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Utilizing carbon dioxide as a regenerative agent in methane dry reforming to improve hydrogen production and catalyst activity and longevity

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ABSTRACT

The study evaluates the effect of forced periodic cycling between methane dry reforming and carbon regeneration using a gasifying agent, such as carbon dioxide. The activity of Ce-promoted Ni–Co/Al₂O₃ catalyst was evaluated in a methane dry reforming process using a fixed-bed reactor under steady-state and periodic operation. Forced cycling reactions (reforming and regeneration) were conducted by manipulating the reactor feed between methane dry reforming and catalyst gasification using CO₂ at cycle periods of 10, 20, and 30 min, and cycle splits of 0.8, 0.6, and 0.4. The physicochemical properties of fresh and spent catalysts were evaluated using several characterization techniques, such as the BET surface area, H₂-chemisorption, and XRD. The results confirmed that methane dry reforming under periodic cycling provides an opportunity to improve methane conversion and increase the catalyst activity and longevity because of the periodic interruption of coke deposition. In particular, methane conversion deteriorated from 68% to 37% under steady-state within five hours of reforming, whereas a modest decrease in methane conversion (from 68% to 63% for a cycle period of 10 min and cycle split 0.8) was observed under periodic operation conditions. The results of catalyst characterization also demonstrated that the on-line removal of carbon during CO₂ regeneration did not lead to any structural effect on the catalyst properties, and it absolutely restored the catalyst properties up to the values measured for the fresh catalyst.

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Introduction

Hydrogen is an attractive energy carrier and a vital feedstock for several major processes in the alternative energy generating sector and petrochemical sector. The utilization of hydrogen has several advantages in terms of reducing greenhouse gas emissions and dependence on fossil fuels [1].

There are a number of sources for producing hydrogen, which include both renewable sources, such as solar photovoltaics, biomass gasification, and non-renewable sources, such as hydrocarbons and coal [2]. The implementations of these processes are influenced by several factors, such as the availability of required feed, application size, production cost and capital cost [3]. Currently, the majority of the production of hydrogen is via hydrocarbon reforming, where

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approximately 50% of the global hydrogen is produced by steam reforming [2]. Therefore, hydrocarbon reforming is considered a primary pathway in the industry to produce hydrogen as an environmentally clean and strategic carrier of energy [4–7]. Recent reports revealed that fossil fuels will be consumed largely in the upcoming decades, causing a significant rise in carbon dioxide emission [8,9]. Therefore, greenhouse gas emission is considered a major challenge facing the energy sector. Consequently, the active use of greenhouse gases, such as methane and carbon dioxide, will have a very important environmental impact because these gases are not environmental friendly. Both carbon dioxide and methane are abundantly available, and they can be converted using a dry reforming process to synthesize gases (mixtures of H₂ and CO) [10]. Hydrocarbon reforming is also a preferred method to produce hydrogen at high purity for small energy technologies such as fuel cells [11]. Overall, the major processes involved in the conversion of hydrocarbons to synthetic gas include dry reforming, steam reforming and partial oxidation [12–14]. Each of these processes tend to have their own advantages and disadvantages based on criteria such as product composition, availability of reactants (CO₂, H₂O, O₂), purity, production scale and cost [15]. The steam reforming process is the most popular route for the production of hydrogen, particularly in both the refining and petrochemical processes [16]. However, the industrial production of synthetic gas using hydrocarbon steam reforming is accompanied by unwanted coke deposition on the catalyst. Coke deposition has distinct disadvantages, including the reduction of catalyst activity and longevity. Within industrial processes, carbon is removed using an excess steam-to-carbon ratio (generally greater than 3) to decrease the rate of coke deposition on the catalyst. Although this method is effective, it requires greater energy consumption as more steam is required than normal steam reforming requires. On the other hand, dry reforming is observed as a promising technology for synthetic gas production, as it offers certain distinct advantages such as follows:

- Depletion of unwanted greenhouses gases (carbon dioxide and methane);
- Gas separation is not required, thereby reducing cost and allowing simple utilization of methane with a high carbon dioxide content;
- Production of synthetic gas with a low hydrogen to carbon monoxide ratio for use in downstream processes such as GTL fuels [10].

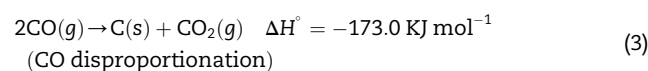
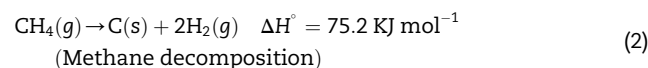
Consequently, dry reforming has received attention because of its industrial and environmental benefits. Hydrocarbon dry reforming has generated interest in the last decade as an alternative route to produce synthesis gas and as a method for recycling carbon dioxide. Recent studies have reported that fossil fuels will be used predominantly in the twenty-first century, causing a significant increase in carbon dioxide emission [8,9]. Thus, one of the largest challenges in the energy generation field at this point in time is to limit the total greenhouse gas emissions.

To develop the dry reforming process, it is necessary to probe the mechanism and identify the most important

challenges that must be accounted for in any efforts toward improving the process. In dry reforming, hydrocarbons, such as methane, react with carbon dioxide in the presence of Ni-based catalyst to produce a synthetic gas mixture at temperature between 700 and 1100 K. Chemically, this reaction can be represented as follows:



Deactivation of catalyst during methane dry reforming is a direct consequence of coke deposition on the catalyst surface [17]. The major reactions are as follows:



While higher temperatures and lower pressures favor methane decomposition, lower temperatures and higher pressures favor the carbon monoxide disproportionation reaction. As clearly observed in reactions (2) and (3), carbon deposition results from both methane decomposition and carbon monoxide disproportionation.

Coke deposition ultimately results in poor catalyst activity, selectivity, and longevity. Consequently, controlling carbon formation has become a top priority at the research level to improve the catalytic system. The two main techniques being implemented to control carbon deposition are based on minimizing coke formation and maximizing coke removal [18–21]. The bulk of the previous research on coke control has depended on developing a carbon resistant catalyst and on using ingenious reactor operation techniques. The development of catalysts with high activity to synthesize gas formation and high resistance to coke formation is being extensively researched [22–24]. It has been found that various catalysts based on nickel and cobalt promoted with low loading of noble metals favor high catalytic activity for dry reforming of methane. However, the higher costs and limited availability of noble metals has favored the utilization of non-precious catalysts such as Ni [25,26]. A bimetallic nickel–cobalt system has been used and compared to other metal-based options to improve carbon-related deactivation of the catalysts. Investigations of both nickel and cobalt as methane dry reforming catalysts have been extensive, but this has been limited by favoring of the deposition of coke [27]. Metal promoters have been introduced to reach the required activity, resistance to coke formation, and cost justification for the nickel–cobalt catalyst system. Recently, the successful use of ceria for dry methane reforming has been reported [9]. Ceria is a promising option given its high resistance to coke formation and its applicability to the nickel–cobalt system. Several studies have demonstrated that ceria-sponsored catalysts have better reforming reactivity and resistance to coke formation in comparison to traditional nickel-based catalysts [28–30]. The reported advantages stem from the redox characteristic of ceria. As dry reforming proceeds, gas solid reactions between various gaseous components (CH₄, CO₂, CO, H₂O, and H₂) and lattice oxygen (O_x) on the surface of ceria occur. The reactions between adsorbed methane and carbon

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