



## In situ detection of coke deposits on fixed-bed catalysts by a radio frequency-based method

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### ABSTRACT

The aim of this work is to study whether a contactless radio frequency-based method is suitable to monitor both coking and regeneration (coke burn-off) of industrial fixed-bed catalysts directly and *in operando*. The tubular steel reactor serves as an electromagnetic cavity and two waveguide feeds (coaxial antennas) are used to impress and receive electromagnetic waves between 1 and 20 GHz. Shifts of the resonance frequencies mirror the coke loading in the lowly loaded state and strongly decreasing power transmission over the entire frequency range goes along with increasing coke load at higher coke loadings. Both the locally homogeneously distributed coking process and the coke burn-off process that starts in the reactor front and moves through the reactor can be observed by the radio frequency-based method.

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### 1. Introduction

In many chemical processes, porous heterogeneous fixed-bed catalysts are used to enhance the rate of chemical reactions and to influence the product selectivity. Major fields of application for solid catalysts are refinery processes and the petrochemical industry, e.g. catalytic reforming of gasoline, dehydrogenation of paraffins or catalytic cracking [1]. A crucial problem during these processes is coke formation in unwanted side reactions. Coke in this context is an abbreviation for various carbonaceous deposits formed inside the catalyst pores. These deposits lead to catalyst deactivation owing to fouling, which is one of the important deactivation mechanisms [2]. The coke deposits block the active sites of the catalysts and hinder the mass transfer in and out of the pores [3]. In addition, the coke deposits decrease the heat transfer and increase pressure drop over the fixed-bed [4]. Depending on the reagents, catalysts, and reaction conditions, coke formation may take a few seconds up to years [1,5]. The chemical composition and structure of coke deposits vary widely [1,5]. At low temperatures, coke shows polymeric structures formed by condensation and rearrangement reactions, whereas at high temperatures, polycyclic aromatic compositions are obtained through dehydrogenation

and hydrogen transfer steps. A very simple scheme of the coking process on acid and bifunctional (noble metal/acid) catalysts with different reactants is given in [6]. The tendency to coke formation depends on the structure of the hydrocarbons used as reactants. Polycyclic aromatics have the highest affinity for coke formation followed by monocyclic aromatics, olefins, and alkanes [7].

To restore the catalytic activity, the coke has to be removed from the catalyst, which is usually done by coke burn-off using oxygen or (in rare cases) by the much slower gasification with carbon dioxide or steam [5,8,9].



Due to the much shorter regeneration time in oxygen (combustion) compared to carbon dioxide and steam (gasification), this regeneration procedure is of much higher interest from the technical and economical point of view [5]. With oxygen, a sufficient conversion rate can usually be obtained at comparatively low temperatures of about 500 °C. This protects the catalyst from irreversible thermal deterioration, e.g. from sintering [10] caused by the highly exothermic oxidation reaction. To avoid excessive high temperatures, the coke is burned off with oxygen diluted with inert gas. Typically, the regeneration is started with only 1 vol.% oxygen [11].

At present, the coke loading of industrial fixed-beds is usually determined *ex situ* via probe sampling in periodic time intervals and a subsequent thermogravimetric or elementary analysis [12].

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Basically, it is also possible to estimate the coke loading as a result of the decreasing catalytic activity or product composition [13]; however, the accuracy is very limited. Hence, a continuous monitoring of the catalyst coke load during deactivation and regeneration would be beneficial with regard to efficiency and safety reasons. Recently, initial successful studies were conducted to investigate a new sensor principle for the detection of the coke loading of fixed-bed catalysts in situ by impedance spectroscopy [14,15]. During these tests, the sensor (an electrically contacted single particle) was located inside the fixed-bed.

In this study, a contactless radio frequency-based measurement technique is examined to monitor the coking and decoking process directly, *in operando* and without the need of installing single particle sensors in the fixed bed. This measurement technique is also known as cavity perturbation method. It is in use for material characterization; see e.g. [16–18]. However, in the present work, the properties of the catalyst materials themselves do not vary. Instead, with coke loading the electrical losses and the permittivity are expected to increase. In strong contrast to classical materials characterization tools, no small samples but entire catalyst-filled fixed-bed reactors are studied. Very preliminary tests using externally coked catalysts that have been filled *ex situ* in a heatable metallic cavity resonator have shown that the coke burn-off of a fixed-bed catalyst can be detected [19]. The utilized technique has also been successfully tested for automotive exhaust gas aftertreatment systems like three-way catalysts [20], ammonia SCR-catalysts [21], lean NO<sub>x</sub> traps [22,23], and diesel particulate filters [24,25].

Recently, a commercially available radio frequency-based sensor has been effectually tested for a diesel particulate filter (DPF) as well [26]. However, the coking process in automotive DPFs and industrial fixed-bed catalysts differ strongly from each other. In DPFs, soot is formed during combustion in the engine and is trapped in the DPF. Soot trapping itself is locally inhomogeneous. In refinery catalysts, coking starts on the active sites of the catalyst pellets inside the catalyst. Unlike in DPFs, usually coke forms homogeneously distributed in the reactor. Hence, it is an interesting question, whether coke formation can also be observed with this radio frequency-based technique.

## 2. Experimental

The radio frequency-based method is applied to a rectangular lab-scale steel reactor with a length of 345 mm and a cross sectional area of 30 mm by 30 mm. The reactor is heated from outside by a heating sleeve and the inlet pipes are wrapped in heating tape to preheat the gas flow. At the operation temperature of 560 °C, the temperature distribution inside the reactor is sufficiently uniform ( $\pm 4$  °C). The catalyst pellets used in all tests are porous cylinders with 4.5 mm in diameter and length. They consist of pure alumina (SN380, former Süd-Chemie, now part of Clariant, particle density: 1.45 g/cm<sup>3</sup>, BET-surface area: 190 m<sup>2</sup>/g, porosity: 0.4, average pore diameter: 6 nm). The total mass of all pellets in the fixed-bed is about 105 g. To locate the catalyst in the center of the reactor, two perforated low temperature cofired ceramic (LTCC) shelves were utilized. They provide a low electric conductivity to allow electromagnetic wave propagation and the many small laser-drilled holes enable the gas flow. The reactor setup is shown in Fig. 1. One can see that there is no contact between the measurement devices (antennas) and the sample. Hence, it is a contactless measurement technique.

At the beginning of each experiment, the reactor was heated up to 560 °C in a gas flow of pure N<sub>2</sub>. For the coking experiments, 33% propane (in N<sub>2</sub>) was used as carbon/coke source (total flow rate of 30 l/h (NTP)). The high propane partial pressure promotes the deactivation due to coke deposits [27]. A simplified coke formation

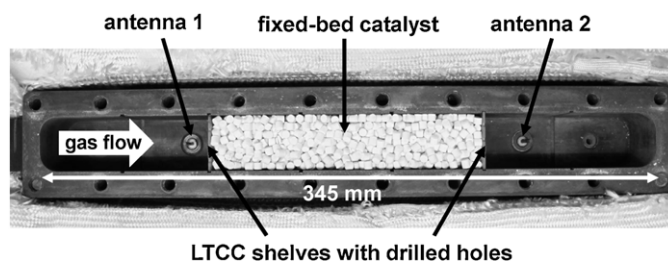


Fig. 1. Reactor setup with the fixed-bed catalyst, the low temperature cofired ceramic (LTCC) shelves and the two antennas.

mechanism, which occurs according to literature with an alkane (e.g. propane) as reactant, is shown in Fig. 2.

In previous studies with electrically contacted single catalyst particles as sensors, it has been shown that there is a clear relation between the amount of coke load,  $L_{\text{coke}}$ , and electrical conductivity [28]. Deposits on the catalyst like ashes or contaminating oxides is highly unlikely and even if small deposits occurred, the huge increase in conductivity due to coke loading would prevail all other minor effects. In [28] it has additionally been shown that even for Cr<sub>2</sub>O<sub>3</sub>-coated catalyst pellets, the semiconductor gas sensor effect amounts only to a factor of 2–2.5 in the resistance for both H<sub>2</sub> or toluene, both dosed in the %–range. Hence, compared to the effect of coke loading with resistance changes of several decades, the gas sensor effect can be neglected. The amount of loaded coke,  $L_{\text{coke}}$ , is here defined as the ratio of the mass of formed coke,  $m_c$ , and the catalyst mass,  $m_{\text{cat}}$ :

$$L_{\text{coke}} = \frac{m_c}{m_{\text{cat}}} \quad (4)$$

For the conditions used here, the coking process lasts 48 h. As shown by a respective mass balance, the conversion of propane along the fixed bed is rather small (about 1.4%), which leads to a homogeneously distributed coke load in axial direction over the entire fixed-bed.

The catalysts are regenerated (coke burn-off) at a total flow rate of 15 l/h (NTP) with 2% O<sub>2</sub> in N<sub>2</sub> for 72 h. Diluted oxygen is required to avoid a temperature runaway and a thermal damage of the catalyst by the exothermic reaction. During regeneration, a reaction front develops in the catalyst bed. Within this reaction front, the oxygen concentration drops from the initial value (here 2%) to almost zero. With increasing burn-off time, the front moves with constant velocity in axial direction through the fixed-bed [29]. The adiabatic temperature increase,  $\Delta T_{\text{ad}}$ , due to the regeneration reaction (Eq. (1)) can be calculated to  $\Delta T_{\text{ad}} = 261$  K from [7]:

$$\Delta T_{\text{ad}} = c_{\text{O}_2} \frac{|\Delta_R H|}{\rho_g \cdot c_{p,g}} \quad (5)$$

with  $c_{\text{O}_2}$  being the concentration of O<sub>2</sub> of 0.29 mol/m<sup>3</sup>,  $\Delta_R H$  the reaction enthalpy of  $-393.5$  kJ/mol,  $\rho_g$  the gas density of 14.6 mol/m<sup>3</sup>, and  $c_{p,g}$  the molar heat capacity of 29.9 J/(mol K). The measured temperature increase,  $\Delta T_{\text{real}}$ , of 10 K differs highly from the calculated value, because the experimental procedure in the lab-scale reactor is non-adiabatic. A significant loss of heat occurs over the reactor walls. Because of the minor value of  $\Delta T_{\text{real}}$ , the effect of temperature is neglected.

To determine the concentrations of CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and O<sub>2</sub>, particularly during regeneration, a gas analyzing system (Fisher Rosemount NGA 2000, BINOS 100) is installed downstream of the reactor.

To excite the electromagnetic waves, two coaxial antennas (waveguide feeds, see Fig. 3) are manufactured and mounted up- and downstream of the fixed-bed (Fig. 1). The antennas are made of stainless steel and feature a “type N” connector plug.

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