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REVIEW

Influence of nanocatalyst on oxidative coupling, steam and dry reforming of methane: A short review

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Abstract The influence of nanocatalyst on three main reactions for natural gas conversion such as steam reforming, dry reforming and oxidative coupling of methane has been reviewed with an emphasis on the literatures' reports and results. Although literatures' experimental results showed that the conversion of methane over the nanocatalysts was higher than that obtained from the ordinary catalysts, there was no correlation between the conversion of methane and the average sizes of the nanoparticles. The results of some nanocatalyst are also compared to ordinary catalysts in the literature which shows the improved influence of nanoscale catalyst performance on methane conversion.

Contents

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1. Introduction

Although methane is an excellent raw material for the production of fuels and chemicals, the main use is as fuel for power generation and for domestic and industrial uses. Large amounts of methane are found in regions that are located far away from industrial complexes and often methane is found off shore. This means its transportation is uneconomical or even impossible. Therefore, parts of the methane obtained, is re-injected, flared or vented at the moment, which is waste of hydrocarbon resource (Farsi et al., 2010; Lunsford, 2000).

On the other hand, both methane and CO_2 are greenhouse gases responsible for global warming and more strict regulations about letting out or flaring are expected in the future (Lunsford, 2000). These transportation and environmental problems and the increasing oil price have led to world-wide efforts for converting methane into easy transportable value added products, such as ethylene, aromatics and liquid hydrocarbon fuels (Amenomiya, 1990; Ross et al., 1996). Methane can be converted into chemicals and fuels in two ways, either via synthesis gas or directly into C_2 hydrocarbons or methanol (Farsi et al., 2010; Lunsford, 2000; Amenomiya, 1990; Ross et al., 1996). For instance, concerning global warning issues both methane and CO_2 can convert greenhouse gases into synthesis gas by dry reforming which is an important feedstock for many industrial processes (Hu, 2010; Xu and Wei et al., 2003; Xu et al., 2003).

Recently, nanocatalysts have attracted much attraction (Shu et al., 2007). In comparison with their micro-sized counterparts, nanocatalysts show higher activity, better selectivity, and outstanding stability because of their large specific surface area, high percentage of surface atoms and special crystal structures (Farsi et al., 2011a; Guo et al., 2000). Nanoparticles can be synthesized by several methods such as sol–gel processing, micro-emulsion, homogeneous precipitation, gas evaporation, laser vaporization, ionized beam deposition, freeze drying and etc (Farsi et al., 2011a; Guo et al., 2000; He et al., 2004a).

The objective of the present review is to provide a tangible account of methane conversion over nano scale catalysts by three reactions namely as steam reforming of methane, dry reforming of methane and oxidative coupling of methane. It is intended that this review provides necessary background information and general direction to those who are involved or about to be involved in this research field.

2. Steam reforming of methane (SRM)

SRM (e.g., $CH_4 + H_2O \leftrightarrow CO + 3H_2$) is a crucial reaction for the production of synthesis gas (Lunsford, 2000). The process is also important for the direct electrochemical conversion of hydrocarbons in solid oxide fuel cells (SOFCs). SOFCs are a very attractive option for electrical power generation in stationary, mobile, and portable applications (Oha et al., 2003; Wu et al., 2009). Commercial catalyst for this reaction is Ni supported on a metal oxide (Wu et al., 2009; Maluf and Assaf, 2009).

The process is run under a wide range of conditions with operating temperatures from approximately 500 to 950 °C (Zhou et al., 2008). One of the critical problems with long-term performance of Ni catalysts is the formation of carbon deposits on the catalyst surface, which evolve into carbon filaments, ultimately diminishing the performance of the catalyst (Wu et al., 2009; Maluf and Assaf, 2009; Zhou et al., 2008).Three main reactions take place as in the following equations:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (3)$$

Both the water–gas shift reaction (Eq. (2)) and reverse methanation (Eq. (3)) are always associated with catalytic SRM at elevated temperatures. Due to their overall high endothermic nature, these reactions are carried out at high temperature to achieve high conversions.

From thermodynamics and reaction engineering perspective, SRM is a highly endothermic process and therefore demands an efficient heat supply to the system. It is usually operated in a temperature range of 700–900 °C to achieve high conversions. It is a very energy consuming and capital-intensive process although the present technology approaches 90% of the maximum thermodynamic efficiency. Although this thermodynamic and kinetic limitation is the opposite of main challenge that occurs for exothermic reactions, further research can be directed to predict a novel strategy for methane activation to produce more substances that are valuable by solving both problems of endothermic and exothermic reactions that designate (Farsi et al., 2011b).

Commercial catalysts for the SRM reaction are Ni on supports, such as Al_2O_3, MgO, $MgAl_2O_4$ or their mixtures (Maluf and Assaf, 2009). Selection of a support material is an important issue as it has been evident that metal catalysts are not very active for the SRM when supported on inert oxides (Sadykov et al., 2009).

Watanabe et al. (2007) studied on nanosized Ni particles. They supported Nickel nanoparticulate catalysts on hollow Al_2O_3 ball by spraying a mixed solution of Nickel and aluminum nitrates. Their solution-spraying plasma (SSP) system is shown in Fig. 1. Their system consists of: (1) an ultrasonic mist generator for a catalyst source solution, (2) a plasma torch reactor and (3) a catalyst particle collector with a water shower supplied by a circulatory pump. They used a fixed bed quartz tubular reactor for SRM. They reported a 92% methane conversion for their nanocatalyst.

Roh et al. (2007) studied highly active and stable nano-sized $Ni/MgO–Al_2O_3$ catalyst. They concluded that the high activity and stability are due to beneficial effects of MgO such as enhanced steam adsorption, basic property, nanosized NiO, crystallite size and strong interaction between Ni and support.

Sadykov et al. (2009) studied on nanocomposite catalysts for SRM. Nanocomposite catalysts comprised of Ni particles embedded into the complex oxide matrix comprised of Y or Sc-stabilized Zr (YSZ, ScSZ) combined with doped