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The SiO_2 supported bimetallic Ni–Ru particles: A good sulfur-tolerant catalyst for methanation reaction

Changkun Yuan, Nan Yao *, Xinde Wang, Jianguo Wang, Deyi Lv, Xiaonian Li *

Institute of Industrial Catalysis, College of Chemical Engineering, Zhejiang University of Technology, 18 Chaowang Road, Hangzhou 310032, China

HIGHLIGHTS

- Addition of H_2S enhances the sintering and oxidation of Ni^0 particle in the methanation reaction.
- Effect of Ru on the sulfur tolerance of the supported Ni catalyst depends on its geometric factor.
- Adsorption of S can only be reduced when S binds with Ni and Ru atoms simultaneously.
- S can bind with Ni and Ru atoms simultaneously on the small bimetallic Ni–Ru particles.
- $NiRu/SiO_2$ catalyst with small bimetallic Ni–Ru particles has enhanced sulfur tolerance.

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ABSTRACT

The long-term stabilities and the sulfur tolerances of SiO_2 supported Ni and NiRu catalysts in the methanation reaction were examined. The presence of H_2S molecules (10 ppm (v/v)) in the syngas led to fast deactivation of Ni/SiO_2 catalyst, because the adsorption of S blocked the active sites as well as accelerated the sintering and the oxidation of Ni^0 particles. The effect of Ru on the reduction of S adsorption over the supported Ni-based catalyst depended on its geometric instead of electronic factor. The S adsorption could only be weakened when S bound with both Ni and Ru atoms simultaneously. The formation of such state was more favorable on the polyethylene glycol (PEG)-additive method derived $NiRu/SiO_2$ catalyst with small bimetallic Ni–Ru particles. As a result, this catalyst could stabilize for ~127 h in H_2S-containing methanation reaction, which was ~1.6–5.8-fold longer than those of PEG-free method derived $NiRu/SiO_2$ catalyst (~79 h) with separated Ru and Ni/SiO_2 catalyst (~22 h).

1. Introduction

The use of natural gas which primarily is consisted of methane as a fuel or a reactant becomes utmost important currently owing to the requirement of environmental protection and the limitation of CO_2 emission. In addition to the direct exploitation of natural gas, the catalytic conversion of stoichiometric syngas ($H_2 + CO$) into methane (the so-called synthetic natural gas (SNG)) provides a promising way to supply this clean fuel in the area with few resource of natural gas [1–9]. Moreover, this SNG process has also been applied to remove trace CO molecules to purify the hydrogen for the fuel cell and the ammonia synthesis [10,11].

Many transition metals (Ni, Ru) have catalytic activities in the methanation process, while the supported Ni-based catalyst is widely accepted as an economical and efficient methanation catalyst [12–15]. Generally, the syngas generated via the gasification of coal or biomass often has high concentration of sulfur-containing compounds (e.g., H_2S). These chemicals are one of the important factors for the deactivation of the supported Ni-based catalysts [16,17]. Although those sulfur-containing compounds can be removed or decreased to a very low concentration before the reaction, it costs huge investment. The development of sulfur-tolerant or sulfur-resistant supported Ni-based catalyst thereby attracts much research interest from both scientific and industrial fields [18–20].

Several methods have been established to enhance the sulfur-tolerance of the supported Ni-based catalyst. The presence of second element like W, alkali or noble metals (Ru, Rh) provides a first reasonable way to design the catalyst with better sulfur-tolerance than the supported monometallic nickel-based catalyst, as these additive metals change their properties [21,22]. For example, Diaź et al. had reported that the addition of alkali elements like Li, K and Na into Ni/SiO_2 not only changed its electronic property, but also blocked some parts of surface Ni sites to limit the adsorption of

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* Corresponding authors. Tel./fax: +86 571 88320930 (N. Yao), +86 571 88320002 (X. Li).

E-mail addresses: kenyao@zjut.edu.cn (N. Yao), xnli@zjut.edu.cn (X. Li).

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H_2S and thiophene. The resultant structure reduced the toxicity of these sulfur-containing compounds [23]. Wang et al. exhibited that the presence of W improved the stability of the supported Ni-based catalysts in the hydrogen production via the sulfur-containing gasoline [24].

The type and the acidity of the support also affect the sulfur-tolerance of the catalyst. As reported in literatures, the TiO_2 supported catalyst showed better sulfur resistance [25]. The CeO_2 could react with H_2S to form $Ce(SO_4)_2$, a compound that promoted the reforming activity [26]. On the other hand, the enhanced acidity of the support could retard the catalyst from S poisoning [27]. Wang et al. demonstrated that the use of acidic ZSM-5 to replace Al_2O_3 as the support could increase the sulfur-tolerant property of the supported Ni catalyst in the steam reforming of liquid hydrocarbons [28].

In addition to the methods as mentioned above, the preparation of the supported monometallic Ni catalyst with highly dispersed Ni^0 particles is expected to be less sensitive to the sulfur-induced deactivation, since the smaller Ni^0 particles can present more available sites for the catalytic reaction and reduce the carbon deposition [29–31]. The investigation reported by Mayne et al. confirmed the larger Ni^0 particles showed a marked deactivation in the autothermal reforming of isooctane with thiophene [31]. However, the attempt of increasing the dispersion of Ni^0 is often limited by the dispersion-reducibility dependence, which inherently exists on the oxide supported nickel-based catalysts [32,33].

Our previous work demonstrated that the polyethylene glycol (PEG)-additive deposition protocol improved the promotional efficiency of Ru and facilitated the formation of small bimetallic Ni–Ru particles with high reducibility on SiO_2 support to break the dispersion-reducibility dependence. Moreover, the bimetallic $NiRu/SiO_2$ catalyst showed the pronounced stability in the methanation reaction [33]. On the basis of these findings, we aim to elucidate the size and structural requirement of the supported Ni-based catalyst for the sulfur tolerance in the methanation reaction here. We use the PEG-additive method to synthesize the supported Ni and NiRu catalysts. The conventional SiO_2 rather than the transition metal oxide and zeolite is used in order to diminish the influence of support on the sulfur-tolerance.

2. Experimental

2.1. Preparation of catalyst

All chemicals used in the present work were analytical reagents. The SiO_2 (B.S.H. Catalyst Inc., specific surface area = 378.1 $m^2\ g^{-1}$, pore volume = 0.97 $cm^3\ g^{-1}$, pore diameter = 10.2 nm) was washed and calcined at 873 K for 16 h before using in the following procedures.

The SiO_2 supported NiRu and Ni catalysts were prepared by either PEG-additive or PEG-free method. For the preparative protocol using PEG-additive method, the $Ni(NO_3)_2{\cdot}6H_2O$ (2.80 g, $\geqslant$98%), $Ru(NO)(NO_3)_3$ (0.24 g, Alfa Aesar) and PEG (2.93 g, average molecular weight = 1000) were added into a 200 cm^3 of solvent containing butanol (50 cm^3, 99%) and deionized water (150 cm^3). This mixed solution was refluxed at 393 K under continuous stirring for 2 h. Subsequently, 5 g of SiO_2 support was added. The formed suspension was heated under vigorous stirring at 393 K in order to evaporate the solvent until the formation of paste-like sample. This sample was calcined in ambient air by increasing the temperature to 673 K at 10 K min^{-1} and holding it there for 5 h to prepare the $NiRu/SiO_2$ sample (10 wt.% Ni, $(Ru/Ni)_{at.}$ = 0.08). With absence of $Ru(NO)(NO_3)_3$ precursor, a monometallic Ni/SiO_2 sample with 10 wt.% Ni could be also prepared by the same method. These two SiO_2 supported Ni and NiRu samples were labeled as Ni/SiO_2-P and $NiRu/SiO_2$-P, respectively. The SiO_2 supported NiRu ($NiRu/SiO_2$-NP, 10 wt.% Ni, $(Ru/Ni)_{at.}$ = 0.08) and Ni (Ni/SiO_2-NP, 10 wt.% Ni) samples were prepared by the above preparative process without PEG polymer.

2.2. Characterization

Powder X-ray diffraction (XRD) experiments were performed by using a Cu Kα X-ray radiation source on a PNAlytical X-ray diffractometer (X'Pert PRO). The XRD patterns were collected by using a step size of 0.0334. The scanning rate was adjusted from 0.0894 to 0.2669° S^{-1} in order to obtain enough intensity for each sample. By using the full width at half maximum (FWHM) of the strongest diffraction peak relevant to NiO crystal ($2\theta \approx 43°$), the average particle size of NiO crystal can be calculated in terms of Scherrer equation.

The reductive behaviors of the SiO_2 supported Ni and NiRu catalysts were examined by a temperature-programmed reduction (TPR) instrument equipped with a thermal conductivity detector (TCD). The samples were treated by 5% H_2/Ar (40 $cm^3\ min^{-1}$) in a quartz reactor. The temperature of the reactor was increased from 303 to 1123 K with a heating rate of 10 K min^{-1}.

The diameters of metallic Ni^0 on the reduced catalysts were calculated according to the H_2 chemisorption uptakes measured by a Quantachrome Autosorb (IQ) unit. The samples were pretreated in pure H_2 (99.999%) at 693 K for 5 h and then evacuated at that temperature for 30 min. After cooling to 323 K, the chemisorption isotherms of hydrogen were recorded and the H_2 uptakes were obtained by extrapolating the isotherms to zero pressure. The contribution of trace Ru to the H_2 uptakes of the supported NiRu catalysts could be ignored, because the supported monometallic Ru catalyst only chemisorbed negligible amounts of H_2 even at ambient temperature [34].

The morphologies and the chemical compositions of the deactivated catalysts after H_2S-containing methanation were characterized by a transmission electron microscope (TEM, Tecnai G2 F30 S-Twin, 300 kV) equipped with an energy-dispersive X-ray analysis (EDX). The size of particle could be measured according to the scale bar as shown in the TEM photo. After H_2S-containing or H_2S-free methanation reaction, the type of carbon species deposited on the supported Ni-based catalysts were examined by the temperature-programmed hydrogenation (TPH) technique. The samples were loaded in a reactor and treated by flowing H_2 (99.999%, 175 $cm^3\ min^{-1}$). The temperature of reactor was increased from 373 to 1123 K with a heating rate of 5 K min^{-1}. A mass spectrometer (Netzsch, QMS403C) was used to record the CH_4 signals formed during the TPH experiments.

The surface oxidation states of Ni elements in the catalysts were determined by an X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD). After placing the catalyst inside the chamber of XPS instrument, the samples were outgassed to achieve the ultra high vacuum. Monochromatic Al Kα X-ray source with 450 W was used to bombard the samples. The binding energies of Ni elements were calibrated by using C_{1S} (284.5 eV) as a reference.

2.3. Methanation reaction

Both H_2S-containing and H_2S-free methanation reactions were carried out in a common fixed-bed reactor instead of other type of reactor [35]. The temperature and the pressure of the methanation reaction were 593 K and 1 MPa, respectively. 1 g of catalyst (0.180–0.106 mm) was homogenously mixed with 0.5 gram of SiO_2 material (0.180–0.106 mm). The mixed powders were loaded in the thermostatic zone of the reactor. Prior to the H_2S-free methanation reaction, the catalyst was pre-reduced in a flowing H_2 [99.999%, 60 $cm^3{\cdot}(\text{g-catalyst min})^{-1}$] at 693 K for 5 h. After