Homogeneous and highly dispersed Ni-Ru on silica support as an effective CO methanation catalyst

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Abstract: The highly dispersed SiO2-supported nickel-based catalysts for CO methanation were prepared by ethylene glycol (EG) modified wet-impregnation method. The results indicate that the highly dispersed 20Ni/SiO2 (EG) catalyst realized good stability and higher catalytic activity than the catalyst obtained from non-pretreated silica support (20Ni/SiO2) in CO methanation, since the smaller nickel particle and strong nickel-silica interaction. By the addition of a small amount of noble metal promoter (Ru, Pt, Pd), the catalytic activity for CO methanation was further improved dramatically. The added noble metal promoter enhanced the reduction of the nickel oxide, and provide more active species for methanation reaction, resulting in 7 times higher CO conversion than non-pretreated 20Ni/SiO2 catalyst.

Keywords: CO methanation, Nickel-based catalyst, Modification.

1. Introduction

In recent years, the debate of the finiteness of fossil resources and high CO2 emissions associated with their combustion caused the increasing attention on the research related to synthetic natural gas (SNG) production from renewable biomass, coke oven gas (COG) or syngas from coal or wood [1]. CO methanation is an important reaction for the production of SNG. Hence, in the present work, the highly dispersed silica supported Ni-based catalysts were prepared by surface modification of silica support. The smaller Ni particle size and strong Ni-support interaction was expected to reduced carbon deposition and nickel sintering, contributing to high activity and excellent stability of Ni/SiO2 catalyst in CO methanation. Furthermore, small amount of noble metal (Ru, Pt, Pd) promoter was added in Ni catalyst in order to improve the activity and stability in methanation reaction. All obtained nickel catalysts were characterized by XRD, TG/DTA, TEM, H2-TPR, H2 chemsorption, XPS and in situ DRIFT.

2. Experimental

The catalysts were prepared by aqueous incipient wetness impregnation method. The loading of nickel were 20 wt. % for all the catalysts. Commercially available silica gel (pore volume 1.061 ml/g, pore diameter 6.7 nm, BET = 451 m2/g) was used as support in this study. Before the impregnation of Ni precursor, the silica gel (5 g) was treated with ethylene glycol (5.305 ml) for 1 h at 50 °C by equivalent-volume incipient-wetness impregnation method. Then the samples were dried in air at 120 °C for 12 h. The aqueous solution (5.305 ml) of nickel nitrate (Ni(NO3)2•6H2O, 6.2 g) was impregnated onto pretreated silica support (5 g) by incipient-wetness impregnation method followed by drying in air at 120 °C for 12 h. After that, the samples were calcinated at 400 °C for 2 h. The catalyst was marked as 20Ni/SiO2 (EG). For comparison, the catalysts obtained from non-pretreated silica support were marked as 20Ni/SiO2. All obtained nickel catalysts were characterized by XRD, TG/DTA, TEM, H2-TPR, H2 chemsorption, XPS and in situ DRIFT.

3. Results and discussion

The catalyst with a large initial particle size suffered a higher extent of sintering compared to a catalyst with a smaller size, and thus leads to rapid deactivation with time on stream (TOS) during the reaction. In contrast, all EG-pretreated catalysts showed a stable catalytic activity for 10 hours, as shown in

Fig. 1. It is well known that the nanoparticles in the highly dispersed catalysts are stable to some extent upon reaction [2]. Hence, the low deactivation rate of these highly dispersed catalysts indicate that the smaller Ni clusters are less prone to deactivation, since the smaller Ni particles can present more available sites for the catalytic reaction and reduce the carbon deposition. On the other hand, the stronger metal-support interaction for the smaller Ni particles can also slow down Ni nanoparticle sintering during the highly exothermic methanation process [3].,

The Ni properties of all catalysts were probed using in-situ DRIFTS, as shown in Fig 2. The higher ratio of CO_L/CO_B means to the higher reaction activity in CO methanation reaction. It can be found that the ratio of CO_L/CO_B increased significantly after EG pretreatment for all samples, and the addition of noble metal promoter also improved this. Hence, it is proposed that the catalytic performance will be significantly improved due to the synergetic effect of noble metal promoter and small Ni particle.

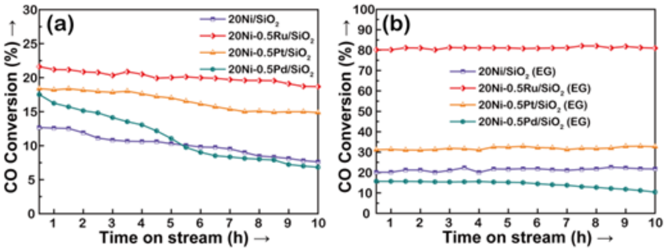

Figure 1. CO conversion as a function of time on stream for the Ni-based catalysts: (a) non-pretreated; (b) EG-pretreated. Reaction conditions: 275 °C, 1 bar, H2/CO = 3, GHSV = 40000 cm3•g−1•h−1, Weight of catalyst = 0.1 g

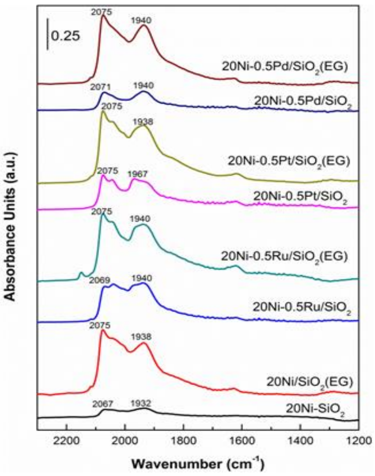

Figure 2. In-situ CO-DRIFT spectra of various Ni-based catalysts.

The characterization results of XRD, TG/DTA, TEM, H2-TPR, H2 chemsorption, and XPS also confirmed the highly dispersed Ni particles contributing to the high activity and stability of noble metal added Ni catalyst prepared by EG pretreatment.

4. Conclusions

Overall, the highly dispersed 20Ni-0.5Ru/SiO2 (EG) catalyst that is simply pretreated by ethylene glycol shows a high resistance for catalyst deactivation with high catalytic performance due to the synergistic effects of small Ni particles and noble metal promoter, and this catalyst can be one of the best catalysts for applying CO methanation reaction.

References

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