VO$_x$ promoted Ni catalysts supported on the modified bentonite for CO and CO$_2$ methanation

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ABSTRACT

Ni catalysts supported on the raw bentonite (RB) and the acid–alkali treated bentonite (B), which were prepared by the impregnation method, were tested for methanation of CO$_2$ and CO respectively to produce synthetic natural gas (SNG). XRD, nitrogen adsorption, SEM, TEM, TG, H$_2$-TPR, and XPS were employed for the characterization of the samples. The results showed that the Ni catalysts supported on the B support were more active than that supported on the RB support because of the improved Ni particles dispersion on the former that had larger specific surface area. After addition of proper amount of the VO$_x$ promoter, the catalytic activity of the B supported catalysts was further improved. This could be attributed to the enhanced H$_2$ uptakes, increased Ni dispersion, reduced Ni nanoparticle size, and the electronic effect of VO$_x$ that can promote dissociation of CO in the methanation reaction. In the lifetime test of CO$_2$ and CO methanation under atmospheric pressure, the Ni/B catalysts promoted by the VO$_x$ promoter were highly stable as they had superior anti-coking and anti-sintering performance to the catalyst without the promoter. This type of the catalysts is promising for industrial production of SNG.

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1. Introduction

Production of synthetic natural gas (SNG) via methanation of carbon oxides (CO and/or CO$_2$) is of great interest in industry, because natural gas is a clean fuel with a relatively high heating value and low carbon emission [1]. Coal conversion to CH$_4$ through gasification and methanation, a process known as coal to SNG, may meet the market demand for natural gas production in coal-rich regions. As shown below, the basic methanation reactions of syngas are highly exothermic: (1) CO + 3H$_2$ ↔ CH$_4$ + H$_2$O, $\Delta H_{298K} = -206.1$ kJ mol^{-1}, and (2) CO$_2$ + 4H$_2$ ↔ CH$_4$ + 2H$_2$O, $\Delta H_{298K} = -165.0$ kJ mol^{-1} [2,3]. In these methanation reactions, Ni-based catalysts are attractive and promising because of their relatively high activity, low cost and good availability as compared to noble metal catalysts. Among various supports, Al$_2$O$_3$ is the most commonly used and studied [4–6]. However, the Ni/Al$_2$O$_3$ catalysts often suffer from serious sintering and coking problems at high reaction temperatures, causing catalyst deactivation. In the last decade many efforts have been made to improve the catalytic performance of the Ni/Al$_2$O$_3$ catalysts, including the use of specific preparation methods such as the solution combustion [7], in situ reducing metal precursor [8] and plasma assisted methods [9], as well as the

addition of promoters such as MgO [4], ZrO$_2$ [10] and CeO$_2$ [11]. Although some promoted catalysts show improved catalytic performance, few of them can prevent the coke formation and the sintering of Ni particles simultaneously.

VO$_x$ as a promoter has been studied in different catalysts and reactions recently. Kip et al. [12] studied the location of the VO$_x$ promoter in Al$_2$O$_3$ and SiO$_2$ supported Ru catalysts and revealed the intimate contact between rhodium and VO$_x$. Mori et al. [13] found that the dissociation of the adsorbed CO on Ru/Al$_2$O$_3$ could be enhanced through oxidation–reduction cycle of VO$_x$ in the pulse methanation reaction. Guerrero-Ruiz [14] discovered that the promotion effect of the VO$_x$ promoter is related to the local electrostatic field or the chemical interaction between the promoter and the adsorbed species. However, the CO and/or CO$_2$ methanation over Ni catalysts added with the VO$_x$ promoter has rarely studied yet.

Recently, progress has been made in reducing metal particles sintering by placing the metal particles in the support matrix [8] or mesopores [15–18], e.g., Ni-incorporated MCM-41 catalysts [19–21]. However, high Ni loadings (exceeded 10 wt.%) were observed to cause serious pore clogging because of the narrow pore size (less than 10 nm). Wang et al. [22] synthesized NiCeAl oxide catalysts with ordered mesoporous structure by a one-pot method for the methanation reaction and found excellent resistance of the catalyst to the formation of graphitic carbon species. Zhou et al. [23] prepared KIT-6 as support

and found that the highly ordered mesoporous structure of KIT-6 improved the selectivity for methane. Unfortunately, the high production cost limits the industrial application of these catalysts.

Over the past several years, natural clays have attracted considerable attention due to their environmental compatibility, low cost, high selectivity, reusability and operational simplicity. Usually raw clays are not suitable for the catalyst support due to their small specific surface area. However, after proper modifications, e.g., by forming the pillared structure [24] or by the acid treatment [25], the surface areas can be increased significantly. The reason why the removal of a fraction of aluminum in clay via the acid treatment can lead to a much larger specific surface area is due to the formation of macro-mesopores, which can be further used to confine Ni species or fix them at specific sites to prevent them from sintering to a certain degree during the reaction. In addition, the reduction of the aluminum content in clay can lower the formation of spinel phase of nickel aluminate [26].

Following up our previous work in methanation study [27–29], in this study, we prepared Ni catalysts for CO_2 and CO methanation for the production of SNG. The catalyst supports are bentonite treated by acid and alkali (B) and the raw bentonite (RB), and VO_x is added as the promoter. It is found that the Ni catalysts supported on the B support promoted by VO_x exhibit much better catalytic activity and resistance to sintering and coke formation than that supported on RB, suggesting that the B support treated by an appropriate method would be a good alternative to the conventional Al_2O_3 support, and the VO_x is a good promoter for supported Ni catalysts for methanation.

2. Experimental section

2.1. Materials

Sodium hydroxide (KOH) and nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) of analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd., China, the raw clay was purchased from Shanghai No. 4 Reagent & H.V. Chemical Co., Ltd., and vanadyl acetylacetonate was purchased from Acros Organics, and used without further treatment.

2.2. Preparation of Ni catalysts

The raw bentonite (RB) was first treated by an acid solution [25] and the obtained support was denoted B (ac), which was then treated by potassium hydroxide solution. Typically, 10.0 g B (ac) was dissolved in 20 mL of deionized water, followed by dropping 0.1 mol L^{-1} KOH solution until the pH value reached 8 approximately. The slurry was stirred for 1 h, followed by filtering and washing until pH became around 7, and the solid was dried at 100 °C and denoted B. The Ni catalysts were prepared by co-impregnation (CIP) method. Firstly, 20 mL of anhydrous alcohol (99.7%, Beijing Chemical Works) was placed in a glass reactor with appropriate amount of vanadyl acetylacetonate, meanwhile 3.1 g of ($Ni(NO_3)_2 \cdot 6H_2O$) was dissolved in 20 mL of anhydrous alcohol. The above two solutions were mixed up, followed with addition of precalculated B to form a slurry, which was kept at room temperature for 12 h under vigorous stirring. The slurry was then heated to 80 °C to evaporate the liquid under continuous stirring, followed by drying at 110 °C overnight to obtain the solid samples. The solid samples after calcined at 400 °C for 5 h in air were denoted 20NxV/B, where, N referred to NiO loading of 20 wt.%, and x = 3, 5, and 8 the mass percentage of V_2O_5. For comparison, the 20N/RB and 20N/B catalysts without the addition of the VO_x promoter were prepared by the conventional wetness impregnation (IP) method. In addition, in order to know the state of V species in the reduced catalysts, the 20N30V/B and 50V/B catalysts were prepared by the same methods as described above and the related characterizations were described in the SI.

2.3. Characterization

N_2 adsorption at − 196 °C was analyzed using a Quantachrome surface area and pore size analyzer (NOVA 3200e). Before the analysis, the sample was degassed at 200 °C for 3 h under vacuum. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.2. The pore size distribution (PSD) was calculated by the Barett–Joyner–Halenda (BJH) method by the adsorption isotherm branch. Powder X-ray diffraction (XRD) patterns were recorded by a PANanalytical X'Pert PRO MPD with Cu Kα radiation (λ = 0.1541 nm) at 40 kV and 40 mA. The crystallite size of the particles was calculated by the Debye–Scherrer equation. The elemental contents of the supports were analyzed by X-ray fluorescence (XRF) (AXIOS-MAX, PANalytical B.V.). The microscopic feature of the samples was observed by a field emission scanning electron microscope (SEM) (JSM-6700F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2010F, JEOL, Tokyo, Japan). Before the TEM measurements, the Ni catalysts were first reduced in fixed bed at 550 °C for 1 h under H_2. Thermogravimetric (TG) analysis was conducted (EXSTAR TG/DTA 6300, Seiko Instruments) in air at a flow rate of 100 mL min^{-1} and a temperature ramp of 10 °C min^{-1}. The surface chemical composition of the samples was determined by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 250 spectrometer (Thermo Electron, U.K.), using a non-monochromatized Al Kα X-ray source (1486 eV). Temperature-programmed reduction with H_2 (H_2-TPR) was carried out on an automated chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome), and the operations are similar to our previous work [4–6]. For the H_2-TPR test, 0.07 g catalyst was loaded into a quartz U-tube and heated from room temperature to 300 °C at 10 °C min^{-1} and maintained for 1 h under Ar flow. Then, the catalyst was cooled down to room temperature and then heated to 1000 °C at 10 °C min^{-1} in the flow of a binary gas (10.0 vol.% H_2/Ar) at 30 mL min^{-1}. For H_2-TPD, 0.2 g catalyst was used and reduced in situ by H_2 flow previously. Then, the catalyst was cooled down to room temperature and saturated with H_2. After removing the physically adsorbed H_2 by flushing with Ar for 2 h, the catalyst was heated to 500 °C at a ramping rate of 10 °C min^{-1} in Ar flow (30 mL min^{-1}). The released H_2 was detected continuously as a function of increasing temperature using a thermal conductivity detector (TCD).

The dispersion of Ni was calculated based on the volume of chemisorbed H_2 using the simplified equation [11]:

$$D(\%) = \frac{2V_{ad} \times M \times SF}{m \times P \times V_m \times d_r} \times 100 \qquad (1)$$

where V_{ad} (mL) is the volume of chemisorbed H_2 in the TPD measurement at standard temperature and pressure (STP) conditions; m is the weight of the sample (g); M is the molecular weight of Ni (58.69 g mol^{-1}); P is the weight fraction of Ni in the sample determined by ICP; SF is the stoichiometric factor (the Ni:H molar ratio in the chemisorption), which is taken as 1 and V_m is the molar volume of H_2 (22.414 L mol^{-1}) at STP; d_r is the reduction degree of Ni calculated based on H_2-TPR.

The number of surface Ni sites per unit mass of catalyst was determined by means of H_2-TPD and the peak area of the H_2-TPR of a standard CuO sample was used to normalize that of the H_2-TPD graph of the samples. The turnover frequency (TOF) values of CO_2 and CO are calculated based on the formula below [29]:

$$TOF_{CO_i} = \frac{V_{CO_i,in} - V_{CO_i,out}}{R_{H_2/Ni} \times V_m} \times \frac{m_{cat-TPD}}{m_{cat-Reaction}} \times \frac{A_{CuO-TPR}}{A_{cat-TPD}} \times \frac{M_{CuO}}{m_{CuO-TPR}} \qquad (2)$$

where $V_{CO_i,in}$ and $V_{CO_i,out}$ are the volume flow rates of CO_i (here, $i = 1$ or 2) at the inlet and outlet of the reactor respectively under standard temperature and pressure (STP), mL s^{-1}; $R_{H2/Ni} = 2$, the stoichiometric factor of the H_2: Ni ratio in the chemisorption; $V_m = 22.414$ L mol^{-1}, the