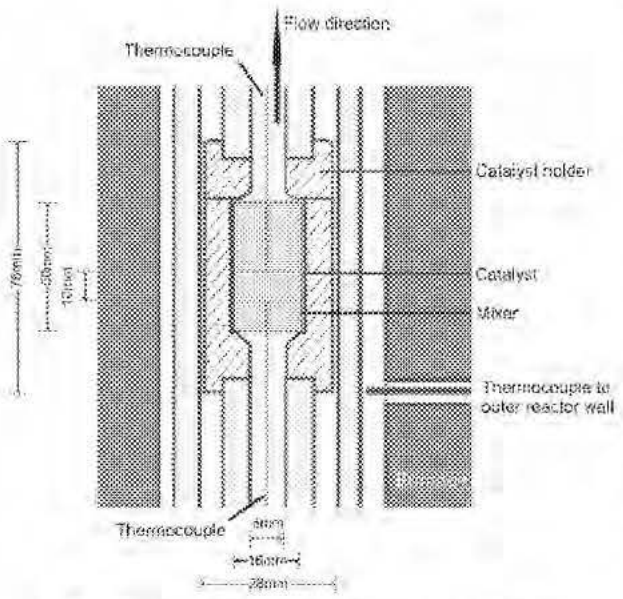

Fig. 1. Catalyst holder in the reactor surrounded by the furnace.

thermostat and the heat exchanger MGW Lauda M5. This flange temperature is chosen because it prevents condensation of the water and melting of the silicon glue (melting point ~200 °C). The catalyst inside the reactor is placed in a holder made out of pyrophyllite and is kept at its position using Pythagoras tubes with a smaller diameter. Those tubes have an inner diameter of 8 mm leading to smaller dead volume and faster transport to the catalytic section. The dimensions of the inner tubes ensure reasonably flat temperature profiles at the catalyst entrance.

Monoliths with an overall length of 50 mm and an outer diameter of 1.5 cm can be placed inside the reactor. In the experiments presented here three cordierite monoliths were placed inside. In the upstream position, an uncoated foam monolith with 10 mm in length is placed guaranteeing flat inlet velocity profiles at the entrance of the following catalytically coated honeycomb monolith, also 10 mm in length. Downstream another honeycomb monolith is placed with a length of 30 mm. A ceramic cloth, approximately 1-mm thick, was wound around the monoliths to diminish bypass of gas.

The entire reactor was placed inside a tubular furnace allowing the operation of the reactor at controlled temperatures. The gas temperatures at the front and at the exit of the catalytic monolith are monitored using Rh/Pt-thermocouples type S. The temperature measured at the rear end of the catalyst is chosen as reference temperature in the charts. The temperature of the outer reactor wall measured by a third thermocouple was used to control the power of the furnace. The reactor was operated at slightly higher pressures than atmospheric (1.05 bar).

The product composition was analyzed using a quadrupole mass spectrometer (AIRSENSE 500) and a gas chromatograph (a modified Varian CP-3380 equipped with a Chrompack Silica Plot 8567 and a Chrompack 7514 Fused Silica Carbo Plot P7). The water in the product stream was condensed in a cold trap [35] before entering analysis devices. The mass of the condensed water was determined for every individual experiment at given constant external conditions.

The applied catalyst was provided by Umicore AG & Co. KG Hanau, Germany. In catalyst preparation, alumina slurry containing rhodium as active catalytic component and further additives, which will not be disclosed, were coated on the inner channel walls of the cordierite honeycomb monoliths. Most of this slurry is deposited in the corners of the rectangular shaped channels where the washcoat is up to 150-μm thick. The thickness of the washcoat in the remaining 75% of the channel wall area is between 5 and 25 μm.

Honeycomb monoliths with hydraulic diameters of ~0.9 mm (900 cpsi (channel per square inch)), and 1.3 mm (600 cpsi) were examined. BET-measurements of a catalyst with 900 cpsi lead to a total surface area of 42.97 m^2/g, and chemisorption measurements using hydrogen estimate a specific surface area of 0.98 m^2/g. The latter value was used to calculate the ratio of the active surface area to the geometrical surface of the channel walls ($F_{cat/geo}$) to be 143. The parameter $F_{cat/geo}$ serves as parameter for the description of the effective catalytic area in the model (Eq. (5)).

In all experiments (Table 2), the gas hourly space velocity (GHSV) was 40,000 h^{-1}. The dilution of the feed stream by 75 vol.% argon leads to an effective GHSV of 10,000 h^{-1} for the potentially reactive gases. The dilution helps to preserve isothermal conditions. All measurements were conducted under steady-state conditions. The measuring time of the mass spectrometer at each temperature was 1 h; alternatively, three repetitive measurements were carried out with the GC analysis. The total amount of condensed water during this measurement series for one set of external conditions was analyzed.

3. Modeling and simulation approach

In modeling the reactor, the following simplifications have been made:

(1) Since the measured temperature difference between the front and back of the catalyst were always below 10 °C, isothermal conditions can be assumed. The foam monolith in front of the catalyst ensures a uniformly distributed inlet flow at the catalyst front face. Hence, all channels behave essentially alike and only one channel of the monolith needs to be analyzed.
(2) The coating led to almost round channel cross-sections. Therefore, the channel flow can be treated two-dimensional assuming cylindrical coordinates with the axial and radial position as independent variables.
(3) An averaged washcoat thickness of 20 μm was assumed. Along the channel, a uniform distribution of the catalyst can be assumed.
(4) Pressure measurements between the feed section and the vaporizer revealed pressures slightly higher than standard pressure. Since the vaporizer and the foam monolith cause the comparably highest pressure drops, standard pressure is taken as input parameter of the simulations.
(5) The temperature in the combined vaporizer and mixing chamber is 200 °C, which is taken as inlet flow temperature.
(6) The flow in the small channels is laminar indicated by the Reynolds number of approximately $Re = 100$ for 900 cpsi and 700 °C.
(7) Since the Péclet number can be defined as $Pe = Re \cdot Sc$ with the Schmidt number for gases being $Sc \sim 1$, a Péclet number of $Pe \sim 100$ can be calculated for 900 cpsi. Hence, in axial direction, convective transport is more important than diffusive transport and axial diffusion can be neglected [36].

Assumption (7) implies that the flow can be modeled by the so-called boundary-layer equations instead of the full Navier–Stokes equations [36]. Mathematically, the character of the equations is simplified from elliptical to parabolic with a time-like coordinate along the channel axis. These assumptions result in the following