

In-situ spatially-resolved measurements of gas composition profiles and catalyst surface temperature to obtain high quality kinetic data. Study case: CO₂ methanation.

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Highlights

- A much larger set of kinetic data can be collected via spatially resolved techniques.
- IR thermography allows to determine surface temperature over the whole catalyst area.
- CO₂ methanation under industrial relevant conditions was studied.

1. Introduction

Modelling and optimization of industrial scale chemical reactors require a very good understanding of the reactions mechanism with the corresponding kinetic description. Therefore, high quality kinetic data are needed, which can be challenging to obtain, especially for fast and highly exothermic reactions such as the CO₂ methanation. Traditionally, kinetic studies rely on measuring the exit gas composition using differential reactors (< 10% conversion) with diluted catalyst beds and diluted reactants to avoid temperature increase. However, these experimental parameters do not reflect industrial relevant conditions. Gathering information on gas composition profiles along the reactor axis allows the investigation of the kinetics in much greater detail, while reducing the number of experiments [1,2]. The advantage of this technique is that it combines integral with differential reactor concepts, therefore it is not limited by the reaching equilibrium or complete conversion.

2. Methods

An optimized optically accessible channel reactor with dimensions of 40 x 100 x 5 mm was designed. At the bottom of the channel a catalyst coated plate is placed, while the top is closed with quartz glass plate. The latter allows determining the catalyst surface temperature by means of non-intrusive infrared (IR) thermography (FLIR SC2500). The reactor is equipped with a thin (O.D. 0.5 mm) movable sampling capillary to quantify the axial gas species composition profiles with a high spatial resolution (1 mm) above the catalyst via calibrated mass spectrometry (Hiden, HPR-20). The height of the capillary above the catalyst can be adjusted (1.0 to 3.5 mm) to obtain radial concentration profiles. Ordered mesoporous nickel-alumina (OMA) catalysts were synthesized following the evaporation induced self-assembly method [3]. Catalysts with a particle size of 20 – 45 μm were coated onto a metal plate and placed in the reactor. The catalyst mass distribution (kg_{cat} m⁻²) was determined by measuring the height of the coating with profilometry, while the catalyst was characterized with BET, H₂-uptake, XRD, SEM and TEM. Kinetic data for the CO₂ methanation were collected at temperatures ranging from 300 to 450°C, SCa total pressure of up to 5 bar_{abs}, a GHSV of 10 to 150 L_N g_{cat}⁻¹ h⁻¹ and varying partial pressures of the reactants (H₂, CO₂) and the products (CO, CH₄, H₂O).

3. Results and discussion

Figure 1 A-D illustrates the picture, height profile, SEM and TEM of the catalyst coated plate (OMA-15Ni, denotes 15 wt% Ni on the ordered mesoporous alumina support), respectively. The first 30 mm and the last 10 mm of the plate were not coated. The measured height profile of the coated area ranged from 20 – 45 μm,

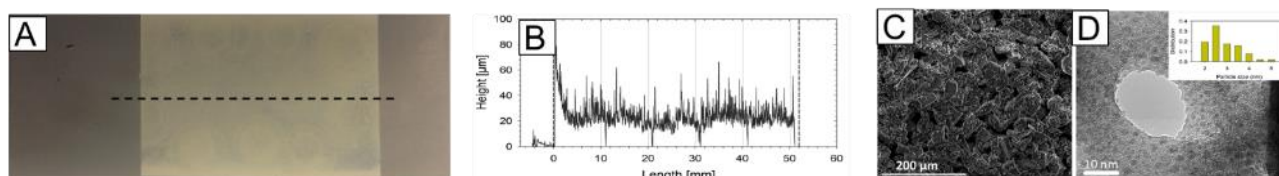


Figure 1. Results for the OMA-15Ni (A) Picture of a coated FeCrAlloy plate; (B); Catalyst height profile (profilometry) (C) SEM of a coated plate; (D) TEM of the catalyst (nickel crystallite).

indicating a one-layer particle coating (Figure 1 B) with total catalyst loading of 130 mg. A closer examination of the coated area by SEM confirmed a homogeneous coating coverage (Figure 2 C). This is important for the development of a mathematical description of the reactor, which will be used for the kinetic parameter estimation and model discrimination of proposed reaction mechanisms. The OMA-15Ni catalyst had a mesoporous surface area of $232 \text{ m}^2 \text{ g}^{-1}$, with an average pore size of 10 nm and highly dispersed nickel with an average crystallite size of 2.8 nm (Figure 1 D).

The results of the CO_2 methanation are exemplarily shown for the experiment conducted at 400°C , 1 bar and $\text{GHSV} = 50 \text{ L}_N \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ are depicted in Figure 2. The top view shows the reactor indicating the flow direction of the gas (left to right) and the IR emissions of the coated (yellow), and uncoated (orange) areas illustrating the temperature distribution. A thermo-couple was used to calibrate the IR camera and relate the measured photon emission with the real surface temperature. As expected, the surface temperature of the uncoated area was constant, while the temperature of the catalyst surface was slightly elevated due to the reaction from 405 to 408°C (Figure 2 B top). Figure 2 B bottom shows nicely, the axial gas composition profiles along the reactor length over the uncoated and coated area with 40 data points per species and run. The gas composition did not change before the coating begins. Thereafter, H_2 and CO_2 decreased from 45 to 28 mol% and from 9.5 to 5.5 mol%, respectively. While CH_4 and H_2O increased to 5.5 and 11.3 mol%, respectively, which was very close to stoichiometric ratio of 2 ($\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$). Small amounts of CO were formed with a maximum of 0.5 mol% at around 20 mm, then it decreased slightly towards the end to 0.2 mol%. The increase in the CO concentration might be due to the reversed water gas shift ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) and the decrease due to CO methanation. In total, more than 800 high quality data points per gas species were collected.

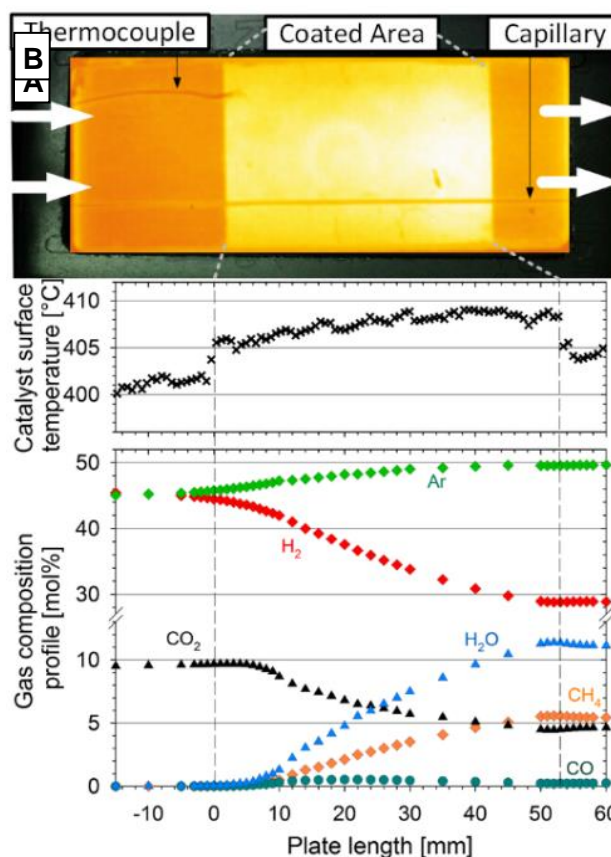


Figure 2. Results for OMA-15Ni catalyst. (A) Picture of the plate reactor with IR-image; (B) Measured axial gas composition profiles and catalyst surface temperature.

4. Conclusions

A comprehensive experimental study on the CO_2 methanation was conducted over ordered mesoporous nickel catalysts in an optically accessible channel reactor using a wide range of temperatures, partial pressures and gas hourly space velocities. A catalyst coating procedure was developed yielding a homogenous catalyst mass distribution. By means of spatially resolved measurements of the axial gas species composition and catalyst surface temperatures along reactor axis, the effects of reactants (H_2 , CO_2) and products (CH_4 , H_2O , CO) on the rates were analyzed. With this technique, a significantly larger set of data for the kinetic parameter estimation was collected than by use of a typical steady-state reactor with concentration measurements at the outlet only, which makes this setup very suitable to study kinetics of heterogeneous catalyzed reactions.

References

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Keywords

Spatially resolved measurement; IR thermography; kinetic data collection; catalyzed reaction