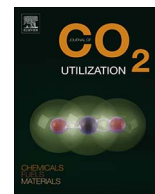




Contents lists available at ScienceDirect

Journal of CO₂ Utilizationjournal homepage: www.elsevier.com/locate/jcou

Active and stable hydrotalcite derived Ni catalysts for CO₂ reforming of methane: Comparison with catalysts by incipient wetness

Dori Yosef Kalai^a, Kristian Stangeland^a, Yiyi Jin^b, Zhixin Yu^{a,*}^a Department of Petroleum Engineering, University of Stavanger, Stavanger 4036, Norway^b School of Environment, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Keywords:

Dry reforming
Hydrotalcite
Incipient wetness
Nickel catalyst
Biogas

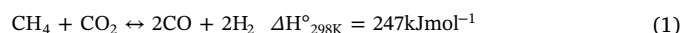
ABSTRACT

Dry reforming of methane (DRM) for synthesis gas production has a promising future in technological developments due to the utilization of CO₂, the principal anthropogenic greenhouse gas. However, this process is still far from industrialization because of catalyst deactivation by coking and sintering. In this study, a series of Ni (Mg)-Al hydrotalcite (HT) derived catalysts were prepared and compared to catalysts prepared by the conventional incipient wetness method. The as-prepared and calcined catalysts were characterized by N₂ adsorption-desorption, X-ray diffraction, temperature programmed reduction, H₂-chemisorption and scanning electron microscope. DRM experiments were carried out at a very high gas hourly space velocity of 240,000 ml/(g_{cat} h) to compare the activity and stability of the catalysts. The 20Ni-Mg-Al HT showed remarkably high and stable conversions in DRM at 750 °C, while the 12Ni-Al HT catalyst presented the poorest activity, resulting from impure HT structure and consequently unstable Ni particles. The 20Ni-Mg-Al HT was further proved to be active and stable under various biogas compositions, even in the deficiency of CO₂. This study demonstrates that pure HT-derived Ni catalysts are superior for DRM at different reaction conditions, and can be utilized for direct biogas upgrading.

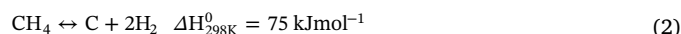
1. Introduction

Anthropogenic emissions of greenhouse gases (GHG), namely CO₂ and CH₄, are proposed to cause an increase in surface temperature of the earth. GHG are strongly related to the world population growth and consequently to the growing energy demand. To address the concerns, different solutions have been proposed, among which carbon capture and storage (CCS) and carbon capture and utilization (CCU) stand out as important alternatives. CCS provides a relatively technological mature solution but has critical limitations: high capital investment costs, uncertain storage capacity, large energy consumption and increasing public resistance [1]. Instead of treating CO₂ as a waste, it can be regarded as a chemical feedstock for the major chemical synthesis process that partly replaces fossil fuel based feedstock. The CCU technology aims to convert CO₂ into gasoline, diesel, jet fuel and commodity chemicals in an economical and practical way. Mainland Europe (in particular Germany), the US and Australia are well advanced in research and development of CCU technologies; Substantial investments were made in those countries by extending CCS technology to incorporate CO₂ utilization in addition to storage [1]. Among the proposed solutions for CO₂ conversion and utilization, dry reforming of methane

(DRM, Eq. (1)) for synthesis gas (syngas) production emerges as a promising technology compared to the industrially applied methane reforming technologies, e.g., steam reforming and partial oxidation, due to the utilization of two GHG gases CH₄ and CO₂. DRM could also be more attractive than steam reforming because it produces H₂/CO ratio that is close to unity, which is favored by the subsequent Fischer-Tropsch processes [2,3].

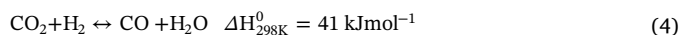
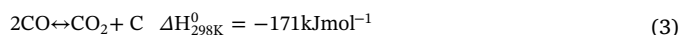


Group VIII metals are the most active catalyst materials for DRM, among which, the nickel (Ni) based catalysts are promising for potential commercialization, due to its high activity and relatively low cost. However, Ni-based catalysts present low stability due to their tendency towards sintering or coke formation at DRM conditions. Coke formation occurs mainly through two side reactions, namely methane decomposition (Eq. (2)) and Boudouard reaction (Eq. (3)). DRM process is also influenced by the simultaneous occurrence of the reverse water gas shift reaction (RWGS, Eq. (4)), which results in an increased CO₂ conversion and consequently, a syngas ratio less than unity.



* Corresponding author.

E-mail address: Zhixin.yu@uis.no (Z. Yu).<https://doi.org/10.1016/j.jcou.2017.12.018>Received 13 October 2017; Received in revised form 23 December 2017; Accepted 31 December 2017
2212-9820/ © 2017 Elsevier Ltd. All rights reserved.



Both support (*i.e.*, metal oxide) and promoter could be effective for improving the resistance against coke deposition for the Ni-based catalysts. Proper selection of supports such as Al₂O₃, MgO, SiO₂ or their combination, enhances the CO₂ adsorption and promotes carbon gasification, resulting in less deposited coke [4,5]. Strong metal-support interactions (SMSI) between the metal particles and the support are suggested to account for the retention of small Ni particle size which improves particle stability against sintering and inhibits the growth of carbon whiskers [6]. Xu et al. [7] reported that the structure of the Ni active phases strongly depends on the interactions of the metal and the support. It was shown that addition of La₂O₃ or MgO as γ -Al₂O₃ modifiers, resulted in Ni species in a different “bound-state”, *e.g.*, NiAl₂O₄ spinel, which was beneficial for the performance of the catalyst. However, the same study showed that “free state” NiO was formed when the supported Ni catalysts (Ni/ α -Al₂O₃, Ni/SiO₂, or Ni/ γ -Al₂O₃) were promoted by K₂O and Li₂O. The formation of free Ni species resulted in significant deactivation that was attributed to weak SMSI effect.

Despite all the efforts to prepare highly active, selective and stable Ni-based catalysts, studies show that catalyst deactivation remains a significant challenge. Several researchers have reported that hydroxalcalite (HT) derived Ni catalysts showed good performance for DRM in a broad range of reaction conditions including low temperatures, *i.e.*, 500 °C [8,9]. HTs, or layered double hydroxides (LDH), consist of positively charged two-dimensional sheets of mixed hydroxides, with water and exchangeable charge-compensating anions placed between the sheets, forming brucite crystallographic structure [10]. The HTs have the general formula [M_{1-x}²⁺M_x³⁺(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·mH₂O where M²⁺ and M³⁺ are the divalent and trivalent metal cations, respectively. *x* is the layer charge density, equal to M³⁺/(M²⁺ + M³⁺) and usually varies in a narrow range of 0.20–0.33 [11–13]. Aⁿ⁻ is the exchangeable interlayer anion for charge balance, and *m* is the hydration degree. The beneficial effect of HT-derived catalysts on DRM originates from their unique physicochemical properties, such as high surface area, strong basicity, the formation of homogeneously mixed oxides after calcination, and the possibility of intermix different metal species into their layers by ion exchange.

Several groups have realized that the M²⁺/M³⁺ ratio has a significant influence on the properties of Ni-Mg-Al HT catalysts. However, there is no consensus regarding the optimum M²⁺/M³⁺ ratio for DRM applications [12,14]. It is agreed that while only Ni is active in DRM, Mg content can influence the overall basicity, which is crucial for enhanced stability against coke formation [15,16]. Perez-Lopez et al. [17] studied the effect of Ni-Mg-Al composition on catalytic performance for DRM using different M²⁺/M³⁺ and different Ni/Mg ratios. They showed that the activity was influenced more by the M²⁺/M³⁺ ratio than the Ni/Mg ratio. The best catalytic performance was obtained for catalysts with M²⁺/M³⁺ = 2 and Ni/Mg in the range of 1–5. They concluded that the catalytic performance was simultaneously influenced by these parameters through Ni crystal size and the obtained surface acid-basicity. Zhu et al. [15] compared the catalytic activity of 8Ni-Mg-Al HT-derived catalysts at 800 °C with Mg/Al ratios from 5/1 to 1/5. The Ni-Mg₁-Al₁ catalyst exhibited the best activity and stability, ascribed to the formation of pure HT precursors. Among the other catalysts, it is evident that higher Mg/Al ratios provided better activity, indicating that the magnesium oxide also plays a key role in the DRM reaction. They concluded that there are two factors which enhance the activity: the first is the formation of HT precursor, and the second is high Mg/Al ratio. These factors are related to the stabilization of Ni particles during DRM at high temperatures.

It is accepted that Ni loading influences the catalytic activity, whereas there is no agreement in the literature concerning the optimal

Ni loading. Dudder et al. [18] studied the catalytic activity of Ni-Mg-Al HT-derived catalysts with different Ni loadings in the range of 0–50 mol % at temperatures of 800 and 900 °C. As expected, the catalyst with Ni content of 50 mol% showed the highest CH₄ conversion, attributed to the higher amount of reduced active species. González et al. [19] studied the influence of Ni loadings of Ni-Mg-Al HT catalysts for DRM at 800 °C. Unexpectedly, activity and stability followed the order of 15Ni > 19Ni > 4Ni, which was explained by the relatively lower reduction degree of the 19Ni catalyst, as revealed in their TPR study. The lower reducibility of the 19Ni catalyst was ascribed to the NiO species that intermix with MgO and strongly interact with the support. Debek et al. [20] prepared Ni-Mg-Al catalysts with Ni loadings from 4 to 60 wt. %. Both CH₄ conversions and H₂/CO ratios were higher for the catalyst with high Ni loading, pointing to a strong influence of Ni content on the activation of H₂ producing reactions. It is proposed that increased Ni content results in increased Ni particle size, which promotes the simultaneous occurrence of methane decomposition. Dissimilar to CH₄ conversions, CO₂ conversions were not strongly depended on the Ni loading. The highest CO₂ conversion was attained by the catalyst with 19.6 wt.% Ni, which was ascribed to the highest total surface basicity.

From another perspective, biogas is composed of primarily CH₄ (55–75%) and CO₂ (25–45%), which could be generated from wastewater treatment, sewage or agricultural waste of organic substances [2,21]. Biogas is proposed to be converted to syngas by dry reforming reactions and can eliminate the need for CO₂ removal, which is normally done through the energy-intensive amine absorption process [22]. Therefore, biogas upgrading and utilization by DRM emerges as another attractive technological option. Several groups studied the direct conversion of biogas through the DRM process at a wide temperature range of 500–800 °C [5,23,24]. These studies presented a larger decrease in CH₄ conversions when an excess of CH₄ was applied, whereas the opposite effect was observed in excess of CO₂. That could indicate that the CH₄ concentration in the feed influences the occurrence of side reactions, particularly the direct methane decomposition, which affects the distribution of the obtained products and accounts for coke formation.

To the best of our knowledge, no study has reported a direct comparison between Ni catalysts prepared through HT precursors and by the conventional incipient wetness method for DRM. The main objective of this study is to demonstrate the advantage of the HT-derived Ni catalysts for DRM regarding catalytic activity and stability. In this work, we synthesized Ni-based catalysts with different loadings through two different methods, *i.e.*, HT precursors and incipient wetness impregnation. The catalysts were characterized thoroughly and studied in DRM over a wide temperature range and at a very high space velocity of 240,000 ml/(g_{cat}·h). Furthermore, we applied the best-performing catalysts, *i.e.*, 20Ni-Mg-Al HT in the direct biogas utilization processes with varying CO₂/CH₄ ratios, which showed promising performance under all conditions. Our results demonstrated that pure HT structure is essential for the preparation of Ni-based catalysts for DRM with high activity and stability.

2. Experimental

2.1. Catalyst preparation

A series of Ni(Mg)-Al catalysts were prepared by co-precipitation for HT-like materials and by conventional incipient wetness impregnation method. The denotations and the nominal compositions of the catalysts are summarized in Table 1. The HT materials were synthesized by a method modified from Bhattacharyya et al. [25]. For each preparation, stoichiometric quantities of Na₂CO₃ (Merck KGaA) and NaOH (Merck KGaA) were dissolved in 400 ml deionized H₂O. Another solution with calculated stoichiometric amounts of Ni(NO₃)₂·6H₂O (Sigma-Aldrich), Mg(NO₃)₂·6H₂O (Alfa Aesar) and Al(NO₃)₃·9H₂O (Merck KGaA) were dissolved in 350 ml water. The nitrate solution was added dropwise to

Download English Version:

<https://daneshyari.com/en/article/6528693>

Download Persian Version:

<https://daneshyari.com/article/6528693>

[Daneshyari.com](https://daneshyari.com)