Journal of Industrial and Engineering Chemistry 17 (2011) 723–726

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Water-gas shift coupling with methanation over MO_x modified nanorod-NiO/γ-Al_2O_3 catalysts

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ARTICLE INFO

Article history:
Received 10 October 2010
Accepted 22 November 2010
Available online 13 May 2011

Keywords:
NiO–MO_x/γ-Al_2O_3 catalysts
Water-gas shift
Methanation

ABSTRACT

Water-gas shift coupling with methanation was carried out over metal oxide modified nanorod-NiO/γ-Al_2O_3 catalysts prepared by grind-mixing method in a continuous flow type fixed-bed reactor. The effects of promoter type, Co_3O_4 content, and reaction pressure were investigated. From the experimental results, Co_3O_4 modified nanorod-NiO/γ-Al_2O_3 catalyst exhibited better activity than NiO–CuO/γ-Al_2O_3 and NiO–Fe_2O_3/γ-Al_2O_3 with molar ratio of CO/H_2/H_2O = 3:1:1 at 593 K and atmospheric pressure. The addition of 10 wt%Co_3O_4 to nanorod-NiO/γ-Al_2O_3 catalyst was optimum. The CO conversion of 50 wt%NiO–10 wt%Co_3O_4/γ-Al_2O_3 catalyst was 7.8% and the CH_4 selectivity reached 83.2%. The NiO–MO_x/γ-Al_2O_3 catalysts were analyzed by X-ray diffraction, temperature programmed reduction and thermogravimetry techniques.

1. Introduction

Natural gas has such advantages as high calorific value, complete combustion, smoke-free and slag-free. Furthermore, natural gas is less poisonousness and safer transportation than coal gas. As the main component of natural gas, methane has no C–C bond in its molecular structure, so it is a clean fuel as far as the burning characteristic is concerned. Therefore the application of methane is beneficial to both environmental protection and energy provision. The ratio of natural gas in energy consumption is increasing year by year in China. Many Chinese cities face natural gas shortage. Besides conventionally separated from natural gas, methane can be artificially synthesized by syngas derived from relatively abundant coal resources in China [1,2]. So coal-to-natural gas technology is being researched and developed [3,4]. And if methanation products are transported by the natural gas transmission pipeline, these can greatly reduce the transportation costs and relieve present transportation insufficient.

Since the hydrogenation of CO-to-methane was discovered by Paul Sabatier and Senderens in 1902, the technology of methanation has been widely developed and applied to gas-purification and substitute natural gas [5–7]. According to the stoichiometry of the methanation reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$, that is often carried out in H_2-rich gases [8–10]. However, the products of SCGP, Prenflo and GSP gasification are usually CO-rich syngas [11]. Methanation of CO-rich syngas is attracting increasing attention. Ni-based catalysts are potentially used in methanation due to elevated selectivity and relatively cheaper price of Ni than noble metal [12]. Conventional Ni-based catalysts are susceptible to deactivation by carbon deposition, and the growth of carbon filaments deposited during methanation of a CO-rich gas is observed by Kuijpers et al. using electron microscope [13]. Agrawal et al. reported that the methanation activity of a Ni/Al_2O_3 catalyst in a mixture of 4% CO and 96% H_2 decreased by 10% (at most) per 24 h ($T < 673$ K) [14]. Knowing that deactivation of Ni-based catalysts proceeded even at high H_2/CO ratios, Kuijpers et al. expected that catalysts that were exposed to gas mixtures having a H_2/CO ratio lower than 2 would lose their activity at a much higher rate. Kuijpers et al. [13] also found that even at low H_2/CO ratios the growth of carbon filaments could be avoided by the use of advanced catalysts in which substantially all Ni particles were bonded to the support by means of an interfacial oxidic layer. On the other hand, addition of water vapour to the reactant reduces the deposition of carbon according to $2C + 2H_2O \rightarrow CH_4 + CO_2$ or $C + 2H_2O \rightarrow CO_2 + 2H_2$ [15–17], and that also favors the water-gas shift (WGS) reaction, $CO + H_2O \rightarrow CO_2 + H_2$ [18]. The WGS and CO methanation reactions are both exothermic and calories produced by the former reaction can inhibit the methanation due to thermodynamic limit, but the catalytic WGS reaction is generally utilized to adjust the H_2/CO ratio. Therefore WGS coupling with methanation, $3CO + H_2 + H_2O \rightarrow CH_4 + 2CO_2$, will be an attractive technology. It is possible to produce substitute natural gas with better thermal efficiency and lower investments.

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1226-086X/$ – see front matter © 2011 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.
doi:10.1016/j.jiec.2011.05.014

Catalysts frequently used for WGS reaction are Fe–Cr series, Cu–Zn series and Co–Mo series [19]. Based on previous studies, a nanorod-Ni/γ-Al_2O_3 catalyst prepared by grind-mixing method exhibited good activity for methanation [20]. In this study, metal oxide modified nanorod-NiO/γ-Al_2O_3 catalysts have been developed by grind-mixing method. Such a combination requires a methanation catalyst which also catalyzes WGS reaction. The characterizations and catalytic performances of special Ni-based catalysts used in water-gas shift coupling with methanation tests are presented.

2. Experimental

2.1. Catalyst preparation

Appropriate amount of nickel acetate was dissolved in ethylene glycol (EG) at 393 K, maintained at the same temperature for 0.5 h. Then 0.2 mol/L Na_2CO_3 aqueous solution was slowly added to the Ni^{2+}–EG solution, and the precipitate of $Ni(OH)_2$ was aged in the liquid for another 1 h. After filtration, it was washed thoroughly with distilled water. Then, the precipitate was dried at 393 K for 8 h and calcined in air at 773 K for 4 h. NiO with nanorod shape was obtained by the calcination of $Ni(OH)_2$ and designated as nanorod-NiO. CuO, Fe_2O_3 and Co_3O_4 were prepared by the same method. Then CuO, Fe_2O_3 and Co_3O_4 were grinded with adequate nanorod-NiO and γ-Al_2O_3 by weight, respectively. With this technique, the content of introduced Co_3O_4 (5%, 10%, 15%, 30% and 50%) could be controlled simply. NiO–MO_x/γ-Al_2O_3 catalyst was shaped and broken into 20–40 mesh catalyst for reserve. CuO, Fe_2O_3 and Co_3O_4 were designated as MO_x.

2.2. Catalyst test

Water-gas shift coupling with methanation was carried out in a continuous flow type fixed-bed reactor. The catalyst (1.0 ml, 20–40 mesh) was diluted with ground quartz to prevent the overheating of the catalyst due to the exothermic reaction. The catalyst was reduced in a flow of H_2 (20 ml/min) for 1 h at 673 K before reaction, and tested at 593 K. H_2, CO, CH_4 and CO_2 were monitored using a GC-4000A gas chromatograph (East & West Instruments, Inc., China) with a TDX-01 column and thermal conductive detector (TCD). CH_4 and other reaction products were analyzed by a GC-9A gas chromatograph (Shimadzu Co., Japan) equipped with a GDX-403 column and flame ionization detector (FID). The composition of reaction products was obtained by CH_4 normalization method.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were conducted on a Bruker Advanced X-Ray Solutions/D8-Advance using Cu Kα radiation. The anode was operated at 40 kV and 40 mA. The wavelength and the step size were 0.15406 nm and 0.02°/S. The 2θ angles were scanned from 10° to 80°.

Temperature-programmed reduction of hydrogen (H_2-TPR) was carried out in a fixed-bed reactor system equipped with a TCD detector. The sample (0.10 g) was pretreated at 673 K under an Ar flow (34 ml/min) for 2 h and cooled down to room temperature, then 10% H_2 in Ar was introduced into the flow system and the TPR spectra were recorded from room temperature to 973 K at temperature rising rate of 5.5 K/min.

The amount of carbon deposited on the catalyst was determined by TG analysis. The TG analysis was carried out in a NETZSCH STA 409 PC/PG thermoanalyzer. The sample was heated in flowing air from 308 K to 1323 K at a heating rate of 10 K/min.

3. Results and discussion

3.1. Effects of MO_x modified nanorod-NiO/γ-Al_2O_3 catalysts

The activities over NiO–MO_x/γ-Al_2O_3 catalysts with molar ratio of $CO/H_2/H_2O$ = 3:1:1 at 593 K are presented in Table 1. Compared with nanorod-NiO/γ-Al_2O_3, CO_2 selectivity all increases over Fe_2O_3, CuO and Co_3O_4 modified nanorod-NiO/γ-Al_2O_3. These show that the addition of Fe_2O_3, CuO or Co_3O_4 could enhance the water-gas shift reaction. However, over NiO–Fe_2O_3/γ-Al_2O_3, CO conversion and CH_4 selectivity decease 1.6% and 13.1%, respectively. While over NiO–Co_3O_4/γ-Al_2O_3, CO conversion and CH_4 selectivity are significantly improved 1.4% and 1.1%, respectively. The changes are intermediate over NiO–CuO/γ-Al_2O_3. Therefore, the activities of catalysts for WGS coupling with methanation are in the order of NiO–Co_3O_4/γ-Al_2O_3 > NiO–CuO/γ-Al_2O_3 > NiO/γ-Al_2O_3 > NiO–Fe_2O_3/γ-Al_2O_3. The differences in activities among Fe_2O_3, CuO and Co_3O_4 modified nanorod-NiO/γ-Al_2O_3 catalysts are possibly within the range of experimental error, but the order is justified by repeatability of experiments. Furthermore, from Fig. 1, additions of 5–30 wt%Co_3O_4 to nanorod-NiO/γ-Al_2O_3 catalyst all improves CO conversion and CH_4 selectivity in comparison with nanorod-NiO/γ-Al_2O_3 catalyst. These also indicate that WGS can cooperate properly with methanation over NiO–Co_3O_4/γ-Al_2O_3 catalyst.

3.2. Effects of Co_3O_4 content on the performance of NiO–Co_3O_4/γ-Al_2O_3

In order to increase the CO conversion and keep high CH_4 selectivity, the effects of Co_3O_4 percentage composition for water-gas shift coupling with methanation are investigated and depict in Fig. 1. Increasing Co_3O_4 content, water-gas shift is effective and CO_2 selectivity increases, with CO conversion and CH_4 selectivity being slightly improved. The addition of 10 wt%Co_3O_4 is optimum.

Table 1
Water-gas shift coupling with methanation over NiO–MO_x/γ-Al_2O_3 catalysts.

Catalyst	CO conversion (C-mol%)	Selectivity (C-mol%)		
		CH_4	CO_2	Other H.C.
NiO–Fe_2O_3/γ-Al_2O_3	4.8	69.0	18.1	12.9
NiO–CuO/γ-Al_2O_3	7.2	82.2	14.5	3.3
NiO–Co_3O_4/γ-Al_2O_3	7.8	83.2	12.3	4.5
NiO/γ-Al_2O_3	6.4	82.1	9.1	8.8

Reaction conditions: n(CO):n(H_2):n(H_2O) = 3:1:1, *T* = 593 K, atmospheric pressure, GHSV(CO + H_2) = 11940 h^{-1}, LHSV(H_2O) = 0.6 h^{-1}. NiO loading: 50 wt%, MO_x: 10 wt%.

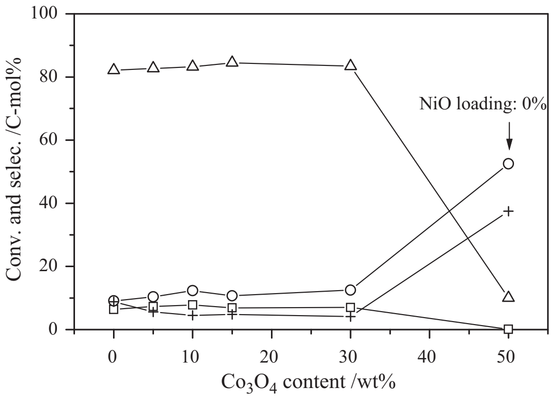

Fig. 1. Water-gas shift coupling with methanation over different Co_3O_4 contents modified 50 wt%NiO/γ-Al_2O_3 catalyst: □, CO conversion; selectivity for △, CH_4; ○, CO_2, +, other H.C. *Reaction conditions*: n(CO):n(H_2):n(H_2O) = 3:1:1, *T* = 593 K, atmospheric pressure, GHSV(CO + H_2) = 11940 h^{-1}, LHSV(H_2O) = 0.6 h^{-1}.