Active and stable Ni based catalysts and processes for biogas upgrading: The effect of temperature and initial methane concentration on CO₂ methanation

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HIGHLIGHTS

- Active and stable Ni based catalysts are demonstrated for direct biogas upgrading.
- Ru promotion increased activity significantly and improved CH₄ selectivity.
- Initial CH₄ concentration in biogas has low impact on the catalysts.
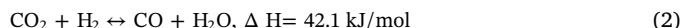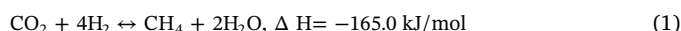- Direct biogas upgrading without CO₂ removal is practically feasible.

ARTICLE INFO

ABSTRACT

CO₂ hydrogenation to methane (CO₂ methanation) is gaining increasing interest as a major chemical synthesis process for chemical storage of fluctuating renewable energy and producing synthetic natural gas by providing an effective process for biogas upgrading. In this study, a series of 12 and 20 wt% Ni/Al₂O₃ catalysts, either unpromoted or promoted by 0.5 wt% Ru, were prepared by the incipient wetness method for the CO₂ methanation reaction from a feed of pure CO₂ or biogas. The catalysts were characterized by N₂ physisorption, XRD, TPR and H₂ chemisorption. The activity for the 12 wt% Ni catalyst increased continuously in the temperature range from 250 °C to 400 °C. Increasing the Ni loading and Ru promotion greatly improved the activity of the catalyst. At 350 °C, the highest CO₂ conversion of 82% and CH₄ selectivity of 100% was achieved over the 20Ni0.5Ru/Al₂O₃ catalyst. Thereafter, methanation of a simulated biogas mixture was investigated over the 20Ni/Al₂O₃ and 20Ni0.5Ru/Al₂O₃ catalysts. The results showed that the CO₂ conversion and CH₄ selectivity were only mildly affected by the feed composition. Furthermore, the stability of the catalysts was similar regardless of the feed composition. This study demonstrates that high purity CH₄ can be achieved from a biogas feed over our Ni based catalysts.

1. Introduction

The CO₂ concentration in the atmosphere is continuously increasing, which is considered to be one of the main anthropogenic causes of global warming and has led to growing interest in CO₂ capture, utilisation and storage (CCUS). CO₂ is not only a waste but could be a renewable carbon feedstock for making fuels, chemicals, materials and carbohydrates (i.e., foods) [1,2]. CO₂ hydrogenation to methane (CO₂ methanation), or the so-called Sabatier reaction, uses CO₂ as a primary feedstock and could theoretically be highly efficient for recycling CO₂. Methanation of CO₂ is an exothermic reaction in which H₂ and CO₂ react to form CH₄ and H₂O. The process is often coupled with the reverse water gas shift (RWGS) reaction, which produces the main byproduct CO. The reaction stoichiometry of the CO₂ methanation reaction and the RWGS reaction is shown in Eqs. (1) and (2) respectively [3].

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O, \Delta H = -165.0 \text{ kJ/mol} \tag{1}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \Delta H = 42.1 \text{ kJ/mol} \tag{2}$$

Currently, significant efforts are being made to replace conventional fossil fuels by renewable energy sources such as wind and solar energy. One of the applications that the CO₂ methanation process has great potential for is intermittent renewable energy storage in power-to-gas technology [4,5]. Furthermore, investigations of the potential of CO₂ methanation process as a biogas upgrading technology are being carried out [6,7]. Biogas consists of mainly CO₂ and CH₄, where the CO₂

content can vary from 25% to 55% depending on the source. Today, biogas upgrading is performed by cleaning the gas to reduce the concentration of impurities, such as sulphides and ammonia, followed by CO_2 removal [8–10]. Converting the large CO_2 fraction in biogas to CH_4 would increase the yield of CH_4, and could be a more attractive option for biogas utilisation. There are two different ways in which the Sabatier reaction can be applied for biogas upgrading. One is the traditional Sabatier process where the CO_2 removed from the biogas can be used as feedstock, while the other is direct biogas upgrading that is performed with a mixture of CO_2 and CH_4. Directly utilising biogas could be very attractive as it would eliminate the need for CO_2 removal, which is normally performed by the energy intensive amine absorption process. Jürgensen et al. [6] performed thermodynamic simulations on the direct biogas upgrading based CO_2 methanation process. The results predicted that the initial CH_4 concentration will have a small impact on the CO_2 conversion, CH_4 selectivity and carbon deposition, particularly at elevated pressures.

Thermodynamically, CO_2 is a very stable molecule, and its conversion is energy intensive. Therefore, efficient catalysts and catalytic processes are required to make CO_2 conversion viable. CO_2 methanation has been investigated over a number of catalysts based on VIIIB metals (for example, Ru, Rh, Ni, Co, Fe), typically on high surface area supports (i.e., Al_2O_3, SiO_2, ZrO_2, TiO_2, CeO_2) [11,12]. Most of the reported research on CO_2 methanation currently focuses on Ni based catalysts, due to their relatively high catalytic activity and low cost. However, Ni based catalysts often suffer in terms of poor activity at low temperatures and deactivation at high temperatures due to sintering and coke deposition [13]. Recently, improvement in catalytic performance has been achieved with hydrotalcite-derived Ni catalysts, and promoters have been demonstrated to further enhance such catalysts [14–16]. Commercially, in addition to Ni, Ru based catalyst are also available and are suitable for low-temperature applications [17]. Ruthenium has been shown to be a promising active metal for CO_2 methanation by many research groups [17–20]. Garbarino et al. [17] compared a commercial 3% Ru/Al_2O_3 to a commercial 20% Ni/Al_2O_3 catalyst and found that the Ru based catalyst performed equally or better than the Ni based catalyst, depending on the reaction conditions. Nevertheless, Ru is considerably more expensive than Ni and has limited use in large scale catalytic processes.

Bimetallic catalysts can greatly improve the catalyst's performance and often show a synergistic effect between the metals. Promotion by a small amount of noble metal has been shown to improve Ni based catalysts in several processes [21–23]. Hwang et al. [24] investigated the effect of Ru content in mesoporous Ni (35 wt%)-Fe (5 wt%)-Ru (x wt%)-alumina xerogel catalysts (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) for CO_2 methanation. Both the CO_2 conversion and the CH_4 yield showed a volcano-shaped trend with respect to Ru content, which indicates that the Ru loading can be optimised to maximise the catalyst's performance. Zhen et al. [25] prepared bimetallic Ni(10 wt%)-Ru(x wt %)/Al_2O_3 nanoparticles (x = 0.5, 1.0, 2.5 and 5.0) by different impregnation methods. The activity tests also revealed a volcano-shaped trend for the catalysts with respect to Ru loading, where the optimum was found to be 1.0 wt%. Furthermore, the bimetallic catalyst showed promising stability over 100 h time on stream.

Impurities are common in many CO_2 sources as well as in biogas, which could have a great impact on the catalyst [8,9]. Jürgensen et al. [7] studied the effect of H_2O and NH_3, common traces in biogas, on CO_2 methanation with an industrial silica-alumina supported Ni catalyst. Lower H_2 conversions were observed with H_2O in the feed, which can be explained by the inhibition effect of H_2O on CO_2 methanation and the associated water-gas shift reaction [26]. On the other hand, small amounts of NH_3 was found to be beneficial for catalyst stability, and NH_3 removal from the biogas was deemed unnecessary. Among other traces in biogas, H_2S is typically always present in small quantities, even after treatment [8,9]. H_2S is generally a problem in catalysis as it can lead to deactivation of the catalyst. Yuan et al. [27] found that

small Ni-Ru bimetallic particles supported on SiO_2 have greater H_2S resistance compared to pure Ni/SiO_2.

Based on an extensive literature review, many challenges must be addressed before the CO_2 methanation technology can be applied for efficient biogas upgrading. The catalyst needs to be active at lower temperatures and stable under real feed conditions (i.e., CH_4 and other trace impurities present in the feed gas). Besides, although the Sabatier process has been well investigated, few studies have focused on the development of efficient catalysts and catalytic processes for the direct biogas upgrading related CO_2 methanation process. Therefore, studying Ni based catalysts for direct biogas upgrading under different reaction conditions is of considerable interest.

In this study, we prepared a series of Ni/Al_2O_3 and bimetallic Ni-Ru/Al_2O_3 catalysts by the incipient wetness method. The Ni loading, as well as the precious metal Ru promotion effect, have been compared to find the most suitable catalyst for direct biogas upgrading. Furthermore, the effect of the process conditions, such as temperature and synthetic biogas feed composition, have been studied to evaluate the CO_2 conversion and CH_4 selectivity. Long-term stability tests have also been performed. The results demonstrate that our 20Ni/Al_2O_3 and 20Ni-0.5Ru/Al_2O_3 catalysts are only mildly affected by the CH_4 concentration in biogas regarding activity, selectivity and stability, and could be practically feasible for small scale direct biogas upgrading.

2. Experimental

2.1. Preparation of Ni-(Ru)/Al₂O₃ catalysts

All catalysts were prepared by the incipient wetness impregnation method. The γ-Al_2O_3 support (SCCa 5-200, from Sasol Germany) was calcined in flowing air at 600 °C for 6 h prior to impregnation. Ni $(NO_3)_2 \cdot 6H_2O$ and $Ru(NO)(NO_3)_2 \cdot xH_2O$ precursors were purchased from Sigma-Aldrich. For the monometallic Ni catalysts, a calculated amount of the aqueous solution of Ni salt was added to the support material to achieve the desired loading. Bimetallic catalysts were prepared by co-impregnation where the support was impregnated with the aqueous solution mixture of Ni and Ru salts. The catalysts were dried at 120 °C for 24 h, followed by calcination in flowing air, where the temperature was increased from room temperature to 600 °C at a ramp rate of 10 °C/min, and maintained at 600 °C for 6 h. The Ni loading was 12 wt% and 20 wt%, while the Ru containing catalyst had a fixed Ru loading of 0.5 wt%. The prepared catalysts were denoted xNi/Al_2O_3 and xNi0.5Ru/Al_2O_3 (x = 12 and 20).

2.2. Catalyst characterization

N_2 physisorption measurements on the calcined support and catalysts were performed at -196 °C using a Micromeritics Tristar 3000 apparatus. Prior to the measurements, the samples were outgassed at 160 °C for 24 h in vacuum. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface areas. The pore volumes were determined at p/p_0 = 0.9975. Barrett-Joyner-Halenda (BJH) method analysis (4 V/A) of the desorption branch was used to obtain the pore size distribution.

The X-ray diffraction (XRD) patterns were recorded for the calcined support and catalysts on a Bruker-AXS Microdiffractometer (D8 ADVANCE) using Cu K_α radiation source (λ = 0.154 nm). The patterns were collected in the range of 10–90° (2Θ) with a step interval of 2.25 °/min. Peaks were indexed according to the database established by Joint Committee on Powder Diffraction Standards (JCPDS).

Temperature programmed reduction (TPR) measurements of the calcined catalysts were done with a Micromeritics Autochem II ASAP 2920. Before TPR measurements, the samples were dried at 200 °C in He flow for 30 min. A 7% H_2/Ar mixture at 50 mL/min were used while the temperature was ramped from ambient to 950 °C at 10 °C/min.

The H_2 adsorption capacity of the catalysts was investigated by a