Catalysts for Hydrogen Production in Membrane Reformers

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Abstract

This paper reports on the research of catalysts for application in membrane reformers. Such reformers are operated at lower temperatures than conventional steam reformers and therefore customized catalysts are required, which are resistant to carbon formation and active at low temperatures. Noble metal based catalysts on various supports are screened for activity and stability under relevant conditions. As a result, ceria–zirconia promoted Rh catalysts are found to be highly active. Stability of these catalysts seems to strongly depend on the solid-solution character of the ceria–zirconia support: reduced CeO_x species are believed to encapsulate Rh particles and thus deactivate the catalyst. Still, many catalytic aspects remain unclear, illustrating the importance of extensive catalyst research for such reformer applications

Keywords: CO_2 capture, catalyst, membrane, steam reforming

Introduction

H_2-permeable membranes are an important technology for the CO_2-free production of electricity from fossil fuels via the so-called precombustion decarbonisation route. At ECN we are developing a membrane reactor for the production of hydrogen by catalytic steam reforming (SR) of methane:

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \qquad (1)$$

The produced H_2 permeates through the membrane, parallel to the reaction. Apart from the advantage of producing separate H_2 and CO_2-streams, the removal of hydrogen from the reaction zone also shifts the equilibrium of the reforming reaction to the product side. This makes that high conversions can be reached at relatively low temperatures. The final goal of this project is the development of a palladium membrane reactor.

In membrane reactors a customized catalyst is required for reforming of methane, which should be active at low temperatures and resistant to coke formation under the carbon-rich membrane reactor conditions. In addition, catalyst costs should not exceed Pd-membrane costs, which are in the order of 1000 €/m^2.

By means of an extensive catalyst screening program, a set of promising catalysts has been selected for further research on catalysts stability during membrane conditions. Among the catalysts screened, are noble metal catalysts on various supports, a reference nickel-based catalyst and two commercial catalysts. For two of these catalysts, the intrinsic kinetics will be determined to provide information for reactor design and optimization.

Catalysts in Membrane Reformers

In order to understand the possible problems relating to the catalyst in a membrane reformer (MR), we should first realize the principle discrepancies between reforming in a conventional reactor and reforming in a membrane reactor. In general, the following differences can be distinguished:

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- Membrane reactors operate at relatively low temperatures, i.e. 400–600°C in stead of 800–1000°C, mainly due to their limited thermal stability. Therefore, performing steam-methane reforming in a MR requires catalysts that are highly active at low temperatures.
- In a membrane reactor, the H_2 concentration in the reaction gas mixture is low compared to a conventional SR reactor. Consequently, an increased steam-to-carbon ratio is in principle be required to prevent carbon formation. However, Lægsgaard Jørgensen *et al.* [1] concluded that, based on thermodynamic calculations, a steam-to-carbon ratio (S/C) of 2.5 at 500°C and 7 bar would suffice to prevent carbon formation. During conventional SR, a S/C of around 3 is usually applied. This suggests that – in theory – the same S/C as applied for conventional SR can be applied for SR in a membrane reactor. The catalyst, however, should not be selective for carbon formation reactions. For instance, Ni-based catalysts could even cause carbon formation during thermodynamically ‘safe’ conditions [2]. Therefore, a safety margin beyond the conventional S/C of 3 would be sensible.

  In addition, the catalyst should be active and stable in the atypical gas compositions encountered during low-temperature reforming in membrane reactors.
- The steam reforming reaction under standard conditions is accompanied by a volume expansion of the reaction gas mixture. As a result, an increased pressure negatively affects the CH_4 conversion and decreases H_2 production. In contrast, in a membrane reactor an increased pressure will in principle positively affect the methane conversion, since due to the H_2 removal from the reaction zone, the volume of the reaction gas mixture is reduced during reaction. This has been confirmed by, e.g., Lin *et al.* [3]. Also, elevated pressures will increase the driving force for H_2 permeation through the membrane.

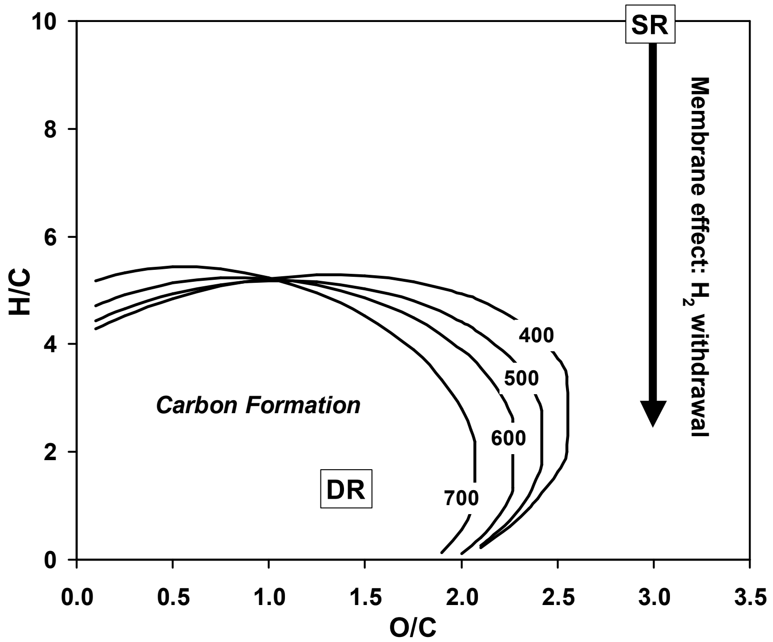

Figure 1 H/C,O/C phase diagram indicating the carbon formation limits at 40 bar (temperatures indicated in °C). DR denotes “Dry Reforming” and is near the center of the carbon formation conditions. SR denotes “Steam Reforming” (S/C=3). The arrow indicates the H/C,O/C–trajectory due to the effect of H_2-removal.

Carbon formation can thus be expected to be a serious problem during operation in a membrane reactor using conventional (Ni-based) catalysts. This is confirmed by the thermodynamic phase diagram in Figure 1, which denotes the carbon formation limits as a function of gas composition. Here, the (membrane) effect of removing H_2 from the gas mixture is indicated, illustrating that membrane reactors indeed operate in the high risk region near the carbon formation limits.

In literature, the application of ceria (CeO_2) as a promoter for reforming catalysts is extensively discussed (see Ref. [4] and references therein). Although the details of the mechanism are still unknown, ceria is known to add resistance to carbon formation and to enhance catalytic activity. Therefore, ceria is considered as an important ingredient for the catalysts developed for this project. Another result is the application of noble metals in stead of nickel, mainly for two reasons: nickel is prone to carbon formation, even during 'mild' reforming conditions, and nickel is catalytically less active than noble metals, an important issue at the relatively low temperatures in membrane reformers.

Catalyst Preparation

As mentioned above, in literature it is reported that ceria promoted catalysts offer resistance to carbon formation. Therefore, a series of ceria-promoted catalysts was developed and we focussed at noble metal-based catalysts.

The catalysts were prepared mainly by impregnation of metal salt solutions onto the support. The ceria–alumina supports have been prepared by co-precipitation methods and the ceria–zirconia supports are either prepared by co-precipitation, or are obtained commercially (as indicated in the Figures below). All other supports are obtained commercially as well. Table 1 below outlines a selection of the most important catalysts examined in this work. After synthesis, all catalysts have been calcined in air at 600°C for 5 hours.

Table 1 Selection of the most important ECN catalysts screened. Ru,Pt,Pd-containing catalysts, such as Ru/Al_2O_3, are prepared in a similar fashion as their Rh counterparts.

Catalyst	**Description**
Rh/Al_2O_3	1 wt% Rh impregnated on γ-Al_2O_3
Rh/ZrO_2	1 wt% Rh impregnated on ZrO_2
Rh/TiO_2	1 wt% Rh impregnated on TiO_2
Rh/CeO_2	1 wt% Rh impregnated on CeO_2
Rh/LCC	1 wt% Rh impregnated on $LaCaCrO_x$
$Rh/MgAl_2O_4$	1 wt% Rh coprecipitated with Mg and Al (ex-hydrotalcite)
Rh/CZ	1 wt% Rh impregnated on $Ce_xZr_{1-x}O_2$; x varies for different supports from approximately 0.15 to 0.85
Rh/CA	1 wt% Rh impregnated on CeO_2–Al_2O_3
Rh/CZA	1 wt% Rh impregnated on $Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3
Rh/Mordenite	0.35% Rh on Mordenite zeolite, via wet ion-exchange

Two commercial catalysts have been used for screening and testing purposes. However, due to the Confidentiality Agreements signed by ECN and the manufacturers, these catalysts will not be explicitly mentioned when presenting the results below. In stead, they are referred to as catalyst X_1 and X_2.

Catalyst Testing: Methodology

Initially, catalyst activity was screened during 'standard' steam-methane reforming gas conditions: 7.5% CH_4 and 22.5% H_2O in N_2 at 1 bar, and between 370 and 530°C (all compositions are molar compositions). Catalyst stability was then screened for a selection of the most promising catalysts under a wide range of reforming gas compositions (CH_4=1.67–5%, H_2O=16.67–25%, CO_2=0–3%, CO=0–1.5%, H_2=0–1.5%).

In order to understand better the differences in catalytic activity, CO pulse-chemisorption measurements are performed. With such experiments, a CO molecule adsorbs on a metal atom (e.g., Rh) and thus gives, with known metal loading, an indication of the metal dispersion on the catalyst.

Catalyst screening was performed on a microflow test rig, with a fixed catalyst bed and gas streams up to 100 ml/min. CO pulse chemisorptions were performed on *in situ* reduced catalysts on a AMI-200 system from Altamira.

Catalyst Testing: Activity and Stability

In order to compare the activity of the noble metals Ru, Rh, Pd, and Pt on ceria-based catalysts, standard SR-activity screening experiments are performed. The results are shown in Figure 2. It can be seen that, on weight basis, Rh is by far the most active metal on this type of support. Based on these results, Rh is selected for further catalyst development.

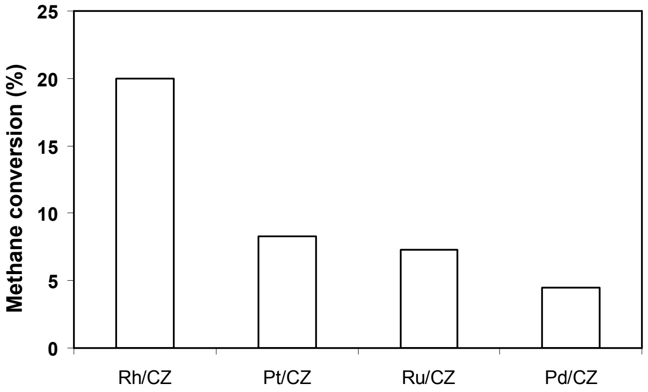

Figure 2 Activity as a function of the active metal for CZ-supported catalysts ($Ce_{0.2}Zr_{0.8}O_2$ support prepared by co-precipitation, 1wt% of metal loading). 'Standard' SR conditions at 400°C are applied.

It is well known that the support can affect the catalytic properties of catalysts to a large extent. In order to establish suitable candidate supports for further research, several Rh catalysts with different supports are screened.

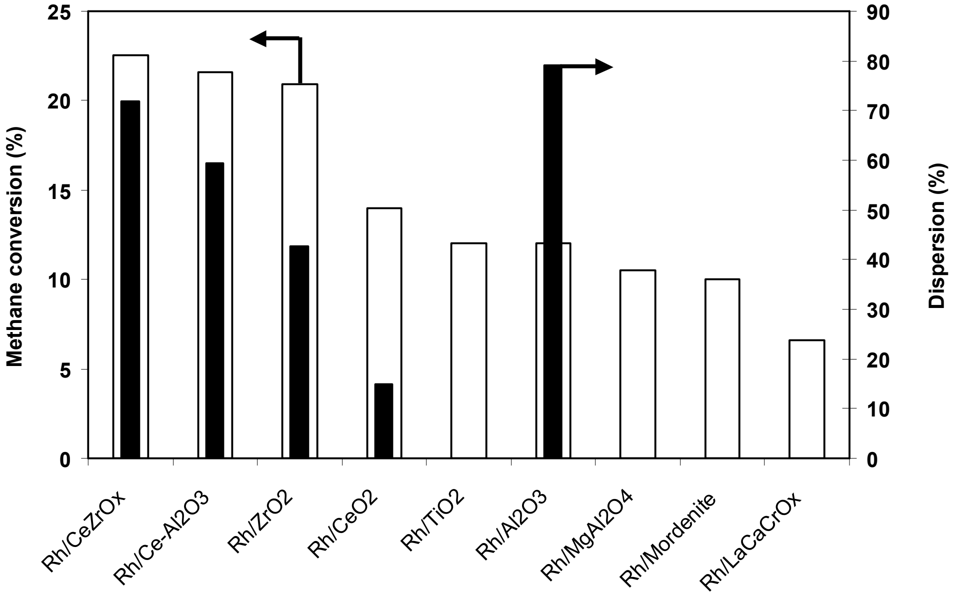

Figure 3 Activity as a function of the support for Rh-based catalysts ($CeZrO_x$ support based on $Ce_{0.2}Zr_{0.8}O_2$ from MEL Chemicals). Standard SR conditions at 400°C are applied. For some catalysts the dispersion is also indicated.

From Figure 3 it is obvious that Ce and Zr-containing catalysts exhibit high activity for reforming at 400°C. It can also be seen that the Rh dispersion, which is a measure for the amount of Rh on the catalyst which is actually available for reaction, of Rh/Al_2O_3 is the highest. Still, the activity of

Rh/Al_2O_3 is significantly lower than the activity of the Ce or Zr-containing catalysts. This suggests that the Rh particles on Al_2O_3 are less active than the Rh on the Ce or Zr-containing catalysts. In other words: dispersion does not exclusively determine the catalyst activity. We believe that synergetic effects between Rh and Ce or Zr exist, which enhance catalytic activity per Rh particle. This synergy could then be explained in terms of oxygen conduction mechanisms or enhanced H_2O activation [4]. These phenomena, however, are still subject of our research.
Note also, that the dispersion of Rh/CeO_2 is extremely low. We suspect this to be the result of encapsulation or agglomeration of the Rh particles by *in situ* reduced CeO_{2-x} [5]. This is in line with our observations (but not shown here) that de initial activity of Rh/CeO_2 (i.e., the activity displayed in Figure 3) rapidly decreases during time-on-stream in the H_2-rich steam-reforming conditions, in contrast to the other Ce-containing catalysts. We suppose that ceria needs to be stabilized (e.g., in a $Ce\text{-}ZrO_2$ or $Ce\text{-}Al_2O_3$ solid-solution matrix) in order to express its promoting effects and suppress its deactivation effects.

Stability and additional activity information was gained in during experiments aimed at obtaining the kinetics of selected catalysts. In order to determine the intrinsic kinetics of these catalysts, their behavior under a wide range of conditions is screened. Moreover, since the same catalysts will be applied for *sorption-enhanced reforming* applications, simulated sorption reformer conditions (i.e., H_2-rich) are also applied.

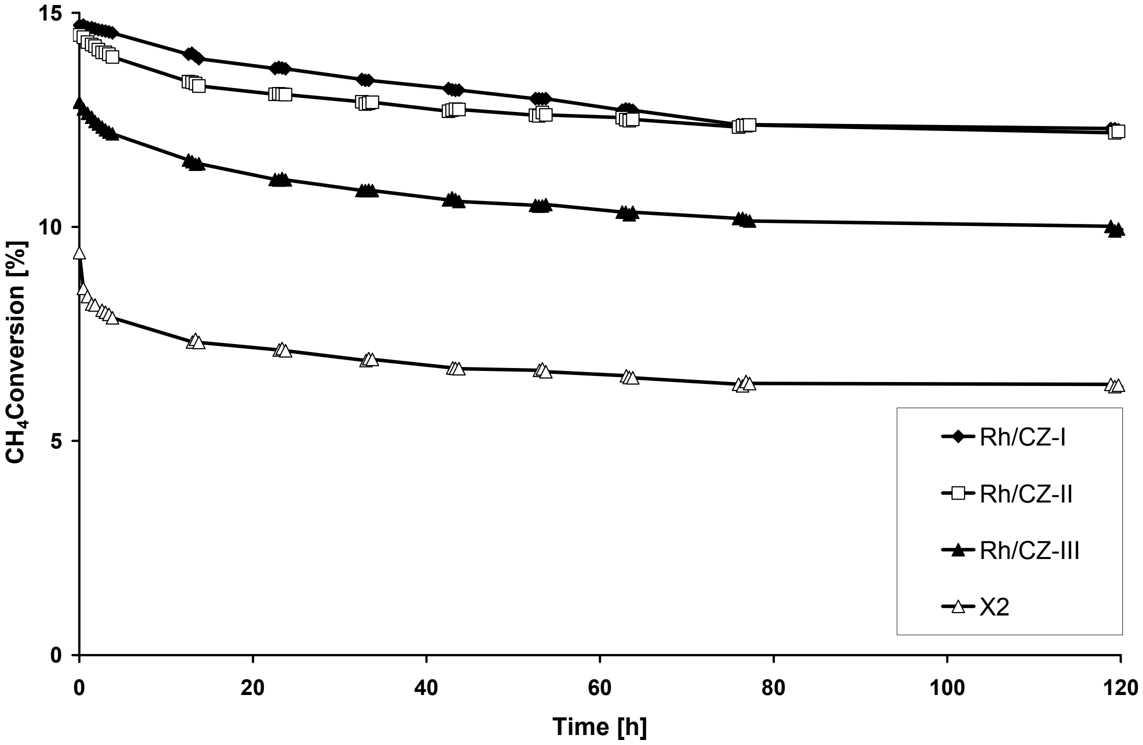

Figure 4 Catalyst stability under a wide range of conditions at 400°C and 1 bar. Only the conversion during a 'reference condition' is shown. The CZ-I, CZ-II, and CZ-III supports are based on $Ce_xZr_{1-x}O_2$ obtained from MEL, Rhodia, and Praxair, respectively.

The catalysts based on ceria-zirconia supports and commercial catalyst X_2 shows initial deactivation, but then tend to stabilize.

Future Plans

The results outlined above clearly indicate that many aspects of catalytic reforming in membrane reactors are still unclear. This emphasizes the fact that extensive catalyst research for such applications is indispensable.

Future plans therefore include more in-depth catalyst research in order to understand the deactivation mechanisms involved and obtain a stable catalyst. Also, the nature of the synergy between Rh and Ce and Zr will be investigated. Furthermore, the intrinsic reaction kinetics of one commercial catalyst and a Rh/CZ catalyst will be studied in order to enable reactor modeling.

Acknowledgment

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