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Preparation of aluminum silicate, $Ca_{12}Al_{10}Si_4O_{35}$, using waste materials and its activity for combustion of hydrocarbons

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Abstract

The aluminum silicate, $Ca_{12}Al_{10}Si_4O_{35}$, was produced by calcining hydrogarnet at 800 °C as a precursor phase. Hydrogarnet was synthesized hydrothermally below 200 °C using molten slag obtained from municipal solid wastes as a raw material. For the combustion of hydrocarbons such as benzene, toluene and propylene, $Ca_{12}Al_{10}Si_4O_{35}$ obtained from molten slag exhibited the oxidation of hydrocarbons at >300 °C.

Keywords: $Ca_{12}Al_{10}Si_4O_{35}$; Silicates; Surfaces; Functional applications; Waste materials; Slags

1. Introduction

High temperature gasifying melting combustors have been used as a combustor for various municipal solid waste which generate molten slag in quite a large amount. The development of a technique for the utilization of molten slag is, therefore, essential for alleviating this situation and also for recycling waste materials. For the past few decades, fly ash, bottom ash or slag has increasingly been utilized in construction and other application fields. A number of studies have been conducted to develop an effective method for the utilization of molten slag in applications such as agriculture, cement, road construction and soil stabilization.

$Ca_{12}Al_{10}Si_4O_{35}$ was able to fix HCl gas at the high temperature range of 400–950 °C and to combust hydrocarbons such as benzene, toluene and propylene at above 400 °C.[1–3] $Ca_{12}Al_{10}Si_4O_{35}$ could decompose chlorobenzene which is one of dioxin precursor compounds, and further, could inhibit the formation of dioxins in a pilot plant of a fluidized bed combustor using refused-derived fuel (RDF).[4] $Ca_{12}Al_{10}Si_4O_{35}$ forms a framework of $(Al,Si)O_4$ tetrahedra and includes superoxide anion (O_2^-) and peroxide species (O_2^{2-}) in a large cavity of the framework. Hydrocarbons were oxidized by O_2^- and O_2^{2-} radicals in the $Ca_{12}Al_{10}Si_4O_{35}$ lattice, decomposing into carbon oxides (CO_2 and CO) and H_2O at >400 °C.[3–5] Chlorinated hydrocarbon such as chlorobenzene was decomposed into $CO_2(CO)$, H_2O and HCl with oxygen radical anions; chlorinated-$Ca_{12}Al_{10}Si_4O_{35}$ [$Ca_{12}Al_{10}Si_4O_{32}Cl_6$] was formed by reacting $Ca_{12}Al_{10}Si_4O_{35}$ with by-product HCl [$Ca_{12}Al_{10}Si_4O_{35}$ $\{Ca_{12}Al_{10}Si_4O_{32}(O_3)\} + 6HCl \rightarrow Ca_{12}Al_{10}Si_4O_{32}(Cl_6) + 3H_2O$].[3] $Ca_{12}Al_{10}Si_4O_{35}$ is a promising material for combustion of harmful compounds such as volatile organic compounds (VOCs). Over the last several years, the release

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of VOCs has received much attention. In view of the magnitude of the problem presented to the chemical and processing industries, the major challenge they face is to reduce the emission of pollution without stifling economic growth.

The aim of this study is to synthesize $Ca_{12}Al_{10}Si_4O_{35}$ using molten slag as a starting material for recycling the waste materials and to examine its combustion activity for hydrocarbons such as benzene, toluene and propylene.

2. Experimental

2.1. Sample preparation

Pure phase $Ca_{12}Al_{10}Si_4O_{35}$ was produced by heating hydrogarnet $[Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}]$ at 800 °C. Hydrogarnet was synthesized via hydrothermal reaction of a stoichiometric mixture of alumina-sol (Nissan Chemical Industries, Alumina-Sol 520), amorphous silica (Japan Silica Industries, VN3) and calcium oxide (Kanto Chemical, reagent grade calcium oxide). The mixture was put in a Teflon-lined stainless steel autoclave (25 ml volume) with distilled water, and then heated with rotation at 50 rpm. The water to solid ratio was 12:1 (w/w). The autoclave was placed in the temperature-controlled oven under the saturated vapor pressure of water, the temperature of which was controlled so as to increase from room temperature to 200 °C in 2 h. The mixture was kept at 200 °C for 15 h. The solid products were filtrated and then dried at 110 °C for 24 h. $Ca_{12}Al_{10}Si_4O_{35}$ obtained from molten slag was similarly produced by heating hydrogarnet as follow: Hydrogarnet was hydrothermally synthesized from stirred aqueous suspension of a mixture of slag, CaO, and $Al(OH)_3$ under steam pressures <200 °C. Table 1 summarizes the chemical composition of slag. The total amount of CaO, Al_2O_3 and SiO_2 was 80 wt.%. The oxides of Fe, Mg, K, Na, Ti, and P were present in the slag as minor components, and Zn and Cr as trace elements. The molar ratio of the starting material was adjusted to Ca:Al:Si = 3:2:0.8. The particle size of the slag was maintained below 20 μm by sieving. Autoclaves were held at a desired temperature of 80–200 °C.

Table 1
Chemical compositions of molten slag (wt.%)

SiO_2	26
Al_2O_3	22
CaO	32
MgO	5.6
Fe_2O_3	3.0
Na_2O	1.1
TiO_2	1.5
K_2O	0.2
P_2O_5	5.7
Cr_2O_3	0.1
ZnO	0.1
Total	97.3

2.2. Analysis of toxic chromium ion after hydrothermal treatments

The chromium ion in slag was analyzed according to the method by the Environment Agency of Japan. Distilled water of pH 6.1 was added to 30 g of slag and the total volume was adjusted to 300 ml. The solution was placed into a 300 ml triangular flask and shaken under 200 rpm at 20 °C for 6 h. After extraction was completed, the eluting liquid was separated by filtration. The content of chromium ion eluted was determined by using an atomic absorption spectrometer (Hitachi, model Z-5000). The solid products after hydrothermal treatment were dissolved by 1N HCl solution under the saturated vapor pressure at 150 °C–5 h in a Teflon-lined stainless steel autoclave. The total chromium ion of hydrogarnet was analyzed in a same way. Furthermore, the solvent in the autoclave after the separation of solid products was also analyzed.

2.3. Catalytic activity

The catalytic activity was measured with a conventional plug flow type quartz glass microreactor in the range of room temperature to 500 °C. The reaction gas was controlled by mixing synthetic air (N_2: 80%, O_2: 20%), so that the concentration of hydrocarbon was 1000 ppm by volume. A stream of 1000 ppm of benzene and toluene was obtained by bubbling air through a temperature-controlled impinger. The total gas flow was 100 ml/min and the space velocity (SV) was 10,000 h^{-1}. The catalyst, sieved to a particle size of 300–500 μm, was placed in the reactor between plugs of silica wool. Reactants and products were analyzed by an on-line gas chromatograph (Shimadzu, Gas Chromatograph GC-8A) with Porapak P and 5A molsieve columns for outlet organic gases and with active carbon column for CO_2 and CO. The selectivity was expressed as percentage of the hydrocarbon converted after correcting the difference in the carbon number.

2.4. Characterization of synthesized products

X-ray powder diffraction data were obtained by a diffractometer (Rigaku, RINT2000) with Cu Kα radiation (30 kV, 40 mA). The surface area was measured by using an N_2 adsorption–desorption equipment (Bell Japan, BELSORP 28SP) at 77 K with a BET method. The chemical composition of the solid products was determined by X-ray fluorescence spectroscopy (Shimadzu Co., Lab center, XRF-1700WS sequential X-ray fluorescence spectrometer) and an atomic absorption spectrometer (Hitachi, model Z-5000).

3. Results and discussion

3.1. Preparation of hydrogarnet

The XRD patterns of hydrogarnet prepared from slag at 80, 110, 130, 150, 170 and 200 °C are shown in Fig. 1. Molten

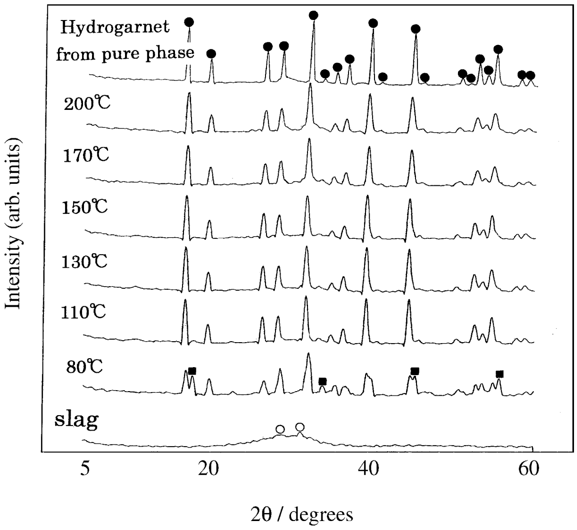

Fig. 1. X-ray diffraction patterns of hydrogarnet obtained from pure phase and slag–CaO–Al(OH)$_3$–H$_2$O at various temperatures. ●: $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$ (hydrogarnet), ○: $Ca_2Al_2SiO_7$ (gehlenite), ■: $Ca(OH)_2$.

Table 2
Total chromium ion content in liquid (mg/l) and solid samples (ppm) after elution test

Slag		Hydrogarnet (110 °C[a])		Hydrogarnet (200 °C[a])	
Liquid	Solid	Liquid	Solid	Liquid	Solid
0.1	913	0.0	505	0.0	503

[a] Reaction temperature of hydrothermal treatment using slag.

slag was largely in a state of glass as a result of rapid water-quench, the XRD pattern of which showed a broad and diffuse diffraction peak with a maximum intensity of around $2\theta = 30°$. However, gehlenite, $Ca_2Al_2SiO_7$, was also identified. The hydrothermal treatment at 80 °C produced a hydrogarnet phase together with $Ca(OH)_2$, which disappears at 110 °C. Thus, hydrogarnet using waste material is produced above 110 °C. In Fig. 1, hydrogarnet obtained from reagent $CaO–Al_2O_3–SiO_2$ is shown as reference. Table 2 displays the total chromium ion contents in liquid and solid samples after the elution test. Table 3 shows the total chromium ion in residual liquids after hydrothermal syntheses. It was noteworthy that a part of chromium ions in slag was eluted as chromium ion, while chromium ions were not eluted from hydrogarnet (Table 2). Furthermore, chromium ions were not detected in the residual liquid after hydrothermal syntheses at 110 and 200 °C (Table 3). It is considered that hydrogarnet obtained from slag retains chromium ion in its structure, because the garnet structure can accommodate a variety of cations.[6–10]

Table 3
Total chromium ion content in solvent after hydrothermal synthesis (mg/l)

Hydrogarnet (110 °C[a])	Hydrogarnet (200 °C[a])
0.0	0.0

[a] Reaction temperature of hydrothermal treatment using slag.

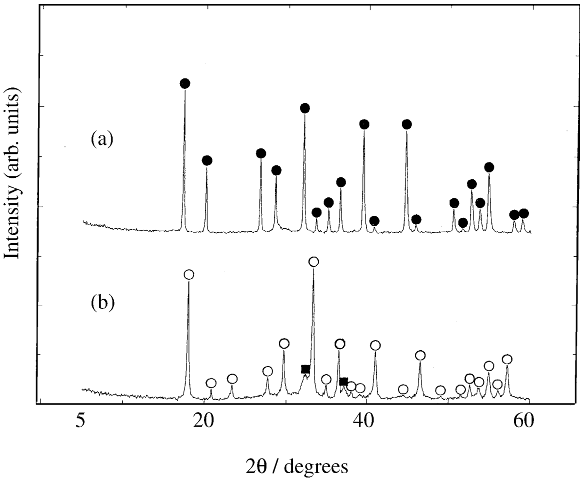

Fig. 2. X-ray diffraction patterns of hydrogarnet obtained from molten slag before (a) and after (b) calcining at 800 °C. ●: $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$ (hydrogarnet), ○: $Ca_{12}Al_{10}Si_4O_{35}$, ■: CaO.

3.2. Preparation of $Ca_{12}Al_{10}Si_4O_{35}$

Fig. 2a and b shows the XRD patterns of hydrogarnet obtained from slag before and after calcining at 800 °C, respectively. As shown, hydrogarnet appeared after the hydrothermal treatment at 150 °C. Transition to hydrogarnet with increasing temperature is given as follows:[3,5]

$$5Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8} \rightarrow Ca_{12}Al_{10}Si_4O_{35} + 3CaO + 22H_2O$$

Hydrogarnet was decomposed to convert to $Ca_{12}Al_{10}Si_4O_{35}$ with a small amount of CaO, while other oxides of Mg, Fe, Ti, K, Na and additional metals with their trace amount were not observed by XRD. $Ca_{12}Al_{10}Si_4O_{35}$ constitutes two tetrahe-

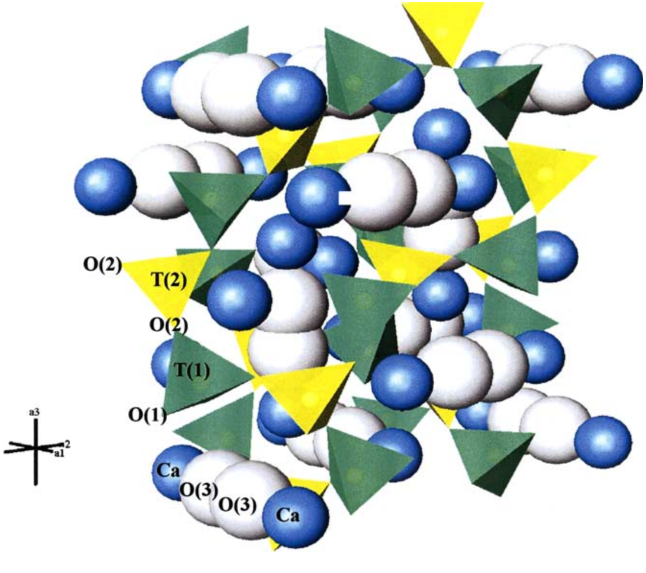

Fig. 3. Crystal structure of $Ca_{12}Al_{10}Si_4O_{35}$, showing the links of tetrahedra. The large and small spheres represent O(3) and Ca ions, respectively.[2]

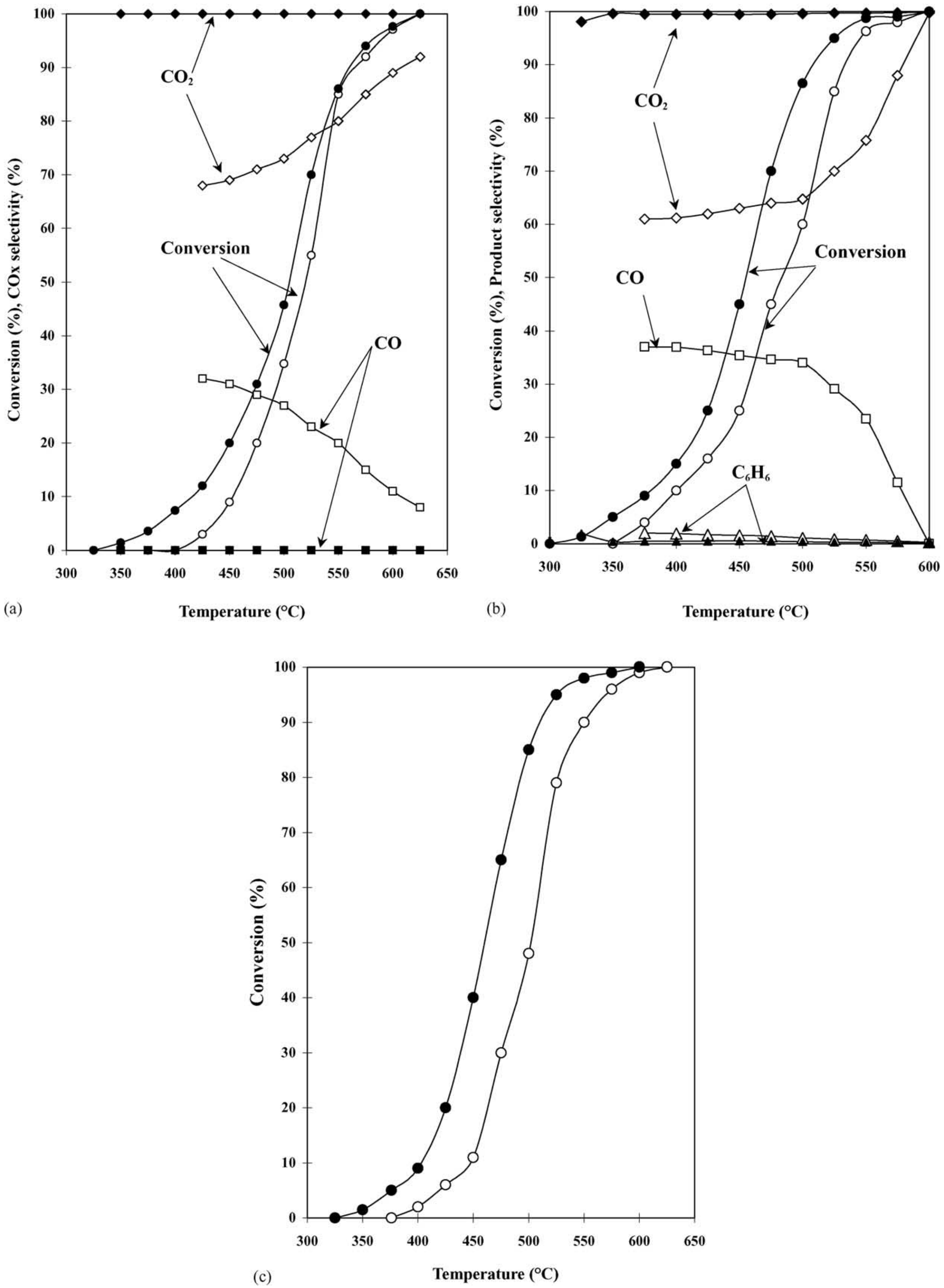

Fig. 4. The conversion and carbon oxide selectivity for each hydrocarbon at various temperatures over catalysts obtained from slag (black symbols) and pure phase (white symbols). (a) benzene, (b) toluene, and (c) propylene.

Table 4
BET surface area (m^2/g) of powders after calcining hydrogarnet obtained from slag and pure phase at 800 °C

From slag	From pure phase
5.9	6.7

dra, T(1):(Al) and T(2):($Al_{1/3}Si_{2/3}$), link together to form the framework structure (see Fig. 3). T(1) cation is bonded to one O(1) and three O(2) anions, while T(2) cation is to four O(2) anions. O(1) oxygen is a nonbridging oxygen with no involvement of the linkage of tetrahedra. The Ca polyhedron consists of two O(1), four O(2), and O(3) anions. A large cavity with the space of 4 Å in diameter in the framework of $(Al,Si)O_4$ tetrahedra accommodates Ca–O(3)–O(3)–Ca linearly coordinated atom groups. Oxygen molecule of O(3)–O(3) exists in the state of both O_2^- and O_2^{2-}.[2,5] It is considered that the ions such as Mg, Fe, Ti, K, Na, and trace elements including Cr and Zn are partially substituted into Ca-polyhedral sites or Al, Si-tetrahedral sites of $Ca_{12}Al_{10}Si_4O_{35}$ structure. The crystal structure of metal substituting $Ca_{12}Al_{10}Si_4O_{35}$ was clarified by some researchers.[11,12] Various kinds of cations were substituted in the polyhedral and the tetrahedral sites of its structure [$Ca_{12}(Al_{6.8}Si_{5.4}Mg_{1.2}Fe_{0.6})_{14}O_{32}Cl_{5.8}$ or $(Ca_{12}Mg_{0.4})_{12.4}(Al_{8.8}Si_{4.0}Fe_{1.0})_{13.8}O_{32}Cl_{5.4}$].

3.3. Combustion of hydrocarbons

Table 4 summarizes the BET surface area of powders after calcining hydrogarnet at 800 °C. Those of pure phase sample are also shown as reference. The surface area after heating hydrogarnet obtained from molten slag was very low, i.e., 5.9 m^2/g. Conversion after 1 h reaction is plotted in Fig. 4 as a function of the reaction temperature. On the catalyst obtained from slag, the oxidation of benzene (Fig. 4a), toluene (Fig. 4b) and propylene (Fig. 4c) started at around 325 °C, and was completed respectively at 625, 600 and 600 °C. On the catalyst obtained from pure phase, on the other hand, the decomposition of hydrocarbons started at around 400 °C. Without the catalyst, 100% conversion for benzene, toluene and propylene were achieved at 800, 700 and 725 °C, respectively. The selectivity towards CO and CO_2, S_{CO} and S_{CO_2}, are calculated as follows:

$$S_{CO}\,(\%) = \frac{C_{CO}}{C_{CO} + C_{CO_2}} \times 100$$

$$S_{CO_2}\,(\%) = \frac{C_{CO_2}}{C_{CO} + C_{CO_2}} \times 100$$

where C_{CO} and C_{CO_2} are the concentration of CO and CO_2, respectively. On the catalyst obtained from slag, the selectivity to CO_2 was virtually 100% from the reaction of benzene, toluene and propylene (the selectivity to CO_2 on catalysts obtained from slag and pure phase was 100 and 100%, respectively for propylene reaction), while CO was also produced on the catalyst obtained from the pure phase, although the selectivity to CO decreased with increasing temperature. On both catalysts, a trace amount of benzene was also produced from the reaction of toluene. It was considered that the combustion of hydrocarbons on $Ca_{12}Al_{10}Si_4O_{35}$ occurred as follows: oxide anions (O_2^- and O_2^{2-}) in the $Ca_{12}Al_{10}Si_4O_{35}$ structure were involved in the oxidation of hydrocarbon followed by their recovery by supplying oxygen and thereby hydrocarbon combustion continued.[2] It is worth noting that metal substituted $Ca_{12}Al_{10}Si_4O_{35}$ obtained from slag exhibited a higher performance for hydrocarbon combustion than the catalyst from pure phase. Metal ions such as Fe, Ti, and so on in the $Ca_{12}Al_{10}Si_4O_{35}$ lattice may be responsible for such a high performance. It is known that metal ions play an important role in oxidative reaction at low temperatures.[13] The $Ca_{12}Al_{10}Si_4O_{35}$ including cobalt ion exhibit a high activity for the combustion of benzene, toluene and propylene at the temperature below 300 °C.[14] The metal substituted perovskite [$LaCo_{1-x}Fe_xO_3$, $LaCoO_3$] shows active performance for VOCs combustion.[15,16] Thus, $Ca_{12}Al_{10}Si_4O_{35}$ obtained from slag exhibited a good stability in its activity on a laboratory basis. Further studies are necessary under more realistic conditions to establish the feasibility and viability for commercial application of our methodology, which are currently in progress.

4. Conclusions

$Ca_{12}Al_{10}Si_4O_{35}$ was formed from calcining hydrogarnet at 800 °C as precursor phase. Hydrogarnet was synthesized hydrothermally below 200 °C using molten slag obtained from municipal solid wastes as raw material. Hydrocarbons (benzene, toluene and propylene) were decomposed into almost CO_2 and H_2O above 300 °C with $Ca_{12}Al_{10}Si_4O_{35}$ obtained from molten slag.

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