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A novel synthesis approach to improve structural and catalytic properties of Mn-Ni-Si mixed oxide powders for water gas shift reaction

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ABSTRACT

Mn-Ni-Si mixed oxide catalyst synthesized via thermal decomposition of $[Mn(H_2O)_6][Ni(dipic)_2]\cdot H_2O$-$SiO_2$ precursor was evaluated for water gas shift reaction and its structural properties and catalytic activity were compared to those of a sample prepared by co-precipitation conventional method. The results reveal that the catalyst obtained by new inorganic precursor approach presents higher BET specific surface area, smaller particle size, and higher activity in comparison with the co-precipitated catalyst, indicating that inorganic precursor route has more advantages than co-precipitation conventional method for the synthesis of Mn-Ni-Si catalyst.

Introduction

The water gas shift (WGS) reaction (1) as an equilibrium-limited and mildly exothermic process [1–3] is industrially catalyzed in two-bed system, a high temperature shift (HTS), operating in 310–450 °C using iron-chromium-based catalysts and a low temperature shift (LTS) carried out in the range of 180-250 °C, over copper-zinc-based catalysts [4–7]. Due to the production of high purity hydrogen, the water gas shift reaction has been applied in ammonia synthesis and Fuel Cell technologies [8–12].

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \rightarrow \Delta H_{298} = -41.1\ \mathrm{kJ/mol} \qquad (1)$$

Because of low price and high catalytic activity, Ni catalyst has been investigated to ascertain its suitability for the water gas shift reaction [13]. Manganese has been widely used as catalyst or promoter in WGS reaction [14,15].

In previous studies, Mn-Ni mixed oxide catalysts have been prepared via different methods such as co-precipitation [16–19], impregnation [14,20], co-precipitation and spray-drying [21] and thermal treatment of carbonate precursors [22]. In present work, inorganic precursor approach (thermal decomposition of $[Mn(H_2O)_6][Ni(dipic)_2]\cdot H_2O$-$SiO_2$ precursor) is used for synthesis of Mn-Ni-Si mixed oxide catalyst and its influence on structural properties and WGS catalytic performance of this catalyst compared with co-precipitation conventional method is investigated. Inorganic precursor route as a facile suitable way enables materials having well defined molar ratio of metals, high BET specific surface area, homogeneous surface and high catalytic efficiency [23–25].

Experimental

Materials

All the used chemicals were regent grade and purchased from Aldrich. To synthesize ammonium 2,6-pyridinedicarboxylate, 2,6-pyridinedicarboxylic acid (1 g) was reacted with ammonia (15 mL) at 70 °C.

Synthesis of $[Mn(H_2O)_6][Ni(dipic)_2]\cdot H_2O$

A mixture containing ammonium 2,6-pyridinedicarboxylate (0.420 g, 2 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.290 g, 1 mmol) aqueous solutions was stirred at room temperature for 4 h. An aqueous solution of $Mn(NO_3)_2\cdot 6H_2O$ (0.287 g, 1 mmol) was then added to this mixture, followed by stirring at room temperature for 1 h and

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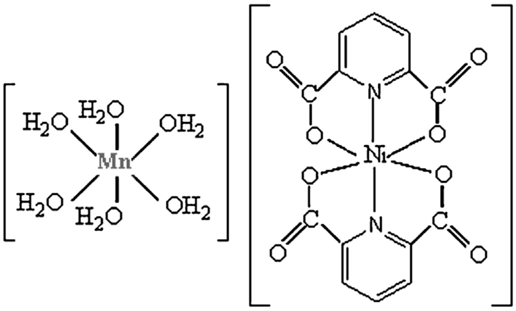

$[Mn(H_2O)_6][Ni(dipic)_2]$

Scheme 1.

evaporation in air at ambient temperature. The formed air-stable crystals were collected and dried in air. Yield: 60% Anal. Calc. for $C_{14}H_{20}MnN_2NiO_{15}$ (569.8): C, 29.51; H, 3.54; N, 4.92. Found: C, 29.78; H, 3.31; N, 4.98%. IR (KBr, cm^{-1}): 3375, 3200, 1630, 1610, 1596, 1431, 1383, 1287, 1081, 770, 730, 693, 600, 550, 440. UV–vis (H_2O, nm): 216, 269. Λ_M (H_2O) = 132 ohm^{-1} cm^2 mol^{-1}.

Synthesis of $[Mn(H_2O)_6][Ni(dipic)_2]\cdot H_2O$-$SiO_2$ precursor

The catalyst precursor was obtained from mixing SiO_2 (0.60 g, 10% wt.) and an aqueous solution of $[Mn(H_2O)_6][Ni(dipic)_2]\cdot H_2O$ (5.70 g, 10 mmol, 90% wt.), stirring and evaporating at 30 °C to dryness.

Synthesis of Mn-Ni-Si mixed oxide catalyst

The manganese-nickel-silicon mixed oxide catalyst was synthesized through calcination of the $[Mn(H_2O)_6][Ni(dipic)_2]$ $\cdot H_2O$-SiO_2 precursor in air using a heating rate of 10 °C/min up to 600 °C and then maintaining in this temperature for 4 h.

Preparation of reference catalyst

For comparison, the Mn-Ni-Si reference catalyst was prepared by co-precipitation conventional method. At first, silica was added to an aqueous solution of nickel nitrate and manganese nitrate. Then, to this mixture was added drop-wise an aqueous solution of Na_2CO_3 at room temperature and pH was maintained at about 10 by adding a NaOH solution. The resulting mixture was stirred for 24 h. The obtained precipitate was filtered, washed several times with distilled water, dried at 120 °C and finally calcined at 600 °C for 4 h.

Sample characterization

Elemental analysis was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Conductivity reading was obtained using a Ciba Corning model check-mate 90 conductivity meter. IR spectra (4000–400 cm^{-1}) were measured on a FT-IR JASCO 460 spectrophotometer with KBr pellets. UV–vis spectroscopy was performed on a JASCO 7850 spectrophotometer. The atomic absorption spectroscopy on metals was carried out by using a Varian AA50 equipment. The weight changes of catalyst precursor were recorded by using TGA-PL England equipment. The sample, ca. 15 mg, was placed in a Pt cell and heated from room temperature to 600 °C at a heating rate of 10 °C min^{-1} with a gas feed (Ar) of 50 mL min^{-1}. DSC was performed on a NETZSCH DSC 200 F3, with a heating rate of 10 °C min^{-1} under a flow of dry air. XRD patterns were recorded on a FK60-04 diffractometer between 5°and 70° (2θ) with a step size 0.02 using Cu Kα radiation. Diffraction patterns were assigned using the PDF database supplied by the international centre for diffraction data (PDF2-Diffraction Database File). Scanning electron microscopy (SEM) studies were conducted using a Jeol JSM 5410 microscope, operating with an accelerating voltage of 10 kV. The BET surface areas and pore volumes were measured with the nitrogen physisorption at −196 °C using a Quantachrome NOVA 4200e apparatus. Each sample was degassed under vacuum at 300 °C for 3 h prior to the measurement.

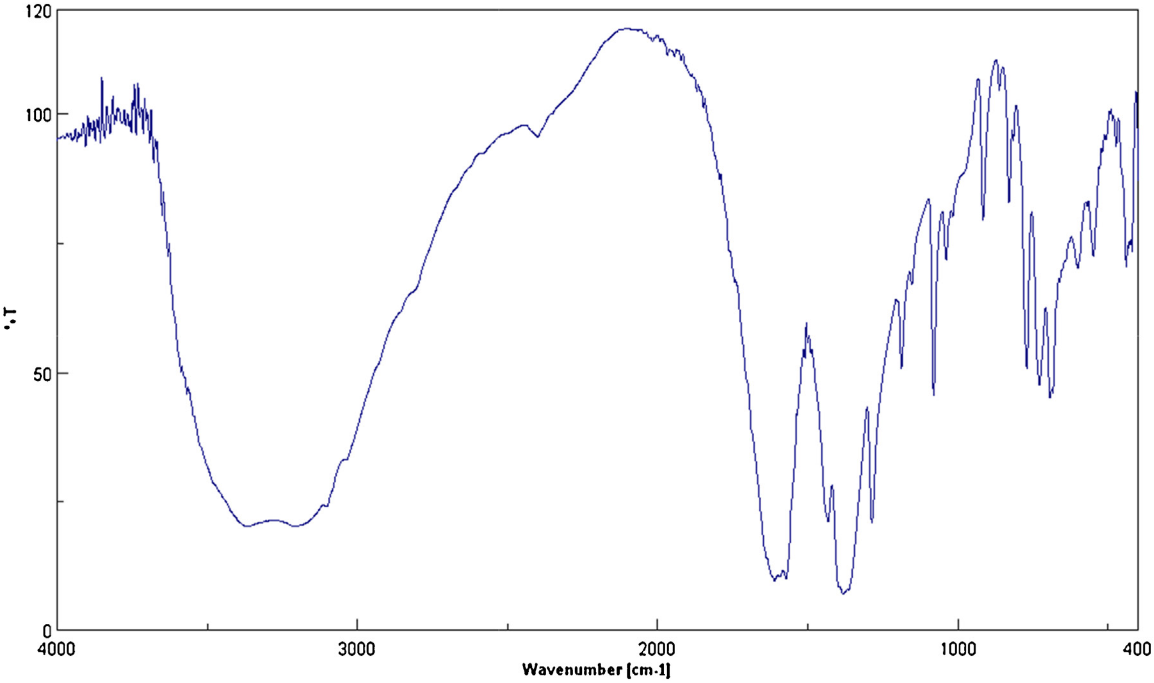

Fig. 1. FT-IR spectrum of $[Mn(H_2O)_6][Ni(dipic)_2]\cdot H_2O$.