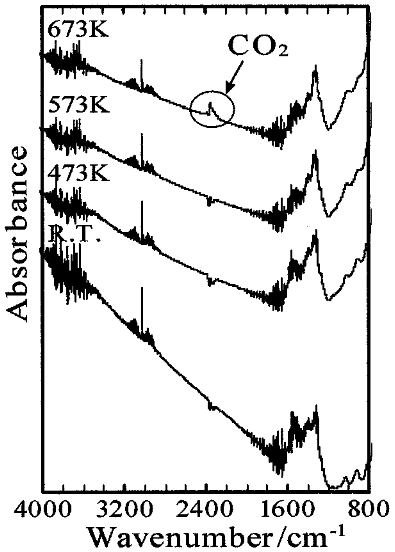

FIG. 7. *In situ* infrared spectra of hematite in methane and oxygen mixed gas at various temperatures.

cell. However, the band assigned to carbon dioxide adsorbed (17) on hematite clearly appeared at 673 K, due to high molar absorption coefficient of carbon dioxide. It was considered that the carbon dioxide adsorbed was generated by methane oxidation. It can be also explained by the IR measurement showing that methane oxidation did progress. Thus the structural change from geothite to hematite at 513–533 K was confirmed in Fig. 6 and methane oxidation was confirmed at 673 K in Fig. 7. These results show that the active catalyst in methane oxidation was hematite.

CONCLUSIONS

This study has shown that 401 goethite is the most effective combustion catalyst among the three types of goethite. The results of *in situ* X-ray diffraction measurements and *in situ* IR absorption measurements show that in methane oxidation, the goethite is converted to hematite and is occasionally changed into magnetite, depending on the conditions. It can be deduced that the active catalyst in methane oxidation is hematite.

REFERENCES

1. T. Imai, Y. Fuji, T. Matsui, M. Isoai, H. Inoue, M. Ishihara, and M. Ukita, *in* "Proceedings of the 9th Annual Conference of the Japan Society of Waste Management Experts," p. 720, 1998. [In Japanese]
2. S. Tanaka, *PACKPIA*, 26 (1996). [In Japanese]
3. B. K. Gullett, K. R. Bruce, and L. O. Beach, *Chemosphere* **20,** 1945 (1990).
4. T. Nakamura and H. Kurokawa, *Phys. Status Solidi A* **155,** 207 (1996).
5. R. M. Cornell and U. Schwertmann, "The Iron Oxides." VCH, Weinheim, 1996.
6. A. C. S. Brown, J. S. J. Hargreaves, and B. Rijniersce, *Catal. Lett.* **53,** 7 (1998).
7. A. C. S. Brown, J. S. J. Hargreaves, and B. Rijniersce, *Catal. Today* **45,** 47 (1998).
8. L. A. Pérez-Maqueda, J. M. Criado, C. Real, J. Šubrt, and J. Bohácek, *J. Mater. Chem.* **9,** 1839 (1999).
9. A. S. J. Baker, A. S. C. Brown, M. A. Edwards, J. S. J. Hargreaves, C. J. Kiely, A. Meagher, and Q. A. Pankhurst, *J. Mater. Chem.* **10,** 761 (2000).
10. S. Sugiyama, Y. Iguchi, H. Nishioka, T. Minami, T. Moriga, H. Hayashi, and J. B. Moffat, *J. Catal.* **176,** 25 (1998).
11. T. Yamazaki, I. Watanuki, S. Ozawa, and Y. Ogino, *Langmuir* **4,** 433 (1988).
12. S. Sugiyama, T. Minami, T. Moriga, H. Hayashi, and J. B. Moffat, *J. Solid State Chem.* **135,** 86 (1998).
13. Y. Amenomiya, V. I. Birss, M. Goledzinowski, J. Galuszka, and A. R. Sanger, *Catal. Sci. Eng.* **32,** 163 (1990).
14. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules." Van Nostrand, New York, 1945.
15. A. Raman, B. Kuban, and A. Razvan, *Corros. Sci.* **32,** 1295 (1991).
16. B. Lee, J. N. Kondo, F. Wakabayashi, and K. Domen, *Bull. Chem. Soc. Jpn.* **71,** 2149 (1998).
17. T. Yamazaki, M. Katoh, S. Ozawa, and Y. Ogino, *Mol. Phys.* **80,** 313 (1993).