

Steady-state and controlled heating rate methanation of CO₂ on Ni/MgO in a bench-scale fixed bed tubular reactor



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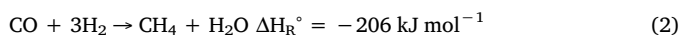
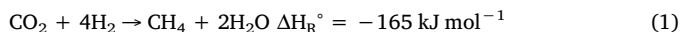
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ABSTRACT

Chemical hydrogen storage via conversion with carbon dioxide into methane is a promising technology in an energy system that relies on renewable energy resources. Robust heterogeneous catalysts are needed for this reaction to proceed at relevant levels. Ni/MgO is a promising catalyst in terms of activity and stability. Although several microscale catalyst studies exist, there is a lack of knowledge on catalyst performance and reactor control at larger scale for carbon dioxide methanation at ambient pressure and a technically relevant stoichiometric H₂:CO₂ (4:1) feed. Two catalysts with a loading of 11 and 17 wt.% nickel were prepared by wet impregnation, producing a Ni/MgO solid solution with a cubic lattice. Controlled increase ('scanning experiment') of the catalyst temperature to 500 °C for the highly exothermic CO₂ methanation was compared to steady-state experiments. Scanning and steady-state experiments yield comparable results in terms of carbon dioxide conversion and methane selectivity, whereas scanning experiments lead to considerable time saving. At a moderate temperature of 325 °C and a feed flow consisting of H₂:CO₂:N₂ = 4:1:5 at a flow rate of 250 cm³_{STP}min⁻¹, CO₂ conversion and CH₄ selectivity near thermodynamic equilibrium are achievable. The long-term stability of Ni/MgO (17 wt.% Ni) at 330 °C was proven during reactor operation for several days.

1. Introduction

The catalytic conversion of carbon dioxide with renewably produced hydrogen to methane (also referred to as CO₂ methanation or production of synthetic natural gas SNG, see Eq. (1)) has gained major interest in recent years [1–4]. One of the reasons for this growing interest can be found in the quest for alternative hydrogen storage systems. In the power-to-gas (PtG) concept [5–8], renewably produced hydrogen is stored as methane, benefitting from the readily available natural gas storage and distribution infrastructure.



Due to the time dependent availability of renewable energy (wind,

hydro, and solar), either large hydrogen buffer storage facilities, making the whole PtG concept questionable, or robust methanation catalysts are needed. The term 'robust' in this context refers to stable CO₂ conversion and CH₄ selectivity not only during long-term operation but also during several operation/down time cycles of the reactor.

Catalytic methanation of CO₂ and CO (Eqs. (1) and (2)) using nickel was first reported more than 110 years ago [9]. Until the beginning of the 21st century, CO and CO₂ methanation was investigated and applied in the context of SNG production from coal, fossil resources, and biomass [10]. Furthermore, catalytic methanation has been used for decades in gas chromatographic analysis of CO and CO₂, first reported by Porter and Volman 1962 [11]. A multitude of different Ni-based catalysts have been reported [4,12–15]. Ni(O)/MgO catalysts exhibit high stability in methane and ethanol reforming [16–24] and for CO

Abbreviations: AAS, atomic absorption spectroscopy; (EF)TEM, (energy filtering) transmission electron microscopy; FID, flame ionization detector; GC, gas chromatography; HT[Nr], numbered (Nr: 1–3) thermocouple position at reactor wall as specified in Fig. 1; ICSD, inorganic crystal structure database at FIZ Karlsruhe; ICP-OES, inductively coupled plasma-optical emission spectroscopy; ID, inner diameter (mm); IR, infrared; Ni[Nr]-MgO, nickel/magnesium oxide catalyst with nickel loading specified in wt.% as [Nr: 11,17]; OD, outer diameter (mm); O(F,T_{tar}), operation point: one specific combination of feed flow rate and target temperature; PtG, power-to-gas; RT, reactor tube; sccm, standard cubic centimeter per minute (cm³_{STP}min⁻¹); STP, standard temperature and pressure 0 °C, 0.1 MPa; SNG, synthetic natural gas; TC, thermocouple casing; TCD, thermal conductivity detector; T[Nr], numbered (Nr: 1–6) thermocouple position inside the reactor as specified in Fig. 1; TOC, total organic carbon; XRD, X-ray diffraction

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Nomenclature	
A_s	Specific surface area determined by Hg-porosimetry ($\text{m}^2 \text{g}^{-1}$)
am_{cat}	Amount of catalyst used in studies cited (mg)
d_{cat}	Diameter of catalyst particle (μm)
d_p	Pore diameter (nm)
F	Feed flow rate at standard temperature and pressure ($\text{cm}^3_{\text{STP}} \text{min}^{-1}$)
h_{cat}	Height of catalyst bed inside the reactor tube (mm)
$\Delta H^\circ_{R,i}$	Standard enthalpy of reaction i (kJ mol^{-1})
m_{cat}	Amount of catalyst used in experiments presented (g)
P	Dry product gas flow rate at standard temperature and pressure ($\text{cm}^3_{\text{STP}} \text{min}^{-1}$)
P_{Hg}	Absolute mercury pressure applied in Hg-porosimetry (MPa)
S_{CH_4}	Methane selectivity (-)
t_{steady}	Time of steady-state operation (h)
t_{store}	Storage time of catalyst (h)
T_{tar}	Target temperature ($^\circ\text{C}$)
v_i	Volume fraction of compound i (vol.%)
w_{Ni}	Nickel loading (wt.%)
X_{CO_2}	Relative conversion of carbon dioxide (-)
y_i	Mole fraction of compound i (-)
<i>Greek symbols</i>	
γ_{Hg}	Mercury surface tension (dyn cm^{-1})
θ_{Hg}	Mercury contact angle ($^\circ$)
ρ_{cat}	Apparent density of catalyst bed (g cm^{-3})
δ_{cat}	Wall thickness (mm)
$\varepsilon_{\text{CO}_2}$	Error of the carbon balance relative to the dry product gas stream (%)

[25,26] and CO₂ [26–30] methanation and therefore seem to be a promising candidate for large scale implementation.

Table 1 summarizes experimental data of studies performed on CO and CO₂ methanation with Ni/MgO catalysts [25–30] relevant for this work. All studies [25–30] were performed with low amounts of catalysts (100–300 mg) in quartz micro-reactors at ambient pressure. Different synthetic approaches (co-precipitation [25,27,28], wet impregnation [26,28,30], mechanical mixing and melting [28]) were applied. In some cases, promoters (tungsten [27], carbon nanotubes [25]) or special structures (SiO₂ shell [29]) were used to enhance catalytic activity. The focus of these studies [25–30] lies on the demonstration of the catalytic activity on a small scale and its dependency on temperature and/or synthesis method and/or catalyst formulation. However, these small scale investigations lack information relevant for technical implementation of Ni/MgO in a fixed bed reactor. The position of temperature measurement referred to in temperature vs. conversion plots was not mentioned [25–30]. The feed flow rate was only varied in one case [29].

In this work, experiments were performed with a bench-scale stainless steel tubular reactor with several temperature measurement positions to demonstrate the applicability of Ni/MgO catalysts in CO₂ methanation with a stoichiometric ratio of H₂:CO₂ = 4:1 feed. Two experimental procedures are compared: (1) scanning experiments with controlled increase of catalyst temperature and (2) steady-state operation. Furthermore, the long-term catalyst stability was evaluated. Two Ni/MgO catalysts with 11 and 17 wt.% nickel loading catalyst were prepared by wet impregnation and characterized by X-ray diffraction (XRD), energy filtering transmission electron microscopy (EFTEM), mercury porosimetry, inductively coupled plasma-optical emission spectroscopy (ICP-OES), and atomic absorption spectroscopy (AAS).

2. Materials and methods

Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99%, p.a., Lactan), granulated spherical (0–8 wt.% < 150 μm , 0–15 wt.% = 150–250 μm , 55–80 wt.% = 250–600 μm) MagGran© (4 MgCO₃·Mg(OH)₂·4H₂O, Ph. Eur., Magnesia AG, Switzerland), deionized water, and concentrated nitric acid (HNO₃, p.a., J.T. Baker) were used. Nitrogen (99.999%), hydrogen (99.999%), and carbon dioxide (99.998%) were supplied by AirLiquide.

Online gas analysis during experiments on the tubular reactor setup was carried out by means of IR absorption (ABB Uras26) for the quantification of CO, CO₂ and CH₄ (0.0–100.0 vol.%), and thermal conductivity detection (ABB Caldos27) for the quantification of H₂ (0.0–100.0 vol.%). The online gas analyzer was frequently recalibrated with three different standard gas mixtures containing certified amounts of

CO, CO₂, CH₄, H₂, and N₂ supplied by AirLiquide. Liquid reaction products were analyzed by means of total organic carbon analysis (TOC-L-CPH, Shimadzu). Atomic absorption spectroscopy was performed on an AAnalyst 400 (Perkin Elmer) device equipped with a nickel hollow cathode lamp set to 25 mA current at a wavelength of 232 nm, applying a compressed air/ethylene flame. Inductively coupled plasma-optical emission spectroscopy was performed on a Spectro Ametek (Spectro Arcos) device. Solid samples for quantification of the nickel content were dissolved in a 1:1 (vol) mixture of HNO₃ (conc.) and H₂O prior to analysis. The TEM investigations were carried out with a Philips CM20, 200 kV, LaB₆ cathode. The microscope is equipped with a Gatan 678 imaging filter for the acquisition of energy filtered images (elemental distribution maps). X-ray diffraction (XRD) patterns of the Ni/MgO catalyst powders were performed on a D8 Advance X-ray diffractometer (Bruker) using CuK α radiation. XRD data were collected in the range of 30–135° 2 θ at a step size of 0.02°2 θ and a counting time of 2 s per step. Rietveld analysis was performed with the software X'Pert Highscore Plus (PANalytical) and with Topas (Bruker). Mercury porosimetry was carried out on a Pascal 140/440 (Thermo Finnigan) with mercury in 99.9995% quality (Roth) and a sample mass of ~ 100 mg. The porosimetry measurements were validated with certified reference material ERM[®]-FD121 provided by the 'Bundesanstalt für Materialforschung und -prüfung' (Germany). Prior to porosimetry measurements solid samples were dried > 12 h at 110 °C, and cooled to room temperature over a desiccant. The Washburn equation assuming a Hg surface tension of $\gamma_{\text{Hg}} = 480 \text{ dyn cm}^{-1}$ and a contact angle of $\theta_{\text{Hg}} = 141.3^\circ$ was used to calculate the pore diameter d_p for cylindrical pores with Eq. (3) from the applied absolute Hg pressure P_{Hg} . The Rootare and Prenzlöw methodology [31] was used to calculate the specific surface area A_s from porosimetry measurements (see Eq. (4)).

$$d_p = \frac{-\gamma_{\text{Hg}} \cdot \cos(\theta_{\text{Hg}})}{2 \cdot P_{\text{Hg}}} \quad (3)$$

$$A_s = -\frac{1}{\gamma_{\text{Hg}} \cos \theta} \int_0^V P_{\text{Hg}} dV \quad (4)$$

2.1. Catalyst preparation

The catalysts referred to as Ni11-MgO and Ni17-MgO were prepared in a four step sequence: (a) preparation of magnesium oxide granulate; (b) impregnation; (c) thermal decomposition; (d) reduction in hydrogen atmosphere.

(a) Fresh magnesium oxide granulate was prepared by thermal decomposition of MagGran© granulate in the tubular reactor in N₂

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