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Decomposition of methane over alumina supported Fe and Ni–Fe bimetallic catalyst: Effect of preparation procedure and calcination temperature

A.S. Al-Fatesh [a,*], **A.H. Fakeeha** [a,*], **A.A. Ibrahim** [a], **W.U. Khan** [a], **H. Atia** [b], **R. Eckelt** [b], **K. Seshan** [c], **B. Chowdhury** [d]

[a] *Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia*
[b] *Leibniz Institute for Catalysis, Rostock, Germany*
[c] *University of Twente, PO Box 217, 7500 AE, Enschede, The Netherlands*
[d] *Department of Applied Chemistry, Indian School of Mines, Dhanbad, India*

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Abstract Catalytic decomposition of methane has been studied extensively as the production of hydrogen and formation of carbon nanotube is proven crucial from the scientific and technological point of view. In that context, variation of catalyst preparation procedure, calcination temperature and use of promoters could significantly alter the methane conversion, hydrogen yield and morphology of carbon nanotubes formed after the reaction. In this work, Ni promoted and unpromoted Fe/Al_2O_3 catalysts have been prepared by impregnation, sol–gel and co-precipitation method with calcination at two different temperatures. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, temperature programmed reduction (TPR) and thermogravimetric analysis (TGA) techniques. The catalytic activity was tested for methane decomposition reaction. The catalytic activity was high when calcined at 500 °C temperature irrespective of the preparation method. However while calcined at high temperature the catalyst prepared by impregnation method showed a high activity. It is found from XRD and TPR characterization that disordered iron oxides supported on alumina play an important role for dissociative chemisorptions of methane generating molecular hydrogen. The transmission electron microscope technique results of the spent catalysts showed the formation of carbon nanotube which is having length of 32–34 nm. The Fe nanoparticles are present on the tip of the carbon nanotube and nanotube grows by contraction–elongation mechanism. Among three different methodologies impregnation method was more effective to generate adequate active sites in the catalyst surface. The Ni promotion enhances the reducibility

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* Corresponding authors. Tel.: +966 1 4676847; fax: +966 1 4678770.
E-mail address: anishf@ksu.edu.sa (A.S. Al-Fatesh).
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of Fe/Al_2O_3 oxides showing a higher catalytic activity. The catalyst is stable up to six hours on stream as observed in the activity results.

1. Introduction

The process of dehydrogenation of hydrocarbons over metal surface has many applications. Among them production of soot and carbon nanotubes (CNT) is an important outcome as revealed in literature [1]. There is continuous interest in the activation and decomposition of CH4 due to its importance in hydrogen production. An increasing concern on the environmental effects of energy use, in the form of global warming, ozone layer depletion, and acid rains has led to intense research on various forms of clean energy. Hydrogen is widely considered to be one of the most promising alternative energy carriers and clean fuel. Among several factors high yields in fuel cells, clean combustion without emission of CO_2, NO_x or SO_x are important from the perspective of renewable energy [1]. Traditionally, dry (with CO_2) reforming and wet (with H_2O) reforming produce synthesis gas [2]. The CO in synthesis gas is converted into pure hydrogen by water–gas shift reaction, however this hydrogen still contains enough CO to poison the catalyst. Among several processes the common feature is the high temperature operation due to the stable C—H bond of CH_4 that makes it very difficult to decompose. In the case of direct thermal decomposition of methane the formation of CO free hydrogen, carbon in the form of carbon nanofibres and carbon nanotube makes this process more interesting because these materials have lots of scientific and technological potential [3].

Among several catalysts, Fe, Cu and Ni based catalysts are found as a promising catalyst for methane decomposition reaction [4]. Recently, both molecular simulation and experimental results suggest that the bimetallic catalysts manifest unique catalytic properties in CNF and CNT growth. The bimetallic interaction of Ni and Fe are well documented in the literature [5–9]. Typically, such catalysts are composed of Al_2O_3 or other oxides as support. Muradov has attempted the pyrolysis of methane to produce CO_2 free hydrogen using alumina supported Fe_2O_3 and NiO (10 wt%) at 850 °C [10,11]. It is proposed that before reaching the steady state methane decomposition the oxide phase reduced to catalytically active metal and carbide phases followed by depletion of these active phases. While reviewing several factors controlling the activity of iron catalyst; the catalyst preparation, calcination temperature, and presence of bi-metallic sites (Ni–Fe) are most important to be focussed. It is reported that 650 °C is the highest temperature for attaining maximum conversion irrespective of Ni loading, however the maximum value of conversion increases with the increase in Ni content [12].

The development of novel materials is a fundamental focal point of chemical research which has been nurtured well in the last decades. Generally, impregnation, co-precipitation and sol–gel methods are widely used for the preparation of different supported catalysts. Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening and agglomeration processes. Impregnation is a method to introduce appropriate active metal constitutions into the support. For supported catalyst, impregnation is widely used because of the simple method and easy dispersion of the active component on the surface of the supporter, which improves its utilization as a catalyst [13]. The sol–gel syntheses of inorganic nanoparticles have been studied extensively by several groups. Generally the hydrolysis of inorganic precursor and condensation of hydroxides are major steps to prepare the interconnected gelatinous material which after drying produces oxide nanoparticles [14]. Therefore the correlation between catalyst preparation method and the catalytic activity is always rewarding from fundamental and application point of view.

In this paper, we report the development of highly active unpromoted and nickel promoted Fe/Al_2O_3 catalyst for methane decomposition reaction. The catalysts are prepared by three different methods, e.g. impregnation, sol–gel and co-precipitation and calcined in two different temperatures i.e. at 500 °C and 800 °C temperatures. The catalysts are being characterized by BET, XRD, TPR, TGA techniques and catalytic activities were tested in the fixed-bed reactor. The spent catalysts have been characterized by TEM, XRD and TGA techniques. An attempt was taken to correlate the catalytic activity with the catalyst characterization results which might be useful to design efficient catalyst for methane decomposition reaction.

2. Materials and methods

2.1. Catalyst preparation

Analytical grades of iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$; 98% pure purchased from Loba chemie®], nickel nitrate [$Ni(NO_3)_3 \cdot 6H_2O$; 97% pure purchased from BDH Chemicals®], aluminium nitrate [$Al(NO_3)_3 \cdot 6H_2O$; 97% pure purchased from BDH Chemicals®] and alumina [SA-6175; purchased from Norton®] were employed without further purification. The catalysts containing different loadings of Fe and Ni were prepared using the following three methods:

2.1.1. Impregnation method (Imp)

The wet-impregnation method was used to prepare the catalysts and the total Fe loading with all catalysts was fixed at 20 wt% with respect to Al_2O_3 support. In a typical wet-impregnation process, the solution having a stoichiometric amount of [$Fe(NO_3)_2 \cdot 9H_2O$] was prepared using double distilled water. Afterwards respective supports were added to the solution with constant stirring at 85 °C. Then catalysts were dried at 120 °C for about 13 h, followed by calcination at 500 °C or 800 °C in atmospheric air for 3 h. To prepare 5 and 10 wt% Ni promoted Fe/Al_2O_3 catalyst, the co-impregnation of nitrate salts of the Fe and Ni with Al_2O_3 support was taken and the same procedure as described above was adapted.

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