Ni-doped high surface area spherical silica catalysts for CO_2 methanation

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Abstract: Nickel-doped spherical silica (SSP) with surface area between 357-868 m^2/g were prepared by gel synthesis using $C_{16}TMABr$, TEOS, and $Ni(NO_3)_2.6H_2O$ as template, silica, and nickel sources with different loading sequences. Alternate loading between Ni and Si (Ni-Alt-Si) resulted in the highest CO_2 methanation activity and methane selectivity at 350°C. As revealed by the H_2-TPR and XPS results, the alternate loading method led to stronger interaction between Ni and SiO_2 in the form of nickel silicate species. All the nickel silicate catalysts, however, showed superior activities than the SSP supported NiO prepared by conventional impregnation.

Keywords: CO_2 hydrogenation, Ni/SiO_2 catalysts, nickel silicate phase.

1. Introduction

Recently, CO_2 methanation has gained much interest for the production of synthetic natural gas from coal or biomass[1]. CO_2 methanation has been investigated using metal catalysts such as Ru, Ni, Fe, Rh and Pd[2] on various oxide supports like Al_2O_3, MgO, CeO_2, SiO_2, ZrO_2 and TiO_2[3]. Among them, nickel-based catalysts remain the most widely studied because of their high catalytic activity and relatively low price but they usually suffered from deactivation due to sintering of Ni particles and carbon deposition[3]. Spherical silica (SSP) is an interesting ordered structure material with high surface area that has been employed as catalyst supports[4]. In this work, Ni source was added during the preparation of SSP to obtain high surface area nickel silicate catalysts. The catalysts were characterized by transmission electron microscopy, N_2 physisorption, X-ray diffraction, and H_2-temperature-program reduction and tested in the CO_2 methanation.

2. Experimental

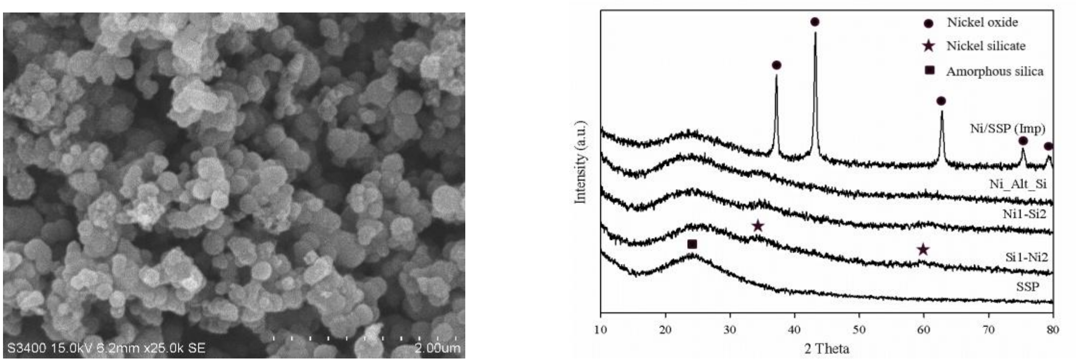
SSP was prepared by gel synthesis with the following molar ratio: 1TEOS: $0.3C_{16}TMABr$: $11NH_3$: 58ethanol : $114H_2O$. At first, ethanol and aqueous ammonia were added to distilled water (DI) under continuous stirring. $C_{16}TMABr$ was dissolved in the mixed solution after stirring for 15 min. After that, TEOS was added with further stirred for 2 h. Finally, dried samples were calcined in air at 550°C. Incorporation of 20 wt% Ni in SSP was done with three different loading sequences: before/promptly/after TEOS addition and are referred to as Ni_1-Si_2, Ni-Alt-Si, and Si_1-Ni_2, respectively. Ni/SSP (Imp) was also prepared by the incipient wetness impregnation for comparison. The sample was dried at 110 °C overnight in air and calcined in air at 550 ℃ for 6 h.

The CO_2 methanation reaction was carried out under atmospheric pressure at 350°C in a quartz micro reactor with WHSV of 36,000 mL/(g_{cat}.h) and H_2/CO_2 ratio of 10/1. Prior to the catalytic test, the catalysts were reduced under H_2 flow at 500 °C for 3 h. The effluent gases were then analyzed by a gas chromatograph attached with thermal conductivity detector to separate CH_4, CO_2 and CO.

3. Results and discussion

Fig 1a. shows the SEM micrographs of the Ni-containing spherical silica catalyst (Ni-Alt-Si). The specific surface areas of the catalysts were varied in the order: Si_1-Ni_2 (868 m^2/g) > Ni/SSP (Imp) (801 m^2/g)

> Ni_1-Si_2 (417 m^2/g) > Ni-Alt-Si (357 m^2/g). The surface area and pore volume of Ni-containing catalysts were less than the bare SSP support (1,213 m^2/g, 1.08 cm^3/g), suggesting partial blocking of the silica pores by nickel species. From the XRD results (Fig 1b), the SSP support exhibited only a broad peak which is a characteristic of amorphous silica. For all the Ni incorporated SSP catalysts, additional peaks at $2\theta=33.7$, 60.4° were detected and attributed to nickel silicate[5]. On the other hand, the diffraction peaks corresponding to nickel oxide were found for the Ni/SSP (Imp). As shown in Fig 2, the CO_2 conversion increased with increasing reaction temperature. At 350℃, the CO_2 conversion was in the order: Ni-Alt-Si (51%) > Ni_1-Si_2 (49%) > Si_1-Ni_2 (28%) > Ni/SSP (Imp) (10%) with methane selectivity $\geq$ 80%. Despite their lower surface area than the impregnation-catalysts, the superior performances in CO_2 methanation of all the nickel silicate catalysts are suggested to be attributed to the strong interaction between Ni and SiO_2 as illustrated in the H_2-TPR results (not shown), which resulted in the highly active and stable active nickel species.



(a) **(b)**

Figure 1. SEM micrograph of Ni-Alt-Si catalysts (a) and the XRD patterns of SSP and Ni-containing SSP catalysts (b)

4. Conclusions

The hydrogenation of CO_2 was studied over Ni-containing spherical silica catalysts prepared with different Ni loading sequences. Among all the catalysts tested, the Ni_Alt_Si catalysts showed only nickel silicate phase and was found to exhibit the best catalytic performances at the reaction temperatures 350°C with higher methane selectivity than the other prepared catalysts.

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