

Hydrothermal Synthesis of La-Mn-hexaaluminates for the Catalytic Combustion of Methane

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Abstract—Hydrothermal synthesis by using urea hydrolysis at 1.0-3.0 MPa and 120-130 °C was employed to prepare Mn-substituted hexaaluminate catalysts for methane combustion. The results from DTA-MS demonstrated that CO₃²⁻ and OH⁻ anions co-exist in the hydrothermal reaction. XRD reveals that the components of carbonates and hydroxides in the hydrothermal reaction are more favorable than those in the (NH₄)₂CO₃ co-precipitation for the formation of the Mn-substituted hexaaluminate phase. After calcination at 1,200 °C for 2 h, LaMnAl₁₁O₁₉ is the major phase of the catalyst prepared by the hydrothermal synthesis method while LaAlO₃ is the major one of the catalysts prepared by NH₄OH and (NH₄)₂CO₃ co-precipitation. The catalyst prepared by hydrothermal synthesis has higher activity than that prepared by NH₄OH and (NH₄)₂CO₃ co-precipitation. The major reason is that more Mn²⁺ ions have incorporated into the hexaaluminate lattice. The effect of drying methods on the formation of hexaaluminate phase was also discussed.

Key words: Methane, Catalytic Combustion, Hydrothermal Synthesis, Hexaaluminate, Urea Hydrolysis

INTRODUCTION

Great interest has arisen for using methane as an alternative to coal and oil, because the combustion of methane can generate power with lesser green-house-gas emissions due to its high hydrogen to carbon ratio [McCarty, 2000]. In the conventional processes of thermal or flame combustion of methane, the flame temperature may easily rise to 1,500-2,000 °C. In such a temperature range, noxious emission of nitrogen oxides that contribute to the formation of acid rain and smog becomes a problem. By replacing the conventional thermal or flame combustion with catalytic combustion, however, it is possible to reduce the formation and emission of NO_x by more than 90% [Ahlström-Silver and Odenbrand, 1997].

The main problem in the development of catalytic combustion processes is to find suitable catalysts with high thermal stability and high activity [Johansson et al., 1999]. Machida and his co-workers reported that Sr_{0.8}La_{0.2}MnAl₁₁O_{19-α} was found to be one of the most stable and active catalysts [Machida et al., 1989, 1990]. Zarur et al. prepared nanostructural CeO₂-Barium hexaaluminates via a reverse microemulsion synthesis [Zarur and Ying, 2000]. They used an alkoxide hydrolysis method to synthesize these high surface and highly active hexaaluminate catalysts. Groppi et al. employed an aqueous technique of co-precipitation with (NH₄)₂CO₃ to prepare Ba-Mn-hexaaluminates and showed that these catalysts had surface areas and methane combustion activities that were comparable to those prepared by the alkoxide hydrolysis methods [Groppi et al., 1993]. Jang et al. reported that Sr_{0.8}La_{0.2}MnAl₁₁O_{19-α} synthesized by (NH₄)₂CO₃ had higher surface areas and activities than those synthesized by co-precipitation with NH₄OH. The LaMnAl₁₁O_{19-α} catalysts were found to show the highest activity in their study [Jang et al., 1999].

The hydrothermal synthesis method has been applied extensively to the synthesis of molecular sieves. We used this method to pre-

pare Mn-substituted hexaaluminate catalysts for the catalytic combustion of methane.

EXPERIMENTAL

1. Synthesis of Mn-substituted Hexaaluminate (LaMnAl₁₁O_{19-α}) Catalysts

1-1. NH₄OH co-Precipitation

Nitrate salts of the corresponding metals in stoichiometric proportion (La/Mn/Al=1/1/11) were dissolved in deionized water. The precipitation was performed by the addition of ammonium hydroxide solution into the well-stirred metal nitrate solution at room temperature. The resulting mixture was washed with deionized water three times and filtered. The filtrated cake was first washed with absolute ethanol and put into an autoclave to dry with the supercritical ethanol (260 °C and 8.0 MPa) for 2 h. Then the alcohol was slowly released. After drying, the powder was calcined at 500 °C for 1 h and followed by calcination at 1,200 °C for 2 h. The catalyst prepared by this method was designated as LMA-OH.

1-2. (NH₄)₂CO₃ co-Precipitation

A procedure practically similar to that mentioned above was used for the co-precipitation with (NH₄)₂CO₃, except that the ammonium hydroxide solution was replaced by an ammonium carbonate solution. The catalyst prepared by this method was referred to as LMA-CO₃.

1-3. Hydrothermal Synthesis

Nitrate salts of the metals with the same stoichiometric proportion as the LMA-OH were dissolved in deionized water and mixed with urea (4 molar per positive charge), then transferred to the autoclave system. The autoclave system was filled with nitrogen gas and the pressure was adjusted to maintain at 1.0-3.0 MPa as the temperature was raised from the room temperature to 120-130 °C. The system was kept at 120-130 °C and 1.0-3.0 MPa for 2 h and then cooled to room temperature. The mixture was then washed three times with deionized water and followed by filtration. The filtrated

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Table 1. The different preparation and drying techniques for the samples

Catalyst ID	Preparation	Drying	SSA m ² ·g ⁻¹	Chemical composition wt%		
				Al ₂ O ₃	MnO	La ₂ O ₃
LMA-HS	Hydrothermal	Supercritical	29.3	66.4	9.2	24.4
LMA-CO3	Carbonate	Supercritical	40.0	69.4	8.6	22.0
LMA-OH	Hydroxide	Supercritical	20.3	71.2	6.9	21.9
LMA-HC	Hydrothermal	Oven drying	37.8	64.1	8.0	27.9

cake was divided into two parts. One part was dried by supercritical drying method as described above. The catalyst prepared by this process was designated as LMA-HS. The other part was dried by conventional oven drying method at 120 °C in air for 24 h. The powder after drying was calcined at 500 °C for 1 h and followed by calcination at 1,200 °C for 2 h. The catalyst prepared by this process was referred to as LMA-HC. The details of the samples are shown in Table 1.

2. Catalyst Characterization

DTA-MS was conducted with a Perkin-Elmer DTA-7 differential thermal analyzer equipped with a Balzers OmniStar mass spectrometer. The samples were heated at a rate of 10 °C/min under a mixture gas of 2% O₂ and 98% He. The chemical composition of catalysts was measured by using a PHILIPS Magix XRF instrument. The results were shown by weight percents of the corresponding oxides. BET specific surface areas were measured by physisorption of nitrogen at 77 K using a Micrometrics ASAP 2010 instrument. Powder XRD patterns of the catalysts were recorded by a Rigaku D/max-r B X-ray diffractometer with CuK α radiation. The XRD instrument was operated at 40 KV and 50 mA. The spectra were scanned between 5° and 70° at a rate of 5°/min.

3. Catalytic Activity Tests

The catalytic activity for the combustion of methane was tested by a fixed-bed quartz reactor system. The reactor was heated in a tubular furnace and the temperature controlled by a temperature controller. The catalyst bed, supported on quartz wool, was in the middle of the heated zone of the furnace. Electronics mass flow controllers (MFCs) were used to control the gas flow rates. For each experiment, 1 ml of the catalyst (grain size 20-40 mesh) was loaded to the reactor (i.d.=15 mm); 800 mL/min (STP) of 1% CH₄ in air was used as the feed. The gas hourly space velocity (GHSV) was monitored to 48,000 h⁻¹. Effluent gases were analyzed on-line with a GC equipped with a thermal conductivity detector (TCD). A personal computer with GC station software was used to control the gas chromatography detection. The effluent gases were analyzed for CH₄, air, CO and CO₂ using a carbon molecular sieve column. T₁₀ and T₉₀ were used to represent the temperatures required for 10% and 90% CH₄ conversion, respectively.

RESULTS AND DISCUSSION

1. Effect of Pressure on the Hydrolysis of Urea

A wide variety of materials have been synthesized by the hydrolysis of urea, such as Ni/Al₂O₃ [Zhao et al., 2000], Au/Co₃O₄ [Wang et al., 2000], Cu-CeO_x [Li et al., 2000], ZrO₂ [Parida et al., 1994]. It is carried out at normal pressure and 80-100 °C. The hydroxyl groups are formed slowly, and the precipitation takes place homo-

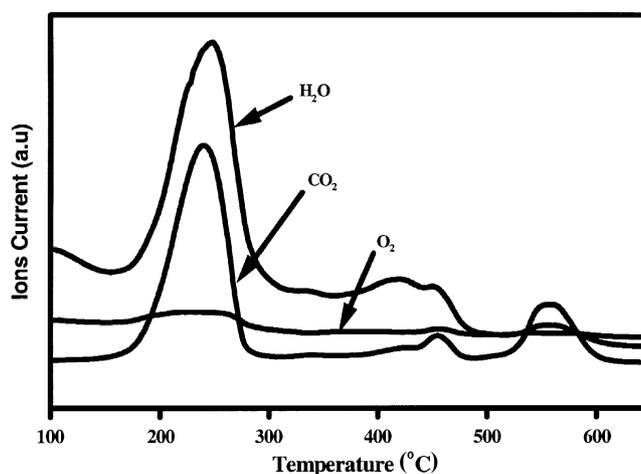
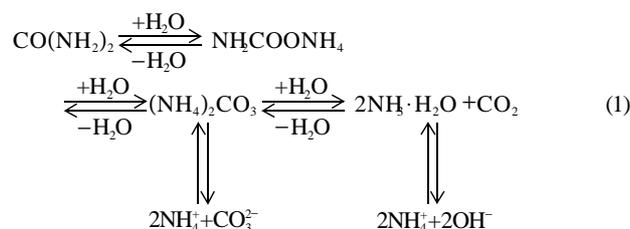


Fig. 1. DTA-MS spectra of the LMA-HC precursor dried at 120 °C for 24 h.

geneously [Shaw and Bordeaux, 1955]. Therefore, this method is usually termed as homogeneous precipitation.

Fig. 1 shows the DTA-MS result of the LMA-HC precursor. There are three peaks (around 230 °C, 460 °C and 560 °C) in the CO₂ curve. They correspond to the decomposition of (NH₄)₂CO₃, MnCO₃ and La₂(CO₃)₃, respectively. The existence of (NH₄)₂CO₃, MnCO₃ and La₂(CO₃)₃ demonstrated that there were CO₃²⁻ anions in the solution during the hydrothermal reaction.

The mechanism of urea hydrolysis can be represented as follows:



In conventional homogeneous precipitation, urea hydrolysis occurs at normal pressure and 80-100 °C. Under such conditions, the hydrolysis equilibria (as shown in (1)) shift to form OH⁻ anions due to the release of the CO₂ gas. Precipitation then takes place and the hydroxide becomes the precursor of the catalyst. In hydrothermal synthesis, however, the hydrolysis of urea is carried out at high pressure, and the release of the CO₂ gas is suppressed. The five equilibria (as shown in (1)) co-exist in the solution and CO₃²⁻ and OH⁻ anions are present in the hydrothermal reaction. These CO₃²⁻ and OH⁻ anions can react with Mn²⁺, La³⁺ and Al³⁺ ions to produce components of the corresponding carbonates and hydroxides, just like

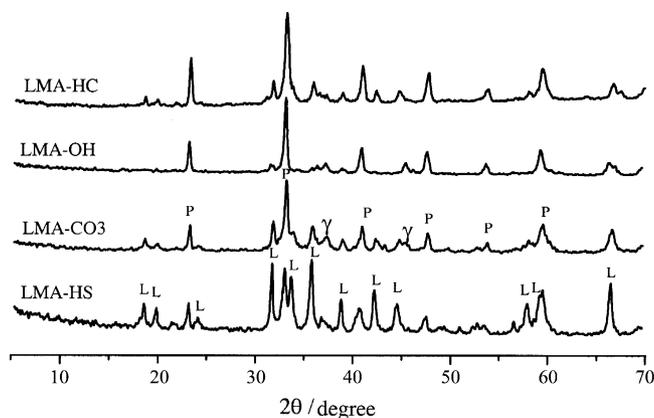


Fig. 2. XRD patterns of the catalysts: L=LaMnAl₁₁O₁₉, P=LaAlO₃, γ -Al₂O₃.

in the case of (NH₄)₂CO₃ co-precipitation. In conventional homogeneous co-precipitation, however, only OH⁻ anions are present [Shaw and Bordeaux, 1955] and hydroxides are the only precursor of the catalyst, which is similar to the case of the NH₄OH co-precipitation.

2. Effect of Preparation Method on the Crystalline Structure of the Catalyst

Fig. 2 shows the XRD patterns of the catalysts prepared by different methods. In the LMA-OH catalyst, LaAlO₃ is the major phase and the characteristic hexaaluminate phases can be observed. Jang et al. reported that although the characteristic hexaaluminate phases could be found in the samples prepared with the NH₄OH co-precipitation method, α - and γ -Al₂O₃ phases were identified as the major phases [Jang et al., 1999]. These results revealed that components of Lanthanum, manganese and aluminum hydroxides are unfavorable to the formation of hexaaluminate phases. In the LMA-CO₃ catalyst, the intensities of the characteristic peaks of the hexaaluminate phase are stronger than that in the LMA-OH catalyst. This result demonstrated that components of carbonate and hydroxides are easier to convert to the hexaaluminate phases than the hydroxide, as reported by Jang et al. [1999] and Ersson et al. [1998]. In the LMA-HS catalyst, the peak intensities of LaAlO₃ phase decrease sharply and the hexaaluminate phase becomes the major one. This reveals that components of carbonate and hydroxides produced in the hydrothermal reaction are more favorable to form hexaaluminate phases compared with those in the (NH₄)₂CO₃ co-precipitation. In the hydrothermal synthesis, the CO₃²⁻ and OH⁻ anions can be formed continuously and the precipitation of the carbonate and hydroxide takes place homogeneously, the same as the formation of OH⁻ anions and the precipitation of the hydroxides in the conventional homogeneous co-precipitation [Shaw and Bordeaux, 1955]. The hexaaluminate phases can be formed easily due to the uniformity of the mixture of the carbonate and hydroxide.

3. Effect of Drying Methods on Formation of Hexaaluminates Phase

The LMA-HC and LMA-HS samples were dried with conventional oven drying and supercritical drying, respectively. As revealed by the XRD patterns in Fig. 2, LaAlO₃ becomes the major phase in the LMA-HC sample, whereas the hexaaluminate phase is the major phase in the LMA-HS sample, as discussed above.

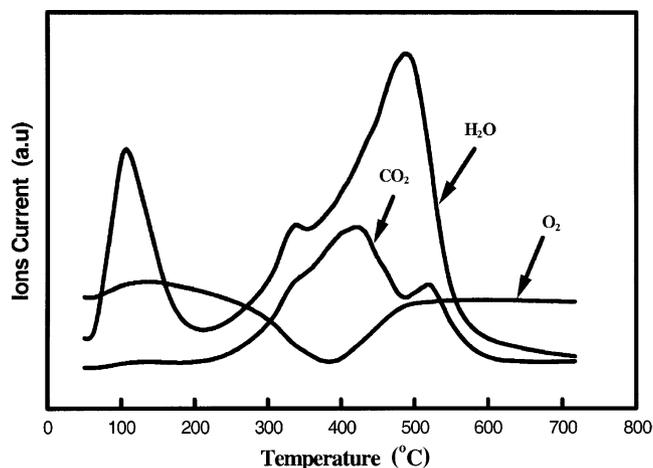


Fig. 3. DTA-MS spectra of the LMA-HS precursor dried by supercritical ethanol.

Fig. 3 shows DTA-MS pattern of the LMA-HS sample. There are three peaks (around 340 °C, 420 °C and 520 °C) in the CO₂ curve, two peaks around 340 °C and 470 °C in the H₂O curve. Only one peak (200-500 °C) appears in the O₂ curve. The peak around 520 °C in the CO₂ curve belongs to the decomposition of La₂(CO₃)₃. The one around 470 °C in the H₂O curve is caused by the dehydration of Al(OH)₃ or AlOOH. The temperature difference between decomposition of La₂(CO₃)₃ and dehydration of Al(OH)₃ or AlOOH is 50 °C. However, as shown in Fig. 1, the temperature for decomposition of La₂(CO₃)₃ is 560 °C. The one for the dehydration of Al(OH)₃ or AlOOH is 460 °C below. The difference between the two temperatures is over 100 °C. Therefore, the temperature difference between La₂(CO₃)₃ decomposition and the dehydration of Al(OH)₃ or AlOOH in the sample dried by supercritical drying is lower than that in the sample dried by the conventional oven drying. The formation of hexaaluminate phase is probably related to such access of the temperature of La₂(CO₃)₃ decomposition to that of dehydration of Al(OH)₃ or AlOOH.

The peaks around 340 °C and 420 °C in the CO₂ curve in Fig. 3 belong to oxidation of ethanol molecules absorbed chemically on the surface of Al atoms. During supercritical drying, ethanol molecules could react with hydroxyl groups on the Al atom surface. Hence, the hydroxyl groups on the Al atom surface could be partly substituted by the oxyethyl groups. Johnson reported that surface hydroxyl groups come into play in the particle growth of transition of alumina. Small particles grow to larger ones due to successive elimination of water from two hydroxyl groups residing on adjacent particle [Johnson, 1990]. With the supercritical drying, the hydroxyl groups on the Al atom surface were partly substituted by the oxyethyl groups. Aggregation of Al atoms was retarded by such a surface modification. The uniformity of the mixture of the carbonate and hydroxide produced by the hydrothermal synthesis was maintained in the supercritical drying process. This is another reason why the hexaaluminate phase is the major one in the sample dried by the supercritical drying.

4. Catalytic Activity for CH₄ Combustion

CH₄ combustion over the different catalysts was also investigated, and the results are shown in Fig. 4. The T₁₀ value for LMA-CO₃

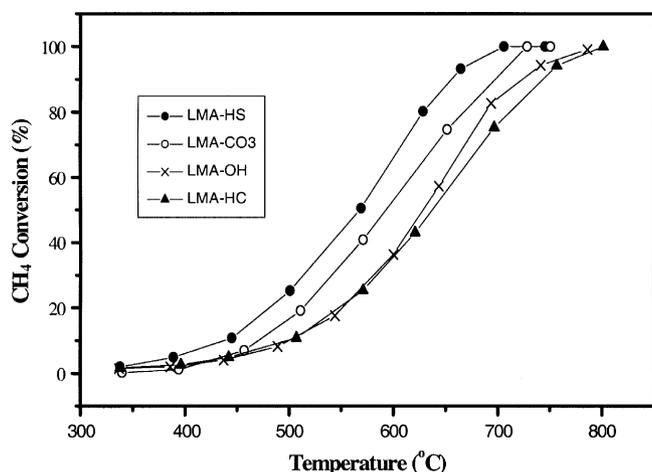


Fig. 4. CH₄ combustion over the three catalysts.

catalyst is 470 °C, which is 25 °C lower than that of the LMA-OH catalyst. Jang et al. reported that the activity of CH₄ oxidation over the Sr_{0.8}La_{0.2}MnAl₁₁O_{19-α} catalysts prepared by (NH₄)₂CO₃ co-precipitation was higher than that prepared by NH₄OH co-precipitation, and the major reason was that catalysts prepared by (NH₄)₂CO₃ co-precipitation have higher surface area [Jang et al., 1999]. As shown in Table 1, the S_{BET} value of the LMA-CO₃ is 40.0 m²·g⁻¹, whereas the one of LMA-OH is 20.3 m²·g⁻¹. So our results demonstrate Jang's viewpoint as mentioned above.

Although its specific surface area was not the highest one, LMA-HS showed the highest activity with T₁₀ at 445 °C, which was about 55 °C and 25 °C lower than those of the LMA-OH and LMA-CO₃ catalysts, respectively. As a sign of the entire conversion of methane, T₉₀ for LMA-HS catalyst is 645 °C, whereas the one for LMA-OH sample is 725 °C. Therefore, besides the surface area, the activity of the catalysts can also be affected by other factors, such as the amount of manganese, the crystalline structure, the rate of the oxidation/reduction cycle and the oxygen desorption capacity of catalysts, as demonstrated by Machida et al. [1990].

Manganese is an active component for CH₄ oxidation. The high activity is associated with the ease of change in oxidation states of the active ions [Zwinkels et al., 1993]. It is well known that manganese ions must substitute the aluminum ions and enter into the hexaaluminate lattice. The reduction/oxidation of manganese, which is reversible between di- and trivalent states in the hexaaluminate lattice, leads to high activity for methane combustion [Machida et al., 1995]. In the LMA-HS catalyst, more Mn²⁺ ions have incorporated into the hexaaluminate lattice. The Mn-substituted hexaaluminate phases are the major phase in the LMA-HS sample. So the high activity of this catalyst could be expected.

CONCLUSION

Hydrothermal synthesis via urea hydrolysis is different from conventional homogenous co-precipitation. Under a high pressure and temperature, CO₃²⁻ and OH⁻ anions can be produced homogeneously in the hydrothermal reaction because the release of CO₂ gas is suppressed. The Mn-substituted hexaaluminate catalysts prepared by this method have catalytic activities for CH₄ combustion higher

than those prepared by (NH₄)₂CO₃ and NH₄OH co-precipitation procedure. Besides the preparation of hexaaluminate catalysts, this method can also be applied to prepare other materials.

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