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# Four challenges for nickel steam-reforming catalysts

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## Abstract

Reforming over supported nickel catalysts has been used commercially for more than 40 years. In this paper four catalytic challenges for nickel steam reforming catalysts are discussed from both a practical and a fundamental point of view. The four challenges are activity, sulphur poisoning, carbon formation and sintering. A coherent microscopic picture of these important aspects of the working catalyst is emerging from classic studies and is now extended by in situ TEM and DFT calculations of atomic-scale relationships between structure and catalyst properties and new knowledge about sintering.

*Keywords:* Steam-reforming; Nickel catalysts; Sulphur poisoning; Sintering; Carbon formation

## 1. Introduction

Heterogeneous nickel catalysts are commonly used for various industrial processes such as hydrogenation reactions, steam reforming, and methanation. The present paper concentrates on the application of nickel catalysts in steam reforming for the production of hydrogen and synthesis gas. Synthesis gas consists of a mixture of hydrogen, carbon monoxide, and carbon dioxide and is an important intermediate in the industrial syntheses of a wide range of bulk chemicals and fuels [1,2]. Steam reforming was commercialized already in the 1960s and in order to keep on improving the efficiency of the process, it has now to be taken to its limits. Information about the process, the catalyst limits, and catalyst improvements requires ever more sophisticated and detailed information about the catalysts even at the atomic level. The steam-reforming process with its combination of high-pressure hydrocarbons and steam is a challenging environment for the industrial nickel catalysts. In this paper, *four challenges for nickel steam-reforming catalysts*, i.e. activity, sulfur poisoning, carbon formation, and sintering are being discussed. The combination of previous studies and recently obtained atomic-scale insight has resulted in a coherent microscopic picture of the most important aspects of activity, sulfur poisoning, carbon formation, and sintering of nickel catalysts for steam reforming.

## 2. The steam-reforming process

The main piece of equipment in a steam-reforming unit is the primary reformer, which consists of approximately 10 m long narrow tubes loaded with the nickel catalyst. The tubes are situated in an oven that supplies the thermal energy needed for the reaction and the desired temperature increase. A typical reforming unit is shown in Fig. 1. In more modern units, an adiabatic pre-reformer is situated upstream of the primary reformer to reduce the load and to minimize the risk of sulfur poisoning and carbon formation in the primary reformer [1,2].

The reactions involved in steam reforming of natural gas are described in Table 1.

Steam reforming is strongly endothermic (as seen from the standard enthalpy of reaction) and leads to an expansion of the gas. Steam reforming must therefore ideally be carried out at high temperature, low pressure, and high steam-to-hydrocarbon ratio in order to achieve maximum conversion. The pressures of 20–40 bar typically applied in industrial reforming units are dictated by the high pressures in the synthesis loops, the necessity of high throughput and low pressure drop on one side and the reduced conversion and increasing cost of using high pressures on the other side.

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Fig. 1. The steam-reforming unit.

## 3. The four challenges for nickel steam-reforming catalysts

The combination of high temperatures and the presence of hydrocarbons and high-pressure steam creates a severe environment for nickel catalysts, and during operation the nickel steam-reforming catalysts encounter *four challenges*. The challenges are strongly interconnected and are shown in Fig. 2 and briefly described below:

(1) *Activity*: The catalyst must have sufficient activity to equilibrate the reaction mixture in the design catalyst volume. This is especially important in the adiabatic pre-reformer, where the effective activity determines the temperature profile in the reactor and thereby the reactor volume needed to equilibrate the gas mixture.

(2) *Sulfur poisoning*: Even after a thorough desulfurization of the feedstock, sulfur-containing compounds in the feed may reach the nickel catalyst at a ppb level. Sulfur is a strong poison for nickel catalysts and blocks the active nickel sites. The sulfur adsorption capacity of steam-reforming catalysts is therefore an important catalyst parameter.

(3) *Carbon formation*: Carbon formation may increase the pressure drop, crush the catalyst pellets, block the active nickel surface, and even form at the inner perimeter of the reforming tubes resulting in a lower heat transfer. Therefore, the limits for carbon free operation are important for the design and operation.

(4) *Sintering*: Nickel particles in the catalyst may grow during operation. This process is called sintering. Sintering influences the three other catalytic challenges so sintering is important in steam reforming due to the high temperatures and high pressures of steam.

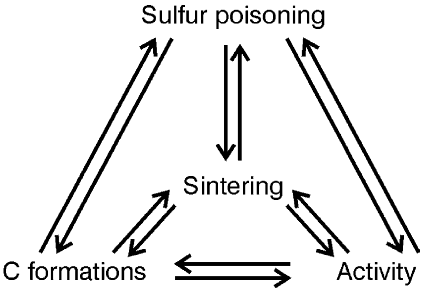

Fig. 2. The four challenges for nickel steam-reforming catalysts.

Table 1
Steam-reforming reactions

| Reactions | $\Delta H^\circ_{298}$ (kJ/mol)[a] |
|---|---|
| 1. $CH_4 + H_2O \rightleftarrows CO + 3H_2$ | −206 |
| 2. $CO + H_2O \rightleftarrows CO_2 + H_2$ | 41 |
| 3. $C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2$ | −1175[b] |

[a] Standard state: 298 K and 1 bar.
[b] For $n$-$C_7H_{16}$.

The four challenges will be discussed in more detail below with the objective of bridging the gap between studies of working catalysts and fundamental knowledge at the atomic level.

## 4. Activity

In a primary reformer, severe sulfur poisoning or sintering is typically the main reason for low activity resulting in higher tube temperatures and even carbon formation. However, in the adiabatic pre-reformer, the activity is a crucial parameter for the lifetime of a catalyst charge. Many studies of the kinetics of nickel steam-reforming catalysts are reported as summarised in Refs. [2,3]. Many of the kinetic expressions show complicated dependencies on the partial pressures of reactants and products. A simple expression for the kinetics of methane steam reforming over nickel catalysts was recently proposed by Wei and Iglesia [3]. They found that the activity at 600–700 °C only depends on the partial pressure of methane implying that abstraction of the first hydrogen atom is the rate-determining step. This conclusion was supported by activity measurements using $CH_4/CD_4$ isotopomers [3]. The active sites were found to be free of any