



## Research Paper

## Highly dispersed Ni/montmorillonite catalyst for glycerol steam reforming: Effect of Ni loading and calcination temperature

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## HIGHLIGHTS

- Highly dispersed Ni/MMT catalysts were prepared by ultrasound cation exchange impregnation method.
- Effect of Ni contents and calcination temperature of Ni/MMT in GSR was evaluated.
- Mesoporous Ni/MMT with 20.9% Ni calcined at 700 °C showed excellent activity and stability.
- Lamellar structure and phyllosilicate content of MMT could improve activity and stability.

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## ABSTRACT

Montmorillonite (MMT) supported nickel nanoparticles (Ni/MMT) were prepared by an ultrasound assisted cation exchange impregnation method with rising pH technique. The Ni/MMT catalysts were characterized by different techniques including thermogravimetric analysis (TGA), N<sub>2</sub> adsorption-desorption, X-ray powder diffraction (XRD), scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM), temperature programmed reduction (TPR), and temperature programmed oxidation (TPO). The characterization results showed the particle size, metal-support interaction, nickel dispersion interrelated with cation exchange capability and confinement effect of montmorillonite lamellar structure. The activity and stability tests were conducted in a fixed bed reaction and the reaction parameters of 600 °C and S/C = 3 were optimized. The effect of Ni loadings and calcination temperature were investigated. The results show that the Ni dispersion, particle sizes of Ni and metal-support interaction (MSI) are closely dependent on the Ni loading and calcination temperature. The MMT support favors dehydrogenation reaction pathway which is effective to suppress the coke deposition and the lamellar structure could provide strong confinement effect which is effective to inhibit Ni sintering. The phyllosilicate content in MMT could promote WGS reaction which is conducive to produce hydrogen rich gas with low CO concentration.

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## 1. Introduction

Concerns about the consumption of fossil fuel reserves and the pollution caused by increasing energy demands make hydrogen a promising alternative energy source [1]. Nowadays, nearly 48% of the worldwide hydrogen is generated through methane steam reforming (SRM) [2]. However, conventional fossil fuel based processes for hydrogen generation have been questioned with respect

to the environmental effect and future energy security [3]. One of the new development directions is to convert renewable biomass or biomass-derived chemicals to hydrogen or syngas. Biomass and biomass-derivatives offer renewable hydrogen sources and a theoretically closed carbon loop since CO<sub>2</sub> could be recycled to plants via photosynthesis [4]. Currently, a glut of glycerol is produced as a by-product in converting triglycerides into biodiesel and it grows as production increases [5]. Increasing availability, renewability, and low cost makes it attractive to develop glycerol steam reforming (GSR) progress for hydrogen generation. Nobel metal-based and non-nobel-metal based catalysts have been investigated for GSR [6]. Ni based catalysts have been widely

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employed in steam reforming process owing to the low cost, wide availability and excellent capability for C–C and C–H bond rupture [7]. Wu et al. [8] have studied the influence of nickel precursors on catalytic performances of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts in glycerol steam reforming. Dou et al. [9] have carried out the continuous sorption-enhanced glycerol steam reforming progress via Ni/NiAl<sub>2</sub>O<sub>4</sub> as a catalyst and CaO as a sorbent in a moving bed reactor. However, Ni-based catalysts generally suffer rapid deactivation caused by sintering of active nickel species and coke deposition [7]. Additionally, the production of hydrogen rich gas with a low concentration of CO is a challenge for nickel catalysts, which are not so active in water gas shift (WGS) reaction [10]. Thus, all these three challenges should be considered to develop a kind of high performance Ni based catalyst.

Recently, controlling the size of nickel particles to several nanometers is conducive to suppress coke deposition [11]. Chen et al. [12] have demonstrated that small-sized Ni crystal could increase saturation concentration of carbon nanofibers and thus reduce the driving force for carbon diffusion through the Ni crystals. However, maintaining a small crystal size is a formidable task, especially for low Tammann temperature metals, since Ni nanoparticles could subject to sintering or coalescence to minimize their surface energy under harsh reaction conditions [13,14]. The most straightforward way of stabilizing the metal nanoparticles is confining or embedding them in porous or lamellar structure [15,16]. Using lamellar mineral-type precursors with exchangeable metal cations homogeneously distributed in a well-defined crystal, metal nanoparticles highly dispersed on thermally and chemically stable oxides are readily formed upon calcination and reduction [10]. Montmorillonite (MMT) is a kind of natural 2:1 type phyllosilicate layered clay mineral with high cation exchange capacity, low cost and high surface area [17]. It could accommodate the nanoparticles and stabilize them even in harsh reaction conditions. The enhanced resistance to sintering originates in the confinement effect of lamellar structure, strong metal-support interaction (MSI) and cation exchange capacity. It has been reported that Rh nanoparticle intercalated into MMT (Rh-MMT) achieved high metal ions dispersion in the clay mineral matrix compared with metal impregnated alumina catalyst, which is due to high cation exchange capacity [18]. And also, Peng et al. [19] have demonstrated that electrostatic force between MMT and metal nanoparticles is stronger than that the physical absorption existed in other porous supports due to the stronger MSI. Meantime, the alumina content of MMT would modify catalyst on the prevention of sintering of the Ni nanoparticles without arousing a reduction in catalytic activity by formation of a Ni–Al solid solution (Ni<sub>3</sub>Al) [20]. Moreover, the phyllosilicate content in MMT could effectively improve WGS and weaken methanation reaction, which is crucial to achieve hydrogen rich gas with a low CO concentration. It could be owing to multilayer-induced dissociation of water on the silica surface and the enhanced reaction of adsorbed hydroxyls with CO [21,22]. Thus, MMT is an ideal support to combine all the strategies to address above three challenges.

It has been well established that the calcination temperature leads to the different MMT structure characteristics and thus shows different catalytic activity and stability. Zhang et al. [23] have concluded that the average pore size increases and the specific surface area decreases with increasing calcination temperature, which may be caused by the growth of TiO<sub>2</sub> crystallite between the layers of MMT. Chen's group investigated the influence of calcination temperature on structure and photocatalytic activity of Titanium oxide pillared MMT. They concluded that the d<sub>001</sub> basal spacing of Ti–Na–MMT decreased with the increase of the calcination temperature, and the calcination temperature on the absorptive ability was similar with photocatalytic activity [24].

We developed a Ni-based MMT catalyst and described our understanding of the influence of calcination and loading on the catalytic properties in GSR. A series of Ni–MMT catalysts were prepared by ultrasound-assisted cation exchange impregnation method, and their physical-chemical properties were studied by N<sub>2</sub> adsorption-desorption, inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), transmission electron microscopy (TEM), H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), H<sub>2</sub> pulse chemisorption, and temperature-programmed reduction (TPO). The catalysts activity was tested in GSR at a temperature of 400–600 °C and a steam to carbon (S/C) ratio of 3. Stability tests of 30 h were also conducted to investigate the origin of deactivation of the Ni–MMT catalysts.

## 2. Experimental method

### 2.1. Preparation of catalysts

Ni–MMT catalyst in this study was prepared by an ultrasound assisted cation exchange impregnation method. The Ni/MMT mole ratios were tuned, which are 0.5:1, 1:1 and 2:1, respectively, and calcination temperatures were at 600, 700 and 800 °C. The obtained catalysts were denoted as 1Ni–1MMT–600, 1Ni–1MMT–700, 1Ni–1MMT–800, 0.5Ni–1MMT–700 and 2Ni–1MMT–700. In a typical synthetic process, a MMT suspension was prepared by diluting 5 wt.% MMT powder with the addition of dodecylamine dropwise at 2.5 mmol dodecylamine/g–MMT with vigorous stirring at room temperature overnight. The resulting mixture further sonicated for 0.5 h to intercalate surfactant into clay matrix, which could expand the basal space. A certain amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in deionized water and then the solution was dropped slowly into the MMT suspension under sonication assisted treatment. The precipitant agent of 1 M NH<sub>4</sub>OH was added to the aforementioned MMT suspension to obtain corresponding Ni loading. The precipitation was performed at 60 °C with moderate stirring until the final pH of 9 was arrived. The precipitates were filtered and washed at 60 °C, followed by drying in air at 110 °C for 14 h. The resultant powder was finally calcined at 700 °C with a ramping rate of 3 °C/min and maintained for 3 h. For comparison, a conventional Ni–Al<sub>2</sub>O<sub>3</sub> with Ni/Al mole ratio = 1:1 (denoted as 1Ni–1Al–700) was also prepared by co-precipitation method with a rising pH technique [25].

### 2.2. Characterization

The textural properties were determined from N<sub>2</sub> adsorption and desorption data using a Micromeritics Tri-Star 3000 at 77 K. Before the tests, all samples were degassed at 573 K for 3 h. The specific surface areas were obtained from the Brunauer–Emmett–Teller (BET) method. The average pore diameters and the cumulative volumes of pores were calculated from Barrett–Joyner–Halenda (BJH) method from the desorption branch of the nitrogen isotherms.

The quantitative amount of Ni in prepared samples was determined by the ICP-OES (Optima2000DV, PerkinElmer). Before the tests, all the samples were digested in HF aqueous solution assisted by sonication.

XRD measurements were carried out to identify crystalline chemical species by using Shimadzu XRD-6000 with the CuK $\alpha$  radiation (40 kV/30 mA) and the data were collected in 2 $\theta$  range from 10 to 85° with a step interval of 0.04° and step time of 2 s. The Scherrer's equation was applied to calculate the average Ni crystalline size in terms of the diffraction peaks of the Ni facet.

Morphologies of the fresh and spent catalysts were investigated by high resolution transmission electron microscopy (HRTEM)

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