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Methane steam reforming and CO₂ methanation over commercial Nickel/Calcium aluminate catalysts: experimental study and laboratory reactor modelling

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Highlights

- Methane steam reforming and CO₂ methanation are studied on two commercial SR catalysts.
- The investigated commercial SR catalysts are both active for CO₂ methanation.
- Alkali presence reduces catalytic activity in both SR and CO₂ methanation.
- A laboratory reactor model has been implemented for both reactions.

1. Introduction

Nowadays, methane or natural gas Steam Reforming (SR) is realized to produce hydrogen and syngases, for the manufacture of NH_3, CH_3OH, higher hydrocarbons, as well as for hydrogenations and fuel cells feeding [1]. The product of methane SR, when followed by a low temperature Water Gas Shift (WGS) step, is a nearly 4:1 mixture of H_2:CO_2 through the so-called global steam reforming reaction: $CH_4 + 2\,H_2O \leftrightarrows CO_2 + 4\,H_2$.

On the other hand, the reverse of the above reaction, usually denoted as "Sabatier's reaction" represents an interesting option for the reuse of CO_2, e.g. from exhaust combustion gases, when waste or renewable H_2 is available [2]. Nickel metal catalyzes efficiently both reactions. However, while the methanation reaction is exothermic, thus being necessarily performed at relatively low temperatures (T < 773 K), steam reforming one is endothermic, being performed at T > 973K. At the present, commercial SR catalysts are constituted by Ni supported on refractory and highly stable crystalline supports, while methanation can be performed on $Ni/\gamma\text{-}Al_2O_3$ catalysts. In the present communication, we report on our experimental studies of methane steam reforming and CO_2 methanation, performed over commercial SR catalysts. The obtained data are evaluated through a laboratory reactor model, in order to achieve a deeper understanding of the chemical engineering of both SR and methanation reactions, which is a preliminary step for industrial reactor modelling [3].

2. Materials and methods

Commercial JM57-4Q and JM25-4Q SR catalysts have been tested. The former one is Ni on calcium aluminate, while the latter is a slightly alkalized version of the 57 series, doped with small amounts of K_2O [4]. As a reference, a home-made methanation (Ni/Al_2O_3) catalyst (HMMC) has been tested in the same conditions. All experiments have been performed by loading 88.2 mg of catalysts diluted in silica glass (440 mg for SR and 700 mg for methanation). The following gas composition has been used for SR experiments: 5% CH_4, 20% H_2O and He balance with a total flow rate of 120 Nml/min. For methanation the same composition reported in [5,6] has been used (total flow rate of 80 Nml/min).

Two different simulation models have been developed for the laboratory reactor, under the hypothesis of steady-state operating conditions and cylindrical symmetry. The first model is 2-D and is based on mass, energy and momentum microscopic balances. Balance equations are coupled to local reaction kinetics, based on the equations proposed by Xu and Froment for a Ni- based catalyst [7]. The model equations are integrated numerically using a Finite Element Method (FEM) implemented through COMSOL Multiphysics 5.2 [8]. The second model, denoted as 'kinetic model', is 1-D and it is based on the hypothesis of isothermal

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plug-flow reactor, with the same kinetic equations implemented in the FEM model and integrated through Matlab R2017a.

3. Results and discussion

Fig. 1 reports experimental data and modelling results obtained in both methane steam reforming and methanation mode. Both experimental and simulation results are represented through the $\prod_i p_i^{v_i}$, which, at thermodynamic equilibrium, corresponds to K_p. In Fig. 1, a fitting of K_p literature values [1] is included. For methane SR, both models evaluate a rapid kinetics for all the reactions involved, and as a consequence, the modelling results collapse with thermodynamic equilibrium in the whole temperature range (T>773K). This is partly confirmed by the experimental data obtained from the HMMC catalyst. Considering the methane SR reaction, alkalized JM25-4Q is the less active catalyst, while the JM57-4Q is only slightly below the reference HMMC catalyst. Under CO_2 methanation (T<773K), significant deviation from thermodynamic equilibrium is demonstrated by both the modelling and the experimental results. The modelling results show a larger deviation from equilibrium, and thus a slower kinetics, than the corresponding experimental data. In CO_2 methanation, the alkalized JM25-4Q is the less active catalyst, while the JM57-4Q is practically as active as the reference HMMC catalyst.
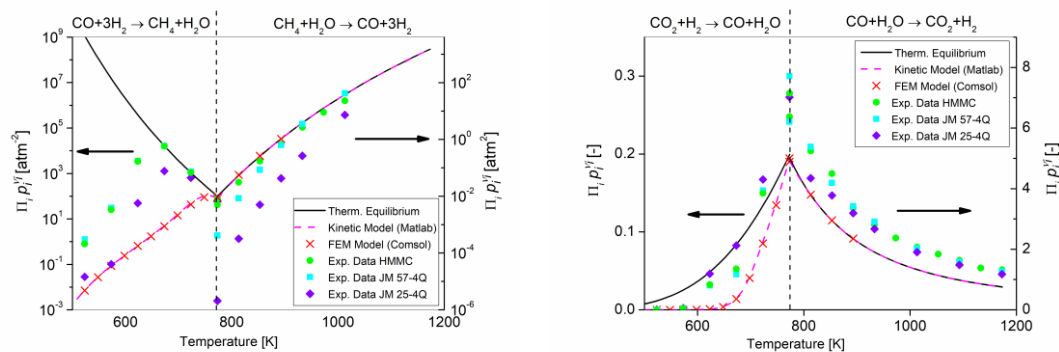

Figure 1. Laboratory reactor results: methane steam reforming and CO methanation (left); direct and reverse water gas shift (right).

4. Conclusions

A kinetic model, previously proposed by Xu [7], is taken as the basis for an FEM and an isothermal plug-flow models, developed for a laboratory reactor. Both models give identical results under the range of operating conditions investigated. The results indicate that the models overestimate the experimental reaction rate under direct operating mode (methane SR reaction), while they underestimate the experimental reaction rate under reverse operating mode (CO_2 methanation). A kinetic study is in progress in order to identify appropriate kinetic laws for the commercial SR catalysts under investigation.

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