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Mass production of CNTs and COx-free hydrogen in fluidized bed reactor by catalytic decomposition of methane using nickel-based Cu-Zn promoted alumina supported catalyst.

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Highlights

- Direct decomposition of methane can be a replacement process for a commercially available steam reforming process.
- More than 90% initial methane conversion was achieved in fluidized bed reactor.
- Produced carbon is in the form of multiwalled bamboo shaped CNTs with high L/D ratio.
- Continuous CNT separation process can be developed by using ultrasonication.

1. Introduction

Energy is the most prominent need of today's world and to develop sustainable and reliable sources of energy is one of the major challenges. Due to increase in global population, the demand for cleaner sources of energy i.e. sources with minimum negative impact on the environment is continuously increasing. The energy resources like bio, solar and wind might be considered as a replacement for the fossil fuels but their technology is not yet fully developed enough to act as a major source of energy and hence, they are highly expensive for large-scale applications. The current research has now been focused on the development of energy sources which lead to a reduction in fossil fuel consumption, have the promising renewable technology and create less or no negative issues for the environment. The technology that needs to be developed aims at giving no GHG emissions or capturing them if they occur.

Hydrogen energy seems to be the most appropriate solution for the energy issue in today's world. This is due to lesser negative impacts on the environment and also high energy potential. Currently, hydrogen is mainly used in oil refineries, methanol and ammonia production most of which is being fulfilled through the Stream reforming process (SMR). This process produces approximately 13.7 kg of CO_2 per kg of H_2 in the gas stream and thus product has to be purified to remove COx.

An alternate way to produce hydrogen is through thermo-catalytic decomposition (TCD) of methane gas in which hydrogen and carbon are the only products. The energy input requirements per mole of methane, for TCD process, is appreciably less than that of SMR (75.6 and 165 kJ/mol CH_4, respectively).The carbon can be produced in the form of valuable by-products like CNTs. The present study aims at investigation on TCD of methane in a fixed bed as well as fluidized bed reactor. Significantly high amount of hydrogen and carbon nanotubes were produced over the selective nickel-based catalyst.

At the industrial scale, fixed bed reactor is very difficult to handle due to the high rate of cocking and deactivation of the catalyst. Fluidized Bed Reactor (FBR) with regeneration unit is employed to overcome the difficulties of a fixed bed reactor. In the regenerator unit, CNTs are separated from the catalyst by the ultra-sonication method and the catalyst is regenerated for the reaction. Efforts are being made to make the separation process continuous.

2. Methods

A Copper-Zinc promoted and alumina supported Nickel based catalyst is prepared by a wet impregnation process. It was characterized by TPR, XRD, BET, TGA, SEM and TEM analysis. Thermal mass flow controllers were used to provide an accurate flow rate of the gas in the FBR. Fresh catalyst was in-situ

reduced in Hydrogen stream before the reaction in a 12 mm ID FBR. The exit gas was analyzed by using calibrated Gas Chromatograph. After the reaction, obtained CNTs was characterized by FE-SEM, TEM, TGA and Raman Spectroscopy to find out their ID, OD, length, purity and morphology. To study the hydrodynamic behaviour of the catalyst, a transparent acrylic tube with the same ID was used. The hydrodynamic study involves fluidization behaviour of different sized catalyst particles, experimental measurement of minimum fluidization velocity and fluidization behaviour of spent catalyst particles.

3. Results and discussion

In FBR, at optimum temperature condition, more than 90% initial methane conversion was achieved (Figure 1a). Produced carbon byproduct is in the form of bamboo shaped carbon nanotubes (Figure 1b). Hydrodynamic behaviour of the catalyst is a crucial parameter in this process. As reaction proceeds, continuous carbon deposition on the catalyst may lead to change in its hydrodynamic behaviour and finally hampering the methane conversion. According to Geldart classification, Geldart A and B are ideal for fluidization while Geldart C particles show cohesive nature and not used in the reactions. Here, the catalyst particle changes its behaviour from Geldart A/B to Geldart C. So, regeneration is required by separating the CNTs.

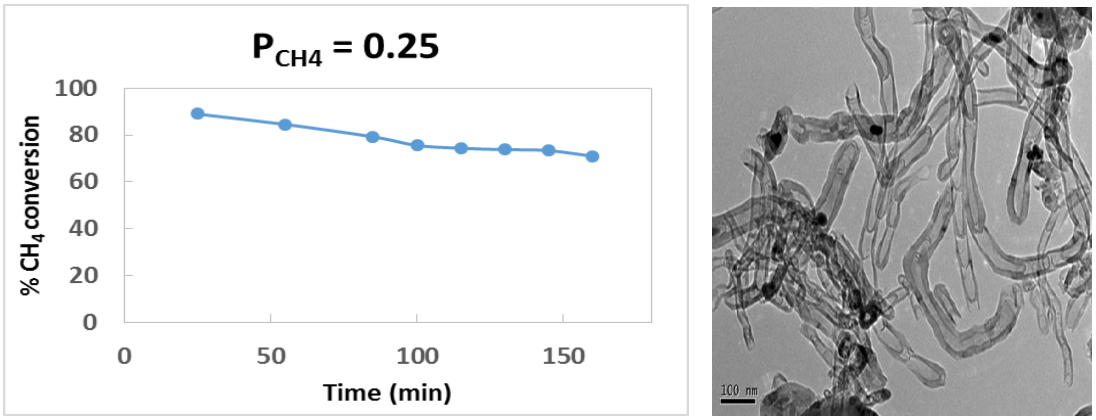

Figure 1. (a) Methane conversion with time on stream, P_{CH4} = 0.25, (b) Transmission Electron Microscopy image of produced bamboo shaped CNTs.

4. Conclusions

More than 90% initial methane conversion was achieved in the Fluidized Bed Reactor over a selected catalyst and produced carbon is in the form of Bamboo shaped multi-walled nanotubes (Diameter: 20-100 nm, Length: 20 microns). The process is developed for the continuous separation of CNTs from the spent catalyst by using ultrasonication. Thus, TCD may potentially serve as a link between present-day hydrocarbon reforming technologies due to zero CO_2 emission and non-fossil based hydrogen production technologies of the future.

References

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"Fluidized bed reactor", "Methane Decomposition", "Hydrogen", "Carbon nanotubes"