In operando detection of coke deposits on a fixed-bed catalyst by a microwave method

Peter Fremerey [1,2], Dieter Rauch [1,2], Andreas Jess [1], Ralf Moos [2]

[1] Department of Chemical Engineering, [2] Department of Functional Materials, University of Bayreuth,
Zentrum für Energietechnik, 95440 Bayreuth, Universitätsstraße 30, Germany,
peter.fremerey@uni-bayreuth.de

Abstract:

The intention of this work is to investigate a contactless in situ microwave-based technique to detect coke deposits in an industrial fixed-bed catalyst. The steel reactor is thereby used as an electrical cavity resonator. The perturbation in the resonator is measured in the microwave range by a vector network analyzer and two waveguide feeds (coaxial antennas). Due to coke loading, the electrical conductivity of the catalyst pellets increases strongly. This leads to changes in the resonance behavior that are mirrored by the scattering parameters. Therefore, the locally homogeneously distributed coking process and the coke burn-off process that starts at the front of the reactor and moves through the fixed bed can be observed by the microwave-based method.

Key words: contactless microwave method, coke deposits, soot sensing, cavity perturbation, electrical conductivity

Introduction

The formation of carbonaceous deposits on the internal surface of porous heterogeneous catalysts is a serious problem in chemical industry using organic compounds as reagents. These coke deposits lead to catalyst deactivation owing to fouling. They hinder the mass transfer into the pores [1] and block the active sites of the catalyst. In addition, the coke deposits decrease the heat transfer and increase pressure drop over the fixed-bed [2].

Coke formation starts by the formation of polymeric structures via condensation and rearrangement reactions. At high temperatures, polyaromatic compositions are obtained through dehydrogenation and hydrogen transfer reactions. A simple scheme of the coking process on acid and bifunctional (noble metal/acid) catalysts is given in [3].

In the regeneration process with oxygen, an adequate conversion rate can be obtained at comparatively low temperatures of about 500 °C, which protects the catalyst from irreversible thermal deterioration, e.g. sintering [4] caused by the highly exothermic oxidation reaction. To avoid sintering, the coke is not burned off with pure oxygen but with diluted oxygen in inert gas like nitrogen. Typically, the regeneration is proceeded with only 1 vol-% oxygen [1].

At the moment, the catalyst state with respect to coke loading cannot be monitored directly and continuously. This would be, however, beneficial for efficiency and safety reasons. Here, a microwave-based measurement technique is examined to monitor the coking and the decoking process directly and *in operando.* This measurement technique was successful tested in [5]. A similar method has already been introduced to determine the status of several different automotive exhaust gas aftertreatment systems: three-way catalysts [6], lean NO_x traps [7], ammonia SCR-catalysts [8], or diesel particulate filters [9].

Experimental setup

The microwave-based method is applied to a lab-scale steel reactor with a length of 345 mm and a cross sectional area of 30 x 30 mm^2. The reactor is heated from outside by a heating sleeve. In contrast to [5] the new setup with the perforated sheets after the gas inlet and before the gas outlet is shown in figure 1. In successful simulation studies we found out that the gas inlet has a great influence on the microwave measurement. To avoid this, the perforated metal sheets are installed in the reactor. The measurement temperature is 550 °C ±4 °C. During coking, 33 % propane (coke source) mixed with N_2 is used at a total flow rate of 30 l/h (1 bar, 20 °C). This high propane partial pressure promotes the deactivation by coke formation [10]. The catalyst is regenerated at 560 °C and a total flow rate of 15 l/h (1 bar,

20 °C) with 2 % O_2 in N_2. During regeneration, a reaction front develops within the catalyst bed. Within the reaction front, the oxygen concentration drops from the initial value to almost zero. With increasing burn-off time, this front moves with constant velocity in axial direction through the fixed-bed [11].

To determine the concentrations of CO, CO_2 and O_2, during regeneration, a gas analyzer (Fisher Rosemount NGA 2000) is installed downstream of the reactor.

The catalyst pellets used in the experiments are porous, pure alumina cylinders with 4.5 mm in diameter and length (BET-surface area:

190 m^2/g, particle density: 1.45 g/cm^3, porosity: 0.4, average pore diameter: 6 nm). The total mass of all pellets in the fixed-bed is about 105 g.

To excite the electromagnetic waves, two coaxial antennas are mounted up- and downstream of the fixed-bed catalyst. The antennas are connected to a vector network analyzer (Anritsu VNA Master MS2028B) via coaxial lines. The scattering parameters of the reactor are measured between 1 and 20 GHz and are subsequently evaluated usually between 3 and 7.5 GHz.
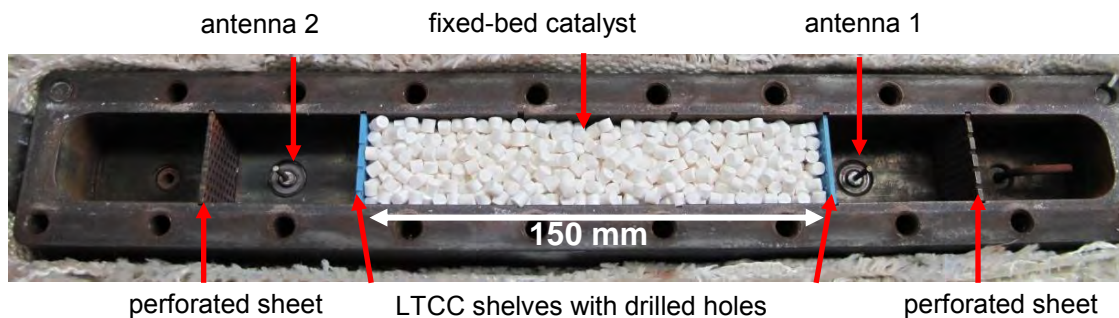

Fig. 1: Reactor setup with the two antennas, fixed-bed catalyst, and the low temperature co-fired ceramic (LTCC) shelves with a low electric conductivity to allow electromagnetic wave propagation and many small laser-drilled holes for the gas flow

The scattering parameters S_{xy} express the ratio between the complex wave amplitudes of the ingoing (a_x) and outgoing (b_y) waves.

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} S_{11}(f) & S_{12}(f) \\ S_{21}(f) & S_{22}(f) \end{pmatrix} \cdot \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (1)$$

For a two-port resonator, as assembled in this work, there are four parameters. S_{11} and S_{22} describe the reflected power at each port at matched input and S_{12} and S_{21} describe the transmitted power from one port to the other. Resonance frequencies, f_{res}, at which resonant modes are formed in the cavity resonator, can be obtained from a plot of the magnitude of the S-parameters over frequency. Usually, the S-parameters are plotted in dB ($20 \cdot \log |S_{xy}(f)|$). The resonance frequencies can be evaluated at the local extrema of the curves. Moreover, the attenuation of the electromagnetic waves can be observed in this plot. More details of this method are described in [12]. In general, the coke deposits change the electrical properties of the resonator filling, particularly of the conductivity. This leads to noticeable shifts of the resonance frequencies and of the attenuation.

Measurement results

The evolvement of a distinct single resonance mode of the reflection parameter $|S_{11}|$ is displayed during coking (Fig. 2).
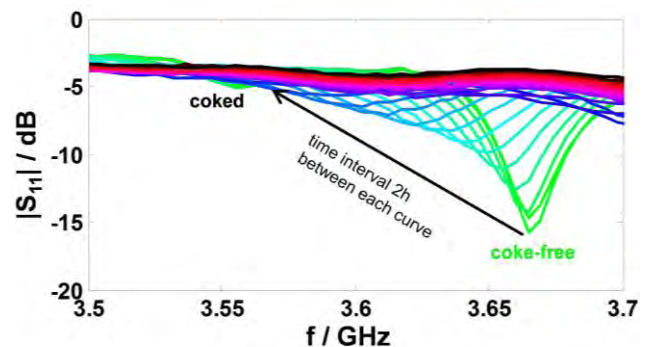

Fig. 2: A single resonance mode of $|S_{11}|$ for different coking times

Figure 3 shows the transmission parameter $|S_{12}|$ for the same experiment. The black lines are the state after 60 hours of coking. At this point of time, the catalyst had reached a carbon load of about 10 g per 100 g catalyst, i.e. L_{coke} = 10 %, as determined by comparison of the weight of the fixed-bed before and after coking.
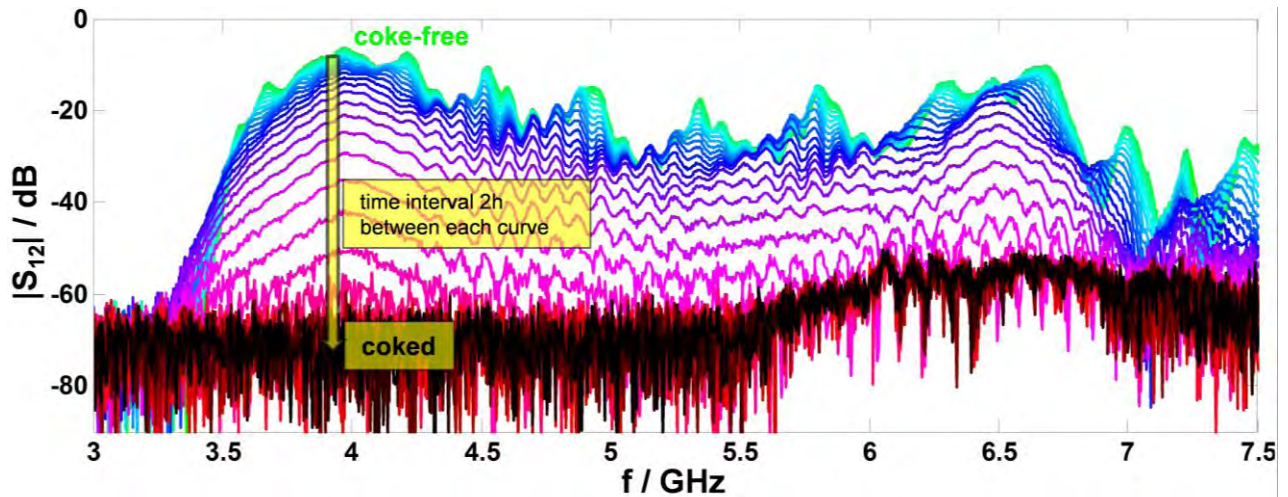
Fig. 3: Transmission parameter |S_{12}| during coke loading

It was proven that both antennas remained always free of coke. Both parameters, |S_{11}| and |S_{12}|, reveal an obvious dependence on the coke loading. The regeneration can be also monitored with this system and the spectra of the completely regenerated catalyst are identical to the spectra at initial coke-free conditions. No aging effect over several measurements with the same antennas can be observed. Also the spectra from a fixed-bed existing of pure alumina measured with these antennas do not change with varying oxygen concentration.

Similar measurements at room temperature show that the electrical conductivity of coke increases with temperature, as already shown in [13]. Additionally the catalyst absorbs the air humidity which also leads to a higher conductivity.

Since the transmission parameters like |S_{12}| do not show any distinct peaks (Fig. 3), the influence of the coke loading is characterized by the average value of |S_{12}| in the range of 4 to 6 GHz:

$$\left|\overline{S_{12}}\right|/\mathrm{dB} = \frac{1}{n_{\mathrm{total}}} \sum_{i(4\mathrm{GHz})}^{i(6\mathrm{GHz})} \left|S_{12}(f_i)\right|/\mathrm{dB} \qquad (2)$$

with n_{total} being the number of sampling points between 4 and 6 GHz. This average value is plotted in figure 4.

With the used setup, no attenuation below about -70 dB could be measured. Therefore, data for very high coke loadings (coking time of more than 50 h; $\overline{|S_{12}|}$ < -70 dB) may not be reliable.

A full coking process followed by a complete regeneration was investigated in the next experiment, which is shown in figure 4. Here, the average value of |S_{12}| is plotted over the coke mass. The red curve displays the coking process and the black line the regeneration

process. After 55 h, the coking process is stopped. This results in 8.5 g coke on 100 g catalyst. During the coking process, 95 % of the propane leaves the reactor without participating in the reaction; as confirmed by gas chromatography. Therefore, the coking process is largely homogenous over the whole fixed bed, which agrees with [13]. Hence, we can assume that the coke loading is constant allover the bed and only changes with time.

In contrast to the coking process, the coke mass at the regeneration is calculated from the CO and CO_2 data of the gas analyzer. Due to the reaction front over the catalyst filling and into the pellets at high regeneration temperature, the coke burns off only at the beginning of the experiment linearly where all oxygen is used. Therefore a C-balance using gas analyzer data defines the coke mass over the whole time precisely.

In general, coking and regeneration differ with regard to the axial coke distribution. This can also be seen in the signal of the VNA which is an average signal about the whole catalyst filling. As described in [13] the electrical conductivity of one pellet changes while conductive paths (percolation paths) of coke are formed through the pellet. This occurs during the coking process after approximately 1 g coke per 100 g catalyst is accumulated in the filling. Until this point, the coke deposit in the catalyst filling does not change the material parameter in a measurable extent, i.e. average value of the transmission parameter is almost constant.

The regeneration displays a different curve. A reason could be that the coke burn-off is not homogeneous over the whole filling, i.e. the single catalyst particles have not the same coke loading during regeneration. In the front section of the bed, the particles are coke free whereas in the rear section the particles still have their

initial coke loading. Only within the reaction front, there are particles with a coke loading between these two extremes, which is most probably the reason for the different curves during coking and decoking (figure 4).

Another aspect may also have an influence: During regeneration at high temperatures (e.g. 500°C), pore diffusion limitations lead to the development of a distinct radial coke profile within the particles [11], which may also have an influence on the electrical signal. At lower temperature (less than 400 °C) these intra-particle diffusion limitations are negligible [11]; respective measurements are currently done. For a proper comparison with the respective signal during coking (which is too slow at such a low temperature to be measurable), it is also necessary to know and to measure how the resonance frequencies shift at different temperatures [14].
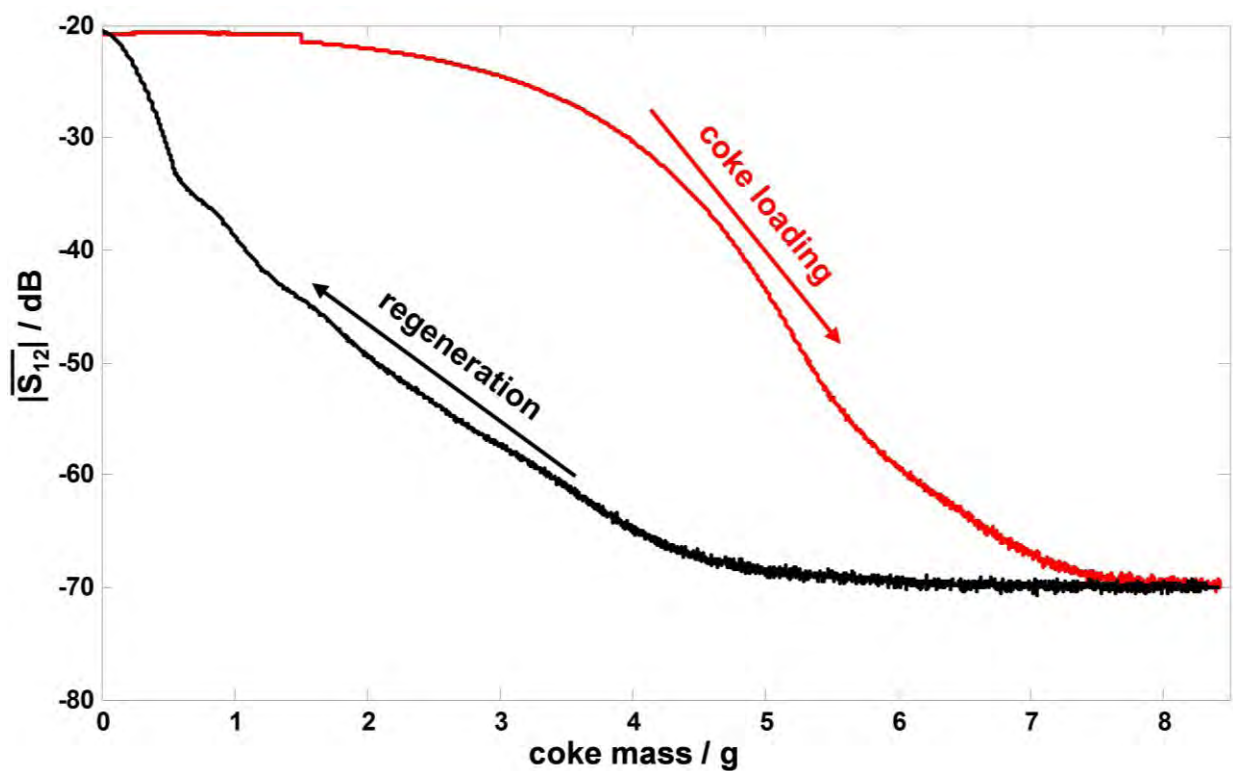

Fig. 4: A coke loading process following directly by a regeneration process. For both processes the average signal of S_{12} is displaced over the coke mass (mass of the unloaded fixed-bed:100 g)

Conclusion and outlook

In this work, it could be shown that the investigated microwave method is suitable to monitor coking and regeneration of a fixed-bed catalyst directly. A strong decrease of the transmission of the electromagnetic waves is observed with increasing coke load of the catalyst bed. For monitoring the coke loading, the attenuation of the transmission parameters tracks the process for a longer time compared to the frequency shift or attenuation increase of the reflection parameters. As a result, the detection of smaller levels of coke load can be measured by the reflection parameters and higher levels by the transmission parameters.

For a better understanding of the system and of the microwave-based technique manual mixed catalyst fillings of pure alumina and defined coke-loaded alumina pellets are under examination.

In future, measurement with the antennas placed directly in the fixed-bed will also been done. In case of success, no LTCC shelves would be needed, which would simplify the new measurement system.

Finally, experiments will be done with a bigger reactor in order to investigate the influence of the reactor size and length-to-diameter ratio.

Acknowledgements

References

[1] C. Kern, A. Jess, Verkokung und Koksabbrand in heterogenen Katalysatoren, *Chemie Ingenieur Technik* 78, 8, 1033-1048 (2006); doi: 10.1002/cite.200600051

[2] D.L. Trimm, Control of Coking, *Chemical Engineering and Processing: Process Intensification* 18, 137-148 (1984); doi: 10.1016/0255-2701(84)80003-3

[3] M. Guisent, P. Magnoux, Organic chemistry of coke formation, *Applied Catalysis A: General* 212, 83-96 (2001); doi: 10.1016/S0926-860X(00)00845-0

[4] C. Royo, J. Santamaría, A. Monzón, Effect of thermal aging upon the regeneration kinetics of a coked Cr_2O_3-Al_2O_3 catalyst, *Thermochimica Acta* 274, 249-259 (1996); doi: 10.1016/0040-6031(95)02714-9

[5] D. Rauch, P. Fremerey, A. Jess, R. Moos, In situ detection of coke deposits on fixed-bed catalysts by a radio frequency-based method, *Sensors & Actuators: B. Chemical* (2013); manuscript number: SNB-D-12-01999R1

[6] R. Moos, M. Wedemann, M. Spörl, S. Reiß, G. Fischerauer, Direct Catalyst Monitoring by Electrical Means: An Overview on Promising Novel Principles, *Topics in Catalysis* 52, 2035-2040 (2009); doi: 10.1007/s11244-009-9399-6

[7] P. Fremerey, S. Reiß, A. Geupel, G. Fischerauer, R. Moos, Determination of the NOx Loading of an Automotive Lean NOx Trap by Directly Monitoring the Electrical Properties of the Catalyst Material Itself, *Sensors* 11, 8261-8280 (2011); doi: 10.3390/s110908261

[8] S. Reiß, D. Schönauer, G. Hagen, G. Fischerauer, R. Moos, Monitoring the ammonia loading of zeolite-based ammonia SCR catalysts by a microwave method, *Chemical Engineering and Technology* 34, 791-796 (2011); doi: 10.1002/ceat.201000546

[9] G. Fischerauer, M. Förster, R. Moos, Sensing the Soot Load in Automotive Diesel Particulate Filters by Microwave Methods, *Measurement Science and Technology* 21, 035108 (2010); doi:10.1088/0957-0233/21/3/035108

[10] M. Larsson, N. Henriksson, B. Andersson, Estimation of reversible and irreversible coke by transient experiments, *Catalyst Deactivation* 111, 673-680 (1997); doi: S0167299197802133

[11] C. Kern, A. Jess, Regeneration of coked catalysts – modelling and verification of coke burn-off in single particles and fixed bed reactors, *Chemical Engineering Science* 60, 4249-4264 (2005); doi:10.1016/j.ces.2005.01.024

[12] G. Fischerauer, M. Spörl, A. Gollwitzer, M. Wedemann, R. Moos, Catalyst State Observation via the Perturbation of a Microwave Cavity Resonator, *Frequenz* 62, 180-184 (2008); doi: 10.1515/FREQ.2008.62.7-8.180

[13] N. Müller, Direkte Bestimmung von Koksdepositen auf Festbettkatalysatoren durch elektrische Sensoren, Bayreuther Beiträge zur Sensorik und Messtechnik, Band 8, Shaker, Aachen, 2011

[14] M. A. Rzepecka, M. A. K. Hamid, Modified perturbation method for permittivity measurements at microwave frequencies, *Journal of Microwave Power and Electromagnetic Energy* 9, No. 4, 317 -328 (1974)