



## Direct detection of coke deposits on fixed bed catalysts by electrical sensors

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### ABSTRACT

The activity and the rate of deactivation of heterogeneous fixed bed catalysts are substantially influenced by the formation of coke deposits. In the chemical industry, especially in refineries and in petrochemical processes, the continuous direct and in situ monitoring of the level of the coke load in a catalytic reactor would be an additional controlling instrument of high value. In order to contribute to the development of such sensors, a representative pellet of an alumina-based chromium-oxide-coated catalyst was used in this work as a model system. The pellet was contacted and electrically measured by impedance spectroscopy. By combination with a gravimetric method, a clear relationship between coke loading and the respective electrical signal could be observed, both during coke formation and during the regeneration by coke burn-off.

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### 1. Introduction

Fixed bed catalysts are used in refinery processes and in the petrochemical industry for a variety of processes to convert crude oil fractions and organic intermediates fast and highly selective to required products [1]. The catalysts thereby differ with regard to physical structure and chemical composition. Typically, a pellet of a porous Al<sub>2</sub>O<sub>3</sub> support with a noble metal or a transition metal oxide dispersed on the inner surface is used [2]. In many processes, the catalysts deactivate due to coke formation, e.g. during the reforming of gasoline to enhance the octane number. In general, coke formation is an unwanted side reaction which influences the reaction rate and the product composition [3].

The term coke is used for a variety of carbonaceous deposits. It may vary from graphitic carbon to condensed high-molecular hydrocarbons and is formed by catalytic as well as by thermal reactions. In general, coke formation may be regarded as some kind of polymerization [4]. The coke grows in the pellets.

It is state-of-the-art to determine the coking level *ex situ* by sampling catalyst pellets from time to time and analyze them by thermogravimetric methods or by other means, e.g. by elementary analysis (C- and H-content). It is also possible to find an indirect correlation between the reaction rate (decrease of catalytic activity), product composition and the carbon load [5]. However, these indi-

rect methods are not very accurate and do not allow to obtain a continuous information about the actual status of a “working” catalyst.

To restore the activity of the catalyst, regeneration is necessary. This is usually accomplished by a controlled burn-off of the coke by means of little oxygen (<2%) in an inert gas stream to avoid an overheating of the catalyst by the exothermic reaction. During regeneration, a reaction front moves through the fixed bed reactor in axial direction with an almost constant velocity, which can be monitored by temperature sensors in the reactor [6].

The direct and in situ detection of coke formation would allow to measure easily and effectively the catalyst status and to respond instantaneously to irregularities during the chemical process. During regeneration, such a coke sensor (as investigated in this work) could not only detect the position of the regeneration front but also monitor the remaining degree of coking. This additional information could help to improve the catalyst regeneration with respect to efficiency and safety.

Similar issues arise in the automotive industry. In order to detect soot in automotive exhaust gas streams, several possibilities are known [7]. However, in contrast to coke formation in fixed bed catalysts, soot particles are formed during the combustion and grow in the exhaust pipe [8]. Hence, soot particles adsorb on the surface of the sensor and can be detected, e.g., by planar sensors covered with interdigital capacitors [9]. The more soot particles adsorb on the sensor, the lower is their resistance [8]. When the sensor is loaded up to a critical value, it becomes “blind”. Since in diesel engine exhaust gases enough oxygen is always available, regeneration is achieved by heating and burning off the soot. In contrast to the automotive application where soot is already available in the

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gas flow, in a refinery catalyst, the concentration of coke/soot in the gas flow is negligibly low. Instead, the coke is formed in the porous catalyst particle on the active centers. Therefore, the basic idea of this work is to use selected particles (equipped with a respective sensing setup) that show the same coking behavior and can therefore directly represent the status of the coke level. Since the coke sensor should also detect the regeneration, one has to keep in mind that the coke may be burned-off at conditions, where mass transfer limitations may influence the process. This may lead to the situation that the coke burns off from the outside towards the center of the catalyst particle (shrinking particle behavior). Therefore, the sensor should have the same or at least a similar geometry like the catalyst particles.

The aim of this explorative study was to investigate for the first time, whether a device that measures directly and in situ the electrical properties of a single representative catalyst pellet can be efficiently be used to monitor the degree of coke loading of catalyst pellets during the actual process and during the regeneration.

## 2. Experimental

The investigations were conducted with pellets of a typical dehydrogenation catalyst. The catalyst consists of porous  $\text{Al}_2\text{O}_3$  pellets as a support material coated with  $\text{Cr}_2\text{O}_3$  as the active component. One representative pellet in the fixed bed catalyst served as a sensing element. Its complex electrical impedance,  $Z$ , was measured with the setup as shown in Fig. 1. The sensor particle was contacted with gold paste. After sintering, a wire was welded on the gold layer. To reduce the physical strain at the contacts and to protect the sensor in the catalyst bulk, the particle was clamped into a steel bracket. Between the bracket and the sensor particle, alumina plates were fixed. The wires passed a ceramic tube which served as a feed through and were connected to the impedance analyzer (HP 4284A). Impedance spectra were taken from 100 Hz to 1 MHz with amplitude of 1 V. The effect of coke loading could even be seen optically, when samples were taken out of the reactor to conduct the coking level in the thermobalance. In Fig. 2, a fresh (left) and a partially coked sensor (right) is shown.

In Fig. 3, the experimental setup is shown schematically. The saturator, the pipes and the tubular reactor system (temperature  $550^\circ\text{C}$ , pressure 1 bar) were heated up under inert conditions. After the designated working temperature was reached, the catalyst pellets were calcined. Thereafter 5 vol% hydrogen was added for 30 min to the nitrogen flow to ensure the same starting parameters for each

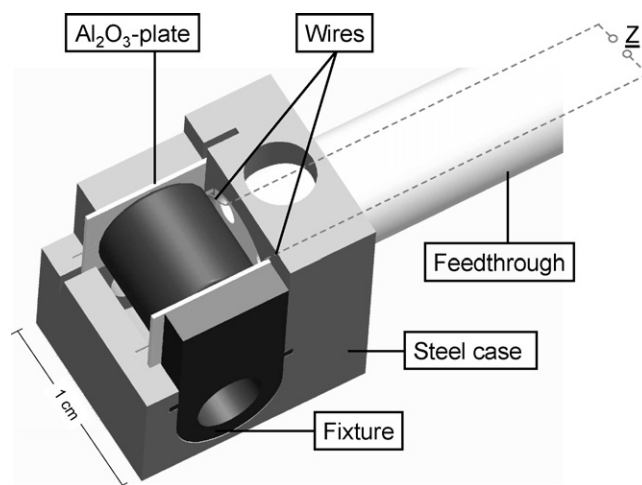


Fig. 1. CAD picture of the sensor.

experiment. Then, hydrogen was turned off and toluene (saturated in nitrogen) was added to the gas flow. Here, toluene served as a model hydrocarbon since it is a typical hydrocarbon that leads to the formation of catalytic coke in refinery/petrochemical processes. The gas flow passed the catalyst pellets and the reaction started. This went along with the formation of coke on the inner surface of the pellets. In industrial processes, the characteristic of time for coke formation may be up to months before regeneration is needed as the (hydrogen) pressure is then up to 30 bar [10]. Here, coke formation was accelerated by a high residence time (quotient of catalyst bulk volume and the flow rate is about 1 s) and a low pressure. In contrast to automotive exhaust gas converters, reforming reactors work under stationary conditions, hence one does not need to take the sensor dynamics into account.

The formation of CO,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{O}_2$  were determined by a gas analysis (Fisher Rosemont NGA 2000, BINOS 100), whereas the products were analyzed periodically by an online gas chromatograph (HP 5890 CP SIC PONA CB). The gas analyzer is used to control the regeneration progress ( $\text{CO}$ ,  $\text{CO}_2$  and  $\text{O}_2$  detection) and to control the hydrogenation procedure. The gas chromatograph enables the monitoring of the catalyst deactivation by analyzing the change in the product yield and product composition.

In order to find a suitable correlation between the impedance signal and the coke content, pellet samples were taken out of the

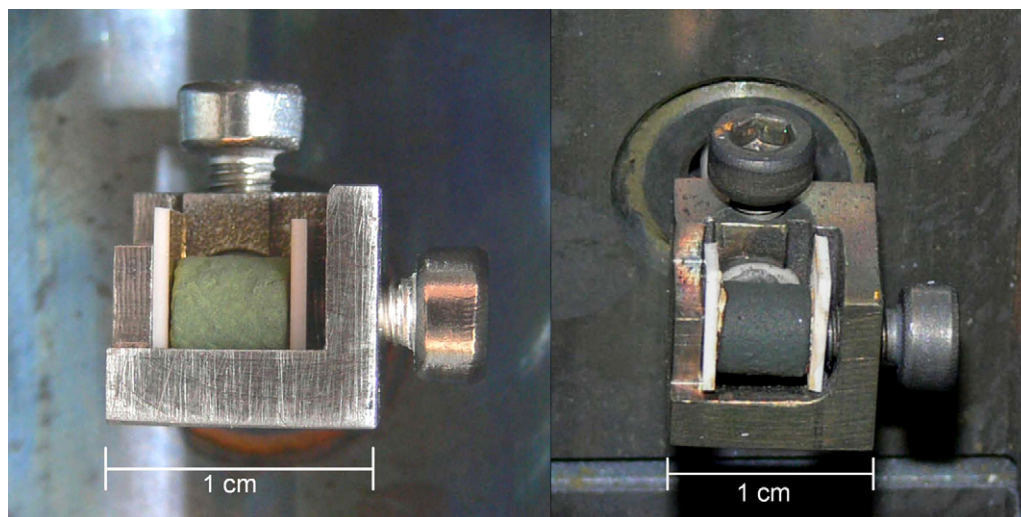


Fig. 2. Photograph of the fresh sensor particle (left) and the coked sensor particle (right).

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