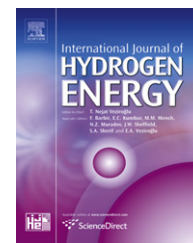


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Thermodynamic and experimental study of combined dry and steam reforming of methane on Ru/ ZrO₂-La₂O₃ catalyst at low temperature

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ABSTRACT

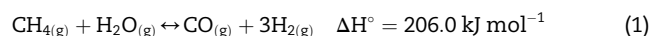
Analysis of the effect of adding small amounts of steam to the methane dry reforming feed on activity and products distribution was performed from thermodynamic equilibrium calculations of the system based on the Gibbs free energy minimization method. This analysis is supported by new insights from the direct experimental investigation of the influence of co-feeding with H₂O over a Ru/ZrO₂-La₂O₃ catalyst. Activity measurements were carried out in a fixed-bed reactor but using the operating conditions applicable in a Pd membrane reactor, that is, at maximum reaction temperature below 550 °C. Experimental results were in good agreement with thermodynamics predictions. It was observed that the addition of H₂O into the dry reforming feed strongly affects activity and products distribution. The co-feeding of steam resulted in increasing methane conversion and hydrogen yield but decreasing carbon dioxide conversion and carbon monoxide yield. At a given temperature, syngas composition (H₂/CO ratio) can be tuned by changing the amount of H₂O co-fed. Interestingly the stability of the Ru/ZrO₂-La₂O₃ catalyst was improved by adding steam to the dry reforming reactant mixtures.

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1. Introduction

Methane is the major component of natural gas and a very stable compound that is difficult to activate [1]. In general, methane is converted to useful products by two different routes: direct and indirect [2]. The direct route is a one-step process, in which, the natural gas reacts with oxygen to give the desired product directly. While, the indirect route is a two-step process whereby natural gas is first converted into synthesis gas (a mixture of H₂ and CO) and then

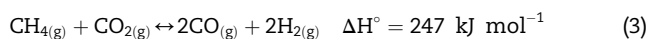
transformed into the required product. The conversion of methane into synthesis gas is usually carried out by the steam reforming process (SRM) according to Eq (1) [3], which is generally accompanied by the water–gas shift reaction (WGS) (Eq.(2)).



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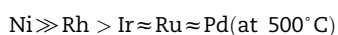
With the growing concerns about negative environmental impact of CO₂ (i.e. global warming) the dry reforming of methane (DRM) (Eq. (3)) is getting more attention as an alternative to SRM [4,5].



Also, the DRM process becomes advantageous compared to SRM since the lower H₂/CO ratios are preferable as feed for use in Fischer-Tropsch synthesis of long chain hydrocarbons (e.g. gasoline or diesel, etc), or oxygenated compound (e.g. alcohols, esters, etc) [6–9].

DRM is a highly endothermic process and requires severe operational temperatures (800–1000 °C) to reach high conversion levels in conventional fixed-bed reactors (CR). These severe operating conditions result in catalysts deactivation by coke deposition [10–12] mainly due to deep cracking of methane, which is thermodynamically favoured at high temperatures. This problem can be overcome either (i) by developing catalysts that minimize the coke formation, (ii) by adding steam [13–17] or oxygen [13,17–22] or (iii) by working at low temperature (<550 °C), as coke deposition via methane decomposition is thermodynamically limited under these conditions [23] although other coke formation reactions as Boudouard reaction might feasibly occur in this low temperature range. In this third case, the use of membrane fixed-bed reactors (MR) would then be required to reach higher conversions by continuously extracting H₂ [24–26].

Most of the reported research on DRM relates to Ni-based catalysts. However, Ni catalysts are prone to carbon deposition which causes its deactivation [11,12,27]. The catalysts based on noble metals are reported to be less sensitive to coking compared to the Ni-based catalyst for DRM [27,28]. According to Rostrup-Nielsen et al. [11], the amount of deposited carbon on the metal catalysts decreases in the following order:



Another factor affecting carbon deposition is the catalyst surface basicity. In particular, it has been demonstrated that carbon formation can be diminished or even suppressed when the metal is supported on a metal oxide carrier with Lewis basicity [11]. Thus, the selection of the support can greatly modify the catalytic properties of a given metal under DRM conditions and give rise to changes in the tendency towards sintering and resistance to carbon deposition [27].

When the DRM is carried out simultaneously with SRM (i) The carbon formation is reduced due to the oxidation of the carbon precursors species (partially hydrogenated CH_x species) [13,14,16] and (ii) a desirable H₂/CO ratio can be obtained conveniently via adjustment of the CH₄/H₂O ratio in the feed [13,14].

On the other hand, the preferential removal of one of the products with a membrane operating simultaneously with a catalyst would cause a shift in the reaction thermodynamic equilibrium [29]. Thus, the application of membrane technology to separate hydrogen from the reaction environment is expected to offer significant advantages in this transformation: a higher energetic efficiency, enhancement of methane conversion at lower operation temperatures

and simultaneous reaction and separation of hydrogen [30–32].

Thermodynamic studies about the syngas production from methane reforming reactions have been previously reported [14,21,33,34]. However, information relative to thermodynamic studies of the low temperature combined DRM-SRM (<600 °C) using small amounts of steam has not been reported.

The combination of DRM with SRM was evaluated over supported Ni catalysts at high temperatures [14–17]. To the best of our knowledge, no studies about the simultaneous dry and steam reforming of methane at low reaction temperatures (below 550 °C) have been carried out.

In the present contribution a thermodynamic analysis of the DRM and the combined DRM-SRM reactions at low temperatures has been carried out by means of the Gibbs free energy minimization method via ASPEN-HYSYS. Thermodynamic calculations were performed keeping constant the CH₄/CO₂ ratio (=1) and varying the steam proportion (small amount of H₂O were added to the feed, 1–5% vol.). This work studies the effect brought about by the addition of small amounts of H₂O to the DRM feed on activity and products distributions from a thermodynamic and experimental point of view. Experimental results obtained under the same operating conditions as those employed in the thermodynamic analysis were compared with thermodynamic calculations.

The low temperature combined DRM-SRM reaction was evaluated over a Ru/ZrO₂-La₂O₃ in a (CR). This catalyst was chosen due to its good performance in methane reforming reactions, as reported in [35,36]. With the aim of studying the catalysts stability (the evolution of CH₄ conversion with time-on-stream) as a function of the feed composition, we have worked under non-equilibrium conditions.

2. Materials and methods

2.1. Synthesis of catalysts

The supported Ru catalyst was prepared using a commercial support: ZrO₂ stabilized with La₂O₃ (7.0%) provided by MEL. Prior to metal loading the support was calcined in air at 500 °C for 4 h. After calcination the specific surface area of the support was 105 m²/g. Then the support was impregnated with Ru (4% wt) by means of the wet impregnation method using an aqueous solution of RuCl₃·H₂O (Sigma–Aldrich) precursor. After Ru impregnation the catalyst precursor was dried in air at 110 °C overnight. Sample was labelled as Ru/ZrO₂-La₂O₃.

2.2. Thermodynamic analysis

Gibbs free energy is the most commonly used function to identify the equilibrium state [37]. A minimization of total Gibbs free energy is a suitable method to calculate the equilibrium compositions of any reacting system. This is based on the fact that the system is thermodynamically favoured when its total Gibbs free energy, expressed as a function of temperature, pressure and component concentrations, is at its minimum value [38,39].

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