Enhanced catalytic performances of Ni/Al$_2$O$_3$ catalyst *via* addition of V$_2$O$_3$ for CO methanation

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A B S T R A C T

Highly active and coking resistant Ni-V$_2$O$_3$/Al$_2$O$_3$ catalysts were prepared by co-impregnation method for CO and CO$_2$ methanation. The influence of vanadium oxide addition on catalyst structure, distribution and reducibility of Ni species, morphology and surface characteristics, was investigated in detail. Compared to the catalyst without vanadium, the Ni-V$_2$O$_3$/Al$_2$O$_3$ catalysts showed significant improvement in the activity, thermal stability, and resistance to coke formation in CO methanation. In addition, these catalysts also showed high activities for CO$_2$ methanation at both atmospheric and 2.0 MPa pressures. It was found that Ni$_3$V$_2$O$_8$ was formed during the calcination of the Ni-V$_2$O$_3$/Al$_2$O$_3$ catalysts, which led to the formation of smaller Ni particle sizes (ca. 3.0 nm) as compared to the case without vanadium oxide addition. The higher catalytic activity over the Ni-V$_2$O$_3$/Al$_2$O$_3$ catalysts for CO methanation was mainly due to the larger H$_2$ uptake, the higher Ni dispersion as well as the smaller metallic Ni nanoparticles. The oxidation–reduction cycle of V$_2$O$_3$ could increase the oxygen vacancies, which enhanced the dissociation of CO$_2$ by-product and generated surface oxygen intermediates, thus preventing carbon deposition on the Ni particles in CO methanation.

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1. Introduction

Methanation of carbon oxides (CO and/or CO$_2$) with hydrogen to produce methane was firstly reported by Sabatier and Senderens in 1902 [1], and has been widely used in various industrial processes such as removal of trace amounts of CO from H$_2$ rich feed gas or purification of the reformate gas for NH$_3$ synthesis and fuel cell application, and processes in relation to Fischer–Tropsch synthesis [2,3]. Recently, there is an arising interest to produce synthetic natural gas (SNG) *via* syngas methanation approach in China [4], as the basic pattern of China energy is characterized by "rich in coal, poor in oil and natural gas". The strategy that relies on the rich coal resources in China while energetically developing "Coal to Natural Gas" not only meets the development direction of coal clean utilization, but also guarantees the effective supplement of natural gas [5].

In recent years great efforts have been made to develop highly efficient catalysts for syngas methanation, and the requirements for the excellent methanation catalysts include high activity at low temperature (ca. 300 °C) and high stability at high temperature (ca. 600 °C) [6]. It is acknowledged that Ru-based catalyst is the most active for syngas methanation, however, limited resource and high cost of Ru restrict its large-scale commercialization [7]. Therefore, Ni-based catalysts are more preferred for syngas methanation due to their low cost, good availability and high activity. However, for Ni-based catalysts, a high reaction temperature (above 320 °C) is generally required to achieve the maximum CO conversion at atmospheric pressure [8–10], and the coke formation is usually serious under the harsh conditions, which reduces the catalytic activity obviously [11–13]. To overcome these limits, various promoters [10,12,14], supports [5,13,15] and preparation methods [6,16] have been selected and tested. However, the above reported catalysts seldom show both high low-temperature activity and good high-temperature stability, as most of approaches are only effective on one of them. Therefore, developing catalysts that can work well at both low and high temperatures still remain as the main challenges.

For Ni-based catalysts, it has identified that the rate-determining step in the methanation reaction is the hydrogenation of CH$_x$ species [17]; for promotion of catalytic activity, it is crucial to realize a fast removal of these surface CH$_x$ species by surface-dissociated hydrogen. It has reported that the surface defects in metallic Ni serve as capture traps for surface hydrogen which

reduces the activation energy of hydrogen dissociation [18], and the largely increased surface defects can be achieved by decreasing the supported Ni particles size into nano-scale with a simultaneously increased Ni dispersion [18]. Moreover, the rate of carbon filament formation is proportional to the particle size of Ni, and below a critical Ni particle size ($d < 2$ nm), the formation of carbon becomes dramatically slow [19]. Therefore, it is proposed that a Ni-based catalyst with small Ni nanoparticles will show much improved low-temperature activity and anti-coking property.

Vanadium oxides are used extensively in industrial catalysts as active component or catalyst supports for many reactions including oxidation of sulphur dioxide, partial oxidation of hydrocarbons and selective reduction of nitric oxide [20]. It was reported that V could obviously restrain the Rh particle size over SiO_2 support through formation of $RhVO_4$ [21–25], and the Rh-V/SiO_2 catalysts could have improved activity and selectivity in CO hydrogenation for the production of C_2 oxygenates such as ethanol and acetic acid [21,23,26,27]. In addition, some authors have reported that V was a good promoter to Ni/Al_2O_3 catalyst in CO hydrogenation to produce C_2–C_4 hydrocarbons [28], but the correlation between the catalyst structure and performance has not been well clarified yet. In addition, it is known that nickel vanadates such as $Ni_3V_2O_8$, $Ni_2V_2O_7$ and NiV_2O_6 can be synthesized by the reaction of V_2O_5 with different amount of NiO [29], which may have the similar performance to $RhVO_4$ in reducing the metallic particle size.

In continuation of our previous work on CO methanation [8–12,30–32], in this work we have developed a Ni-V_2O_3/Al_2O_3 catalyst by co-impregnation method. It is found that the addition of vanadium oxide is capable of improving both the low-temperature catalytic activity and the anti-coking property of the Ni catalyst in the CO methanation even under very harsh conditions. In addition, CO_2 methanation is also studied over the Ni-V_2O_3/Al_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation

All the chemicals with analytical grade including nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd., China, and used without further treatment. Vanadyl (IV) acetylacetonate was purchased from Acros. The commercial porous γ-Al_2O_3 (Zibo Honghe Chemical Co. Ltd., China) with a surface area of 164 m^2 g^{-1} was calcined at 400 °C in air for 2 h before use.

The NiO/Al_2O_3 catalyst was prepared by the wet impregnation method. The stoichiometric quantity of Ni(NO$_3$)$_2$·6H$_2$O was dissolved in ethanol, followed with addition of the γ-Al_2O_3 support to form a slurry. The slurry was vigorous stirred at room temperature overnight, and then heated to 70 °C to evaporate the liquid, followed with drying at 100 °C for 24 h and further calcination at 500 °C for 2 h in air with the heating rate of 2 °C min^{-1}. The collected catalyst with a NiO loading of 20 wt% was denoted as 20NA.

The NiO-V_2O_5/Al_2O_3 catalysts with various V_2O_5 contents were prepared by the co-impregnation method following with the above procedures by adding stoichiometric quantities of Ni(NO$_3$)$_2$·6H$_2$O and vanadyl (IV) acetylacetonate in ethanol simultaneously. The finally obtained samples were denoted as 20NAxV (x = 2, 5, 10 and 16), where x represented the mass percent of V_2O_5. In addition, $Ni_3V_2O_8$ was also prepared with the same procedure mentioned above only without addition of γ-Al_2O_3 [29]. V_2O_5/Al_2O_3 was prepared by the same method as 20NA10V only without addition of NiO, and the pure V_2O_5 was obtained by calcining vanadyl (IV) acetylacetonate at 500 °C for 2 h in air with the heating rate of 2 °C min^{-1}.

2.2. Catalyst characterization

N$_2$ adsorption at −196 °C was measured using a Quantachrome surface area and pore size analyzer NOVA 3200e. Prior to the measurement, the sample was degassed at 200 °C for 4 h under vacuum. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.3. The pore size distribution (PSD) was calculated with the Barett–Joyner–Halenda (BJH) method using the adsorption isotherm branch.

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO MPD with a step of 0.02° using the Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA, and checked with the card number of Joint Committee on Powder Diffraction Standards (JCPDS). The crystal size of the sample was calculated using the Debye–Scherrer equation.

H$_2$ temperature-programmed reduction (H$_2$-TPR), H$_2$ temperature-programmed desorption (H$_2$-TPD) and CO$_2$ temperature-programmed desorption (CO$_2$-TPD) were carried out on Quantachrome Automated chemisorption analyzer (chemBET pulsar TPR/TPD). For H$_2$-TPR, 0.05 g sample was loaded in a quartz U-tube and heated from room temperature to 200 °C at 10 °C min^{-1} and maintain for 1 h under He flow. Then, the sample was cooled to room temperature and followed by heating to 1000 °C at 10 °C min^{-1} under a binary gas (10 vol% H$_2$/Ar) with a gas flow of 30 mL min^{-1}. For H$_2$-TPD, 0.2 g catalyst was used and reduced in situ by H$_2$/Ar flow previously. Then, the sample was cooled to room temperature and saturated with H$_2$. After removing the physically adsorbed H$_2$ by flush with Ar for 2 h, the sample was heated to 1000 °C ramping at 10 °C min^{-1} in Ar flow (30 mL min^{-1}). The consumed or desorbed H$_2$ was detected continuously as a function of increasing temperature using a thermal conductivity detector (TCD). The number of surface Ni sites per unit mass of catalyst was determined by means of H$_2$-TPD assuming the adsorption stoichiometry of H/Ni = 1:1. The peak area of H$_2$-TPD profile was normalized by that of H$_2$-TPR of a standard CuO sample. The dispersion of Ni was calculated based on the volume of chemisorbed H$_2$ using the following simplified equation [12]:

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

where V_{ad} (mL) represents the volume of chemisorbed H$_2$ at the standard temperature and pressure (STP) conditions measured in the TPD procedure; m is the sample weight (g); M is the molecular weight of Ni (58.69 g mol^{-1}); P is the weight fraction of Ni in the sample as 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 molar volume of H$_2$ (22414 mL mol^{-1}) at STP; d_r is the reduction degree of nickel calculated based on H$_2$-TPR. For CO$_2$-TPD, 0.2 g catalyst was used and reduced in situ by H$_2$/Ar flow previously. Then, the sample was cooled to room temperature in H$_2$ flow and saturated with CO$_2$ (30 mL min^{-1}) for 1 h. After removing the physically adsorbed CO$_2$ by flush with He for 2 h, the sample was heated to 500 °C ramping at 10 °C min^{-1} in He flow (30 mL min^{-1}). The turnover frequency (TOF) was calculated according to the formula described in our previous work [9].

The surface chemical composition was analyzed by an X-ray photoelectron spectroscopy (XPS) test conducted on a VG ESCALAB 250 spectrometer (Thermo Electron, U.K.) with a non-monochromatized Al Kα X-ray source (1486 eV).

The microscopic feature of the samples was observed by field emission scanning electron microscope (SEM) (JSM-6700F, JEOL, Japan) and transmission electron microscopy (TEM) (JEM-2010F, JEOL, Japan). Before the TEM measurement, the H$_2$-reduced catalysts were cooled to room temperature in H$_2$ flow and then