Fe Supported Alumina Catalyst for Methane Decomposition: Effect of Co Coupling

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Abstract

In recent years hydrogen production received enormous attention, since it is an environmentally friendly, energy source. The aim of this research was to examine the hydrogen production with the help of methane's catalytic decomposition. 30% Fe coupled with different % of Co over alumina support, were examined by catalytic decomposition of methane for the production of hydrogen. The catalysts were prepared by impregnation method. The catalytic activity results revealed that the catalysts, coupled 15% Co gave the highest conversion of 72.5% as depicted by the three hour time on stream profile. The fresh and spent catalysts were characterized using different techniques such as BET, H_2-TPR, and XRD.

Keywords: Al_2O_3, Carbon Nanotubes, Co, Fe, Hydrogen, Methane

Introduction

Nowadays, hydrogen is regarded as ideal fuel that can replace the fossil, particularly when it is produced without carbon oxides. Hydrogen can easily be used not only directly as a clean and valuable fuel for heating, industrial processes and automobile, but also as a storable energy carrier as it can be transported economically as well as efficiently over extensive distances. Hence, hydrogen is being looked upon as an ideal energy carrier. Hydrogen production processes are many, for instance, steam, CO_2 reforming of methane, reforming of biomass, partial oxidation of natural gas, coal gasification and water photolysis [1–7]. The main disadvantage of these processes is the combination of CO and CO_2 gases with H_2 gas production [9]. Thus, it is necessary to perform the separation of carbon oxides to avoid the rapid catalyst deactivation due to the use of impure hydrogen and therefore the cost of hydrogen

production rises [10]. Consequently, hydrogen formation via catalytic decomposition of methane (CDM) was found as a potential process for COx-free hydrogen production [11,12]. Furthermore, the CDM process is associated with the coproduction of valuable nano carbon materials such as multi-walled carbon nanotubes, which possess superb properties that rends them useful for a variety of applications [13]. Conversion of methane depends upon the catalyst matrix which comprises the active material and the support [14]. Transition metals of Group VIII such as Ni, Co and Fe have been widely employed in CDM at moderate conditions [15,16].. Pradhan et al[17] have utilized Fenton Chemistry to degrade PNP using Fe^{+2}/H_2O_2 along with HC to great effect, achieving maximum PNP removal of 63.2%. The following work attempts to build upon this synergism between HC and H_2O_2 to achieve higher PNP degradation extents.

Experimental

Catalyst Performance Evaluation

Catalytic methane decomposition experiments over Fe based catalysts were performed at atmospheric pressure within the vertical stainless steel fixed-bed tubular (9.1 mm i.d. and 30 cm long) micro-reactor (PID Eng & Tech micro activity reference). 30% Fe/Al_2O_3 e was coupled with various loadings of cobalt (0%, 6%, 15% and 30%).The reaction setup used in this study was shown in Figure 1. The setup comprised three major segments: feed gas delivery, catalytic reactor, and products analysis section. The feed section contained two gas cylinders of CH_4 and N_2. All gases were of high purity and purchased from local suppliers. Reactant gases coming from the regulators were passed through in-line filters, and then introduced to the mass flow controllers (MFC). The gases after mixing are fed to the reaction section. Online samples of the feed gas mixture were directed through a sampling valve to the gas chromatograph (GC) for analysis.
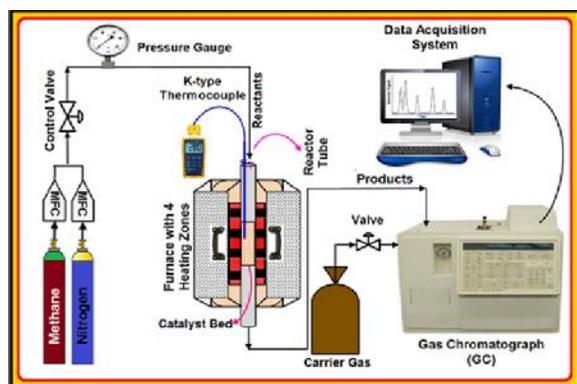

Fig. 1 Schematic Diagram of Experimental Setup

A typical activity test was conducted over a fixed mass (0.3 grams) of catalyst, and it was placed over a quartz wool bed. In order to monitor the actual temperature in the reactor, a K-type stainless steel sheathed thermocouple was placed axially at the center of the catalyst bed. After loading the catalyst, a constant flow of N_2 (20 ml/min) was introduced to the reactor, to purge the moisture, air and other gases from the reactor. Before carrying out activity tests, the catalysts were exposed to reduction treatment under a continuous flow of H_2 (40 ml/min) at 500 °C for 90 min. After reduction, the system was again flushed with N2 about 20 min to flush out any physisorbed and residual hydrogen from the reactor. Then, the temperature of the reactor was increased to the desirable temperature of the reaction (700 °C) in the presence of N_2.

Once the desired temperature was achieved, a feed mixture of pure methane and N_2 gas was fed into the reactor to accomplish the methane decomposition. In a typical test, the volume ratio of the feed gas mixture, i.e., methane/nitrogen was 1.5/1; whereas, the accumulative flow rate was found to be 25 ml/minute, having the space velocity of almost 5000 ml/h.gcat. The composition of the outlet gas was tested online with the help of gas chromatography (Shimadzu GC-2014). It was embedded with thermal conductivity detector using the PP-Q column. Afterwards, the reactor was cooled to room temperature. Subsequently, the cooled catalyst was taken for characterization.

CH_4 Conversion was calculated by using the following formulae:

$$CH_4 \text{ Conversion (\%)} = \frac{CH_{4\,in} - CH_{4\,out}}{CH_{4\,in}} \times 100$$

Catalyst Preparation

Analytical grades of Iron and cobalt nitrates and high activity gamma alumina were employed for the preparation of catalysts using the impregnation methods. In this the active metal precursor i.e. Fe and Co nitrates were added in distilled water and subsequently the alumina support. The mixture was heated at 80°C for 3 hr under constant stirring to impregnate the active metal over supports. After that impregnated catalysts were placed in the furnace at the temperature of 120°C overnight. It was then followed by the calcination at 450°C for 3h.

Results and Discussion

In this work, investigation of catalytic decomposition of methane to produce hydrogen and carbon was conducted at 700°C reaction temperature using iron based supported catalysts on alumina. The active metal was coupled with different loadings of cobalt. Pure methane and nitrogen were fed to the reactor. The inert gas N_2 constituted 10% of the feed. No appreciable amount of methane decomposed during the test of feed in the absence of catalysts under the similar experimental conditions of temperature and therefore, no hydrogen was detected by gas chromatography. Catalyst activities toward hydrogen production and stability tests and their corresponding characterization results were presented. The textural properties of the catalysts have been extracted from the N_2 adsorption–desorption isotherms. Analysis of the isotherms of the prepared catalysts (Fig.2) revealed hysteresis loops of slightly different shaped; however, the observed adsorption-desorption isotherms were similar to type IV. The hysteresis loops were of type H_2 shaped. It was also clear that the amount N_2 adsorption-desorption increased with the increase of the relative pressure. When the 30% Fe/Al was coupled with 6% and 15% Co the amount N_2 adsorption-desorption decreased but it increased when 30% Co. This was consistent with relative changes of the textural properties of the catalysts and hence the variation of the surface area.
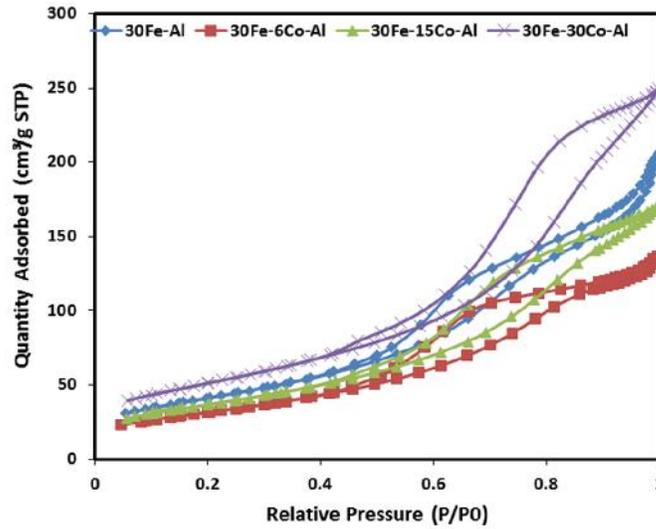
Fig.1 N_2 Adsorption-Desorption Isotherms for Fresh 30Fe-xCo/ Al Catalyst Series for Different Loading of Cobalt

To understand the basis of the enhancement in catalytic activity, H_2-TPR was performed. Fig. 3 exhibited the H_2-TPR profile for alumina supported iron catalyst coupled with loadings of cobalt. TPR patterns for different cobalt loading catalysts are fairly similar to each other specifying that catalysts had undergone similar reduction behavior. The response of cobalt loadings and 30% Fe/Al_2O_3 temperature scan using hydrogen as reducing agent provides three peaks in the TPR profiles. Indeed, this is a common feature of Fe based catalyst [17]. Their signals appear around 272-462, 409-745, 760-902°C with peak maximum centered at 385,

575 and 843°C respectively. These regions of temperature obviously identify that catalytic methane decomposition follows three mechanisms that are predominant at different temperatures. The first peak is attributed to the transformations of FeOOH Fe_2O_3 while the second peak is ascribed to the reduction of Fe_2O_3 Fe_3O_4, whereas the third peak denotes the transformation of Fe_3O_4 Fe [18]. The increment in the cobalt loading from 6% to 15%, shifted the reduction peaks to higher temperatures. This could be due to the variation of the extent of metal to support interactions in these catalysts.
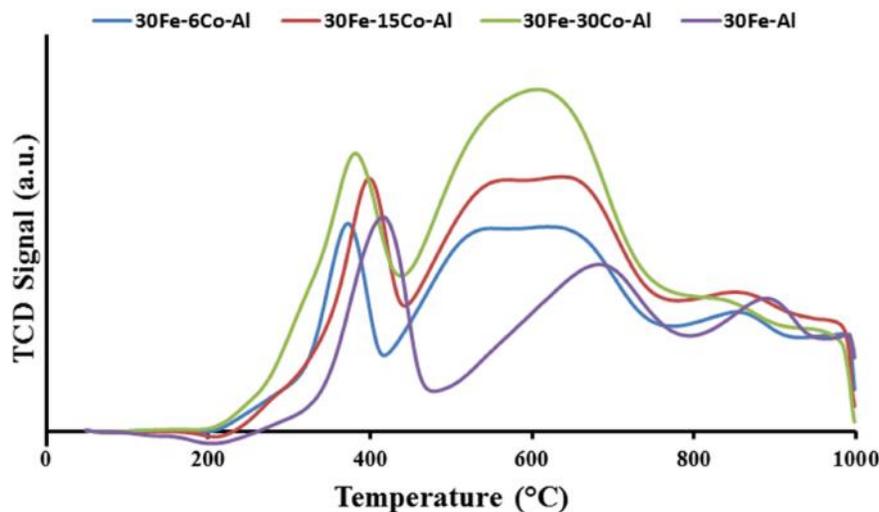

Fig.3 H_2 -TPR Patterns for Fresh 30 Fe-Al Catalysts Series for Different Cobalt Loadings.

The results of 30% Fe /Al catalysts in terms of CH_4 conversion of different Co loadings (0%, 6%, 15% & 30%) were presented in Fig. 4. From the obtained results, it was apparent that the Co loading had fairly impact on their catalytic performance. It was obvious from Fig. 4 that the activity of CH_4 increased with the increment in of the Co loading up to

15%. However, further increment in loading caused reduction in CH_4 conversion. For instance, for 30% Co had shown 63.2% initial methane conversion; while, after three hours, the same catalyst had shown 70.6%. The 15% Co catalyst has given better trends of CH_4 activity, since it varied from 64.1% to 72.5% with the same time span.
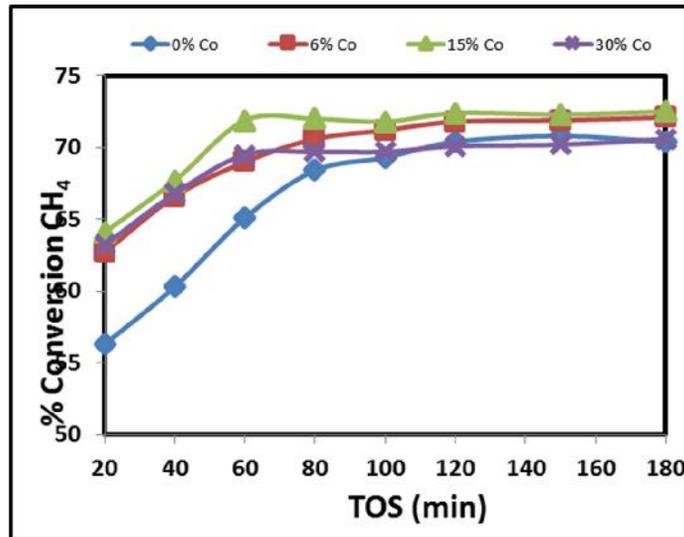

Fig.4 Variations of Hydrogen Conversion for Three Hours' Time on Stream of 30% Fe- xCo/Al₂O₃   Catalyst Activated at 500 °C
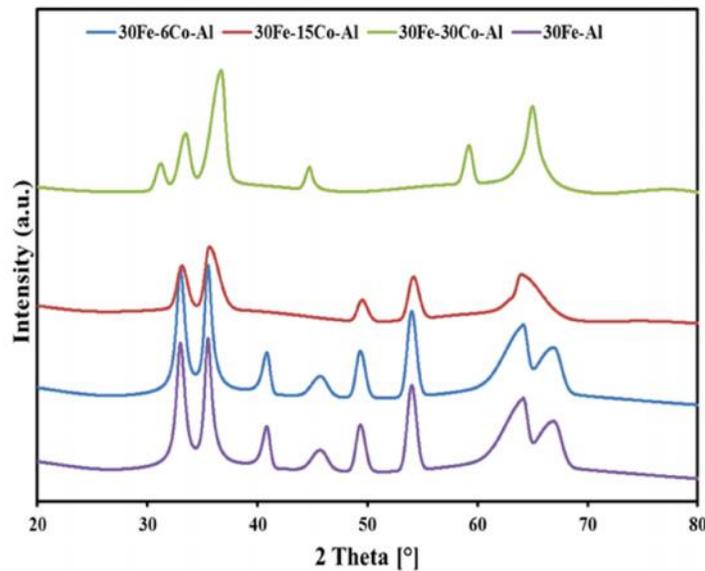

Fig. 5 XRD Patterns in 30Fe-Al Catalyst Series of Different Co Loadings

Figure 5 presented the XRD patterns in 30% Fe alumina supported catalyst series of different Co loadings. It is apparent from XRD diffractograms that the catalysts had shown crystallinity behavior, since obvious reflections were observed in XRD profiles. The intense diffraction lines were observed at $2\theta = 32.8°, 35.4°, 40.6°, 49.1°, 53.8°, 63.7°$ and

$2\theta = 66.1°$, correspond to Fe_2O_3 hematite (JCPDS: 01-084-0309). The coupling of 6% Co did not change the pattern at all while the higher loadings 15% Co and 30% Co had less number of peaks which modified the interaction between active metals and the support. This was also reflected in the enhancement of conversion for 15% Co.

Conclusion

Catalytic thermal decomposition of methane to COx-free hydrogen and carbon nanomaterials was studied over 30% Fe catalysts supported on /Al_2O_3. The effect of Co coupling with 30% Fe/Al, ranging from 0 to 30% Co loading, over impregnated catalysts was investigated. The activity results revealed that the 15% Co loading was relatively better than other Co loadings. It was found that 15% Co catalyst has given better trends of CH_4 activity. The methane conversion values varied from 64.1% to 72.5% during the three hours time on stream.

Acknowledgements

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