Montmorillonite-supported Ni nanoparticles for efficient hydrogen production from ethanol steam reforming

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HIGHLIGHTS

- Montmorillonite is an attractive catalyst support for ethanol steam reforming (ESR).
- Ni^0 as active sites are generated in the montmorillonite clay.
- The alkaline treatment created more mesopores and neutralized acid sites.
- Montmorillonite supported Ni^0 show excellent catalytic activity and stability in ESR.

GRAPHICAL ABSTRACT
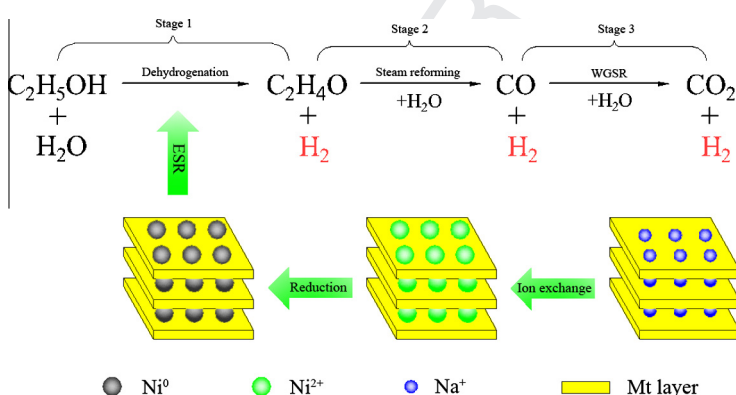
ABSTRACT

Alkaline-promoted of NiAl–montmorillonite (NiAl–Mt) catalysts were prepared by ion-exchange method, tested in ethanol steam reforming (ESR) for hydrogen production, and characterized by a combination analysis of XRD, TPR, SEM, HR–TEM, EDS and N_2 adsorption–desorption. Characterization results indicated that the textural properties of the as-prepared catalysts are strongly dependent on the alkaline treatment. More importantly, a clear improvement on stability and catalytic activity, especially for the high selectivity to hydrogen, was observed in ESR. For NiAl–Mt/NaOH catalyst, ~74.7% selectivity of hydrogen was kept at 773 K during 10-h test, while that of NiAl–hydrotalcite (NiAl) catalyst decreased from 20.4% to 5.3% within 10 h, and the selectivity of hydrogen on NiAl–Mt was ~55.1%, accompanying with byproducts of acetaldehyde and ethylene. The improved activity and stability were attributed to the neutralization of acid sites by alkaline treatment, which accelerated the dehydrogenation and suppressed the dehydration of ethanol.

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1. Introduction

With increasing concern about the shortage of fossil fuels and environmental problems, certain renewable sources of energy are expected to substitute for the conventional energy resources [1,2]. Given the increasing demand for new and clean energy, hydrogen is considered to be an ideal energy carrier to support sustainable energy development. It can be used as feed in fuel cells for power generation with high efficiency and it is extremely clean as the only by-product is water [3,4]. There are various resources for hydrogen production such as coal, natural gas, propane, methanol, and ethanol. Among all these resources ethanol is superiorly attractive because of its relatively high hydrogen content,

availability, non-toxicity, storage and handling safety, and more importantly, it can be produced by fermentation of biomass [5]. The target reaction of ethanol steam reforming (ESR) is represented as below:

$$C_2H_5OH + 3H_2O \rightleftharpoons 2CO_2 + 6H_2 \qquad \Delta H^{\ominus}_{298} = +347.4 \, \text{kJ/mol} \qquad (1)$$

For the efficient production of hydrogen, the catalyst plays an important role. In other words, how to design and develop efficient catalyst with high activity and selectivity is very crucial. Up to now, many kinds of metal catalysts have been employed in this reaction process, including precious metal and non-noble metal catalysts [6]. Precious metal catalysts, such as Ru, Pt, Rh and Ir exhibited higher activity and selectivity, whereas extremely high cost associated with such catalytic system and less availability limited their application [7,8]. Thus, many studies tend to choose Ni, Cu, Co and non-noble metal as potential alternatives [9,10]. Of all the non-noble metal catalysts, nickel catalysts have been widely used in the ESR due to their high dehydrogenation activity and low cost [11,12]. Unfortunately, Ni-based catalysts suffer from significant deactivation caused by sintering and carbon deposition. It has been reported that alumina can improve the dispersibility of Ni and efficiently prohibit the carbon deposition and nickel sintering during the steam reforming reactions [13,14]. In the same way of the metallic phase, the choice of the support is also very important in order to prevent these drawbacks. The physical and chemical properties of the support as well as the extent of interaction with the active metal would play a crucial role in the complex chemistry of supported metal catalysts.

The montmorillonite (Mt) clay is considered as environmentally benign, cheap, easily available and robust supporting/stabilizing material for the synthesis of different metal nanoparticles [15–18]. It has several obviously advantages as support matrices: (1) Mt is abundant worldwide and does not require laborious and time-consuming efforts for their synthesis as well as surface functionalization, which may often poison the catalytic active sites of the supports and the particles; (2) Mt has even more open framework structure than other porous materials and does not cause significant mass-transfer limitation; (3) Mt has much higher chemical and heat stability; and (4) the electrostatic force between Mt and metal nanoclusters is stronger than the physical absorption existed in other porous supports. To the best of our knowledge, few reports have studied on the use of Mt in the ESR.

Herein, we want to report the utilization of the alkaline treatment in Ni, Al intercalated Mt, which served as a novel catalyst in ESR efficient for hydrogen production. The physicochemical properties of the fabricated catalysts were investigated through a combination analysis of XRD, XRF, TPR, SEM, HR-TEM, N$_2$–BET, etc. The role of alkaline treatment in the design of the catalysts for ESR and the structure–activity relationship of the as-prepared catalyst were systematically studied.

2. Experimental

2.1. Materials

Ni(NO$_3$)$_2$·6H$_2$O (Aladdin, >98.0%), Al(NO$_3$)$_3$·9H$_2$O (Aladdin, >99.0%), NaOH (Kermel, >98.0%), ethanol (Kermel, >99.7%), Na–montmorillonite was purchased from Zhejiang Sanding Science and Technology Co., Ltd. Na–montmorillonite (Na–Mt) was used after sedimentation to remove a small amount of impurity. The cation exchange capacity (CEC) was around 110 meq per 100 g clay. The chemical composition of Na–montmorillonite wt%: SiO$_2$ 65.14, Al$_2$O$_3$ 17.05, Fe$_2$O$_3$ 3.12, TiO$_2$ 0.77, K$_2$O 1.52, MgO 3.12, CaO 0.35, Na$_2$O 2.15, loss on ignition (LOI): 6.52.

2.2. Catalyst preparation

Preparation of NiAl–montmorillonite (NiAl–Mt) catalysts. 5.0 g purified Na–Mt was dispersed in 200 mL of an aqueous Ni(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O solution (the Ni/Al molar ratio was 5). This slurry was magnetically stirred for 3 h to ensure ionic-exchange adequately (5 wt% of Ni with respect to the clay weight). The NiAl–Mt powder was collected by filtration and then thoroughly washed with deionized water to remove the excess salt. Then, the sample was dried at 353 K, and calcined at 873 K under static air condition for 3 h with a ramp of 5 K/min.

Preparation of NiAl–hydrotalcite (NiAl) catalysts. The NiAl derived catalyst was prepared by a coprecipitation technique. The Ni/Al molar ratio was 5, and the Ni loading was fixed at 5.0 wt%.

Preparation of NiAl–montmorillonite/NaOH (NiAl–Mt/NaOH) catalysts. The resulted NiAl–Mt was dispersed in deionized water and a desired amount of aqueous NaOH (1 mol/L) was slowly added to the solution with maintaining a constant pH of 9–10. The hydrothermal treatment, drying process and calcination were identical with NiAl–Mt.

2.3. Characterization of catalysts

The X-ray diffraction (XRD) patterns were performed on Rigaku D/max-2500 instrument (40 KV, 100 mA) using Cu Kα radiation at a scanning speed of 8° (2θ)/min, with the scanning range of 3–70°.

N$_2$ adsorption–desorption isotherms were measured with Micromeritics ASAP 2020 instrument. Prior to each measurement, the samples were degassed under vacuum at 573 K for 4 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size and pore volume were determined on the basis of the Barrett–Joyner–Halenda (BJH) method using the data of adsorption branches.

X-ray fluorescence (XRF) spectra was recorded on S8 TIGER X-ray fluorescence spectrometer (Bruker, Germany).

H$_2$–temperature programmed reduction (TPR) was performed on a Micromeritics AutoChem 2920 apparatus equipped with a TC detector. Prior to each TPR, the samples, about 30 mg, were thermally treated under air stream at 573 K to remove water and other contaminants. TPR profiles were obtained by heating the samples under a 10% H$_2$/Ar flow (50 mL/min) from 298 to 1173 K at a linearly programmed rate of 10 K/min.

The surface morphology images were examined with the SU-1500 (Hitachi, Tokyo, Japan) scanning electron microscope (SEM).

The microstructures of catalysts was investigated using transmission electron microscope (TEM, JEM-1011) equipped with an energy-dispersive X-ray spectrometer (EDS).

2.4. Catalytic performance test

Catalytic performance tests were performed in a tubular fixed-bed steel reactor at atmospheric pressure. 0.5 g of catalyst mixed with 2.5 g of quartz particles (all catalysts were crushed into particles of 20–40 mesh in size). Prior to each reaction, the system was out-gassed with N$_2$ for 30 min, then the catalysts were reduced in H$_2$/Ar at 923 K for 2 h, and then switched to the reaction temperature with N$_2$ flow protection. The liquid mixed reactant with a water to ethanol molar ratio of 8:1 was fed into the reactor through a electronic peristaltic pump at a rate of 0.1 ml/min before mixing with N$_2$ (as a carrier gas, 70 ml/min), and then vaporized at 423 K. The total liquid hourly space velocity (LHSV) was 1.9 h^{-1}. The effluent gaseous products were analyzed on-line by a haixin 950 gas chromatograph equipped with a TCD and a FID detector and two packed columns. TDX-01 packed column was used to separate H$_2$ and N$_2$, whereas CO, CH$_4$, CO$_2$, C$_2$H$_4$ were separated using a GDX-