Tailoring the properties of electrolyzed Ni/mesostructured silica nanoparticles (MSN) via different Ni-loading methods for CO$_2$ reforming of CH$_4$

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A B S T R A C T

A series of Ni/mesostructured silica nanoparticles (NiM) catalysts from an electrolyzed Ni precursor were prepared by in-situ (NiM_IS), impregnation (NiM_IM), and physical mixing (NiM_PM) methods for CO$_2$ reforming of CH$_4$. N$_2$ physisorption indicated that all preparation methods decreased the surface area and pore volume of the mesostructured silica nanoparticles (MSN) which may be attributed to the blockage of the pores by the deposition of NiO particles onto the MSN support. The XRD and H$_2$-TPR analyses indicated that the in-situ method dispersed smaller Ni^0 crystallites and exhibited a stronger metal-support interaction compared to the other methods. IR results indicated that the presence of an alkaline electrolyte during the introduction of Ni promoted sequential desilication-substitution of MSN, forming Si−O−Ni. CO$_2$ adsorbed IR and ESR spectroscopies showed that NiM_IS possessed a higher basicity and more defect structures compared to NiM_IM and NiM_PM, owing to the abundant silanol groups and the formation of metal-deficient Ni$_2$O$_3$. At 800 °C, the CH$_4$ and CO$_2$ conversions occur in the order of NiM_IM (CH$_4$ = 45.6 %, CO$_2$ = 52.4%) <NiM_PM (CH$_4$ = 60.5 %, CO$_2$ = 83.9 %) <NiM_IS (CH$_4$ = 94.3 %, CO$_2$ = 91.7%). The amount of carbon deposited for NiM_IM, NiM_PM and NiM_IS was 2.97%, 2.35% and 0.84%, respectively. The promoting effect of the highest catalytic activity and lowest carbon deposition for NiM_IS was related to an intimate association between better dispersion and strongly interacted Ni, as well as high basicity and concentration of surface defects in the catalyst.

1. Introduction

Catalytic CO$_2$ reforming of CH$_4$ to synthesis gas (H$_2$ and CO) has been proposed as one of the promising technologies for the simultaneous utilization of these two greenhouse gases. This reaction not only provides a feasible approach for resource utilization and environmental management, but also produces the chemical feedstock needed for many manufacturing processes [1]. Thus, CO$_2$ reforming of CH$_4$ has a wide application prospect. Developing a practical catalyst with high activity and good stability is not only the research hotspot of the catalyst field, but also the key of achieving CO$_2$ reforming of CH$_4$ for commercialization. Current research results indicate that noble metal catalysts have good activity and carbon deposition resistance to the reforming reaction [2]. However, Ni has drawn remarkable attention in this area, owing to its wider availability and lower cost. For the current research situation, Ni-based catalysts easily lose their activity, because of serious carbon deposition [3].

There are two main properties of a catalyst that affect carbon deposition, that is, surface structure and surface basicity. Generally, there are two major techniques that have been highlighted for improving the catalytic activity of this catalyst: (i) increasing the surface area of the metal active sites by synthesizing nano-sized materials and (ii) adding a support, such as silica, alumina, metal oxide, and so forth, to improve the dispersion of the metal and to increase the basicity of the catalyst [4,5]. In parallel with this, we have successfully synthesized Ni supported on mesostructured silica nanoparticles (MSN) for CO$_2$ reforming of CH$_4$ [6]. We found that this catalyst showed appreciable activity and stability compared to Ni/MCM-41, owing to the presence of interparticles pores that promoted a better reducibility of Ni and basicity of the catalyst. However, the incorporation mechanism of Ni into MSN is not well reported.

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Owing to this advantage, an extension of this study is worth pursuing.

It is well known that methodologies of promoted catalyst preparation have a significant effect on the physicochemical properties of catalysts and their catalytic performance [7]. In our previous study, we successfully synthesized several nano-sized particles of ZnO, CuO, and α-FeOOH supported on silica by a simple electrochemical method [8–11]. Their outstanding uses as photocatalysts in the photodegradation of organic pollutants as well as in isomerization encouraged further applications of this method for designing various types of catalysts for various applications. Recently, an electrolyzed Ni catalyst also showed better catalytic performance compared to the salt-derived Ni catalyst in CO_2 reforming of CH_4 [6]. Besides shortening the conventional synthesis time, this method can also be carried out under mild conditions without using strongly acidic conditions, hydrothermal treatment, higher temperature, and/or reactive compounds.

Therefore, in this study, we further explored the effect of Ni-loading method of the electrolyzed Ni precursor onto MSN using three methods, which is in-situ electrolysis (IS), impregnation (IM), and physical mixing (PM). Subsequently, their physicochemical properties were interpreted using MP-AES, XRD, N_2 adsorption, TEM, H_2-TPR, IR-KBr, CO_2 adsorbed IR, ESR, and TGA analyses. The relationship between the effect of the Ni-loading method and the catalytic activity in CO_2 reforming of CH_4 was investigated through a fixed bed continuous flow reaction. Depending on the preparation method used, different species and different Ni sizes were observed with variation in the reducibility and concentration of basic and structure defects. A new structural model for NiM_IS was proposed on the basis of the literature, characterizations and catalytic testing results. A relationship between these features and the catalytic performance was also discussed.

2. Experimental

2.1. Synthesis of mesoporous silica nanoparticles (MSN)

MSN was prepared by co-condensation and sol–gel method as previously reported [12,13]. In brief, the cetyltrimethylammonium bromide (CTAB, Merck), ethylene glycol (EG, Merck) and ammonium (NH_4OH, QRec) solution were dissolved in 700 mL of double distilled water with the following mole composition of CTAB:EG: NH_4OH:H_2O = 0.0032:0.2:0.2:0.1. After vigorously stirring for about 30 min at 50 °C, 1.2 mmol tetraethylorthosilicate (TEOS, Merck) and 1 mmol 3-aminopropyl triethoxysilane (APTES, Merck) were added to the clear mixture to give a white suspension solution. This solution was then stirred for another 2 h at 80 °C, and the as-synthesized MSN sample was collected by centrifugation at 20,000 rpm. The as-synthesized MSN was dried at 110 °C and calcined at 550 °C for 3 h to form surfactant-free MSN. Complete removal of the surfactant was verified by means of infrared spectroscopy, which did not reveal the presence of any residual organic species.

2.2. Preparation of Ni supported on MSN (NiM) catalysts

In this study, three types of preparation methods, in-situ electrolysis (IS), impregnation (IM) and physical mixing (PM) were carried out. For the in-situ electrolysis method, a 10 mL DMF solution was added to a one-compartment cell fitted with a platinum (Pt) plate cathode (2 cm × 2 cm) and a nickel (Ni) plate anode (2 cm × 2 cm) containing TEAP, naphthalene and MSN. Naphthalene was used as a mediator in the system to produce radical anions, which then reduced the nickel cations to give smaller nickel nanoparticles [14]. Then, the electrolysis was conducted at a constant current of 480 mA cm⁻² and 0 °C under a N_2 atmosphere under continuous stirring. The desired Ni content supported on the MSN and the time required for complete electrolysis was calculated based on the Faraday's law of electrolysis, as shown in the following equation;

$$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right) \qquad (1)$$

where n is the number of moles of Ni, I is the constant current of electrolysis (A), t is the total time the constant current was applied (s), F is Faraday's law constant (96,487C mol⁻¹), and z is the valence number of ion of the substance (electron transferred per ion). The number of moles of Ni required was calculated based on the total time, t of the electrolysis. For example, 1137 s is the time required to produce 5 wt% of Ni in 1.5 g MSN. After electrolysis, the solvent was removed before being dried overnight at 110 °C and calcined for 3 h at 550 °C to give a dark grey colored NiM_IS catalyst. For the impregnation and physical mixing methods, a required amount Ni was firstly prepared using electrolysis procedure as describe above. After the electrolysis, the electrolyzed Ni solution was added into MSN for incipient wetness impregnation process at 80 °C. Then, the product was dried overnight at 110 °C and calcined for 3 h at 550 °C, and finally, a light green colored NiM_IM catalyst was obtained. For the physical mixing method, the electrolyzed Ni solution was directly subjected for drying at 80 °C before being dried overnight at 110 °C and calcination at 550 °C for 3 h. As a result, a black NiO powder was obtained. Finally, a desired amount of black NiO was physically mixed with MSN and calcined for 3 h at 550 °C to give a dark grey colored NiM_PM catalyst. In this study, Ni loading of NiM catalysts was adjusted at 5 wt%. In order to determine the amount of Ni in the NiM catalysts, the corresponding catalysts were dissolved in HF solution before subjected to MP-AES analysis. It was found that approximately 5 wt% Ni was successfully loaded into the NiM catalysts (Table 1).

2.3. Characterization

The elemental analyses of Ni in the catalysts were determined by microwave plasma-atomic emission spectrometer (MP-AES) using 4100 MP-AES Agilent Technologies model 98000A. The crystalline structure of the catalysts was determined with X-ray diffraction (XRD) recorded on powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of $2\theta = 1.5$–80^0. The crystallite size of NiO and metallic Ni (d_{Ni}^0) was calculated by means of the Scherrer equation:

$$d_{NiO} = \frac{0.9\lambda}{B\cos\theta} \qquad (2)$$

where λ is the X-ray wavelength corresponding to Cu-Kα radiation (0.154 nm), B is the broadening (in radians) of the NiO and Ni^0 reflection at 43.3 and 44.6^0, respectively and θ is the angle of diffraction corresponding to the peak broadening. Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100F microscope. The samples were ultrasonically dispersed in acetone and deposited on an amorphous, porous carbon grid. Nitrogen adsorption–desorption isotherms were used to determine the

Table 1
Electrolysis time, contact time between Ni solution and MSN, and the amount of Ni detected in MSN for NiM_IS, NiM_PM and NiM_IM catalysts.

Catalysts	Electrolysis time (min)[a]	Contact time between Ni solution and MSN (min)	Ni detected in catalyst (%)[b]
NiM_IS	19	139	4.97
NiM_PM	19	–	5.01
NiM_IM	19	120	4.98

[a] Calculated based on Faraday's law.
[b] Ni detected by MP-AES.