Preparation of high-performance Co_3O_4 catalyst for hydrocarbon combustion from Co-containing hydrogarnet

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Received 12 August 2002; accepted 22 November 2002

Supported Co_3O_4 catalysts were prepared via the calcination of Co-containing hydrogarnet, $(Ca_{3-x}Co_x)Al_2(SiO_4)_{3-y}(OH)_{4y}$, at 400 °C. Such precursors with various extents of substitution were synthesized from the hydrothermal reaction of a stoichiometric mixture of calcium oxide, amorphous silica, alumina sol, and cobalt hydroxide at 200 °C. It was found that the catalyst consisted of Co_3O_4, CaO, and mayenite and exhibited a high activity for the combustion of propylene, benzene, and toluene at temperatures below 300 °C.

KEY WORDS: cobalt-containing hydrogarnet; mayenite; cobalt oxide; combustion; hydrocarbons.

1. Introduction

Over the last few years, environmental legislation has imposed increasingly stringent limits for permitted atmospheric emission levels. The release of hydrocarbons, especially volatile organic compounds (VOCs), has also been receiving much attention, because VOCs are possible compounds for causing cancer. Thermal combustion is a way to reduce VOCs in the atmosphere, although it requires temperatures above 1000 °C. The use of a combustion catalyst can significantly lower the operating temperature. Indeed, the oxide of a metal such as cobalt, copper, or manganese is active for the combustion of hydrocarbons in the temperature range 300–600 °C [1–3].

Hydrogarnet ($Ca_3Al_2(SiO_4)_{3-y}(OH)_{4y}$, $0 \leq y \leq 3$) has the garnet structure, in which a variety of cations can be accommodated. The general formula for a collective garnet is expressed by $X_3Y_2Z_3O_{12}$, where X, Y, and Z are divalent (Ca^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+}, Zn^{2+}), trivalent (Al^{3+}, Cr^{3+}, Fe^{3+}, Ti^{3+}, V^{3+}, Zr^{3+}, Sn^{3+}), and tetravalent cations (Si^{4+}), respectively. Structurally, the tetrahedral $(SiO_4)^{4-}$ in hydrogarnet is replaced by $(O_4H_4)^{4-}$. Such an extensive solid solution involving the $(O_4H_4)^{4-}$ group is not found in other common garnets and is highly unusual in silicate groups in general [4–6]. The feature of the substitution with a variety of cations in the lattice is similar to that of layered double hydroxides (LDHs) $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot mH_2O]^{x-}$, where M(II) and M(III) are a divalent and trivalent cation, respectively, and A^{n-} is a charge compensating anion such as CO_3^{2-}, NO_3^-, Cl^-, polyoxometallate, or other macrocyclic ligand. LDHs are readily decomposed at around 400 °C to mixed oxides, the catalytic properties of which are well studied [7–11]. The purpose of the present study is to synthesize Co-containing hydrogarnets with various extents of substitution and to examine their catalytic activity for hydrocarbon combustion.

2. Experimental

2.1. Preparation of hydrogarnet

Cobalt-containing hydrogarnets with various extents of substitution ($(Ca_{3-x}Co_x)Al_2(SiO_4)_{0.8}(OH)_{8.8}$: $0 \leq x \leq 0.2$, Co/Ca = 0–0.0714; $x = 0.0$ (Co/Ca = 0), $x = 0.03$ (Co/Ca = 0.0101), $x = 0.05$ (Co/Ca = 0.0169), $x = 0.06$ (Co/Ca = 0.0204), $x = 0.07$ (Co/Ca = 0.0238), $x = 0.08$ (Co/Ca = 0.0273), $x = 0.09$ (Co/Ca = 0.0309), $x = 0.10$ (Co/Ca = 0.0344), $x = 0.11$ (Co/Ca = 0.0380), $x = 0.15$ (Co/Ca = 0.0526), $x = 0.20$ (Co/Ca = 0.0714)) were prepared via the hydrothermal reaction of a stoichiometric mixture of alumina-sol, amorphous silica, calcium oxide, and cobalt hydroxide. Cobalt hydroxide was obtained by mixing $Co(NO_3)_2\cdot 6H_2O$ with a 0.3 M NaOH solution by adjusting its pH to 13. Hydrothermal treatments were performed as follows. The mixture of raw materials was put in a teflon-lined stainless steel autoclave (25 mL volume) with distilled water followed by heating under rotation at 50 rpm. The weight ratio of water to solids was 12. The resultant mixture was heated from room temperature to 200 °C in 2 h and held for 15 h. The prepared compounds were washed until their pH became 7 and then separated by

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filtration followed by drying at 110 °C for two days. The Co_3O_4/Al_2O_3 catalysts with Co_3O_4 contents of 0.3, 1.0, 2.5, 5.0, 10, and 15 wt% were prepared by the impregnation of Al_2O_3 (Catalyst and Chemicals Ind. Co. Ltd) with an aqueous solution of $Co(NO_3)_2$.

2.2. Characterization

X-ray powder diffraction data of catalysts were obtained using a Rigaku RINT 2000 diffractometer with Ni-filtered CuKα radiation (40 kV, 30 mA). The phase evolution up to 600 °C was monitored by *in situ* high-temperature X-ray diffraction with a Rigaku RINT 2000 temperature controller under ambient atmosphere (air). Samples were heated at a rate of 5 °C/min, and held before each measurement for 1 h. The specific surface area was measured using an N_2 adsorption–desorption equipment at 77 K (Bell Japan, BELSORP 28SP).

2.3. Catalytic activity for hydrocarbon combustion

The combustion of hydrocarbons was performed using a conventional quartz glass microreactor from room temperature to 500 °C. The concentration of hydrocarbons was 1000 ppmv. By mixing synthetic air (80% N_2 and 20% O_2) the flow rate was controlled to be 100 ml/min corresponding to a space velocity of 10 000/h. The catalyst was pelletized to a 300–500 μm particle size and put in the reactor between plugs of silica wool. Analysis of the effluent gases was performed using an on-line gas chromatograph (Shimadzu GC-8A) with Porapak P and 5A molsieve columns for the assignment of organic compounds and with an active carbon column for CO_2 and CO.

3. Results and discussion

3.1. Characterization of Co-containing hydrogarnet

Figures 1 and 2 illustrate XRD patterns of Co-containing hydrogarnets with various extents of substitution and their lattice parameter *a*, respectively. Substitution was confirmed for the range of Co/Ca from 0 to 0.0344 with the additional Co_3O_4 phase for the Co/Ca range 0.0380–0.0714. The lattice parameter *a* decreased from 1.24078 to 1.23131 nm with increasing cobalt content in the Co/Ca range 0–0.0344, while for Co/Ca = 0.0344, 0.0380, 0.0526, and 0.0714, a constant value of $a = 1.2313$ nm was observed. In the hydrogarnet structure, the substitution of Co^{2+} into the calcium sites should result in a decrease in the value of *a* due to the different ionic radius: 0.112 nm for Ca^{2+} vs. 0.090 nm for Co^{2+} [12]. The solid solution containing Ca^{2+} and Co^{2+} was formed within the Co/Ca ratio 0–0.0344, namely $(Ca_{3-x}Co_x)Al_2(SiO_4)_{0.8}(OH)_{8.8}$: $0 \leq x \leq 0.1$. Table 1 summarizes the lattice parameters of the Co-containing hydrogarnet.

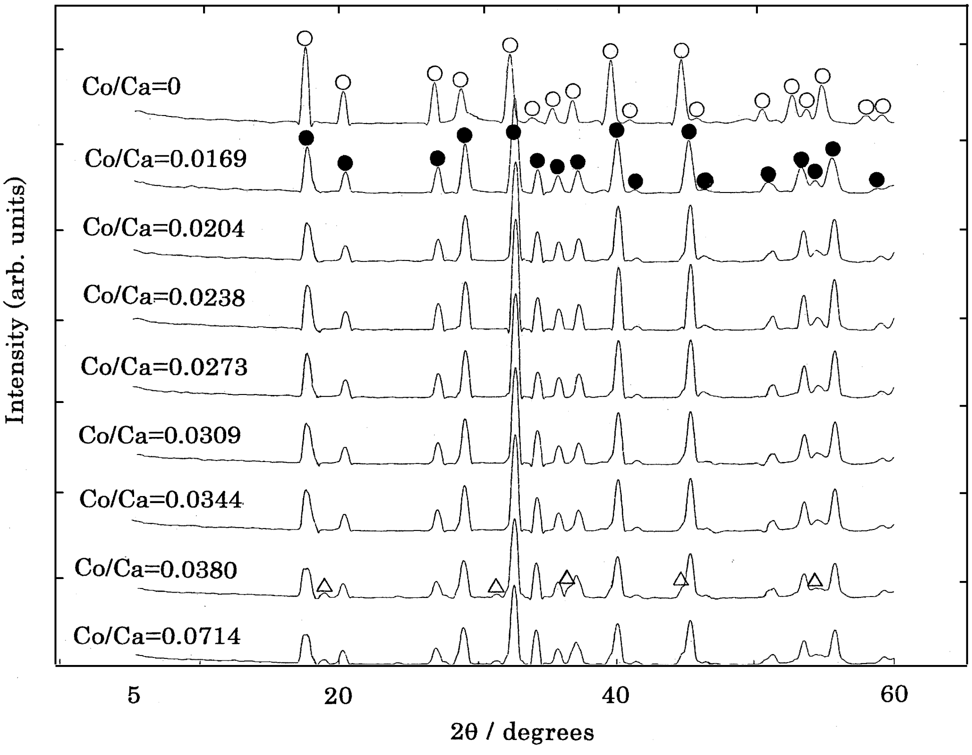

Figure 1. XRD patterns of Co-hydrogarnet obtained from hydrothermal syntheses. (○) Hydrogarnet ($Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$), (●) Co-hydrogarnet ($(Ca_{3-x}Co_xAl_2(SiO_4)_{0.8}(OH)_{8.8}$: $0 \leq x \leq 0.2$, Co/Ca = 0–0.0714), (△) Co_3O_4.

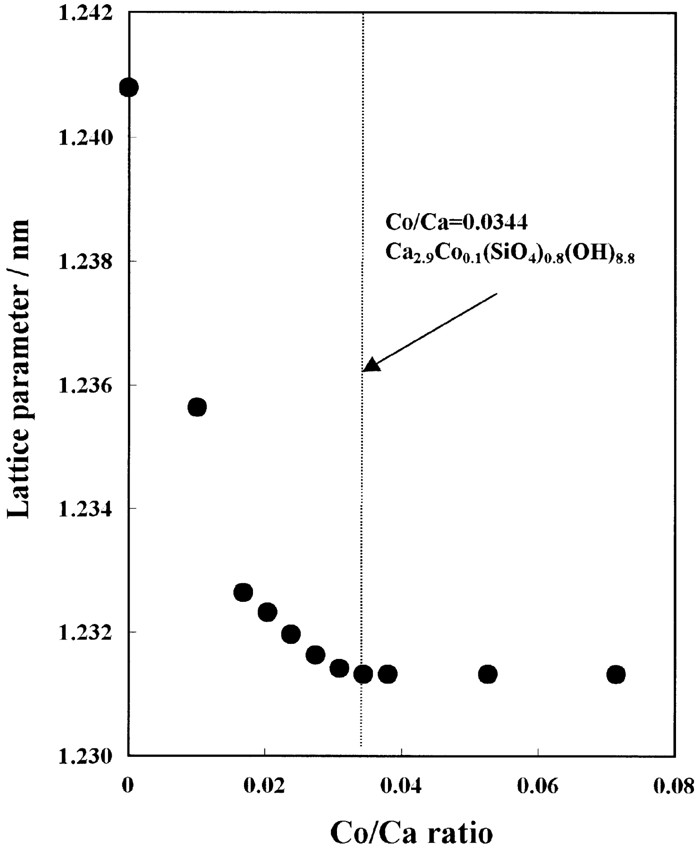

Figure 2. Lattice parameter *a* of Co-hydrogarnet for various compositions.

Figure 3 shows *in situ* high-temperature XRD patterns of the hydrogarnet with a Co/Ca ratio of 0.0344 after heating at various temperatures. Co-containing hydrogarnet remained unchanged after heating at 300 °C but converted to a mixture of CaO, Co_3O_4, and hydrous mayenite at 350 °C. Above 400 °C, the Co-containing hydrogarnet was converted to a mayenite-supported Co_3O_4 catalyst (oxide loading 2.4 wt%).

As figure 4 shows, the BET surface area of the mayenite-supported Co_3O_4 was very small, the largest value of which was 6.5 m^2/g. Although the surface area was very small, it should be noted that mayenite had a framework of $(Al,Si)O_4$ tetrahedra and occluded hydroxide (OH^-), superoxide anion (O_2^-), peroxide anion (O_2^{2-}), and oxygen radical (O^-) in a large cavity of the framework [13–16].

3.2. *Combustion of hydrocarbons*

Prior to the examination of combustion activity, it was confirmed that the Co-containing hydrogarnet itself exhibited no activity for hydrocarbon combustion at a temperature <300 °C. A previous study also revealed that mayenite could catalyze the combustion of benzene at >400 °C [16]. Figure 4 shows the conversion of hydrocarbon over Co-containing hydrogarnets after heating at 400 °C. It was obvious that the incorporation of Co cations into hydrogarnet resulted in a significant increase

Table 1
Lattice parameters of Co-containing hydrogarnet ($(Ca_{3-x}Co_x)Al_2(SiO_4)_{0.8}(OH)_{8.8}$: $0 \le x \le 0.10$)

Chemical formula		*a* (nm)	*V* (nm^3)
$Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.0$ (Co/Ca = 0)	1.24078(15)	1.910
$(Ca_{2.97}Co_{0.03})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.03$ (Co/Ca = 0.0101)	1.23563(6)	1.886
$(Ca_{2.95}Co_{0.05})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.05$ (Co/Ca = 0.0169)	1.23263(6)	1.872
$(Ca_{2.94}Co_{0.06})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.06$ (Co/Ca = 0.0204)	1.23231(7)	1.871
$(Ca_{2.93}Co_{0.07})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.07$ (Co/Ca = 0.0238)	1.23196(6)	1.869
$(Ca_{2.92}Co_{0.08})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.08$ (Co/Ca = 0.0273)	1.23162(12)	1.868
$(Ca_{2.91}Co_{0.09})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.09$ (Co/Ca = 0.0309)	1.23141(13)	1.867
$(Ca_{2.90}Co_{0.10})Al_2(SiO_4)_{0.8}(OH)_{8.8}$	$x = 0.10$ (Co/Ca = 0.0344)	1.23131(10)	1.866

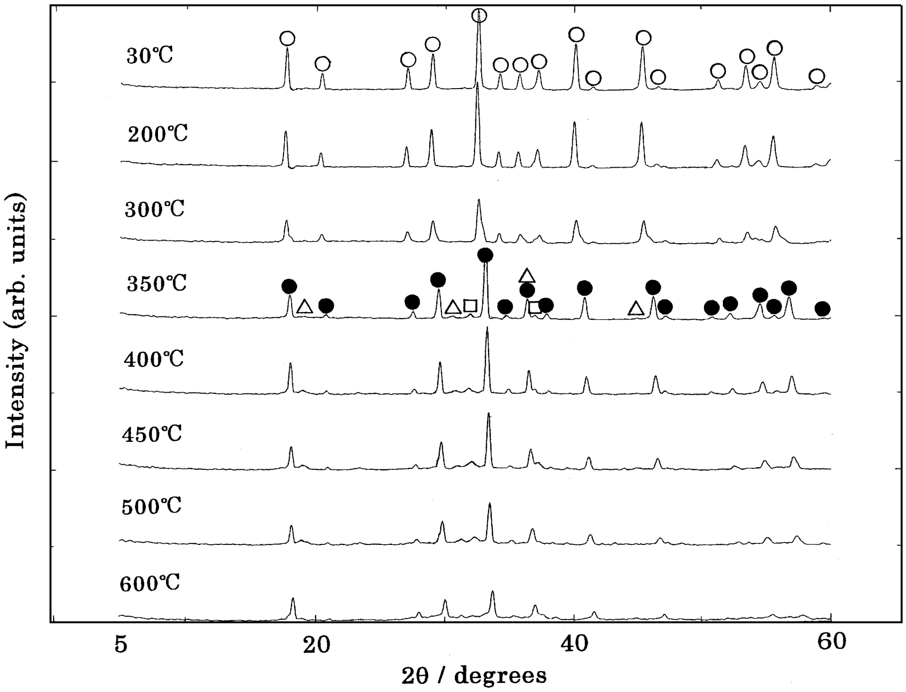

Figure 3. *In situ* high-temperature XRD patterns of Co-hydrogarnet (Co/Ca = 0.0344) at various temperatures. (○) Co-hydrogarnet, (●) mayenite, (△) Co_3O_4, (□) CaO.

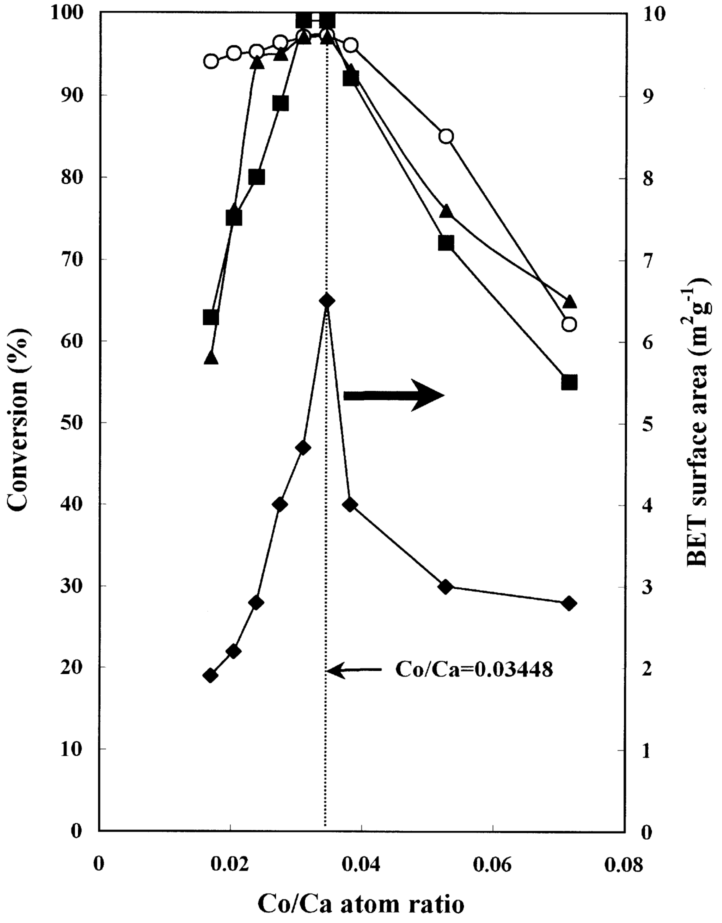

Figure 4. BET surface area and conversion of hydrocarbons at 300 °C on catalyst (Co_3O_4 supported on mayenite) after heating Co-hydrogarnet at 400 °C with various Co/Ca compositions. (○) Propylene, (■) benzene, (▲) toluene.

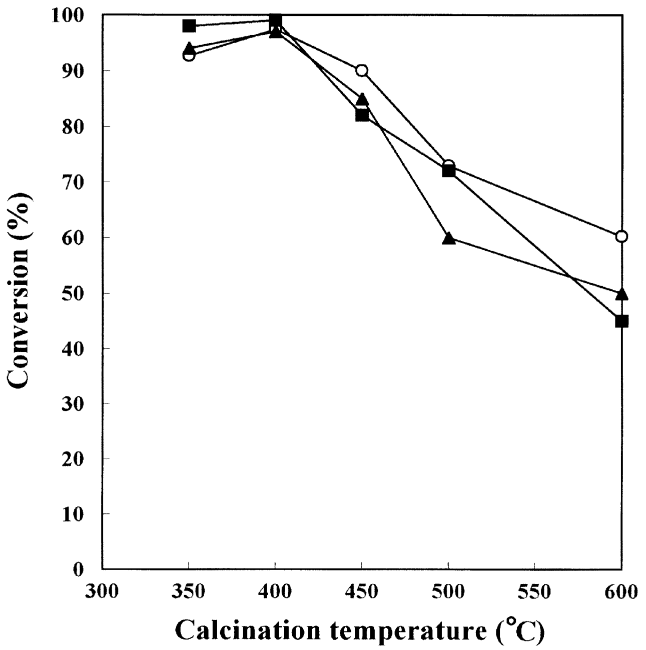

Figure 5. Conversion of propylene (○), benzene (■), and toluene (▲) at 300 °C on catalyst (Co_3O_4 supported on mayenite) with Co/Ca = 0.0344 after calcining at various temperatures.

in the combustion activity for all hydrocarbons examined and that the largest conversion was obtained for a Co/Ca ratio of 0.0344.

Figure 5 and table 2 show the effect of the calcination temperature of the Co-containing hydrogarnet on the combustion of propylene, benzene, and toluene at 300 °C for the catalyst with Co/Ca = 0.0344. As shown, the conversion decreased with increasing calcination temperature.

For the catalyst with Co/Ca = 0.0344 after calcination at 400 °C, the catalytic performance is illustrated in figure 6 for the combustion of propylene, benzene, and toluene. Combustion began at around 200 °C for all hydrocarbons and was completed at 325 and 300 °C for propylene and benzene, respectively. Toluene oxidation was completed at 325 °C with the formation of a small amount of benzene. The Co-containing hydrogarnet-derived catalyst exhibited a good stability in its activity on a laboratory basis. Since isolated Co_3O_4 was formed after heating Co-containing hydrogarnet at 400 °C, its particle size was determined from X-ray diffraction and the result is summarized in table 3. The size was quite small for Co/Ca = 0.0169, 0.0238, and

Table 2
Textural properties of mixed oxides after calcining Co-hydrogarnet with Co/Ca = 0.0344

Calcined temperature (°C)	350	400	450	500	600
BET surface area (m^2/g)	5.7	6.5	4.2	3.5	2.4
Co_3O_4 particle size[a] (Å)	260	275	447	489	856

[a] Particle size of Co_3O_4 obtained from Scherrer equation $d_{(111)}$.

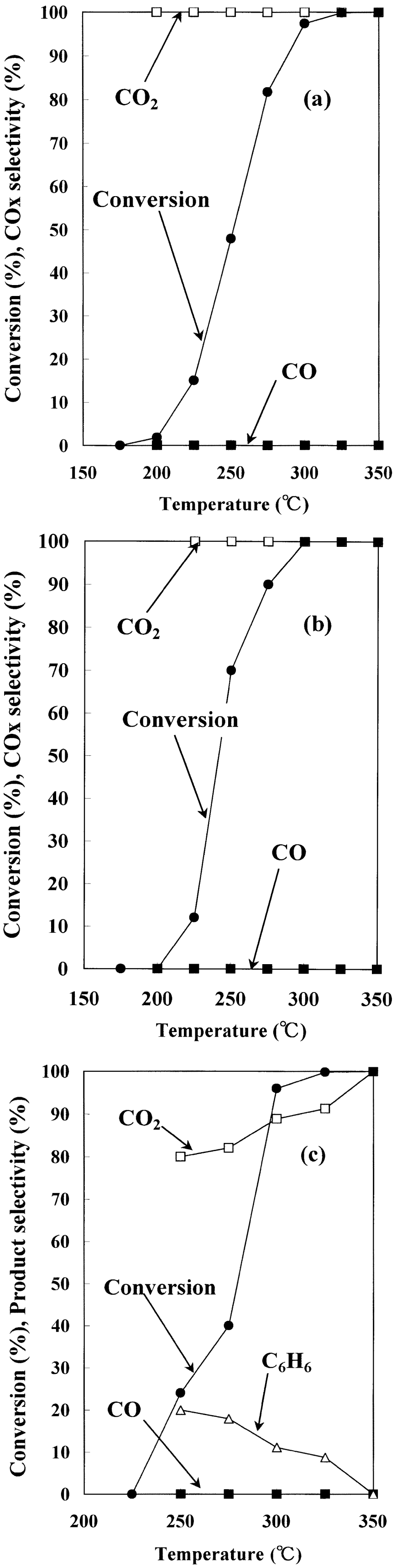

Figure 6. Oxidation curves of (a) propylene, (b) benzene, and (c) toluene on catalyst (Co_3O_4 supported on mayenite) after calcining Co-hydrogarnet at 400 °C with Co/Ca = 0.0344.

Table 3
Textural properties of mixed oxides after calcining Co-hydrogarnet at 400 °C

Co/Ca atom ratio	0.0169	0.0238	0.0344	0.0714
BET surface area (m^2/g)	1.9	2.8	6.5	2.9
Co_3O_4 particle size[a] (Å)	250	260	275	850

[a] Particle size of Co_3O_4 obtained from Scherrer equation $d_{(111)}$.

0.0344, but not for 0.0714. Therefore, the combustion activity must be explained in terms of the size of Co_3O_4 particles deposited on mayenite. The high activity observed for Co/Ca = 0.0344 should be ascribed to a small size of Co_3O_4 particles, while the low activity for Co/Ca = 0.0714 to a larger size of Co_3O_4 particles. The activity of the catalysts with Co/Ca = 0.0169 and 0.0238 was not high, although the size of Co_3O_4 particles was small. This might result from a small number of Co_3O_4 particles, because the extent of substitution was small for these catalysts.

In the above context, it should be noted that the Co_3O_4/Al_2O_3 catalyst exhibited a low activity for the combustion under the same experimental conditions. The conversions for the combustion of benzene at 350 °C were 8.0, 15, 19, 32, 65, and 85% for Co_3O_4 contents of 0.3, 1.0, 2.5, 5.0, 10, and 15 wt% with a particle size of 250–260 Å. It is interesting to note that the activity of the Co_3O_4/Al_2O_3 catalyst was less than that of the mayenite-supported Co_3O_4 catalyst, although the size of Co_3O_4 particles was similar between them. Mayenite has a structure of a framework of $(Al,Si)O_4$ tetrahedra and hydroxides (OH^-), superoxide anions (O_2^-), peroxide anions (O_2^{2-}), and oxygen radicals (O^-) are incorporated in the cavity of the framework [13–16]. Therefore, the observed high activity of the mayenite-supported Co_3O_4 catalyst may result from a synergetic effect of small Co_3O_4 particles and mayenite involving oxygen anions. The loss of mayenite phase may be responsible for the loss of catalytic activity at higher calcination temperatures (see figures 3 and 5). This is because the oxidation of hydrocarbons needs active oxygen species like oxygen anions [17] and mayenite itself was revealed to exhibit an activity for benzene combustion at >400 °C [16].

An ideal substitution of Ca ions with Co ions occurred in the Co-containing hydrogarnet with a Co/Ca ratio of 0.0714, together with the formation of the additional Co_3O_4 phase. Calcination of this hydrogarnet should also produce Co_3O_4 particles finely dispersed on mayenite together with additional free Co_3O_4. However, XRD measurements and the activity test gave no evidence for the presence of such fine Co_3O_4 particles for Co/Ca = 0.0714. The free Co_3O_4 particles may disturb the production of Co_3O_4 particles finely dispersed on mayenite, although further study is necessary for clarification.

4. Conclusions

Finely dispersed Co_3O_4 catalysts were prepared by calcining Co-containing hydrogarnet with various Co/Ca ratios at 400 °C. For the combustion of hydrocarbons, the catalyst obtained exhibited a higher activity than a conventional Co_3O_4/Al_2O_3 catalyst because of the smaller size of Co_3O_4 particles. It was concluded that the calcination of Co-containing hydrogarnet provided an excellent way to produce a finely dispersed Co_3O_4 catalyst active for hydrocarbon combustion.

Acknowledgment

We gratefully acknowledge Dr. S. Velu of Pennsylvania State University for fruitful suggestions.

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