

Available online at www.sciencedirect.com**ScienceDirect**

Energy Procedia 40 (2013) 240 – 248

Energy

Procedia

European Geosciences Union General Assembly 2013, EGU

Division Energy, Resources & the Environment, ERE

Sabatier based CO₂-methanation of flue gas emitted by conventional power plants

K. Müller*, M. Fleige, F. Rachow, and D. Schmeißer

*Applied Physics/Sensorics**Brandenburg University of Technology, Konrad Wachsmann Allee 1, 03046 Cottbus, Germany*

Abstract

The hydrogenation $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ discovered by Paul Sabatier nowadays is discussed as “Power-to-Gas” approach to utilize excess energy from renewable electricity generation. In a laboratory scale, we investigate the Sabatier process in a simulated flue gas atmosphere of conventional base load power plants. The reaction is investigated with regard to conversion rates, yield, selectivity and long-term stability. Using a catalyst based on nickel, we extract selectivities near 100% with a conversion around 85%. Beside the influence of oxygen, we investigate further typical contaminations like NO₂ and SO₂.

© 2013 The Authors. Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](#).
Selection and peer-review under responsibility of the GFZ German Research Centre for Geosciences

Keywords: Power to gas; CO₂-Methanation; Sabatier-reaction; flue gas

1. Introduction

An important aspect for the reduction of direct CO₂ emission is the reintegration of secondary products like H₂ or CO₂ into the energy supply. In the course of renewable energy production, the flexible exploitation and storage of excess energy is necessary. In such a scope, synthetic carriers of energy

* Corresponding author. Tel.: +49-355-69-4067; fax: +49-355-69-3134.
E-mail address: muellerk@tu-cottbus.de

(methane, methanol, hydrogen) are possible, also for mobility and power supply. A special concept in this scope is the production of methane from CO₂. In this case, excess energy produced by renewable energies is converted into chemical energy, with the possibility to feed the produced CH₄ into the existing network of natural gas. This concept is discussed as the “power to gas”-approach with the production of synthetic natural gas. Necessary is a sufficient supply of hydrogen, generated by regenerative energy.

In relation to hydrogen, the production of methane has to be regarded as ennoblement in energy density under incorporation of CO₂. The energy density of methane/natural gas with respect to the volume is higher; we have 40.0MJ/m³ for methane instead of 12.7MJ/m³ for hydrogen [1].

A conversion of CO₂ into CH₄ is possible by the Sabatier reaction



For a commercial nickel based catalyst, the performance for the Sabatier reaction is tested already for typical contaminations for oxyfuel combustion of coal, after flue gas condensation and desulfurisation [2]. A typical CO₂ concentration after oxyfuel combustion is higher than 95% (Wall, 2007), with SO_x and NO_x contaminations in the ppm range, after flue gas condensation and desulfurization. For controlled SO₂ and NO₂ concentrations and also for technical oxyfuel CO₂, no deviations from the catalytic activity without any contaminations are found [2].

Of course, the advantage of oxyfuel combustion is a conversion into almost pure CO₂ as flue gas, due to combustion with almost pure oxygen. On the other hand this process is limited in special applications in terms of carbon dioxide capture and storage. In relation to an approach related to carbon capture and cycling, the conversion of CO₂ directly from the flue gas of a conventional power plant is a new aspect and has several advantages: The conversion of CO₂ into methane could be integrated directly into the combustion process. Even older power plants could be upgraded and used as a possible source for CO₂, in the same sense as the amine cleaning of flue gas, as a post combustion process. Further, waste heat of the power plant could be used as process energy for the catalytic reaction.

A typical composition of the flue gas of a power plant based on brown coal is given in table 1:

Table 1. Typical composition of flue gas of a power plant based on brown coal, before flue gas condensation and desulfurisation [3]

N ₂ , Vol%	H ₂ O, Vol%	CO ₂ , Vol%	O ₂ , Vol%	SO ₂ , Vol%	NO ₂ , Vol%
65.2	18.8	11.6	4	0,35	0.05

The typical ratio of N_2/CO_2 is around five, with a residual amount of O_2 , in the range of 5Vol%. This is a relatively high value, mainly due to an extra addition of oxygen for an optimized combustion [3]. With respect to the Sabatier reaction with a stoichiometric input stream, a mixture of five parts N_2 , four parts H_2 and one part CO_2 reflects a synthetic flue gas composition with H_2 as additive for the methanation, but without oxygen and minor SO_2 and NO_2 contaminations. In this work we investigate the catalytic performance of nickel based catalysts in a synthetic flue gas atmosphere. Also, we, investigate the influence of oxygen as well as SO_2 and NO_2 contaminations.

2. Experimental

As catalyst for the Sabatier based methanation, we use nickel oxide, supported on silica gel with a content of 60wt% NiO (Aldrich) and an average grain size of 0.15 up to 0.25 mm for the silica particles. For each experiment described below we use a fresh prepared NiO/silica catalyst.

To prevent hot spots and related sintering effects [4], we distribute the NiO catalyst in a bed of quartz sand with approximately same grain size (here sieved into 0.25mm). The NiO-catalyst is homogenized in a weight ratio of quartz sand: NiO/silica=15:1. In total 7g of the catalytic mixture is filled into a metallic reactor tube of 8mm in diameter and 100mm in length.

Using a swagelok system for the gas flow, the reactor is mounted into an oven, which supplies a homogeneous temperature distribution during the catalytic reaction. The reactor is build with stainless steel (swagelok Cr-Ni steel, 304/304L, according to American Iron and Steel Institute nomenclature). The incoming gas stream is preheated in a gas tube, formed as a spiral with a length of 224 cm (figure 1). For a direct control of the temperature evolution during the reaction, a thermocouple is mounted inside the reactor tube. After mounting into the furnace, all catalytic charges are activated in a stream of hydrogen with a flow rate of 20ml/min at a temperature of 400°C. The activation is completed when the content of hydrogen is 100% in the output gas stream, measured by our sensing system. The Sabatier reaction is started normally at 350° with a stoichiometric input composition of four parts H_2 and one part CO_2 in gas flow, adjusted as ml/min. All experiments are performed at ambient pressure inside the reactor chamber.

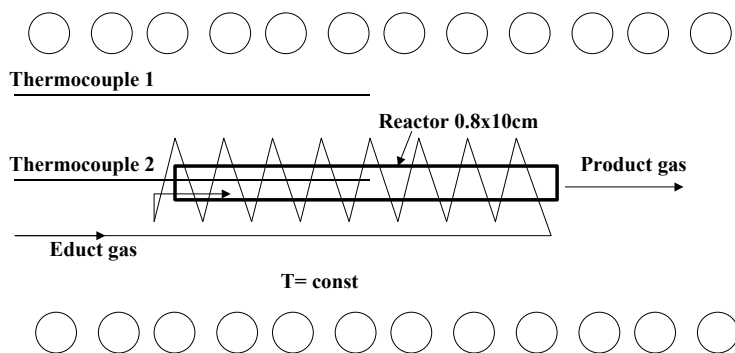


Fig. 1. Schematic of the reactor: The incoming gas is preheated in a swagelok tube, formed into a spiral. The spiral is 224cm in length, with a diameter of the tube of 0.3 cm. After preheating, the gas is guided into the reactor tube with 0.8 cm in diameter and 10cm in length. The product gas is then guided to the analytical system. The reactor is mounted into a Nabertherm oven for an isothermal temperature regime

We perform the following sequence of tests in different educt gas mixtures:

- five parts N₂, four parts H₂, and with one part CO₂ as a reference
- five parts N₂, one part CO₂ and O₂ additives from 1 up to 8% in the flue gas, and four parts H₂
- five parts N₂, four parts H₂, one part CO₂, and added SO₂ and NO₂ contaminations, up to 86ppm in the flue gas.

The oxygen additive is guided in our gas mixture system, the contamination is added as SO₂ or NO₂ in CO₂ or N₂ as carrier gas. The gas is delivered as certificated mixture (Crystal Mixture, Air Liquide), and is added with defined values into the input gas stream.

As analytical system, we use a quadrupole mass spectrometer (e-Vision2, mks) and additionally gas sensors for CO₂, H₂, CH₄ and CO (AGM, Sensors Inc.). For the measurement of the mass flow after the catalytic reaction, we use a flow controller for the product gas stream ("Definer", Bios). With this information on chemical composition and flow rates of the product gas stream, a characterization of the catalytic performance in terms of conversion X, yield Y and selectivity S, according to [5,6] is possible.

For operation, the quadrupole mass spectrometer is installed in a vacuum chamber. The vacuum chamber is connected into the gas stream of the product gases via a pinhole of 6 µm in diameter. With this setup also a characterization of catalysts by performing thermal desorption experiments (TDS), directly in situ is possible [7,8]. A detailed description of the setup for catalysis is given in [5].

3. Results

In a first part (figure 2), we show the measurements for synthetic flue gas without oxygen and further additives. This investigation is a reference and standard for further experiments and shows the catalytic performance in a nitrogen dominated atmosphere. A highly selective conversion of CO₂ with a yield >80% was measured. The performance of the catalyst is obviously not influenced by dilution effects or even additional reactions. Compared to measurements with only four parts of H₂ and one part of CO₂, without nitrogen, no significant change in performance is measured [2,5]. Also, the performance is stable during the time frame of the experiment (two days).

Oxygen plays a dominant role as contamination or residual of the combustion process in flue gas. In a second step, we added oxygen into the gas. The catalytic performance versus the oxygen content in the flue gas is shown in figure 3A. The first observation is a lowering of conversion and yield, but remaining high selectivity. Obviously, the hydrogen-oxygen reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ ($\Delta_f H^0 = -571,6 \text{ kJ/mol}$) plays an important role here. Due to this reaction, in ideal case for every oxygen molecule two molecules of hydrogen are detracted and not available for the Sabatier reaction. In figure 3B, we compare the measured conversion versus oxygen content with a calculation for 100% conversion of hydrogen by the hydrogen-oxygen reaction assumed. For this purpose, we take the molar fraction of oxygen in the flue gas:

$$P_{\text{O}_2} = [\text{O}_2] / ([\text{O}_2] + [\text{CO}_2] + [\text{N}_2])$$

With N₂:CO₂:H₂=5:1:4, the ratio of O₂:H₂ is received as

$$[\text{O}_2] / [\text{H}_2] = \eta_{\text{O}_2} = 3 / (2(1 - P_{\text{O}_2}))$$

Taking the hydrogen-oxygen reaction into account, we should have for conversion (and yield also)

$$X_{CO_2} = X_{CO_2}^0 (1 - 2\eta_{O_2})$$

With $X_{CO_2}^0$ as conversion (or yield) without any oxygen content. With this assumption, we have

$$X_{CO_2}(P_{O_2}) = X_{CO_2}^0 (1 - 3P_{O_2} / (1 - P_{O_2}))$$

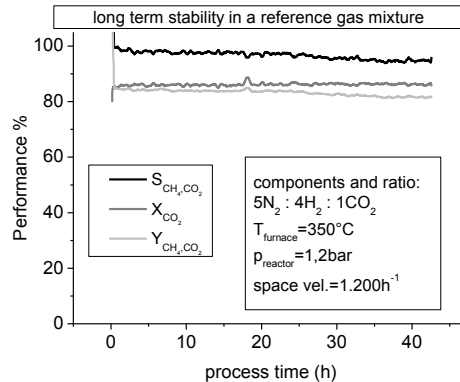


Fig. 2. Catalytic performance, expressed as conversion X of CO₂, yield Y of CH₄ and selectivity S towards the Sabatier reaction versus time for an educt gas stream of 100 ml/min, consisting of 50ml/min N₂, 40ml/min H₂ and 10ml/min CO₂. The reactor temperature is 350°C.

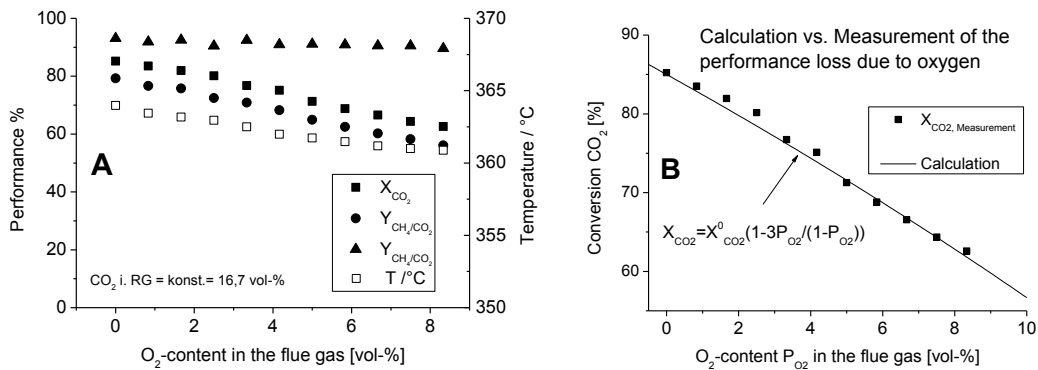


Fig 3: A: Catalytic performance versus the content of oxygen in the flue gas, for an educt gas stream of 100 ml/min, consisting of 50ml/min N₂, 40ml/min H₂ and 10ml/min CO₂ and different additives of O₂. Each point reflects the static performance after oxygen input. Also the temperature of the reactor is drawn, versus oxygen content. B: Conversion X of CO₂ as function of oxygen content in the flue gas, compared to a calculation with a conversion of 100% of oxygen, according to $2H_2 + O_2 \Rightarrow 2H_2O$

A good fitting of the data is obvious, in conclusion, the hydrogen-oxygen reaction is preferentially responsible for the loss in catalytic performance.

The hydrogen-oxygen reaction is strongly exothermic, an influence on the reactor temperature is expected. The temperature inside the reactor during the catalytic reaction is also shown in figure 3A. The temperature remains nearly constant, with a small drop towards lowered temperatures. One possible reason is the lowered efficiency of the Sabatier reaction, which compensates the temperature evolution during the hydrogen-oxygen reaction. Another reason could be a reaction of hydrogen with oxygen already in the metallic tubes, consisting of a Cr-Ni alloy, as already mentioned.

An additional confirmation for the hydrogen-oxygen reaction and the complete removal of oxygen by this reaction is the long time stability of the catalytic performance with a certain amount of oxygen. Figure 4 shows a measurement over a period of 40 hours with a content of 5% in the synthetic flue gas. No differences in performance over time are found: The selectivity remains constant near 100%, with a conversion and yield near 70%.

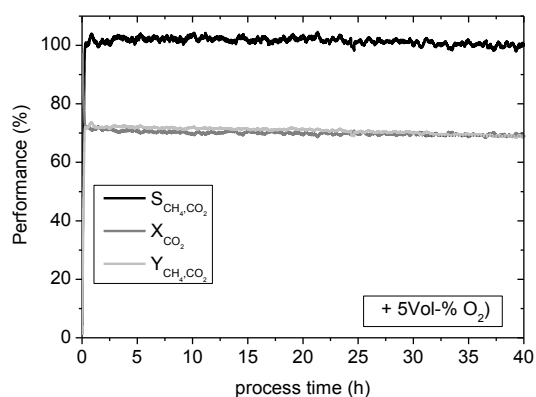


Fig 4: Catalytic performance versus time, with a content of 5% oxygen in the synthetic flue gas. Again for an educt gas stream of 100 ml/min, consisting of 50ml/min N_2 , 40ml/min H_2 and 10ml/min CO_2

A critical contamination is sulphur. In terms of CO hydrogenation, even trace amounts of H_2S in the range of 15-100 ppb can reduce the catalytic performance by several orders of magnitude, for example [9]. This strong influence of a small sulphur content is mainly due to the strong bonding of sulphur and metal atoms.

In contrast to biogas with H_2S as sulphur contamination and its well known influence on activity, for flue gas of conventional power plants the main sulphur contamination is in the form of SO_2 . We have to investigate whether oxidised sulphur in the typical concentration range after desulfurization is deleterious for the catalytic activity of Ni catalysts. For example, Pt electrocatalysts in fuel cells are degraded by SO_2 , due to the formation of strong bonds between the metallic catalytic center and sulphur [10]. Also for the catalyzed combustion of methane, SO_2 plays an important role for degradation of Pd, Ir and Pt catalysts [11,12].

In figure 5, we show a catalytic performance as function of time, the first 12.5h for a reference without any contaminations, and then CO_2 with 516ppm SO_2 additive is used. Because the educt gas is thinned out with four parts hydrogen, the corresponding value for the SO_2 content in the flue gas is 86ppm. For dry flue gas after flue gas condensation and desulphurization, this is a typical value [13]. Directly after

change from reference to the contaminated gas flow, the conversion and yield and the selectivity drops down. The conversion drops for 17% in 12.5 hours, or 1.36% per hour. This deactivation caused by the SO_2 content is low in relation to a possible degradation caused by H_2S .

The next important contamination is NO_2 . Figure 6 shows the performance of flue gas with an NO_2 contamination of 100ppm. For NO_2 , the catalytic performance is not significantly affected for the time frame of 100 hours measurement. The selectivity remains constant at near 100%, also the conversion is high, with a value of greater than 80%.

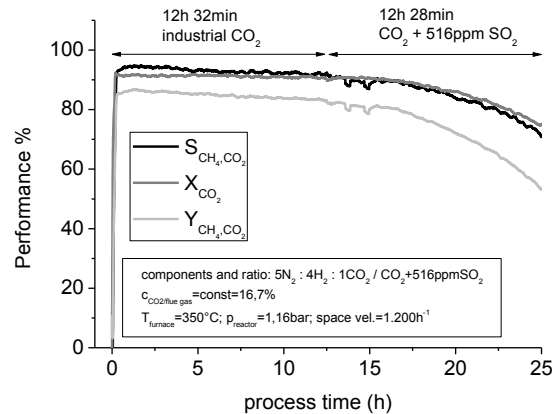


Fig. 5. Catalytic performance versus time, after 12.5h, CO_2 with 516ppm SO_2 is used. This corresponds to a content of 86ppm in the flue gas.

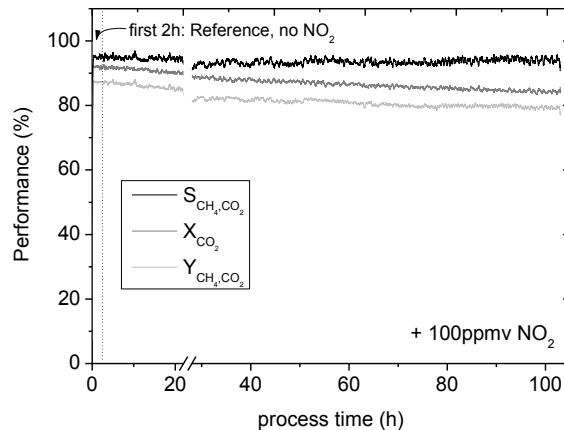


Fig. 6. Catalytic performance versus time, with a NO_2 -content of 100ppm.

4. Summary and Discussion

The investigations in the presented work focus on fuel gases emitted by conventional power plants, as a potential source of CO₂ for the Sabatier reaction. Using a commercial Ni based catalyst on a silica support; we present the catalytic performance in a simulated fuel gas atmosphere with a CO₂/N₂-ratio of 1:5. This is a typical value for conventional power plants on the base of brown coal.

In summary, the catalytic performance is not influenced by dilution effects or additional reactions. As in the case without nitrogen, a selectivity near 100% and a conversion of CO₂ as well as a yield CH₄ of greater than 80% was measured. Also, the performance is stable during the time frame of the experiments.

An investigation of synthetic flue gas with additional contaminations give the following results: For NO₂ in a concentration of 100ppm, no significant change in performance is detected.

Oxygen is an additive for an optimized combustion process in a power plant and a content of around 5 vol-% is typical for flue gas. The catalytic performance for a variation of the oxygen content from 0 up to 8 vol% (and higher) shows no changes in the catalytic acidity, in principle. Nevertheless, the efficiency of the process is lowered by the oxygen-hydrogen reaction. Here, the hydrogen, available for the Sabatier reaction is removed by this reaction, and the conversion and yield is exactly lowered by the amount of subtracted hydrogen. In general, the efficiency of the methanation is lowered by additional oxygen, and the amount of oxygen in the flue gas should be as low as possible. Of course, a compensation of hydrogen loss due to the oxygen hydrogen reaction is an opportunity, but the result is a need for more hydrogen or energy, also with a loss in efficiency.

Sulphur is known to be deleterious for Ni based catalysts, SO₂ in a concentration of around 80ppm is a typical contamination for flue gas. After change from the reference to the contaminated gas flow, the conversion, yield and also the selectivity is lowered for 17% in 12.5 hours, or 1.36% per hour. This deactivation caused by the SO₂ content is low in relation to a possible degradation caused even by traces of H₂S. This difference has to be discussed with regard to the probability of the reaction of the H₂S and the SO₂ molecule with the free surface of the Ni. Here we have to take a look on the molecule stability: A hint for the stability of the two molecules H₂S and SO₂ is their Standard enthalpy of formation $\Delta_f H^\circ_{298}$. A comparison of the standard enthalpies of formation gives only -21 kJ/mol for H₂S [14], but -297 kJ/mol for SO₂ [15]. Because this energy is need again to decompose the molecule, this indicates a much higher thermal stability of the SO₂ molecule, compared to the H₂S. This could be a reason for the relative stability of the Ni based catalysts against SO₂.

A possible way for operation in flue gas with an SO₂ contamination of around 80ppm is the regeneration of sulphur poisoned catalysts. As an example, the regeneration of sulphur-poisoned steam reforming catalysts based on Ni, a treatment with steam, steam-air mixture, and steam-hydrogen mixture (H₂O/H₂ molar ratio of 100) for removing sulphur as SO₂ and H₂S is usual [16]. Further, if necessary, an effective removal of SO₂ in the flue gas is possible by using active coal for SO₂ adsorption. In demonstration plants, a precipitation of SO₂ below the detection limit was shown [17].

For a conversion of 85% and around 100% selectivity, the product gas in our experiments is a mixture of 5 parts N₂, 0.15 parts CO₂, 0.85 parts CH₄ and 0.6 parts H₂, the water is removed in a cooling trap. The relative amount of CH₄ is here 12.9%. In terms of a power to gas approach, we have to take into account, that such a mixture is a typical "lean gas" with a low fuel value ($H_o \leq 9 \text{ MJ/m}^3$) [18]. In consequence, further investigations related to a transition into rich gas are necessary. Opportunities are the separation of nitrogen by pressure swing adsorption or polymer membranes [19]. Other possibilities are the transition into liquid gas, or recuperation approaches, with a storage of excess energy in the form of lean gas and a combustion in the case of demand. Nevertheless, a high potential of the methanation of fuel gas is given by the possibility of upgrading conventional power plants in the sense of a post combustion processes.

Acknowledgements

First of all we grateful acknowledge G. Beuckert, M. Städter, I. Paloumpa for the assistance. The topic of CO₂ methanation is part of GeoEn-Geoenery-Research. GeoEn is funded by the German Ministry of Research and Education (BMBF). It is a joint research project of the German Research Centre for Geosciences (GFZ), the University of Potsdam (UP) and the Brandenburg University of Technology (BTU) and addresses fundamental questions related to the sustainable use of geo-energy. The direct methanation of fuel gas is funded by BMWi under grant 03ET7002A. Based on our results in laboratory scale, a further upscaling is necessary. These experiments are planned and funded by the European Regional Development Fund (ERDF).

References

- [1] Bossel U, Eliasson B. *Energy and the Hydrogen Economy*. Oberrohrdorf, Switzerland: ABB Switzerland Ltd.; 2003.
- [2] Müller K, Rachow F, Israel J, Schmeißer D. Sabatier based CO₂ methanation under oxyfuel conditions. To be published 2013.
- [3] Bernstein W. Energietechnik. In: Hering E, editor. *Grundwissen des Ingenieurs*, München: Carl Hanser; 2007, p. 581–618
- [4] Rostrup-Nielsen JR, Pedersen K, Sehested J. High temperature Methanation Sintering and structure sensitivity. *Applied Catalysis A: General* 2007; **330**:134–138.
- [5] Müller K, Städter M, Rachow F, Hoffmannbeck D, Schmeißer D, Sabatier- based CO₂-Methanation by Catalytic Conversion *Environmental Earth Science*, submitted 2013.
- [6] Dittmeyer R. *Chemische Technik. Prozesse und Produkte*. 5. Ed. Weinheim: Wiley-VCH; 2006.
- [7] Städter M. *Integration eines Quadrupolmassenspektrometers zur Charakterisierung von Hochdruckreaktionen in Katalyse und ALD*. Diploma Thesis, Technical University Cottbus 2011.
- [8] Städter M, Richter M, Rachow F, Müller K, Schmeißer D. Ambient Pressure Thermal Desorption measurements on NiO on SiO₂ catalysts. *Environmental Earth Sciences*, submitted 2013.
- [9] Bartholomew CH. Mechanisms of catalyst deactivation. *Applied Catalysis A: General* 2001; **212**:17-60.
- [10] Gould BD, Baturina OA, Swider-Lyons KE. Deactivation of Pt/VC proton exchange membrane fuel cell cathodes by SO₂, H₂S and COS. *J. Power Sources* 2009; **188**:89–95.
- [11] Escandón LS, Ordóñez S, Vega A, Díez FV. Sulphur poisoning of palladium catalysts used for methane combustion: effect of the support. *J. Hazard Mater.* 2008; **153**:742-750.
- [12] Ohtsuka, H. The Oxidation of Methane at Low Temperatures Over Zirconia-Supported Pd, Ir and Pt Catalysts and Deactivation by Sulfur Poisoning. *Catalysis Letters* 2011; 141:413-419.
- [13] Fleige M. *Die Sabatier-Reaktion unter Rauchgasbedingungen konventioneller Wärmekraftwerke: Experimentelle Untersuchung und Verfahrensaspekte*. Master Thesis BTU Cottbus, 2013.
- [14] Zumdahl, S. *Chemical Principles* 6th ed. Boston: Houghton Mifflin Company; 2009.
- [15] Eckman JR, Rossini F. The heat of formation of Sulfur Dioxide, Bureau of Standards Journal of Research 1929; 3: 597.
- [16] Liyu Li L, Howard C, King DL, Gerber M, Dagle R, Stevens D. Regeneration of Sulfur Deactivated Ni-Based Biomass Syngas Cleaning Catalysts. *Ind Eng Chem Res* 2010; **49**: 10144.
- [17] Ritter G. Möglichkeiten der Schadstoffabtrennung aus Abgasen mit Braunkohlenkoks. In: Steinmetz E, editor. *Adsorptive Nachreinigung von Abgasen aus Verbrennungsanlagen mit Aktivkoks*, Essen: Vulkan; 1992, p. 8–18.
- [18] Cerbe G, Carlowitz O, Hölzel G, Kochs A, Knauf G, Köhler H, Lehmann J, Lethen H, Mauruschat H. *Grundlagen der Gastechnik*. 4th ed. München: Hanser; 1992.
- [19] Ballhorn M. *Entwicklung von Polymermembranen für die Abtrennung von Kohlendioxid aus Gasströmen*. Dissertation, RWTH Aachen, 2000.