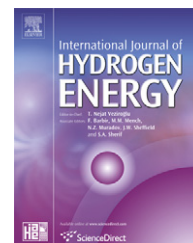


Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/he

Catalytic decomposition of CH₄ over NiO–Al₂O₃–SiO₂ catalysts: Influence of catalyst preparation conditions on the production of H₂

Jangam Ashok, Gangadhara Raju, Padigapati Shiva Reddy, Machiraju Subrahmanyam, Akula Venugopal*

Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Tarnaka, Hyderabad, Andhra Pradesh 500 607, India

ARTICLE INFO

Article history:

Received 24 April 2008

Received in revised form

9 June 2008

Accepted 10 June 2008

Available online 21 August 2008

Keywords:

H₂ production

NiO–Al₂O₃–SiO₂

CH₄ decomposition

Influence of pH

Hydrotalcite structure

Carbon nanofibres

ABSTRACT

This paper presents the synthesis and characterization of NiO–Al₂O₃–SiO₂ catalysts prepared by co-precipitation method and the catalytic activities estimated for the production of H₂ by CH₄ decomposition. The physico-chemical characteristics are evaluated by XRD analysis, TPR and O₂ pulse chemisorption, XPS, CHNS, SEM/EDAX, TEM and BET-surface areas of fresh and used forms of catalysts. XRD studies revealed the presence of hydrotalcite-like precursors in oven dried form and produced dispersed NiO species upon calcination in static air at 450 °C. The catalyst compositions for NiO–Al₂O₃–SiO₂ system are optimized based on various parameters such as varying Ni loadings, change in Al/Si ratios, precipitation at different pH and finally choice of precursors on CH₄ decomposition activities. Based on the results it is concluded that the composition of NiO–Al₂O₃–SiO₂ and preparation conditions played a key role in the decomposition of CH₄. The optimized compositions are established for the production of H₂ that can be utilized in fuel cell applications.

© 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen is an emerging alternative to conventional fuels to reduce CO_x emissions. It is considered as a clean energy source and its market demand is steadily increasing [1,2]. Conventionally, steam reforming, partial oxidation and autothermal reforming of natural gas are the major routes for the production of hydrogen. The main draw back in these methods is association of CO with the produced hydrogen. The hydrogen generated by these methods can be utilized in fuel cells only if the associated CO is completely eliminated [3–5]. However, this problem can be avoided by direct decomposition of methane in the absence of O₂/air environment.

Therefore, recently the catalytic decomposition of methane (CDM) has become a promising approach for many researchers [6–11]. From commercial and economical standpoint CDM is a useful technology since it produces both pure H₂ and carbon nanofibers. The former is a clean fuel, which can be utilized directly in fuel cell and the later is highly valuable graphitized carbon material [12]. The quality of produced carbon depends on the metal supported system, which is employed and also the value of produced carbon will compensate the cost of the catalyst.

Earlier studies on CDM using transition metals such as Fe, Co, Cu and Ni are reported in literature [13–19]. Amongst all, nickel-based catalysts are known to be more active at low

* Corresponding author. Tel.: +91 40 27193510; fax: +91 40 27160921.

E-mail address: akula@iict.res.in (A. Venugopal).

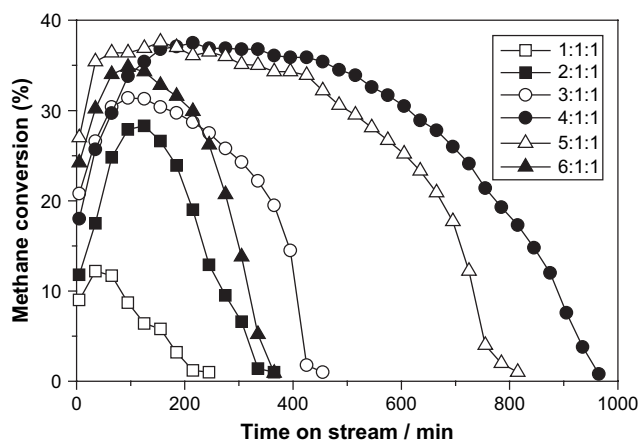


Fig. 1 - The time on stream (TOS) analysis over Ni loaded on Al/Si = 1, (NiO-Al₂O₃-SiO₂) catalysts prepared at pH = 9.0.

temperatures and provide a higher yield of H₂ per mass unit of the active component. For this reason, the nickel-based catalysts seem to be the most attractive for the industrial use. It appears that Ni particle size plays a major role in the CDM activity and life of the catalyst. It is reported that the nickel particles larger than 100 nm in size are incapable of producing carbon filaments [20]. Hence the process of hydrocarbon cracking does not need fine catalyst particles, but the use of supported catalysts is necessary [21]. Takenaka et al. reported the silica, titania and alumina as supports for Ni-based systems for CDM process [22]. Earlier we have reported the CDM activities over Ni/SiO₂ and Ni supported on various zeolite catalysts [13,15]. The use of silica-alumina mixed oxides as a support has received less attention. However, there are few reports on the utilization of Ni/Al₂O₃-SiO₂ system as a catalyst but in different applications [23,24]. In this study we have chosen Si-Al mixed oxides as a dispersing agent for Ni metal component and prepared a series of NiO-Al₂O₃-SiO₂ catalysts by co-precipitation method. The detailed study in this investigation includes parameters such as (1) influence of Ni loading, (2) Si/Al ratio, (3) effect of pH and finally (4) the influence of Ni

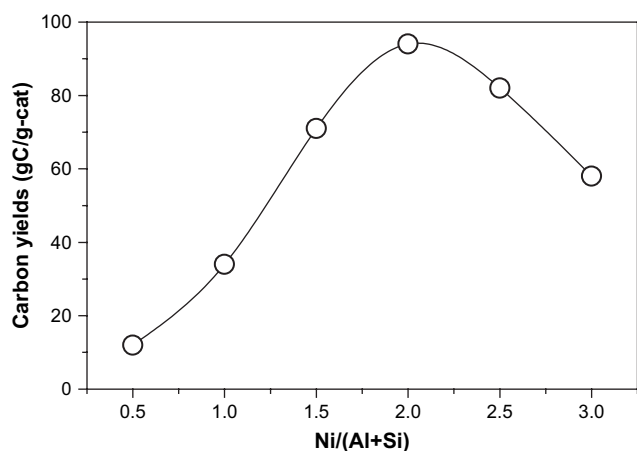


Fig. 2 - The carbon yields obtained after CDM reaction over Ni loadings over NiO-Al₂O₃-SiO₂ catalysts.

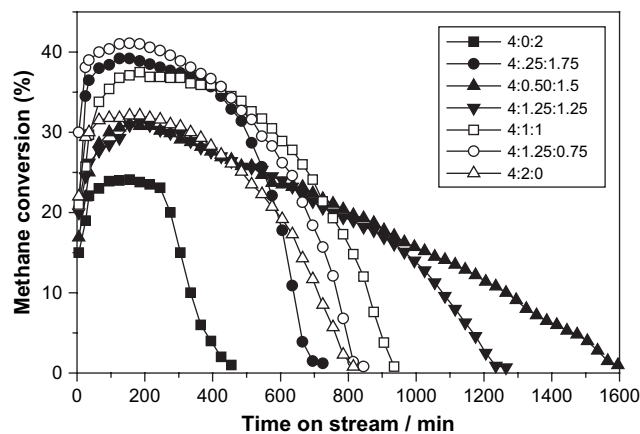


Fig. 3 - The time on stream (TOS) analysis over NiO-Al₂O₃-SiO₂ catalysts with constant Ni content and different Al/Si ratios.

precursor on CDM activity. This study also includes physico-chemical characteristics of the fresh and used forms of the catalysts by various techniques namely BET-SA, XRD, SEM/TEM, H₂-TPR, XPS and CHNS analyses. The CDM activities are measured at a temperature of 550 °C and ambient pressure.

2. Experimental

The catalysts used in this study were prepared by co-precipitation method. In a typical procedure, required amount of tetra ethyl ortho silicate as a source for silica is taken in a beaker having 500 ml distilled water and precipitated using required amount of 0.25 M HCl and stirred for 1 h. The silica gel precipitate is added simultaneously with the solution-A containing mixture of metal (Ni and Al) nitrates and solution-B containing base mixture of 1:1 volume of 2 M NaOH and 1 M Na₂CO₃ were added slowly while maintaining a constant pH ~ 9 throughout the addition. Thus, produced precipitate is thoroughly washed with distilled water until the pH comes down to the pH of distilled water and dried at 100 °C

Table 1 - The O₂ uptakes (pulse chemisorption), H₂ uptakes (TPR) and H₂ yields over NiO-Al₂O₃-SiO₂ (4:0.5:1.5) catalysts precipitated at various pH 7-11

pH	Total run time (h)	H ₂ yeilds ^a (mol/mol Ni)	H ₂ uptakes ^b (mmol/g-cat)	O ₂ uptakes ^c (μmol/g-cat)	S _{Ni} (m ² /g-Ni)
7	44	1729.5	10.6	747.8	49.28
8	35	1536.0	10.2	716.4	47.21
9	27	1451.4	11.9	687.6	45.31
10	20	1088.5	11.1	670.5	44.18
11	16	907.1	11.2	644.5	42.47

a Obtained form CDM activities.

b Calculated by TPR analysis.

c Calculated from O₂ pulse chemisorption.

Download English Version:

<https://daneshyari.com/en/article/1279222>

Download Persian Version:

<https://daneshyari.com/article/1279222>

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