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Contactless temperature measurements under static and dynamic reaction conditions in a single-pass fixed bed reactor for CO_2 methanation

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ABSTRACT

Resolving the temperature profile in catalytic fixed bed reactors is essential for the investigation of reactions. However, this is not readily possible at laboratory scale without affecting the flow regime. Thermography tracks temperature profiles contactless with a high spatial resolution and without influencing the flow regime in the reactor. This study applies thermography for a powder fixed bed reactor at laboratory scale. A parameter investigation was conducted to identify the dependency of hot spot temperatures during the highly exothermic CO_2 methanation reaction on major process parameters like reactant gas dilution, volume flow and cooling temperature. Further, the impact of an upstream cold bed on the temperature distribution in the catalytic bed was investigated. It was found that the cold bed was able to remove the heat of reaction efficiently to prolong an overheating of the catalyst bed. Thermography was also used to study a dynamic phenomenon, namely the in situ sulfur poisoning of a nickel-alumina catalyst. The temperature of the fixed bed was thereby spatially resolved at any point in time during the reaction. It was found that poisoning causes the reactive zone to move through the catalytic bed at a constant velocity. A simple poisoning model was applied to correlate the observed moving velocity to the catalyst's specific active surface area as determined by static H_2 chemisorption at room temperature.

1. Introduction

The increasing climate change forces society to rethink how the required energy is obtained. By focusing on the expansion of renewable energy sources such as wind power, hydropower and solar energy, the dependence of the industry on fossil fuels is to be reduced in order to limit global warming to 1.5 °C above pre-industrial levels by 2050. This, among other aims in Germany, is to be achieved by the Energiewende [1,2]. A problem caused by the transition of energy production to renewable sources is that these sources are subjected to temporal as well as quantitative fluctuations. Furthermore, there is a spatial problem between power generation and consumption. Large off-shore wind parks, for example, generate the electricity which is mainly required in urban conurbations and industrial sites. In order to solve this problems, concepts, which feature suitable storage and transport media have to be developed. One of these concepts is the so-called power-to-gas (PtG) concept [3]. This demonstrates the possibility of converting CO_2 from anthropogenic sources or from the atmosphere to CH_4 by means of H_2 derived from water electrolysis [4]. The basis for this process was laid by Paul Sabatier and Jean Baptiste Senderens in 1902 [5]. Nowadays, the CO_2 methanation has come to the forefront of science [6,7], especially since the passing of the Energiewende. For the catalytic conversion of CO_2 with H_2 to CH_4, many metals were tested. Among them are Ru [8–17], Rh [18–22], and Pd [23–26]. Their high methanation rate, however, is offset by the very high price, which prohibited them from being used industrially. In addition to the noble metals, transition metals such as Co [12,27], Fe [12,28–30], Cu [28], Ir [28] and Ni [31–37] were also applied. Here, Ni predominantly prevails, which, in addition to a very high activity, also shows a high selectivity towards CH_4. Moreover, Ni has a very favorable price in comparison with other metals, which made it the catalyst of choice for industry [38]. In order to further increase the activity of Ni/Al_2O_3 catalysts for CO_2 methanation, different promoter metals have been added. Zhao et al. [39] reported an enhanced activity for Mn promoted systems and the group of Grunwaldt [40] found an increased activity for NiFe alloys.

The overall reaction equation of the methanation is summarized in (1):

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad (1)$$

As the reaction is highly exothermic, there is a risk of creating a hot spot

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in the reactor, which was also observed for other exothermic reactions [41–45]. In addition, sintering processes which significantly impair the life-time of the catalyst may occur due to local temperature maxima. This can be observed not only in industrial applications but also in laboratory scale. Single-pass fixed bed reactors are often assumed to be isothermal, although hardly enough thermocouples can be placed in small fixed beds. If reactors are built large enough, several thermocouples can be placed at selected points [46,47]. Horn et al. developed a reactor design using a movable sampling capillary to measure the spatial reactor profile in terms of mass and temperature within the reactor [48–50]. The sampling capillary was connected to a mass spectrometer and was also equipped with a thermocouple or a pyrometer fiber. However, all these methods potentially disturb the flow within the reactor [51]. Another promising way of dealing with this problem is thermography. Despite the potential of this method, this technique has only begun to prevail in recent years. Above all, fixed beds of active moldings [52,53], foams [54], monoliths [55,56] or overflowed catalyst particles [57], and plate catalysts [58,59] were investigated for determining the kinetics of CO/CO_2 methanation and the partial oxidation of CH_4.

In this work, the applicability of the contactless temperature measurement technique under static and dynamic reaction conditions to permeated, powder fixed beds is shown, using the CO_2 methanation as an example for a strongly exothermic reaction. The work is divided into three parts. The first part deals with a parameter study to investigate the impact of major process parameters like temperature, partial pressure of reactants and volume flow on conversion and the temperature profile in the fixed bed. The second part deals with the question of how to improve the heat transport within the bed by varying the bed geometry and using partially inert fixed beds. For these experiments, a low-loaded, co-precipitated $NiAlO_x$ (Ni/Al = 1/5) catalyst was used [60]. The last part outlines the utilization of this measurement technique for dynamic reaction conditions. Therefore, the time dependent deactivation behavior of a co-precipitated $NiAlO_x$ catalyst (Ni/Al = 1/1) in the presence of a feed gas containing 5 vppm H_2S is shown.

2. Experimental section

2.1. Catalyst synthesis

For the synthesis of the nickel-alumina precursor, the reverse co-precipitation method at constant pH was used following the synthesis route described in [60,61]. The water was purified by a Millipore® water clearing rig. Nickel nitrate, aluminum nitrate, sodium hydroxide and sodium carbonate (Merck KGaA) with the purity of p.a. were used as purchased. Co-precipitation was performed in a 3 L double-walled glass reactor (Büchi) preloaded with 1 L of water, stirred at 150 min^{-1} by a KPG stirrer and heated to 30 °C. For an improved mixing, two flow breakers were additionally inserted in the vessel. 120 mL of the metal nitrate salt solution (1 M $Ni(NO_3)_2{\cdot}6H_2O$ and 1 M $Al(NO_3)_3{\cdot}\ 9H_2O$, both Merck KGaA, p.A) were added by a peristaltic pump (Medorex e.K.) with 2.3 mL min^{-1}. The precipitating agent was a mixture of 0.5 mol NaOH and 0.5 mol Na_2CO_3. A Titrino Autotitrator 716DMS by Methrom® dosed the solution into the vessel to keep the pH value constant during precipitation. The molar ratio of Ni/Al was set to 1/5 and 1/1 (NiAl15 and NiAl11). After precipitation, the product slurry was aged for 18 h under stirring in the mother liquor. Subsequently, the precipitate was washed with purified water until the pH value of the filtrate reached the original one of water. The retentate was first dried overnight at 80 °C and then calcined at 450 °C for 6 h under synthetic air flow (heating rate 5 K min^{-1}).

2.2. Catalyst characterization

For powder X-ray diffraction analysis (XRD), a PANanalytic Empyrean with Cu-K_α radiation and a monochromator was used. The diffractogram resulted from scanning in the range between 2Θ = 5–90° and with an angular velocity of 0.05708° s^{-1}. The specific surface area of the calcined catalyst was determined by N_2 physisorption. Therefore, a Nova 4000e surface area analyzer from Quantachrome was used. The isotherm was measured in the p/p_0 range between 0.05 and 1 and the BET surface area was calculated by using the p/p_0 range between 0.05 and 0.3. As a pretreatment, the sample was heated up to 120 °C under vacuum and kept for 3 h to remove physisorbed water. The specific metal surface area of the catalyst was measured by means of H_2 chemisorption. For this purpose, a Quantachrome Autosorb-1 was used. Prior to the measurement, the catalyst was reduced in 5 vol% H_2 in N_2 at 450 °C for 5 h (heating rate of 2 K min^{-1}). Chemisorption was conducted at 35 °C and the H_2 uptake was calculated by the extrapolation method.

2.3. Experimental setup

For the temperature measurement, an optical accessible reactor setup was employed. The main parts consisted of a gas dosing and mixing section, the reactor section and the analysis section. All gases were purchased from Westfalen AG and had a purity of 5.0. The gases were dosed by mass flow controllers (Bronkhorst). To prevent condensation of produced water, the exhaust line was heated. The reaction section consisted of a massive heating block equipped with two heating cartridges, allowing a maximum temperature of 700 °C. Further, the heating block also had an opening for the contactless temperature measurements. The optical accessible tube reactor was a 30 cm long quartz glass tube with an inner diameter of 4 mm and a wall thickness of 1 mm and was placed in the heating block.

The fixed bed was held in place by silica wool plugs in the isothermal zone of the quartz glass tube reactor. For an additional temperature measurement, a thermocouple was placed at the beginning of the fixed bed. In case of the static measurements, the product gas was analyzed in a SpectrumTwo FTIR spectrometer (PerkinElmer) equipped with a heated flow cell of 120 mL volume and CaF_2 windows using a range of 4000–1100 cm^{-1} with a resolution of 4 cm^{-1}. In the case of the dynamic measurements, the product composition was analyzed every 20 min by a Shimadzu GC-14B equipped with a flame ionization and thermal conductivity detector. The GC was regularly calibrated with gas mixtures of known composition and tested with a bench mark catalyst of known CO_2 conversion. Moreover, activity results obtained by the GC have been compared to the on-line FTIR used for static measurements and found to be very similar. A sketch of the overall testing rig is presented in Fig. 1. It is worth mentioning, that the sampling rate of a GC, which is slow as compared to other gas analyzers, e.g. IR cells, might be a limiting factor for tracking fast dynamic processes. In the current case however, the complete deactivation of 50 mg of a highly active material by a few vppm of H_2S, can be expected to occur on the scale of several days. A response time of 20 min was therefore considered adequate.

For the contactless temperature measurements, a SC-2500 near-infrared camera (FLIR) equipped with an indium gallium arsenide (InGaAs) detector working with a wavelength range of 0.9–1.7 µm and a standard frame rate of 50 Hz was used. The nominal accuracy of the camera is ± 1 °C, which is for example higher than a Type K thermocouple (± 2.2 °C). The choice of the working range allows using the so-called atmospheric windows where no interaction of the emitted IR radiation with the atmosphere occurs. Therefore, the interaction of the emitted IR radiation with heteronuclear molecules of the surrounding atmosphere can be neglected. The working range of the camera also meets perfectly with the optical permeability of quartz glass, whereby only a small attenuation of the emitted infrared radiation is observed.

Another important factor is the emissivity of the investigated material. This emissivity is temperature dependent and decreases with increasing temperature. Therefore, it is very important to consider this change in the temperature calibration of the camera. The following