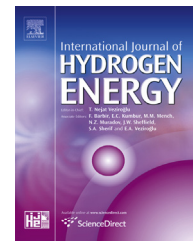


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Influence of the operating parameters over dry reforming of methane to syngas

A. Serrano-Lotina*, L. Daza

Instituto de Catálisis y Petroleoquímica (CSIC), C/ Marie Curie 2 L10, Campus de Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

The influence of operating parameters over dry reforming of methane reaction was evaluated using a Ni-based catalyst obtained after calcination of a hydrotalcite-like precursor. The studied variables were mass to flow ratio (W/F), reaction temperature and CO₂/CH₄ ratio. Maximum methane and carbon dioxide conversions were achieved at W/F ratios above 0.21 g h L⁻¹. The higher the W/F ratio was, the lower amount of water was formed, which led to a higher H₂/CO ratio. The increase in reaction temperature produced an increase in conversions. Water concentration in the outlet stream showed a maximum at 600 °C. At this temperature, reverse water–gas-shift reaction (RWGS) was favoured because it is endothermic. However, steam reforming and carbon gasification were also favoured and they consumed great part of the water produced. CO₂/CH₄ ratios above 1 led to a higher CH₄ conversion but selectivity to hydrogen decreased because RWGS reaction was favoured. When CO₂/CH₄ was below unity, CH₄ conversion decreased but less amount of water was produced so a higher H₂ selectivity was achieved. The catalyst exhibited good stability over dry reforming of methane under all the tested conditions, which may be ascribed to its high basicity. This property improved CO₂ adsorption and then RWGS reaction and carbon gasification.

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1. Introduction

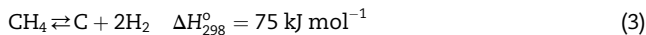
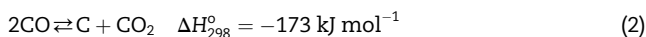
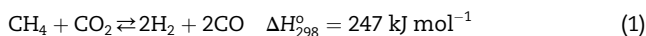
Dry reforming of methane has attracted considerable scientific interest in the past years, since it offers the possibility of simultaneous removal of two inexpensive and abundant carbon containing sources, which are also greenhouse gases. In addition, this technology becomes advantageous compared with steam reforming since (i) H₂/CO ratio is near one, which is suitable for further use in the production of oxygenated compounds and other liquid hydrocarbons [1]; (ii) the separation of CO₂, which is an energy intensive and a rather costly process, is not necessary.

However, there is still no large-scale application of CO₂ reforming of CH₄, due to the lack of efficient and stable catalysts. Therefore, great efforts have been focused on development of reforming catalysts. The major drawback of dry reforming of methane (1), which occurs at temperatures above 640 °C,¹ is the deactivation of the catalysts. This deactivation is mainly caused by deposition of inactive carbon, although metal oxidation or sintering may not be neglected. The origin of inactive carbon during reforming processes may be either carbon monoxide disproportionation (2) which is favoured at temperatures below 700 °C,¹ or methane decomposition (3) which takes place at temperatures above 557 °C¹ [2].

* Corresponding author. Tel.: +34 91 5854793; fax: +34 91 5854760.

E-mail address: asl@icp.csic.es (A. Serrano-Lotina).

¹ When operating at atmospheric pressure.



In order to minimize coke formation two approaches can be taken into account. The first one can be executed by controlling the reaction kinetically by using appropriate catalysts and supports [3–8]. The other alternative is working at high temperatures, high mass to flow ratios (W/F) or high CO_2/CH_4 ratios [5,9]. Many authors [2,10–12] have suggested an operation at CO_2/CH_4 ratios above 1 and temperatures above 800 °C to avoid regions where there is a thermodynamic potential for carbon formation. However, from an industrial standpoint, it may be desirable to work at lower temperatures and CO_2/CH_4 ratios near unity. Furthermore, some methane sources, such as biogas usually exhibits CO_2/CH_4 ratios below one.

Many studies about operating conditions over dry reforming of methane have been reported in literature [13–20]. However, different results have been shown, probably due to the participation of secondary reactions that are favoured in a greater or lesser extent depending on catalysts' properties.

The aim of this work is to study the influence of the operating conditions, (W/F ratio, reaction temperature and CO_2/CH_4 ratio) over the catalytic performance of a catalyst obtained from a hydrotalcite-like precursor, which has shown an excellent performance in dry reforming of methane reaction [21].

2. Experimental

2.1. Catalyst preparation

The catalyst was obtained after calcination at 750 °C of a hydrotalcite-like precursor, which was prepared by coprecipitation, according to a previously reported method [8,22]. The final measured Mg/Al molar ratio was 2.3 whereas Ni and La contents were 2.8 and 1.9%, respectively. The catalyst consists on a La-promoted mixed oxide with cubic structure where Ni^{2+} and Al^{3+} were inside the MgO lattice. From RMN ^{27}Al characterization, presence of tetrahedral aluminium was observed [23] what may indicate the presence of clusters of Mg–Al inverse spinel type, as has been proposed in the literature [24]. This catalyst showed basic properties and a BET area of $109 \text{ m}^2 \text{ g}^{-1}$.

The catalyst was reduced *in situ* at 650 °C with pure hydrogen during 1 h in order to only reduce segregated NiO what leads to a higher catalyst stability according to previous studies [25].

2.2. Catalytic tests

The evaluation of the catalyst was performed at atmospheric pressure in a tubular fixed-bed Ni-free steel reactor, placed inside a Microactivity Reference PID Eng&Tech equipment. Inner diameter of the reactor was 1.08 cm and the reactor length was 28 cm. Reaction products were analysed with an Agilent chromatograph 6890N connected in line, equipped

with a TCD detector and Chromosob 102 and Porapak P5 Q columns. CH_4 , N_2 , H_2 , and CO_2 gases were fed from Praxair gas bottles with a purity of 99.5 for CH_4 and 99.999% for the rest. Excessive pressure drop was avoided by choosing a catalyst particle size between 0.5 and 0.42 mm. Temperature was measured by a K-thermocouple inside the catalytic bed. Preliminary experiments were carried out to determined suitable conditions for which external mass transfer and internal pore mass transfer are not predominant [23]. The tests reported here were performed under such conditions. A blank test with an empty Ni-free steel reactor was also performed to ensure that no carbon formation was produced.

Three different tests were done in order to establish the influence of mass to flow ratio (W/F), reaction temperature and feeding composition, over CH_4 and CO_2 conversion and H_2/CO ratio. All the tests were performed at atmospheric pressure. Plotted results were average results for each condition.

W/F ratio was evaluated between 0.007 and 0.21 g h L^{-1} , working at 700 °C and a CO_2/CH_4 ratio of 1. This was achieved by using a fixed amount of the catalyst (0.25 g) and changing the flow rate of the feed in the range of 20–180 mL min^{-1} . Each flow rate was maintained for 2 h time-on stream. In the second experiment 0.25 g of the catalyst was tested between 450 and 800 °C, with step-wise increments of 50 °C, operating at 0.21 g h L^{-1} (flow rate = 20 mL min^{-1}) and a CO_2/CH_4 ratio of 1. Each temperature was maintained for 2 h time-on-stream. The test was performed decreasing the temperature, from 750 to 450 °C, in order to avoid the possible deactivation of the catalyst due to carbon deposition, which is favoured at low temperatures through CO disproportionation (2) [26]. The catalyst was again heated at 750 °C, showing equivalent conversion. Finally, this same catalyst was heated up to 800 °C. The highest temperature was tested at the end because it was higher than calcination temperature and catalyst structure could be modified. CO_2/CH_4 ratio was evaluated between 0.4 and 1.5 working at 0.21 g h L^{-1} and 700 °C. Each condition was kept for 2 h and no differences between analyses were observed. For the evaluation of CO_2/CH_4 ratio, three experiments were performed with 0.25 g of catalyst and the following CO_2/CH_4 ratio: (i) $\text{CO}_2/\text{CH}_4 = 0.4$, (ii) $\text{CO}_2/\text{CH}_4 = 0.7$, (iii) $1 < \text{CO}_2/\text{CH}_4 < 1.5$. The final condition in all the experiments was $\text{CO}_2/\text{CH}_4 = 1$. Expected conversions were achieved with the exception of experiment 1, where lower conversions were observed despite the catalyst had been stable at $\text{CO}_2/\text{CH}_4 = 0.4$. That is the reason for performing separate experiments.

The calculation of the equilibrium conversions were based on the assumption that only reforming reaction occurred without any side reactions.

3. Results and discussion

3.1. Influence of W/F ratio

Fig. 1 shows that CH_4 and CO_2 conversions approached to equilibrium conversion with an increase in W/F ratio, which agrees with other published results [18,20,27]. At low W/F ratio, contact time between reactants and catalyst is short, so

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