CO methanation over Ni catalysts supported on high surface area mesoporous nanocrystalline γ-Al$_2$O$_3$ for CO removal in H$_2$-rich stream

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In this work, nickel catalysts supported on mesoporous nanocrystalline gamma alumina with high surface area were prepared and employed in CO methanation reaction. The prepared samples were characterized by XRD, BET, SEM, TEM, TPD and TPR techniques. The results showed that the optimized γ-Al$_2$O$_3$ possessed a mesoporous nanocrystalline structure with a high surface area of 328 m^2 g^{-1}. The catalytic results revealed that 25 wt.% Ni/Al$_2$O$_3$ catalyst exhibited the highest catalytic activity and showed 100% CO conversion at temperatures as low as 240 °C. This catalyst exhibited the high stability for CO conversion and CH$_4$ selectivity during 120 h time on stream at 240 °C. In addition, the effect of GHSV, CO:H$_2$ ratio and the effect of CO$_2$ and H$_2$O on the catalytic performance of Ni/Al$_2$O$_3$ catalysts in CO methanation reaction was investigated.

Introduction

Nowadays, direct energy production from hydrogen in fuel cell systems have obtained much more interests, because of its clean fuels, high efficiency and their least air pollutants. Among different types of fuel cells proton exchange membrane fuel cells (PEMFC), is one of the most favorable processes, applied in mobile and stationary applications. Hydrogen-rich stream generated by steam reforming and/or partial oxidation of natural gas, alcohols, and other hydrocarbons [1]. The produced reformate gas after water gas shift reactions typically contains 0.5–2.5 vol.% carbon monoxide [2,3].

For PEMFC applications the hydrogen gas should be free of anode catalyst poisons, as small amount of carbon monoxide deteriorate its efficiency. The maximum content of CO should be lower than 10 and 100 ppm for Pt and/or Pt–Ru based anodes, respectively. There are various methods for CO removal including pressure swing adsorption, membrane separation, CO selective oxidation and CO methanation [4]. Preferential oxidation of carbon monoxide (CO-PROX) has been considered

as a deep-cleaning method. However, by considering pros and cons, recently CO methanation process has been proposed as an attractive alternative method in mobile and small scale applications because of its cost efficiency, space saving, hydrogen yield, safety, simple process, easy control and wide operating temperature window [5]. CO methanation reaction uses the hydrogen present in the gas mixture and hence prevents the need for additional external gas supply. Moreover, no oxidizing and/or inert gas are mixed with hydrogen feed stream. Furthermore, the produced methane is inert to the PEM fuel cell and can be utilized in the afterburner [6].

A reliable methanation catalyst should have a high CO conversion at sufficiently low temperatures with high degree of CO selectivity compared to CO_2. The amount of H_2 consumed in CO hydrogenation reaction is small, in a consequence of low CO concentration [7]; While the great amount of CO_2 content in the reformate gas can consume considerable amount of hydrogen. In addition, reverse water gas shift (RWGS) reactions may convert CO_2 to CO. It should be noted that RWGS reaction may act as a hindrance in the complete methanation of CO in the presence of CO_2 [6]. At last, the stability of the catalyst during long time on stream is another important factor [8]. Therefore, an efficient methanation catalyst must be high active, selective and stable and able to retard both CO_2 methanation and RWGS reactions.

A great deal of studies has been made on the investigation of CO methanation over nickel based catalysts [7,9–15] and noble metals such as Ru-based catalysts [6,16–19]. Supported nickel catalysts represent comparable performance as precious metal catalysts. Because of the cost efficiency and availability of Ni-based catalysts, development of these catalysts is of great interest with respect to Ru-based ones.

In general, three factors can influence the activity of Ni catalysts: i) size of Ni nanoparticles, ii) crystal structure and phase of Ni active site and, iii) interaction between Ni species and support. The effects of different promoters such as Ru [20–22], Fe [23], Zr [24], and Ce [25], on nickel catalysts have been investigated in CO methanation. Nevertheless, to date, there are still some major challenges affect the application of Ni catalysts in CO methanation reactions. From the viewpoint of practical applications, the most appropriate temperature range for CO methanation is about 200–250 °C. Another challenge is attributed to the expense CO_2 in feed gas and its effect on the working temperature window and the selectivity of catalyst. Also, a suitable catalyst should selectively convert CO to CH_4 in hydrogenation reaction with respect to other hydrocarbons.

In this paper nickel catalysts supported on high surface area mesoporous nanocrystalline gamma alumina were prepared and employed in CO methanation reaction. In addition, the effect of GHSV, $CO:H_2$ ratio and the effect of CO_2 and H_2O on the catalytic performance of Ni/Al_2O_3 catalysts in CO methanation reaction was investigated.

Experimental method

Catalyst preparation

Different Al_2O_3 supports under different conditions were synthesized by precipitation method. For this purpose, an aqueous solution of NH_3 was added drop-wise to the 0.05 M $Al(NO_3)_3 \cdot 9H_2O$ solution under vigorous stirring at constant temperature. The resulted solution was aged at constant pH for appropriate time at the same temperature, then filtered and washed with distilled water. The precipitate was dried overnight at 80 °C and calcined in air at 500 °C for 4 h. The detailed synthesis parameters are listed in Table 1.

After preparation of catalyst support, a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 100 ml distilled water and then the powder alumina support was added to nickel nitrate solution under stirring for 4 h at room temperature. Afterwards, the suspension was dried at 80 °C for 12 h and calcined at 450 °C for 4 h with heating rate of 3 °C/min. In this process, the content of Ni is varying from (5–50 wt.%) and prepared Ni-based catalysts were denoted by xNi/Al_2O_3, where x shows the content of Ni in wt.%.

Catalyst characterization

The specific surface area of the catalysts was analyzed by N_2 adsorption–desorption using BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The samples were purged with

Code	Parameters controlling					BET/BJH parameters		
	Synthesis temperature	Aging temperature	NH_3 molarity	Final pH	Aging time	Pore vol. (cm^3/g)	Pore size (nm)	BET (m^2/g)
A1	25	60	12	9	20	0.44	5.4	275
A2	40	60	12	9	20	0.42	4.6	285
A3	60	60	12	9	20	0.45	4.9	295
A4	60	40	12	9	20	0.46	5.4	245
A5	60	80	12	9	20	0.59	8.2	248
A6	60	60	9	9	20	0.39	4.7	295
A7	60	60	6	9	20	0.29	4.1	306
A8	60	60	3	9	20	0.29	3.8	328
A9	60	60	3	10	20	0.35	4.6	327
A10	60	60	3	8	20	0.36	4.9	239
A11	60	60	3	9	12	0.32	4.3	292
A12	60	60	3	9	6	0.35	4.8	285

Table 1 – Structural properties of the prepared Al_2O_3 samples.