

Crystal structure stability and catalytic activity of magnetoplumbite (MP) catalyst doped with Mn and Mg

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Abstract

LaMg_xMn_{1-x}Al₁₁O₁₉ catalysts with Magnetoplumbite (MP) structure were prepared by the reverse microemulsion method, where *x* values were varied in the range of 0–1. The effects of Mn and Mg introductions on crystalline phase compositions, texture and activities of the catalysts were investigated. The catalysts were characterized by XRD, N₂ adsorption, TEM, H₂-TPR, TG-DTA, etc. The results showed that LaMg_{0.5}Mn_{0.5}Al₁₁O₁₉ catalyst had high surface area (40.1 m² g⁻¹/1200 °C 5 h); LaMg_{0.5}Mn_{0.5}Al₁₁O₁₉ catalyst exhibited the high activity for CH₄ combustion (*T*₁₀ = 470 °C, *T*₉₀ = 690 °C). It was believed that a synergetic effect of Mg and Mn is beneficial to enhance the stability and catalytic activity of the crystals.

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1. Introduction

Catalytic combustion of CH₄ at high-temperature is an environmental-benign combustion technology. Compared with flame combustion, CH₄ can burn more efficiently in wider air-to-fuel ratios and NO_x emissions can be reduced greatly [1]. The key of this technology is to design a highly efficient catalyst. Over the decades, hexaaluminates catalysts have been explored extensively [2–11]. In view of synthesis strategy, researchers tried to suppress formation of the impurities crystals (e.g. LaAlO₃ or BaAl₂O₄, α-Al₂O₃) by enhancing homogeneity of precursor. In particular, BaAl₁₂O₁₉ and CeO₂/BaAl₁₂O₁₉ catalysts were synthesized by a reverse microemulsion route, which had so far the highest surface area and activity [12]. Nevertheless, the

impurities crystals were often segregated during the crystallization process of hexaaluminates, which greatly reduced the activities and stability of the catalysts [13,14].

In view of MP crystallography, the unsubstituted LaAl₁₁O₁₈ possesses highly distorted MP structure. [LaAl₁₂O₁₉]⁺ defective cells are present, which consist of [Al₁₁O₁₆]⁺ spinel blocks intercalated by mirror planes of [LaAlO₃]⁰. To maintain electroneutrality of MP crystal, as a result, [Al₁₁O₁₉]⁵⁻ defective cells are generated. This is characterized by the wide Al excess with respect to the nominal LaAl₁₁O₁₈ formulae [2,15,16]. The presence of excess Al would lead to the formation of LaAlO₃, which would reduce surface area of catalyst greatly. Therefore, it is not always effective to refrain the formation of impurities crystal by a synthesis strategy. The design of the catalysts with high thermal stability remains a challenge to researchers. To the best of our knowledge, most of endeavors have been devoted to the development of a new synthesis method, but very fewer reports are available on how to refrain the

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segregation of the impurities crystals from the viewpoint of MP crystal structure [15–17]. The divalent metal ions (Mg and Mn) can suppress the segregation of the impurities crystals and is beneficial to reduce the defectivities of MP crystal effectively [3].

In the work, $\text{LaMg}_x\text{Mn}_{1-x}\text{Al}_{11}\text{O}_{19}$ ($x = 0, 0.2, 0.5, 0.8, 1$) catalysts were synthesized in the reverse microemulsions, using inexpensive inorganic salts as starting chemicals. The samples were characterized by TEM, TG-DTA, XRD, N_2 adsorption, H_2 -TPR, etc. The influences of Mg and Mn on physicochemistry properties of MP catalysts were investigated.

2. Experimental

2.1. Catalyst preparation

In the experiment, all chemicals were of chemical grade and purchased from Liaoyang Chemicals Company, Ltd. They were used without further purification. The used reverse microemulsion system consisted of polyoxyethylene (7) Octanyl phenyl alcohol ether (NP7, molecule weight: 464), *n*-hexanol, cyclohexane and aqueous solution of ammonium carbonate (or stoichiometric nitrates), which were employed as surfactant, cosurfactant, continuous phase and dispersed phase, respectively. The reverse microemulsion synthesis strategy of $\text{LaMg}_x\text{Mn}_{1-x}\text{Al}_{11}\text{O}_{19}$ catalysts is given in Fig. 1.

In a typical procedure, 1.0 M $(\text{NH}_4)_2\text{CO}_3$ solution and 0.5 M mixture solution of nitrates were used, and the weight ratios of water/ C_{13}E_6 /*n*-butanol/cyclohexane were kept at 1.5:1.2:3.5:13.5. At room temperature, the precursors were synthesized by rapid mixing the equal volumes of nitrates-containing microemulsion and $(\text{NH}_4)_2\text{CO}_3$ -containing microemulsion under vigorous stirring. The reaction continued for 5 h under stirring, and then, the mixture was aged for 24 h under undisturbed condition at room temperature. After aging, acetone was added to demulsify the system, and the precursor was recovered by centrifugation. The precursor was washed sufficiently with deionized water and ethanol in sequence, and then dried by supercritical ethanol drying. Supercritical drying process was operated at 260 °C and 7.0–8.0 MPa for 2 h. The details of the drying method were described elsewhere [18]. The samples were calcined at 800, 900, 1000, 1100, 1200 in a muffle under a flowing air for 5 h, respectively.

To investigate effect of introduction of Mg and Mn on $\text{LaMg}_x\text{Mn}_{1-x}\text{Al}_{11}\text{O}_{19}$ catalysts, x value were varied.

2.2. Characterization

The samples were characterized by X-ray diffraction (XRD) on a Rigaku D/MAX-RB X-ray powder diffractometer, using graphite monochromatized Cu K α radiation ($\lambda = 0.154 \text{ nm}$), operating at 40 kV and 50 mA. The patterns were scanned from 5° to 70° (2θ) at a scanning rate of 5° min^{-1} . A nitrogen adsorption isotherm was performed at 77 K and $<10^{-4}$ bar on a Micromeritics ASAP2010 gas adsorption analyzer. Each sample was degassed at 200 °C for 5 h before the measurement. Surface area and pore size distribution were calculated by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods, respectively. The morphology of the catalyst was characterized with a JEOL model 200CX transmission electron microscope with the accelerating voltage of 200 kV. The powders were dispersed in ethanol ultrasonically, and then the samples were deposited on a thin amorphous carbon film supported by copper grids. TGA–DTA was carried out with Pyris 1 TGA thermogravimeter and DTA-7 (US Perkin-Elmer Co.), and the temperature rises from room temperature to 900 °C at a rate of 10 °C min^{-1} .

2.3. H_2 -TPR (Temperature programming reduction)

To evaluate the level of reducible Mn species in the catalyst, H_2 -TPR was conducted on Micromeritics 2900 TPD/TPR. About 0.5 g of catalyst was placed in the analyzing instrument and heated from 30 to 900 °C in a flow of He and H_2 (10% H_2 and 90% He) at a heating rate of 10 °C min^{-1} . Outlet H_2 concentration was monitored using a thermal conductivity detector (TCD), which allowed the evaluation of H_2 consumption.

2.4. Combustion of CH_4 over the catalysts

The reaction of CH_4 combustion was carried out in a conventional flow system under atmospheric pressure. 0.5 ml catalyst (20–40 mesh) was mixed with 0.5 ml quartz powder, and then was loaded in a quartz reactor (i.d. 10 mm), with quartz beads packed at both ends of the catalyst bed. A mixture gas of 1 vol.% CH_4 and 99 vol.% air was fed into the catalyst bed at a gas hourly space velocity

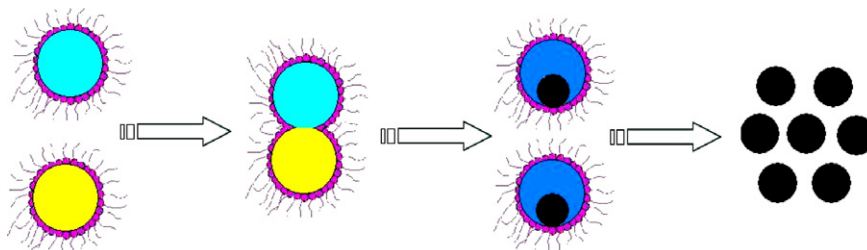


Fig. 1. Diagram of reverse microemulsion synthesis of $\text{LaMg}_x\text{Mn}_{1-x}\text{Al}_{11}\text{O}_{19}$ catalysts.

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