



Template-free synthesis of mesoporous γ -alumina-supported Ni–Mg oxides and their catalytic properties for prereforming liquefied petroleum gas



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ARTICLE INFO

Article history:

Received 7 January 2014

Revised 12 March 2014

Accepted 14 March 2014

Keywords:

Mesoporous alumina

Nickel catalyst

Mixed metal oxides

Liquefied petroleum gas

Steam reforming

ABSTRACT

Mesoporous γ -alumina (γ -MA)-supported Ni–MgO catalysts were first prepared through one-pot hydrolysis of inorganic salts without surfactants and used for the prereformation of liquefied petroleum gas (LPG). The influence of MgO addition on catalyst structure, surface characteristics, distribution of Ni species, and reducibility of Ni²⁺ ions was investigated in detail. The prepared Ni–MgO/ γ -MA catalysts possessed wormhole-like mesoporous structures with large surface areas, narrow pore size distributions, and metallic Ni nanoparticles homogeneously dispersed in γ -MA frameworks. The results showed that MgO could improve catalyst surface basicity and lower metallic Ni particle sizes, resulting in significant enhancements in the activity, stability, and resistance to coke deposition for the prereformation of LPG. Comparative investigation of the prereformation of LPG over Ni–MgO/Al₂O₃ catalysts obtained by different routes revealed that the high stability and coke resistance ability were mainly due to the formation of smaller metallic Ni nanoparticles and stable support structures.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) operating with hydrogen are currently one of the most promising clean energy technologies for stationary and mobile applications because of their high intrinsic energy efficiency, quick start-up, and zero emissions [1–3]. Hydrogen production via fuel processing is one of the key issues in the development of hydrogen-powered fuel cell devices and thus has become an important area of catalysis research [4–6]. Several catalytic reforming approaches for generating syngas and hydrogen from various hydrocarbons and alcohols, such as steam reforming [7–9], partial oxidation [10,11], autothermal reforming [12,13], and CO₂ reforming [14–16], have been extensively investigated. Catalytic steam reforming has been recognized as a promising route for on-board and on-site hydrogen production for PEMFCs because this type of reforming produces higher hydrogen yield and eliminates the needs for an air compressor and related component units [17,18]. Steam reforming of natural gas, which is mainly composed of methane, is currently the most economical process for the supply of hydrogen [19–21]. The facilities for hydrogen production have to be constructed near natural gas pipelines because the storage and transportation of

liquefied natural gas require large energy inputs due to the low liquefaction temperature of methane. However, transmission and distribution infrastructures for natural gas are generally lacking in remote areas or sparsely populated areas, especially in developing countries such as China. Therefore, an alternative energy source is needed for on-site or on-board hydrogen production for fuel cells [22–24].

Liquefied petroleum gas (LPG), a widely used residential fuel composed mainly of propane and butane without sulfur or other electronegative atoms, is a preferred potential feedstock for distributed hydrogen production for fuel cell applications due to its higher energy density than natural gas, easy storage and transportation, and well-established distribution infrastructures for the fuels [25–30]. It is well known that steam reforming of hydrocarbons is a strongly endothermic reaction, and thus the reaction exhibits maximum performance with respect to hydrogen yield at significantly high temperatures. However, the use of higher hydrocarbon can cause significant deactivation and reactor plugging, which results from carbon deposition during the thermal or steam cracking of hydrocarbons at high temperatures [31–33]. An alternative process for solving this problem is catalytic reforming in two stages, with a pre-reformer to first convert the higher hydrocarbons to methane, hydrogen, and carbon oxides at lower temperatures (400–500 °C), followed by the high-temperature reforming of the reformat in a main reformer into hydrogen and

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carbon oxides at temperatures above 700 °C with minimal risk of carbon formation [34–36].

Nickel catalysts, especially those supported on alumina, have been recognized as promising catalysts for the steam reforming of hydrocarbons because of their high catalytic activity and low cost. However, most Ni/Al₂O₃ catalysts suffer serious problems of carbon deposition, nickel sintering, and phase transformation at high temperatures [37–39]. It has been shown that the structure and surface properties of the catalysts depend strongly on chemical composition and synthesis procedures, resulting in significant change in catalytic performance. Therefore, a great deal of effort has been made to improve the activity, stability, and resistance to coke formation of nickel-based catalysts through adding promoters, modifying catalyst supports, improving catalyst preparation routes, etc. [40–45].

In recent years, ordered mesoporous alumina (OMA)-supported nickel and/or nickel-mixed oxides such as Ni–Ce, Ni–Mg, Ni–Ca, and Ni–La oxides, with high surface areas, large pore volumes, and narrow pore size distributions (PSDs), have been synthesized with aluminum alkoxides as aluminum sources via a one-pot surfactant-assisted self-assembly strategy [46–52]. The obtained Ni particles were dispersed uniformly on the mesoporous framework, and showed more excellent catalytic activity and stronger resistance toward catalyst deactivation during the reforming reactions due to the high metal dispersion and the “confinement effect” of the mesoporous structure, compared with the counterparts obtained through a conventional impregnation method. However, the mesoporous alumina supports obtained via the surfactant-assisted method give only amorphous framework walls, which lack the structural stability and surface characteristics of crystalline alumina for use as catalyst supports, while higher-temperature calcinations for the γ -alumina phase result in the formation of a nickel aluminate spinel phase, in which Ni species are embedded in the lattice of the γ -alumina and are difficult to reduce to active metallic Ni atoms at temperatures below 700 °C. Therefore, there is still a great deal of interest in developing a one-step approach to fabrication of stable mesoporous alumina-supported Ni catalysts with both crystalline γ -alumina and high nickel dispersion at lower temperatures.

Very recently, we have successfully synthesized mesoporous crystalline γ -alumina (γ -MA) with high surface area (>380 m²/g), pore volume (~0.3 cm³/g), and narrow PSD through simple partial hydrolysis of Al(NO₃)₃ aqueous solution with (NH₄)₂CO₃ without organic surfactants [53]. In this synthetic process, NH₄NO₃/Al species hybrids containing Keggin-Al₁₃ cations were achieved, and all Al species were almost transformed to γ -alumina at a low temperature of 200 °C. The obtained γ -alumina exhibited a homogeneous wormhole-like mesoporous network structure built up of small interconnected γ -alumina nanoparticles (2.0–2.5 nm) instead of simple packing of the secondary particles, which resulted in high thermal and hydrothermal stability [53]. These results stimulated us to extend this approach to preparation of mesoporous γ -alumina-supported nickel and/or nickel mixed oxides with high surface areas and narrow PSDs at lower calcination temperatures, to avoid the formation of nickel aluminate spinel, for the pre-reforming of LPG.

In the present study, γ -MA-supported Ni and/or Ni–Mg oxides were first prepared at a low calcination temperature of 400 °C through one-pot partial hydrolysis of mixed aqueous solutions of inorganic salts without organic surfactants. Ni and Ni–Mg oxide species were uniformly dispersed in a mesoporous γ -alumina framework, resulting in the formation of homogeneous Ni nanoparticles without changes in the mesoporous structure and the γ -alumina phase after reduction with H₂. Their catalytic behavior for the pre-reforming of LPG was intensively investigated, and also was compared with that of counterparts prepared by the surfac-

tant-assisted route and the traditional impregnation method. A comprehensive understanding is provided to optimally design an effective catalyst for the pre-reforming of higher hydrocarbons for on-board and on-site fuel cell applications.

2. Experimental

2.1. Chemicals and preparation of γ -MA-supported Ni and Ni–Mg oxides

All reagents were analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received without purification, except for Pluronic P123 (M_{av} = 5800, EO₂₀PO₇₀EO₂₀) from Aldrich.

The pure γ -MA and γ -MA-supported Ni and Ni–Mg oxides were prepared via one-pot hydrolysis and co-condensation of an aqueous solution of inorganic metal salt precursors with (NH₄)₂CO₃ as hydrolyzer. In a typical synthesis, 0.1 mol of Al(NO₃)₃·9H₂O, along with required amounts of Ni(NO₃)₂·6H₂O and Mg(NO₃)₂·6H₂O, was dissolved in 50 mL of deionized water at 70 °C. A 1 mol/L (NH₄)₂CO₃ aqueous solution was dropped very slowly (~0.9 mL/min) into the aqueous solution of inorganic salts with vigorous magnetic stirring using a syringe pump until sudden formation of monolithic transparent gel occurred and the stirring was stopped. At this moment, the pH value of the gel was measured in the range of 5.2–5.8, slightly varying with the content of Mg and Ni metal ions. The gel beaker was covered with a plastic film and aged at 30 °C for 48 h. After this, the crude gel was taken out and dispersed in an open glass dish at 100 °C for 24 h. Then, the as-prepared solid was treated in 200 °C in air for 10 h to remove ammonium nitrate. *Caution!* This process must be carried out with care to avoid the explosion of the ammonium nitrate. Finally, the treated solid was further calcined at 400 °C for 10 h in air at a heating rate of 1 °C/min. The preliminary investigation indicated that γ -MA-supported Ni–Mg catalysts containing 15–20 wt% Ni loading showed the optimum catalytic performance for the pre-reforming of LPG. Therefore, the loading of Ni in all the catalysts was fixed at 18 wt% in the present work. The γ -MA-supported Ni–Mg oxides with different Mg/Al molar ratios were denoted as NiO–xMgO/ γ -MA and read as Ni–xMgO/ γ -MA after H₂ reduction, where x represents the Mg/Al molar ratio in the sample.

For comparison, the sample denoted NiO–0.25MgO/ γ -MA-imp, containing 18 wt% Ni, was prepared by an incipient impregnation method. γ -MA powder calcined at 400 °C was added into an aqueous solution of Ni(NO₃)₂ and Mg(NO₃)₂ under stirring and kept at ambient temperature for 2 h. The mixture was evaporated out at 80 °C and then dried at 100 °C overnight, and finally the solid was calcined at 400 °C for 10 h in air.

The other sample containing 18 wt% Ni, denoted NiO–0.25MgO/OMA, was ordered mesoporous alumina-supported Ni–Mg oxide, which was prepared with aluminum alkoxides and nickel and magnesium nitrates as precursors by a one-pot evaporation-induced self-assembly method with Pluronic 123 as the pore-directing agent, according to the procedure reported in the references [47,50]. The final gel was calcined at 600 °C for 5 h at a heating rate of 1 °C/min. The obtained NiO–0.25MgO/OMA was confirmed to have a two-dimensional ordered mesoporous structure with an amorphous alumina pore wall, and Ni and Mg were homogeneously dispersed in the alumina framework by XRD and TEM, as described in Ref. [50].

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Rigaku D/MAX-2200 apparatus using CuK α

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