

Slow aging mechanisms in non-oxidative reaction conditions e.g. dehydrogenation on Pt-ZSM5 catalysts

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Abstract

Control of reaction conditions, short residence times and completely inert surfaces are of major importance when studying aging mechanisms by soot formation. The use of ceramics as reactor material in combination with a special reactor design allows control over industrially relevant reaction conditions ($T_{\max} = 1100\text{ °C}$, $t_{\text{Residence}} = 50\text{ ms}$) and sample shapes while avoiding interfering side reactions. We have successfully tested new ceramic kinetic reactors in two model systems of propane dehydrogenation and reactor coil material. The presented reactor setup allows long-term measurements with industrially relevant material samples under controlled conditions. In both model reactions it was possible to perform studies on regeneration methods by oxidation and to study the effects on the material using different in-situ and ex-situ techniques including ^{31}P MAS NMR measurements.

Keywords

ceramic reactor, materials, coke, aging mechanisms

1. INTRODUCTION

In electrically heated endothermic reactions of hydrocarbons without partial oxidation, e.g. propane dehydrogenation, heavy soot formation occurs during the reaction. In high-temperature reactions, despite the presence of steam or oxygen, metal surfaces of reactor walls catalyze heavy coke formation, which can block reactor tubes within days and affect the alloy composition of the reactor walls. This leads to a slow deactivation of the catalysts or blockage of the reactor. The objective of this study was to provide kinetic reactors and methods able to better understand the slow aging processes due to coke formation and the influence on the used materials due to coke formation and removal.

A major drawback of current experimental setups is that these often do not use the original forms of catalysts (often powders or other model systems are used), which may have strong influences on the aging mechanisms. On the other hand, the actual reaction conditions cannot be fully reproduced (high temperatures, high flow rates, elevated pressures). At the same time, tests on an industrially relevant scale are rarely technically feasible for research applications. In this case, simulations and models are often used as a substitute.

With our development of novel ceramic kinetic reactors, we tried to fill the experimental gap between laboratory scale measurement techniques and pilot plant scale for research in high temperature reaction engineering. The intention was to develop suitable model systems to describe these processes quantitatively and realistically in order to determine optimal process conditions.

2. METHODS

The required conditions for the investigation of the soot forming processes are a) inert surfaces, b) high temperatures, c) large heat exchanging surfaces, d) short residence times without dead volume or preheating of the reaction gas, e) use of air at high temperatures for in-situ coke removal.

For these studies, a novel reactor concept was developed based on proven metallic flatbed reactors for kinetics measurement. The full ceramic kinetics reactor allows permanent maximum temperatures of up to 1100 °C with extremely short residence times of $< 50\text{ ms}$ under controlled isothermal conditions. 997 alumina was used as the main ceramic material. At the same time, no preheating sections were required due to good heat transfer. This was achieved by a high ratio of height to width inside the ceramic reactor. It allowed to use catalyst and material samples in relevant sizes without compromising on controlled reaction conditions. The ceramic reactor is embedded in a heated metal casing, which stabilizes the construction. Ceramic connectors and metal sleeves made of special alloys with low thermal expansion allow to achieve a gas tight setup when implementing the ceramic reactor in a metallic setup.

This approach has been applied to two different reactions. First, propane dehydrogenation, where the aim is to achieve an inert reactor surface and high heat transfer under controlled reaction conditions. Second, ethane cracking, where high temperatures above 900 °C and very short residence times of approx. 50 ms over the material sample are required. Similar studies have been carried out in the past (Muñoz Gandarillas et al., 2014), but without achieving realistic con-



ditions in terms of short residence times and similar flow characteristics over the material sample.

In both cases, good heat transfer is required to keep the gas and catalyst or sample temperature at near isothermal conditions, especially in the presence of strong exothermic or endothermic reactions. Furthermore, any secondary reactions by the reactor walls must be excluded, while the reactor material must be able to withstand an oxidative gas atmosphere for in-situ regeneration with oxygen and fast temperature changes.

3. RESULTS

Our measurements on platinum zeolite catalysts have shown that the macroscopic morphology can have a major influence on the aging kinetics when studying slow aging effects due to soot formation. In the case of powder-based catalyst samples in small quantities and volumes, usually tested in tubular reactors, the conditions are controlled and well defined, but differ drastically from other catalyst shapes, even if the catalyst material and preparation is the same, as can be seen in Fig. 1, where the aging process of different catalyst shapes was tested in the same setup. Therefore, the use of standard equipment based on catalyst powder is a good method to characterize the reaction kinetics of a wide variety of materials, but does not adequately represent the aging behavior of catalysts in industrial use. The aim of this work was to use industrially relevant catalyst shapes and sizes while maintaining control over the reaction conditions. In addition, the residence time of the reaction gas at elevated temperatures can be of critical importance. For studies at temperatures above 550 °C, coke precursors can already form in the gas phase in the preheating sections. This unwanted precursor

formation is exacerbated in a metallic environment because the reactor wall often acts as a catalytic surface.

The controlled reaction conditions during the long term reaction and the in-situ regeneration with lean air have enabled us to produce the samples shown on the poster for the novel catalyst investigations according to Rieg et al. (2021). In this way, small changes in the catalyst structure could be identified for different samples.

When testing reactor materials, e.g. in the development of reactor coils, very short residence times of less than 50 ms on the test sample are also required in addition to the temperature and surface material requirements. Overheating the material sample relative to the gas temperature can improve the comparability with an industrial reactor without the need of a large scale reactor coil. The presented reactor design allows on the one hand to present the shown temperature profiles inside the reactor (see poster). On the other hand, the temperature control allows fast changes in reaction conditions, which means great flexibility in reaction control. In Fig. 2, temperature profiles of sample temperature as well as heater temperatures over time are shown at high reactor temperatures and different residence times down to 10 ms above the sample. At the same time, an instantaneous change of reaction gases is possible. Thus, it is possible to change from reaction gas to an inert gas atmosphere or oxidizing conditions without delay. The first test showed that coking and decoking behavior varied with the number of cycles shown on the Poster. In further tests, different materials will be tested in order to study differences in the behavior of the materials over oxidation cycles as well as over the composition of materials. The results will be used as a basis and validation for the development of quantitative models of the aging mechanism of the tested materials.

The temperature of one of the heating elements and the surface temperature of a metal sample (without reaction) are

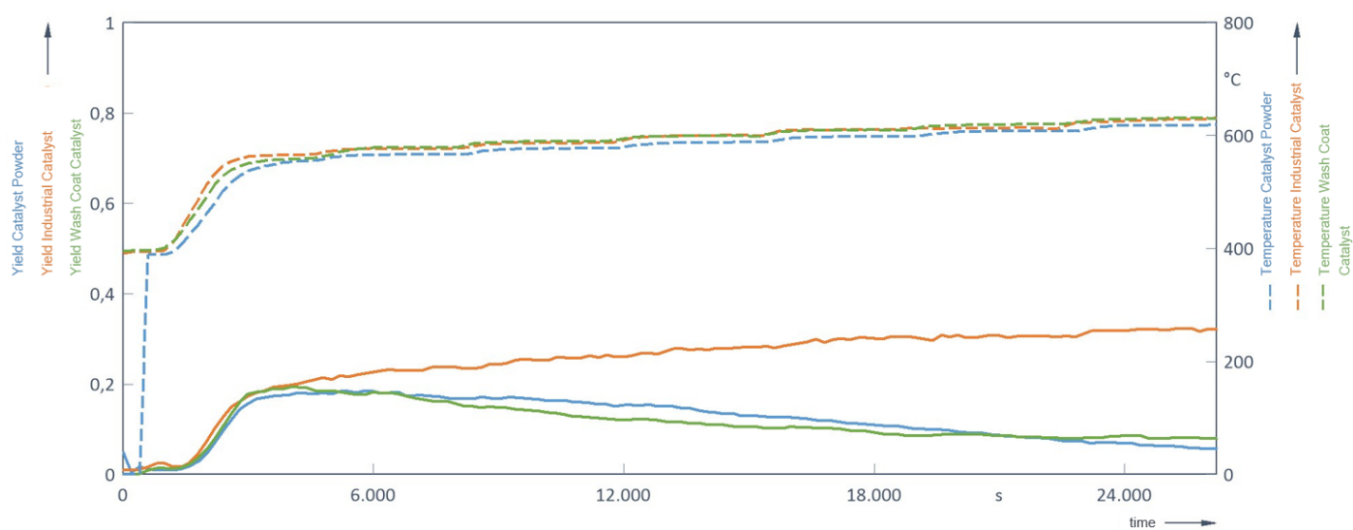


Figure 1. Catalyst aging of same catalyst material in different shapes leading to significantly different behaviour. Here, catalyst as powder of loose ZSM-5 or precipitated as washcoat on a solid surface leads to instant catalyst aging due to coke formation. Industrial catalyst shapes with macro structure show significant resistance to coke formation at comparable activities.

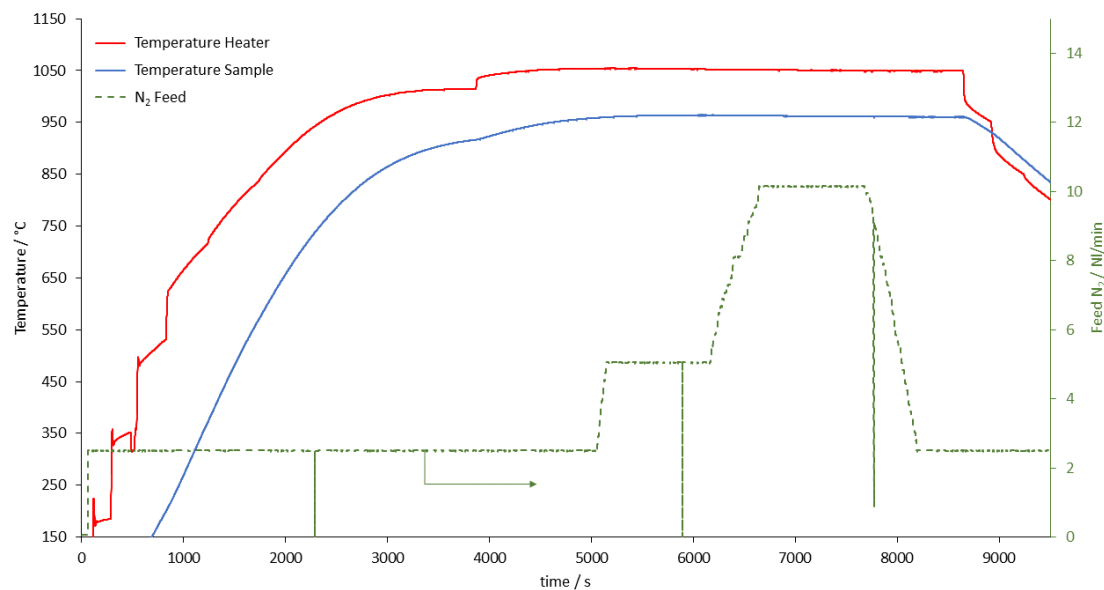


Figure 2. Temperature of the kinetic reactor over time (without overheating the sample).

shown in Fig. 2. The temperature of the test system can be freely adjusted over a wide temperature range in a short period of time. Heating up to 950 °C with approx. 3 s/K is demonstrated here. The gas flow in standard volume per minute has been varied and shows little influence on the temperature. This allows us to reproduce a wide range of reaction conditions. In addition, the conditioning of material samples can be stopped quickly (see the end of measurements). This enables us to condition the samples for ex-situ studies in different aging conditions.

4. CONCLUSIONS

With the use of ceramic kinetic reactors, we were able to investigate aging by soot formation using two different model systems (propane dehydrogenation and the study of reactor coil materials). With the reactor system presented, controlled aging at temperatures up to 1100 °C with short residence times of 50 ms over long time periods is possible. At the same time, in-situ regenerations could be carried out with air or other oxidants showing significant alteration of the

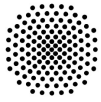
used samples. In this way, realistic model systems can be specifically conditioned for subsequent investigation using ex-situ methods. This is demonstrated by the example of a Pt-ZSM-5 system.

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Motivation and Purpose

In electrically heated endothermic reactions of hydrocarbons without partial oxidation, strong soot formation occurs during the reaction. This leads to a slow deactivation of the catalysts or blockage of the reactor.

The dehydrogenation of propane as well as cracking reactions are processes that exemplify this problem. Zeolite-platinum catalyst have proven to be particularly suitable for propane dehydrogenation because the catalytic surface is protected from deactivation by carbon deposits over long periods of time. Whereas in the case of cracking reactions, the formation of an initial layer of soot must be prevented by means of a suitable reactor material.

However, the mechanisms of slow aging by deposit formation and deactivation upon regeneration by removal of soot using oxygen-containing species has not been fully understood. [1, 2]

The focus of this work is on the study of slow aging by coking on ZSM5 and cracker coil coupons as well as its removal with new measurement technique accessible under controlled inert conditions.

Experimental results show:

- Strong influence of operating conditions on deactivation
- Differences in carbon formation along the reaction coordinate
- History of reaction gas influences coke formation
- Oxidation cycles differ over time due to material changes

The aim of this study is to better understand the slow aging processes of coke formation and material change due to coke removal by oxidation. Eventually to be able to describe them quantitatively with suitable models in order to determine optimal process conditions.

Experimental Study ZSM-Pt Catalyst

Newly developed fully ceramic flatbed reactor concept was used. The key features are:

- Catalyst in relevant scale under highly controlled conditions
- Inert reactor surfaces prevent side reactions
- Isothermal temperature profile despite high reaction enthalpies
- High temperature stability up to 750 °C

Temperature profiles were monitored using fiber optic technology, gas analysis with online GC and MS

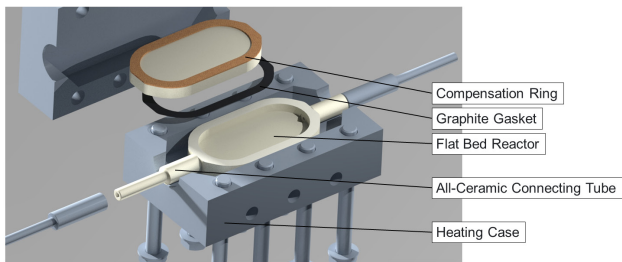
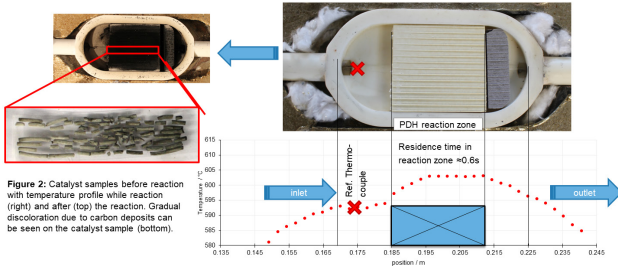


Figure 1: Digital model of the used all-ceramic flat bed reactor setup



Analyses of catalyst samples regenerated with oxygen have shown mobility of platinum clusters outside the zeolite structures. ³¹P MAS NMR measurements give access quantitative information on the origin of catalyst aging while regeneration. [3]

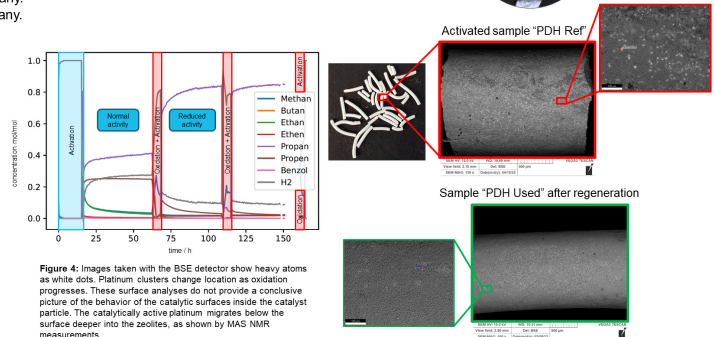


Figure 4: Images taken with the BSE detector show heavy atoms as white dots. Platinum clusters change location as oxidation progresses. These surface analyses do not provide a conclusive picture of the behavior of the catalytic surfaces inside the catalyst particle. The catalytically active platinum migrates below the surface deeper into the zeolites, as shown by MAS NMR measurements.

The difference between triphenylphosphine (TPP) and H₂ adsorption measurements allows a quantitative distinction between inner platinum surfaces inaccessible to TPP and outer surfaces.

The measurements show that the accessible platinum surface becomes less accessible due to regeneration with oxygen and thus migrates into the interior of the zeolite structure. The dispersion of Pt remains the same as before.

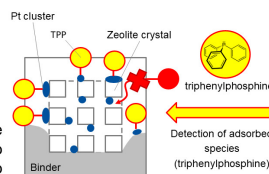


Figure 5: Schematic illustration of the reaction of TPP with catalytically active platinum surfaces. TPP cannot bind to surfaces within the zeolite due to steric effects.

Table 1: ³¹P MAS NMR results and hydrogen chemisorption results. NM loading of 2.563 mmol g⁻¹

Sample Name	Complexed TPP ^a / mmol g ⁻¹	Maximum external sites ^b / %	NM dispersion ^d / %
PDH Ref direct	0.023	0.5	75
PDH Ref equilibrated	0.032	0.6	
PDH Used direct	0.017	0.5	85
PDH Used equilibrated	0.027	0.3	

^a from ICP-OES; ^b from quantitative ³¹P MAS NMR; ^c calculated assuming a 2:1 TPP:noble metal stoichiometry; ^d from H₂-Chemisorption

Experimental Study Cracking Coil

The concept of the ceramic flatbed reactor has been expanded to include:

- Gas temperatures up to 1100 °C and overheated coil coupon
- Very short residence times on the coil coupon < 0.1 s
- Variable hot reaction gas residents time
- Long time measurement >72 h

The temperature profiles were determined with movable thermocouples, the gas analysis is carried out by FTIR.

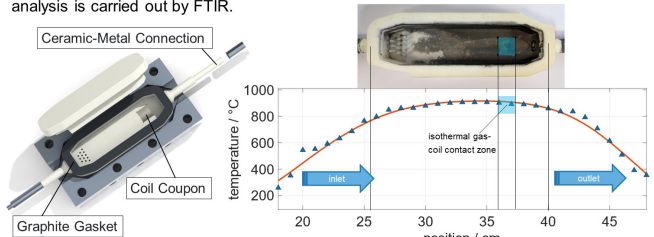


Figure 6: Digital model of the used all-ceramic flat bed reactor setup (left), thermocouple measurement of temperature profile inside the reactor (right)

In order to investigate long-term effects on different reactor materials, several cycles of coking and decoking are carried out in succession, see [4]. The advantage of our setup is low material input and controlled reaction conditions. First test show that coking and decoking behavior varies with the number of cycles (Figure 8).

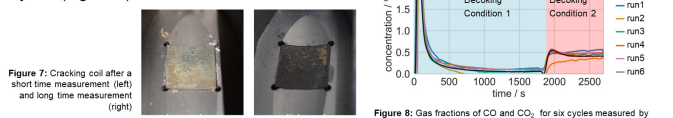


Figure 7: Cracking coil after a short time measurement (left) and long time measurement (right)

Figure 8: Gas fractions of CO and CO₂ for six cycles measured by FTIR during the decoking process under two different conditions.

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