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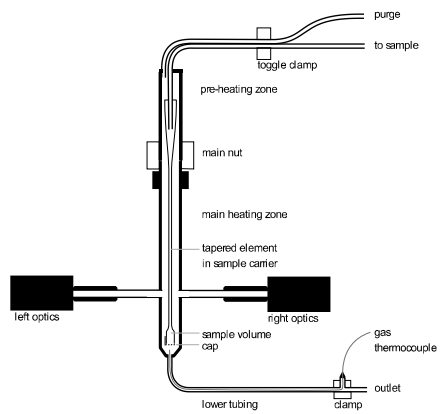


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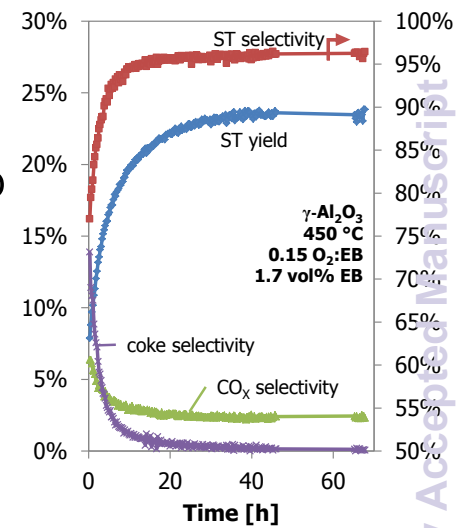
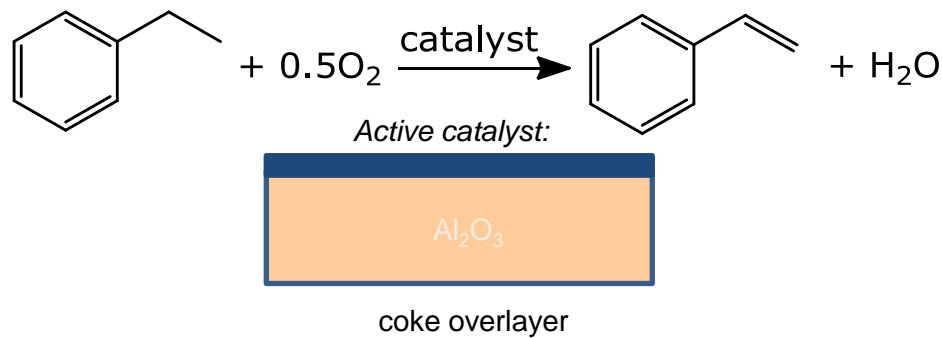
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TEOM



A TEOM investigation on coke formation in the oxidative dehydrogenation of ethylbenzene to styrene

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A packed bed microbalance reactor setup (TEOM-GC) is used to investigate the formation of coke as a function of time-on-stream on γ -Al₂O₃ and 3P/SiO₂ catalyst samples under different conditions for the ODH reaction of ethylbenzene to styrene. All samples show a linear correlation of the styrene selectivity and yield with the initial coverage of coke. The CO_x production increases with the coverage of coke. On the 3 wt% P/SiO₂ sample the initial coke build-up is slow and the coke deposition rate increases with time. On alumina based catalyst samples a fast initial coke build-up takes place, decreasing with time-on-stream, but the coke amount does not stabilize. A higher O₂:EB feed ratio results in more coke, and a higher temperature less coke. This coking behaviour of Al₂O₃ can be described by existing “monolayer-multilayer”-models. Further, the coverage of coke on the catalyst varies with the position in the bed. For a maximal styrene selectivity the optimal coverage of coke should be sufficient to convert all O₂, but as low as possible to prevent selectivity loss by CO_x production, this is in favour of high temperature and low O₂:EB feed ratios. The optimal coke coverage depends in a complex way on all the parameters: temperature, O₂:EB feed ratio, reactant concentrations, and the type of starting material.

Introduction

Studies on the catalyst coking are usually performed to gain insight on the catalyst deactivation. In catalytic cracking, the carbon deposits block the acid sites that are active for the cracking reactions, causing the catalyst deactivation.^{1, 2} The oxidative dehydrogenation (ODH) reaction of hydrocarbons is an exception to this. The selective conversion of ethyl benzene (EB) to styrene (ST) reaction is not catalysed by the catalyst that is loaded into the reactor, but by the coke that is formed during the reaction.³⁻⁸ Similarly in the methanol to olefins (MTO) and related processes firstly a ‘hydrocarbon pool’ has to be formed that generates the desired products in concert with the Brønsted acid sites in the catalyst, but it also leads to deactivation.⁹ By studying the coke formation,¹⁰ information on the real catalyst in these processes can be obtained. In ODH coke can be formed in several ways: oligomerisation of olefins, poly-alkylation of aromatics and condensation of aromatics.² For ODH of EB it is generally accepted that the oxygen groups on the surface of the deposited coke,^{11, 12} especially the quinone groups,¹³ are the catalytically selective active sites. These can undergo a redox reaction where ethylbenzene (EB) is the reducing agent and the oxygen is the oxidizing agent.¹⁴ It is also postulated that (oxygen) radicals take part in the

dehydrogenation mechanism.¹⁵ In the past, a few ODH studies focused on the formation of the carbon deposits on aluminas^{16, 17} and the rate of formation on metal pyrophosphates.⁵ Several factors influence the formation of coke on Al₂O₃ in ODH, namely:¹⁶

- A higher oxygen partial pressure will give more coke
- A maximum is present when varying temperature
- The acidity of the catalyst increases the coke formation

According to Lisovskii *et al.* these factors result in a stable amount of coke on an Al₂O₃ catalyst, a monolayer, that covers the catalyst surface.¹⁶ For alumina the amount of monolayer coke normalised for the specific surface area is about 0.54 mg/m².¹⁶ For the metal pyrophosphate catalysts a monolayer corresponds to about 0.8 mg/m².⁵

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Table 1: Data on the ODH performance in the 6-flow reactor.²³⁻²⁶

Sample	Temp. [°C]	O ₂ :EB	ST yield	ST selectivity	CO _x selectivity
γ -Al ₂ O ₃	450	0.6	29%	82%	16%
1.3P/Al ₂ O ₃	475	0.6	31%	83%	15%
Al-1000	450	0.6	36%	86%	13%
3P/SiO ₂	475	0.6	51%	91%	8%

One of the tools that are available to study coke formation dynamics are microbalance reactors. A special type of microbalance reactor is the tapered element oscillating microbalance (TEOM), that uses the natural frequency of the oscillating tapered element to determine mass changes.¹⁸ The TEOM reactor has a well-defined gas phase (fixed bed reactor), a high mass resolution and stability and can operate under conditions that are relevant to practical operation.¹⁹ It does not suffer from external mass-transfer limitations or gas bypassing, as is the case for hanging basket type microbalance reactors.¹⁸ The TEOM has found applications in many topics such as coke deposition, adsorption and diffusion in zeolites, gas storage, synthesis of carbon fibres.¹⁸⁻²²

In our own work and in the literature many catalyst samples for the ODH of EB have been tested and discussed.^{2-8, 14-16, 23-26} The optimal performances of four of our tested samples are summarized in Table. The γ -Al₂O₃ is the reference sample used in this work, reaching 29% ST yield at 82% ST selectivity. The addition of a phosphorous promoter^{8, 27-29} improves the ODH performance of the Al₂O₃ to some extent, 2% points increase in ST yield and 1% point in ST selectivity. The high temperature (1000 °C) calcined Al₂O₃ sample Al-1000, shows a larger improvement of the performance with 36% ST yield and 86% ST selectivity. The 3 wt% P/SiO₂ sample is one of the best performing samples that was tested, with 51% ST yield at 91% ST selectivity.

The objective of this work is to obtain detailed real-time information on the formation of the carbon deposits on γ -Al₂O₃, Al₂O₃ calcined at 1000 °C, 1.3 wt% P/Al₂O₃ and 3 wt% P/SiO₂ catalyst samples. The real-time information on coke amount as a function of *time-on-stream* is one of the missing pieces in the understanding the ODH process, as this is usually done by post-mortem analysis of the sample by TGA.¹⁷ This will be done using a TEOM-GC reactor setup, which provides continuous data on the catalyst sample mass and the catalyst performance in the ODH reaction with *time-on-stream* (TOS).

Experimental

Catalyst preparation

The γ -Al₂O₃ extrudates (Ketjen CK300, 0.57 ml/g, 190 m²/g, now Albemarle) are crushed, sieved to 212-425 μ m particles, and used as such or calcined at 1000 °C for 8 h (Al-1000), or modified with a phosphorous promoter (H₃PO₄). The SiO₂ support (silica NorPro, SS61138, 1.00 ml/g, 250 m²/g (213 m²/g according to our internal BET measurements)) is crushed

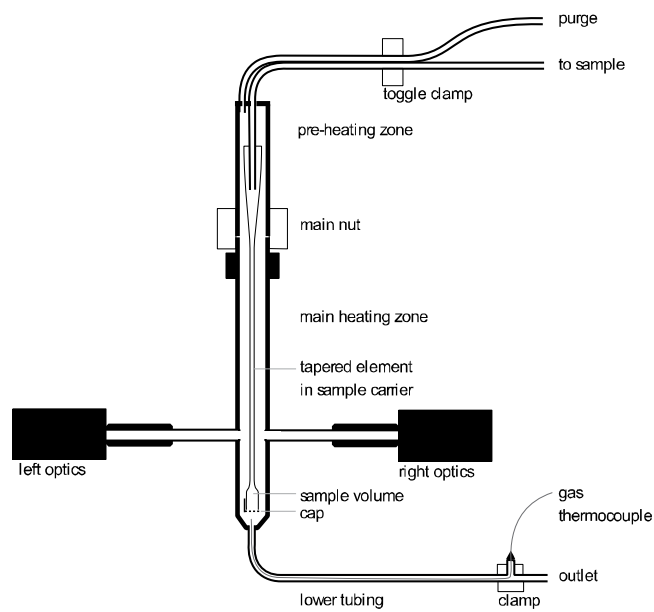


Figure 1: Schematic of the TEOM reactor part.

and sieved to 212-425 μ m and dried at 150 °C in vacuum for 4 hours. The phosphorous is introduced by impregnation using the incipient wetness method with a 5% excess of the pore volume. The required amounts of H₃PO₄ are mixed with Milli-Q[®] demineralised water, after which the support is impregnated with the solution. The wetted support is shaken vigorously with an automatic shaker to homogenize the impregnated support. Next it is dried at 70 °C in static air overnight, followed by calcination in a static air calcination oven at 500 °C for 8 hours. The heating rate is set at 4 °C/min. The P loading is set as wt.% elemental phosphorous (3 wt% is denoted as 3P/SiO₂), but presumably the phosphorous is present in its oxidic form of P₂O₅ after calcination and under ODH reaction conditions. Similarly, sample 1.3P/Al₂O₃ contains 1.3 wt% elemental phosphorous. An overview of the catalyst samples and their properties is given in Table .

The TEOM reactor setup

The tapered element oscillating microbalance (TEOM) reactor setup is an excellent tool for measuring the mass changes of a sample under reaction conditions. This mass change can be the result of coke formation, adsorption, desorption, oxidation, or reduction.^{10, 18-22} A mass change of less than 1 microgram can

Table 2: Specifications of the used catalyst samples in the TEOM.

Sample	S _g [m ² /g]	V _p [ml/g]	Sample [mg]	other
γ -Al ₂ O ₃	272	0.83	60.9	Ketjen CK300
Al-1000	119	0.49	77.6	Calcined at 1000 °C
1.3P/Al ₂ O ₃	245	0.59	60.9	1.3 wt% P on Ketjen
3P/SiO ₂	164	0.76	46.1 ^a / 50 ^b	3 wt% P on SiO ₂

^a 20 h TOS experiment, Figure 11.

^b 130 h TOS experiment, Figure 10.

be measured. That means that already a change in the gas composition can be detected by this method. A commercial (now discontinued) Rupprecht and Patashnick (R&P) 1500 Pulse Mass Analyser is used. A schematic layout of the reactor part is shown in Figure 1.

The working principle of the balance is based on the natural oscillation frequency of the reactor that is at the end of a tapered element. The frequency of this oscillation depends on the weight of the sample. This frequency is accurately measured by an infrared beam, perpendicular to the oscillation. A change of the frequency from f_0 to f_1 from time t_0 to t_1 results in a total mass change (of gas and solids in the sample volume) that is calculated according to Eq. 1. The spring constant K_0 is determined by using a calibration weight on the reactor.

$$\Delta M = \Delta M_S + \Delta M_G = K_0 \left(\frac{1}{f_1^2} - \frac{1}{f_0^2} \right) \quad 1$$

In the reactor setup, a catalyst sample of maximum 100 mg can be used. This is held in position by a quartz wool plug at the top and at the bottom, and a metal cap with small holes in it is used to close the reactor end. There are two temperature zones, a preheating zone that can be heated from 50 °C to 500 °C and a reaction zone that can be heated from 50 °C to 600 °C. The operating pressure is between 0 barg (ambient pressure) and 30 barg. A reaction gas mixture can be formed from three gases and one liquid feed that is evaporated. The flows are all accurately controlled by six mass flow controllers. The connected gases are helium, air and carbon dioxide. All flows are reported at the normal conditions of 20 °C / 1 atm. The ethylbenzene is fed as a liquid (LMFC, max 0.6 g/h).

At the start of an experiment, the reactor (450-500 °C) and preheating zone (200 °C) are heated up under a helium flow (25 ml/min) through the reactor and a helium purge flow (100 ml/min) along the reactor. When the sample mass is stabilised (normalised standard deviation $< 3 \times 10^{-6}$), the reaction was started by switching to the reactor feed that consists of air (0.12-1.07 ml/min), helium (25 ml/min), and the ethylbenzene vapour (0.13 g/h or 0.45 ml/min vapour). This gives an EB concentration of 1.7 vol%. The helium bypass purge flow is not changed. The O₂:EB molar feed ratio is varied between 0.05 and 0.5. The (diluent + O₂):EB molar feed ratio is 58. The W/F_{EB} is between 37 and 64 g-cat·h/mol. The $GHSV_{TOT}$ is 20.000 l/h.

The sample is regenerated in between experiments at the reaction conditions by stopping the EB feed, yielding a diluted air mixture (0.1-0.9 vol% O₂). The experiments are highly reproducible after each regeneration.

An online GC, type Chrompack CP9001, with two channels was used for analysis of the product gas stream. One channel uses an FID for the analysis of hydrocarbons with a 60 cm 12% UCW column. The other channel uses a TCD for the analysis of permanent gases (O₂, N₂, CO, CO₂) with a Poraplot Q and molsieve column. The molsieve column uses a bypass for CO₂ and H₂O analysis. The EB conversion X_{EB} , selectivities of ST,

coke and CO_x (Sel_i) and ST yield Y_{ST} are based on ethylbenzene concentrations and calculated according to Eqs.2-6. M_{coke} is 120 g/mol, assuming a molecular composition for coke of C₈H₈O.²⁹ Although the mass increase by coke is measured, the overall carbon balance does not close at 100% since the CO and CO₂ concentrations were close to the GC detection limit.

$$X_{EB} = \frac{[EB_{in}] - [EB_{out}]}{[EB_{in}]} \quad 2$$

$$Sel_{ST} = \frac{[ST_{out}]}{[EB_{in}] - [EB_{out}]} \quad 3$$

$$Sel_{CO_x} = \frac{([CO_{2,out}] + [CO_{out}]) / 8}{[EB_{in}] - [EB_{out}]} \quad 4$$

$$Sel_{coke} = \frac{\Delta m_{coke} \cdot [EB_{in}]}{M_{coke} \cdot \Delta t \cdot F_{EB}} / ([EB_{in}] - [EB_{out}]) \quad 5$$

$$Y_{ST} = X_{EB} \times Sel_{ST} \quad 6$$

In addition to the calibration procedure of the TEOM setup itself, the setup was also verified by separate determination of the coke amount using a microbalance (MettlerToledo TGA/SDTA851^o).

The 6-flow reactor setup

The data in Table 2 and Figure 14 in this work is based on ODH experiments performed in a parallel fixed bed reactor setup that was described in detail in our previous publications.²³⁻²⁶ To obtain the catalyst samples for Figure 14, the total catalyst amount is split 8 beds with glass beads in between, allowing for individual post-mortem coke amount determination of each of the 8 beds.

Catalyst characterization

The final amount of coke deposit is determined off-line by a TGA (MettlerToledo TGA/SDTA851^o, 20 mg sample of spent catalyst, 100 ml/min air and 50 ml/min He flow mixture) using a ramp of 3 °C/min from RT to 723 °C. Surface area, pore volume and pore size distribution are determined by N₂ adsorption at -196 °C (Quantachrome Autosorb 6B). The samples are pre-treated overnight in nitrogen at 250 °C.

Results

The ODH performance in the TEOM reactor

With the TEOM-GC setup, both the catalyst performance and catalyst weight are monitored with *time-on-stream* (TOS). A typical example of the catalyst performance of Al₂O₃ in the TEOM reactor is shown in Figure 2 (*left*). At the 0.15 O₂:EB feed ratio, a styrene yield of 23 % at a 96% ST selectivity is reached after 20 h TOS and do not change up to a TOS of 70 h.

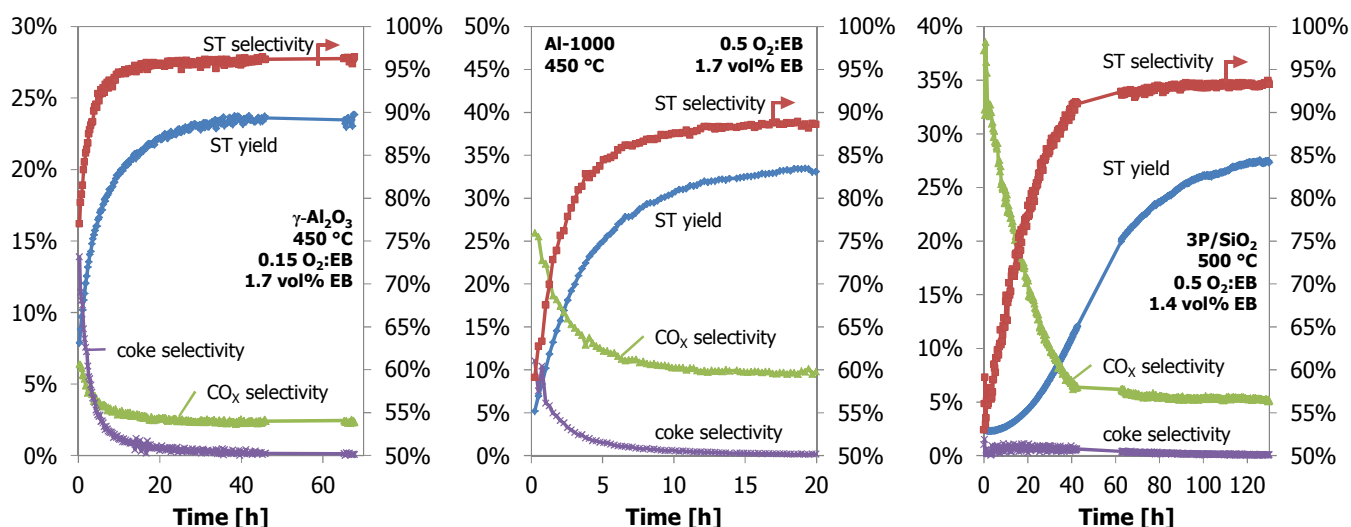


Figure 2: The ODH performance as a function of *time-on-stream* for the γ -Al₂O₃, Al-1000 and 3P/SiO₂ samples in the TEOM reactor.

This performance is better than would be expected from comparable 6-flow experiments at 0.2 O₂:EB feed ratio (14% ST yield at 88% ST selectivity).²³⁻²⁶ The *TOS* required to reach this optimum performance is longer in the TEOM setup. Initially the coke selectivity is high, 15%, this quickly decreases to below 1% after 10 h *TOS*. Initial ST yield and ST selectivity are 8% and 77%, respectively. With *TOS* the ST selectivity and yield increase, coke selectivity and CO_x selectivity decrease. The catalyst performance stabilizes after about 10-20 h, depending on the reaction conditions. The O₂ conversion is around 95% during the whole experiment.

The performances in the ODH reaction for the Al-1000 and 3P/SiO₂ samples are shown in Figure 2 (*middle and right*). With increasing *TOS*, both ST yield and ST selectivity increase. For the Al-1000 they increase from 5% to 34% and from 60% to 89%, respectively. For the 3P/SiO₂ the increase is from 4%

to 16% and from 57% to 87%, respectively. The oxygen conversion for Al-1000 increases from 50% to 90% after 20 h *TOS*. For the 3P/SiO₂ the oxygen conversion is constant at about 50%. Again, the ODH performance of the Al-1000 is better than expected from the 6-flow experiments. The ODH performance of the 3P/SiO₂ is, however, worse than expected.²³⁻²⁶

Catalyst coverage with coke

Many experiments are performed with the bare γ -Al₂O₃ at three temperatures and four O₂:EB feed ratios. These results are shown in Figure 3. It is assumed that all the mass increases are only the result of carbon deposition. At the same O₂:EB feed ratio the final coke coverage in about 20 h *TOS* decreases from 0.71 m²/g to 0.38 m²/g with an increasing temperature from 450 °C to 500 °C. Initially the coke formation rates are the same,

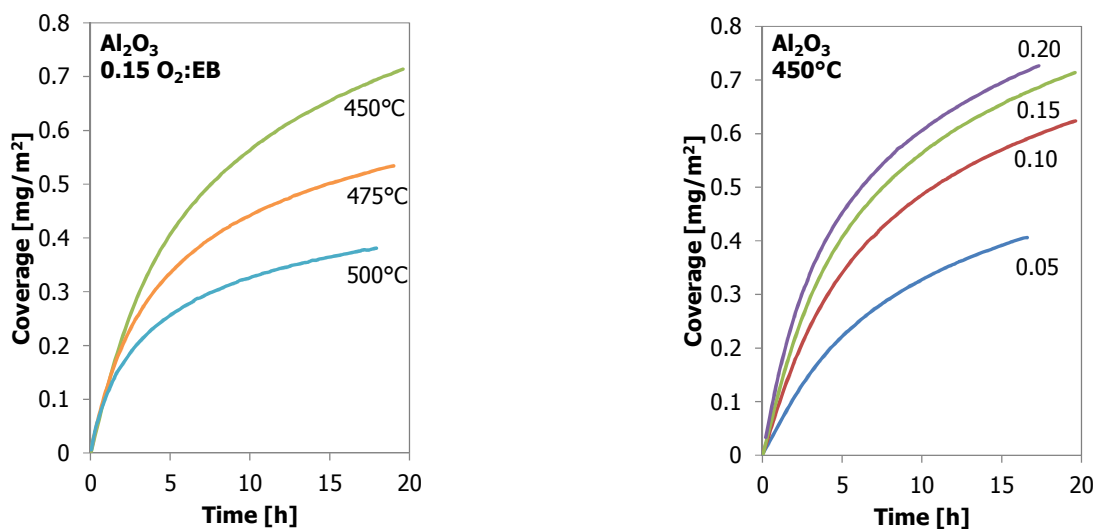


Figure 3: The effect of temperature (*left*) and O₂:EB feed ratio (*right*) on coke coverage (TEOM) for Al₂O₃ as a function of *time-on-stream*.

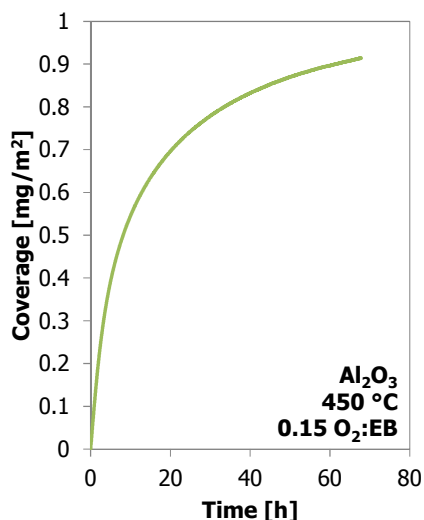


Figure 4: The coke coverage (TEOM) as a function of time for Al_2O_3 up to 70 h *time-on-stream*.

but at a higher temperature the amount of coke levels off earlier. With increasing O_2 :EB feed ratio from 0.05 to 0.20 at a constant temperature the final coverage of coke increases from 0.41 mg/m^2 to 0.72 mg/m^2 . The initial coke formation rates increase with an increasing O_2 :EB feed ratio. With *time-on-stream*, the coke deposition becomes slower. Figure 4 shows that the coke coverage keeps increasing with the *time-on-stream*, although the coke deposition rate decreases with the *time-on-stream*, but does not become zero.

A comparison between bare alumina and phosphorous loaded alumina is shown in Figure 5. The latter shows a better performance in the ODH reaction. The coke coverage evolution is nearly identical to the Al_2O_3 sample, even though the Al_2O_3 support and their surface areas are different (Table). Also a thermal treatment results in a better ODH performance

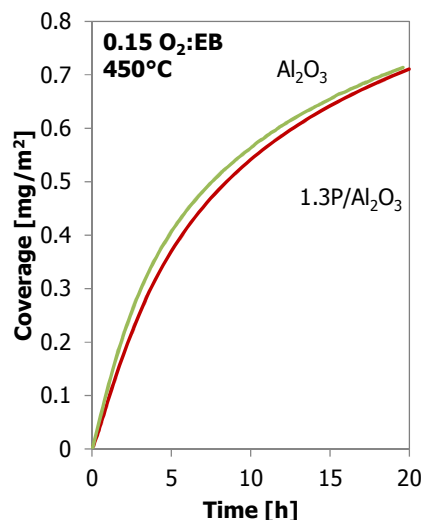


Figure 5: Coke deposition (TEOM) as a function of time for Al_2O_3 and $1.3\text{P}/\text{Al}_2\text{O}_3$ samples.

for the Al-1000 than that of the $\gamma\text{-Al}_2\text{O}_3$.^{24, 25} A phosphorous loaded silica support, such as $3\text{P}/\text{SiO}_2$, shows the best results in the ODH reaction.^{25, 26} Their coke coverage evolution is shown in Figure 6. The $1000 \text{ }^\circ\text{C}$ calcined alumina shows a similar behaviour as the bare alumina, but the coverage by coke is higher, 1.02 mg/m^2 for Al-1000 against 0.70 mg/m^2 for $\gamma\text{-Al}_2\text{O}_3$, after 20h *TOS*. The P/SiO_2 sample shows a completely different coke deposition behaviour. Initially the coke build-up is very slow, but it increases continuously in time. Also a higher temperature is required to observe sufficient coke formation and ODH on the P/SiO_2 sample. After 20 h *TOS* only 0.38 mg/m^2 of coke is deposited.

The experiment with the $3\text{P}/\text{SiO}_2$ sample was repeated under slightly different conditions (30 vs. 25 ml/min helium carrier flow, 50 vs. 46.1 mg sample) to observe the coke build-up

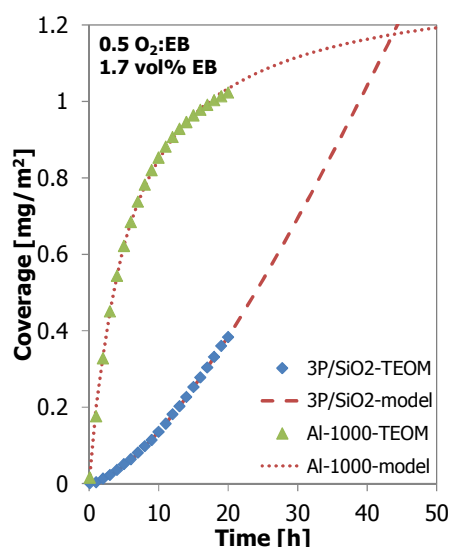


Figure 6: Coke coverage (TEOM) as a function of time for Al-1000 at $450 \text{ }^\circ\text{C}$ and for $3\text{P}/\text{SiO}_2$ at $500 \text{ }^\circ\text{C}$.

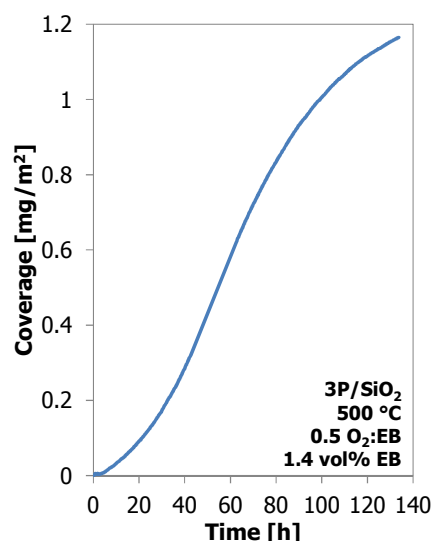


Figure 7: Coke coverage (TEOM) as a function of a longer *time-on-stream* for $3\text{P}/\text{SiO}_2$.

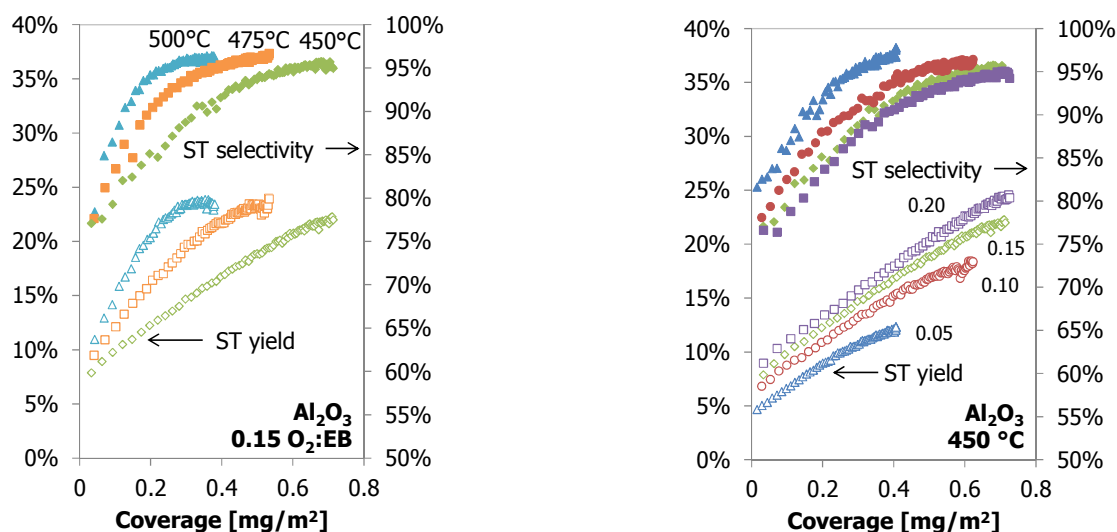


Figure 8: The styrene yield (open symbols) and selectivity (closed symbols) as a function of the coke coverage on the Al_2O_3 , for different temperatures (*left*) and O_2 :EB feed ratios (*right*) up to 20 h *TOS*.

during a longer *time-on-stream* (130 h *TOS*). The results are presented in Figure 7. Initially the coke build-up is very slow, but increases with *TOS*. After 60 h *TOS* or above 0.6 mg/m^2 coverage the coke build-up on 3P/SiO₂ becomes slower and resembles more the behaviour of the Al_2O_3 samples.

Modelling coke coverage

The coke build-up on alumina with time on stream has been modelled with the “monolayer-multilayer” model^{5, 31, 32} (Eq. 7) that describes the formation of coke with two mechanisms: monolayer coke formation on the surface of the catalyst and multilayer coke formation on top of the existing coke. The monolayer amount is related to the physical limitations of the catalyst surface, represented in the model by the constant $k_{Cm,max}$. Both monolayer and multilayer growth are a function of the monolayer coke amount C_m . All constants are considered to be a function of temperature and oxygen concentration (Eq. 8).

$$\frac{dC}{dt} = k_1(k_{Cm,max} - C_m)^{n_1} + k_2 C_m^{n_2} \quad 7$$

$$k_n = k_{n,0} p_{\text{O}_2}^{m,n} e^{\left(\frac{-E_{a,n}}{RT}\right)} \quad 8$$

Individual fitting of each experiment, and plotting of the fit parameters to temperature and O_2 concentration showed that k_1 and $k_{Cm,max}$ are a function of the temperature and k_1 and k_2 are

Table 3: Model parameters found by fitting the coke build-up from the alumina experiments.

Parameter	$k_{n,0}$	$E_{a,n}$ [kJ]	$n_{\text{O}_2,n}$	n_n
k_1 [g coke/g cat/h]	$8.17 \cdot 10^7$	99.2	1	2
k_2 [1/h]	$9.92 \cdot 10^{-2}$		2	1
$k_{Cm,max}$ [g coke/g cat/h]	$6.62 \cdot 10^{-6}$	-61.6		

functions of O_2 concentration. Finally all experiments were fitted as a group together, the resulting fit parameters are given in Table 3.

The data from the experiments with Al-1000 and 3P/SiO₂ is also modelled with the “monolayer-multilayer” model^{5, 31, 32} (Figure 7). For 3P/SiO₂ to fit the model, a low $k_{Cm,max}$ was found and a high k_2 compared to the alumina samples. The S-curve behaviour of the longer *TOS* experiment with 3P/SiO₂ in Figure 8 could not be captured by the “monolayer-multilayer” model in Eq. 7.

Styrene yield as a function of coke coverage

When the catalyst performance and mass data are coupled, a linear relationship is observed for the styrene yield as a function of the coverage of coke (Figure 8). The slope of the curve increases at a higher temperature. For higher O_2 :EB feed ratios the slope does not change, but the off-set value of the ST yield at 0 mg coke increases. At the higher styrene yields and coke coverage, the data from the experiments start to deviate from a linear relation. At the O_2 :EB feed ratio of 0.15 and at 500 °C the deviation starts at a coverage of about 0.25 mg/m^2 , at 475 °C it is 0.40 mg/m^2 and at 450 °C no deviation is observed (Figure 8).

The styrene yield as a function of the coke coverage for a 70h *TOS* experiment over the γ - Al_2O_3 is shown in Figure 9. Under these conditions the styrene yield increases linearly with coke coverage up to 0.70 mg/m^2 (20 h *TOS*). The yield increases slightly, but above 0.80 mg/m^2 (35 h *TOS*) the styrene yield does not change anymore with an increase in the coke coverage.

The styrene yield as a function of the coke coverage for Al-1000 and 3P/SiO₂ is shown in Figure 11. Although the temperature and sample amounts are different, both samples show an almost identical dependency of the styrene yield on the coke coverage. A linear fit gives a productivity of 7 g styrene/g

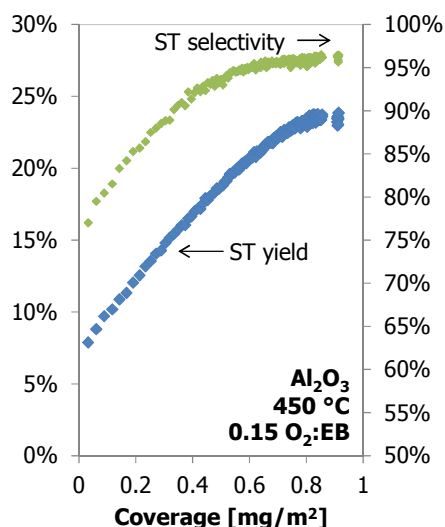


Figure 9: The styrene yield and selectivity as a function of coke coverage for Al_2O_3 up to 70 h *time-on-stream*.

coke/h. Above a 30% styrene yield and a coverage of about 0.80 mg/m^2 , the calcined alumina sample shows a deviation from the linear relation between ST yield and coke coverage.

Also for the 3P/SiO_2 sample under slightly different conditions (30 vs. 25 ml/min helium carrier flow, 50 vs. 46.1 mg sample) the styrene yield increases linearly with the coke coverage up to about 20% ST yield and a 0.6 mg/m^2 coverage, above which it starts deviating from the initial linear relationship (Figure 10). The gap in the GC data is due to a temporary GC failure. The styrene yield curves in Figure 10 and in Figure 11 are exactly parallel. Additionally, above a coke coverage of about 0.2 mg/m^2 the amount of carbon dioxide produced also shows a linear relationship with the coke coverage. At this coverage the amount of CO_2 produced is the minimum.

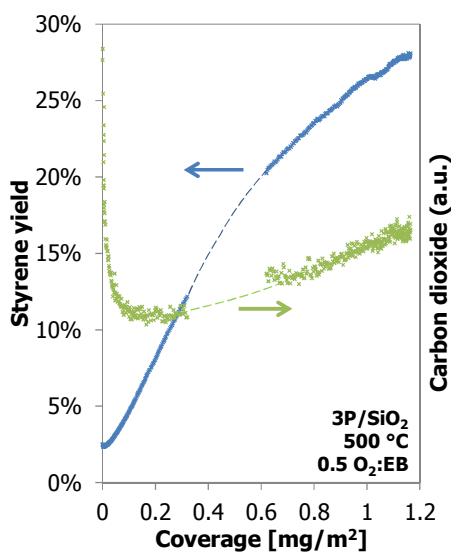


Figure 10: Styrene yield (*left*) and carbon dioxide (*right*) as a function of the coke coverage for 3P/SiO_2 .

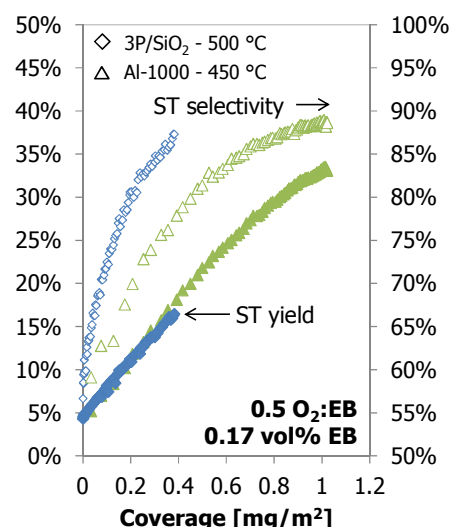


Figure 11: Styrene yield (closed symbols) and selectivity (open symbols) as a function of coke coverage for Al-1000 and for 3P/SiO_2 .

TGA analysis

The spent Al_2O_3 (1000 °C) and 3P/SiO_2 samples are analysed by temperature programmed thermo gravimetric analysis (TGA) in air at 3°C/min , their oxidation profiles are shown in Figure 12. The maximum oxidation temperature of the coke on 3P/SiO_2 is higher than that for alumina based coke, 565°C versus 480°C , respectively. This indicates a higher reactivity of the coke on the Al_2O_3 .

Distribution of coke in a catalyst bed

An experiment was done in the 6-flow reactor setup with $\gamma\text{-Al}_2\text{O}_3$, where the catalyst bed was split up in 8 separate parts. This gives an idea of the build-up of coke over the catalyst bed length. This catalyst was tested in the 6-flow setup using our

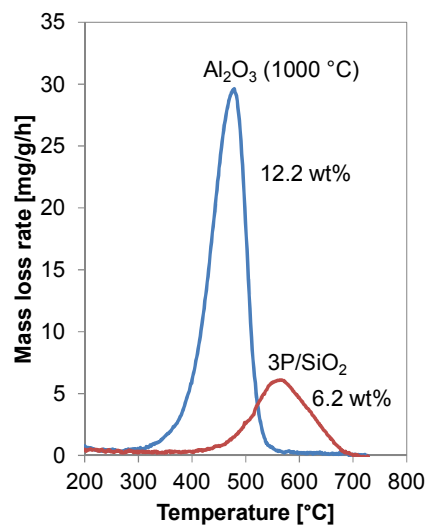


Figure 12: TGA in air profiles of the spent Al-1000 and 3P/SiO_2 samples.

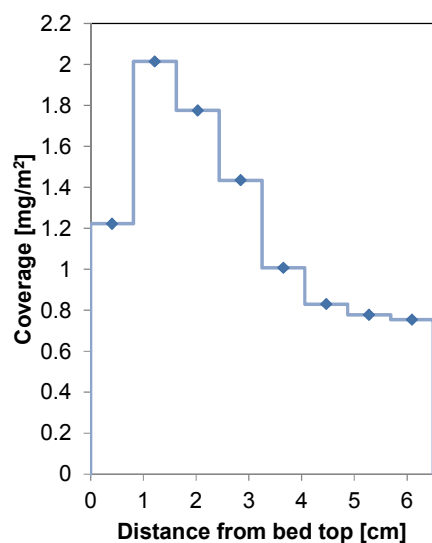


Figure 13: Distribution of the coke coverage on γ -Al₂O₃ as a function of the catalyst bed length, after the standard 62 h testing protocol in the 6-flow reactor.

standard screening protocol.²³⁻²⁶ The coverage of coke as a function of the bed length is shown in Figure 13. The maximum coverage of coke, 2 mg/m², is located in the second section of the catalyst bed. The top section of the catalyst bed has a lower coke coverage (1.2 mg/m²). Towards the end of the bed the coverage of coke decreases to 0.75 mg/m². The reactor is operated in down-flow operation.

The characterisation by TGA also indicates small variations in the temperature of maximum soot oxidation: the top catalyst section at 466 °C, the next at 476 °C, the next two at 472 °C and the bottom four at 470 °C.

Discussion

The oxidative dehydrogenation reaction could be an attractive reaction to replace the industrially used endothermic direct dehydrogenation reaction that is equilibrium limited. The ODH reaction is catalysed by the coke that is formed and not by the initial ‘catalyst’.^{3-5, 7, 8, 11-16, 23-30} Therefore, it is very important to get more insight on this coke and its performance. So far some general correlations have been found,^{5,16,17} that are investigated in more detail in this paper with the TEOM-GC setup.

ODH performance in the TEOM reactor

Before going into detail on the formation of coke and the catalytic activity of this coke, a few other observations need to be discussed, like the different performance of the TEOM reactor compared to the 6-flow reactor. In the TEOM reactor, activation is slower (10-20h vs. 5h) and ODH performance is better (Y_{ST} , 23% vs. 14%; Sel_{ST} , 95% vs. 88%; O₂:EB, 0.15 vs. 0.2). From our previous work it is known that the ODH performance over a bare alumina at different temperatures (450-500 °C) changes no more than 1%.²³⁻²⁶ Also the lower O₂:EB feed ratio contradicts with the higher ST yield.²³⁻²⁶ Such

differences were not expected, as both setups are fixed-bed reactors that operate under similar conditions like space velocity, O₂:EB feed ratio and temperature. The obvious explanation for these differences between the two setups is found in the reactant concentrations. These are lower in the TEOM reactor, the inlet EB concentration is 1.7 vol% against 9 vol% in the 6-flow reactor. At lower concentrations, the processes that occur (coke deposition, coke gasification and ODH) may become slower, but at the same O₂:EB feed ratios the ST yield and selectivity hardly change.¹⁶ This is also seen in the coke build-up experiments on 3P/SiO₂ in Figure 6 and Figure 7 that are done with the same feed of reactants, but with a slightly higher dilution (25 vs. 30 ml/min helium) and thus different concentrations in the gas mixture. This has a large effect on the coke build-up. After 20 h *time-on-stream* the amount of coke in the first experiment is 0.38 mg/m², the second experiment needs 50 h *TOS* to reach this coke coverage. The reactant concentrations appear to have a large effect on the coke build-up at these very low concentrations.

Another possible explanation for the ODH performance differences is the quality of the analysis. With the 6-flow this is more advanced because of the higher concentrations and a more accurate calibration. But even with these low concentrations, an error estimation results in only a $\pm 0.5\%$ point ST selectivity difference and a $\pm 0.1\%$ point difference in ST yield. An error in the O₂:EB feed ratio will result in a little larger deviation, but still smaller than the differences in ODH performance that are observed between both setups.

Axial dispersion phenomena are thought mainly responsible for the improved performance. The Péclet number of the TEOM reactor is about 9× smaller than for the 6-flow reactor, implying more a CSTR-like behaviour with more averaged concentrations of reactants over the catalyst bed than the integral concentration profiles of a plug flow reactor. This can lead to improved performance over an Al₂O₃ catalyst.²⁶

The worse than expected performance in the ODH reaction for the 3P/SiO₂ sample is attributed to side effects of the set-up, especially when operated > 500 °C for this catalyst.²⁵ When oxygen is still available after the reactor, as is the case with the 3P/SiO₂ sample, it will react further resulting in a lower performance than expected. Whenever possible in the experiments, full conversion of O₂ over the reactor was aimed for, but with the 3P/SiO₂ sample this could not be achieved.

Despite the differences between the TEOM and 6-flow setup, it can be stated that the general observed trends are similar. Although the time scales and conditions are different, their performances with regard to temperature, molar O₂:EB feed ratio and catalyst samples are in agreement for both setups.

Modelling coke formation

The temperature and oxygen dependencies of the coke deposition with *TOS* (Figure 4) are very well captured in the “monolayer-multilayer” model. The maximum “monolayer” amount of coke on a catalyst ($k_{Cm,max}$) is a function of temperature, and is less related to the available surface area (physically constant) than thought before. The “monolayer”

growth rate is a function of temperature and $O_2:EB$ (1st order). The “multilayer” growth rate constant in itself is not a function of temperature, however, by its dependency on the “monolayer”, the temperature dependency is already included, and in addition it has a 2nd order $O_2:EB$ dependency for its growth rate. Using this model to optimize the reaction conditions for slow deactivation and thus minimum coke growth, high temperature and low $O_2:EB$ are favourable. This is in line with conclusions from our staged O_2 feeding work.²⁵

A possible extension of the “monolayer-multilayer” model would be to include a saturation of the catalyst with coke, as towards the high coke loadings there will be an effect of pore filling and rapidly reducing available surface area. Data in Figure 14 shows coverages of up to 2 mg/m², much higher than was obtained in the TEOM. According to the model, under those conditions it would take about 30h to reach such coverages, where in reality the experiment lasted for 62h.

The initial coke formation on 3P/SiO₂ can also be described by the “monolayer-multilayer” model, but with a low $k_{Cm,max}$ and a high k_2 it does not fit the description of “monolayer-multilayer” coke formation. Surface-coke (slow) vs. coke-on-coke (fast) formation would be a better description, where coke-on-coke is likely also taking place in the planar direction on the (inactive) surface. For higher coverages on 3P/SiO₂ the “monolayer-multilayer” model cannot describe the coke formation. A different or extended model is required.

Coke coverage and ODH performance

The ODH performance is very dependent on the $O_2:EB$ feed ratio. However, the ST yield as a function of the coke coverage (Figure 8 (right)), initially has the same linear slope for all $O_2:EB$ feed ratios, showing that the initial activity of the coke is similar under different $O_2:EB$ feed ratio conditions. The reaction temperature does not have a large effect on the ODH performance, but it does have a large effect on the coke coverage as a function of *time-on-stream* (Figure 9 (left)). At all 3 reaction temperatures 95% Sel_{ST} at 20% Y_{ST} is reached, but at lower coke coverage for higher temperature. This clearly shows the temperature dependency of a catalyst, like coke is in the ODH reaction.

At increasing coke coverages, the linear correlation between the styrene yield and the coverage of coke does not hold anymore (cf. Figure 8). At the point that it starts to deviate from the initial linear correlation, sufficient coke is available to catalyse the ‘selective’ ODH reaction. The coke formation continues, whilst the ODH performance does not change. Overall, the coke catalyst becomes less efficient. Eventually the excess of coke will have an effect on the ODH performance, as more CO_x is produced and the styrene yield is decreasing (Figure 10).²⁵

Activity of Coke

In the literature it is claimed that adding a mineral acid, like phosphoric acid, changes the composition and reactivity of the coke.^{16, 27-29} Based on the data presented in this work, the largest factor that determines the performance is the coverage

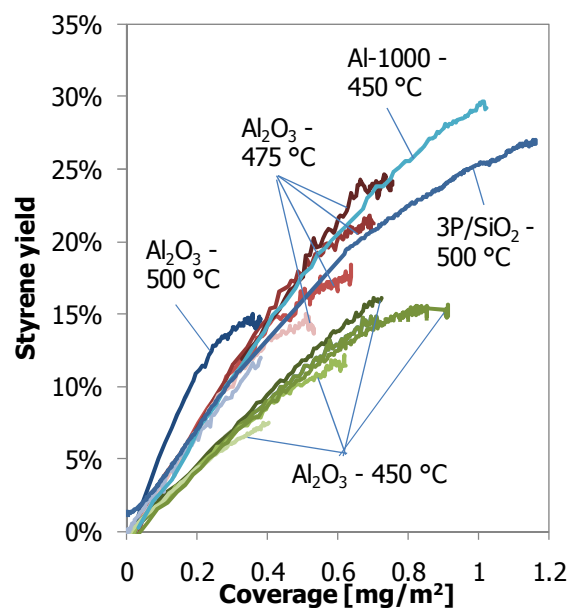


Figure 14: ST yields, corrected for the ST yield at zero coke coverage, as a function of coverage by coke for all experiments.

of coke. Its composition and reactivity can still explain some diverging results. The phosphorous loaded alumina shows nearly the same coke coverage as the γ -Al₂O₃ (Figure 5), but has a slightly better ODH performance in the 6-flow.

The coke deposits on the 3P/SiO₂ and Al-1000 samples have the same productivity, but at a different temperature (Figure 11) and the TGA data (Figure 12) also suggests different reactivity of the coke on the samples. A comparison of all available ST yields as a function of the coke coverage is shown in Figure 14, corrected for the yield at zero coverage. Comparing the styrene yields to the ST yield of normal γ -Al₂O₃ at similar coke coverage and reaction temperature, the coke on Al-1000 is more active and the coke on 3P/SiO₂ is less active than of normal γ -Al₂O₃. This is supported by the activity of the coke in TGA, where the coke on 3P/SiO₂ needs a higher oxidation temperature.^{23, 24} The TGA profiles in Figure 12 cannot be compared directly to the profiles presented by Nederlof *et al.* (2013)²³ because the heating rate was 3 °C/min compared to 10 °C/min in the other papers. This causes a shift in the oxidation temperatures. However, the trend of the activity of the coke for ODH and oxidation temperature in TGA is similar.

Deactivation

All experiments with the alumina based catalysts show the same behaviour of quick initial coke deposition and a decreasing coking rate with *time-on-stream* (Figure 3-7). For a stable catalyst operation this is preferred, as it means that the coverage of coke on the sample will not change fast with longer *time-on-stream*. The ODH performance of alumina is quite stable with time, or in other words, the coke formation and gasification rates are nearly in balance. A very small net coke formation still takes place, but it takes a very long time (> 50 h TOS at 10 vol% EB) before the extra coke has a negative effect

on the ODH performance.^{25, 26} Modelling gives the insight that monolayer coke coverage is quickly approached and mostly multilayer coke deposition takes place. In terms of the catalyst stability the opposite is presented by the 3P/SiO₂ sample that displays a slow initial coke build-up, but increasing coking rates with *time-on-stream* (Figure 6). The ODH performance of 3P/SiO₂ in the 6-flow setup shows an optimum after a 3 h *TOS*, with a minimum CO_x formation, and then deactivates.^{25, 26} This deactivation is caused by excessive coking that shifts the oxygen balance to CO_x production instead of styrene. The 130 h run with 3P/SiO₂ also shows this increase in the CO_x production (Figure 10) after a minimum in the CO₂ production at low coke coverage of 0.2 mg/m². Any further increase in the coke coverage gives an increased CO₂ production. At the optimum ODH performance in the 6-flow setup (3h *TOS*), the coke formation, coke gasification and ODH reactions are not in balance. The TEOM experiment with the 3P/SiO₂ catalyst shows that the coking rate will eventually decrease with time (Figure 7). But by the time that the coke formation will decrease, the performance of the P/SiO₂ will be far from its optimum in comparison with the normal flow experiments.²⁵

Perspective to other work

In the work of Lisovskii *et al.*¹⁶ it appeared that a monolayer coverage of the coke is obtained when the pseudo steady-state is reached (optimal ST yield and selectivity), that was determined at 0.54 mg/m² over several Al₂O₃ samples (at O₂:EB = 1, 0.17 vol% EB and 425 °C). This TEOM study shows that the coke coverage mainly depends on the O₂:EB feed ratio and the reaction temperature (also at the pseudo steady-state). The theoretical coverage of a monolayer of graphene of 0.76 mg/m² is even surpassed by the Al-1000 and 3P/SiO₂ samples, before reaching their optimal ST yield at a high O₂:EB feed ratio of 0.5. Therefore, we hypothesize that coke formation occurs more like stacks of islands (3-dimensional) instead of monolayer (2-dimensional) in the case of graphene-like structures on the support surface, where every layer has a similar ODH activity. The surface density of such coke islands can be higher for supports with a high acid site density such as γ -Al₂O₃ and lower for supports with a low acid site density such as 3P/SiO₂.^{28, 30} Coke is able to form at the acid sites and also at the edges and on top of existing coke ('multilayer'), but at a slower rate. This is supported by the presented modelling results with the "monolayer-multilayer" models.^{5, 31, 32}

The presented data are not in full agreement with the claim by Lisovskii *et al.*¹⁶ that the amount of coke is stable. There is a continuous net build-up of coke on the catalyst (Figure 4), but this is very small and only clearly observed on a longer time scale of tens of hours. On an hour to hour basis the amount of coke is nearly constant, especially when less sensitive equipment than a TEOM is used to determine the amount of coke.

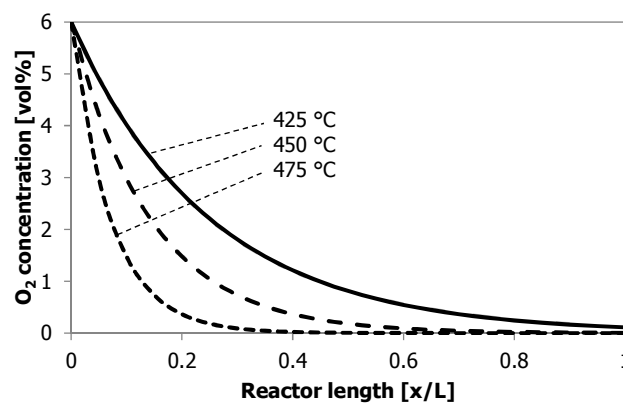


Figure 15: Schematic O₂ concentration profile as a function of the reactor bed length at the different reaction temperatures.

Distribution of coke along the catalyst bed

The build-up of coke along the catalyst bed in the 6-flow setup is intriguing (Figure 13). At the first section of the catalyst bed where the oxygen concentration is the highest, less coke is present than in the next section of the catalyst bed. The reactivity of the coke is also highest in this top section, as indicated by the temperature of maximum coke oxidation. Perhaps most of the CO_x is already formed in the top part of the catalyst bed, reducing the local coverage of coke, but also lowering the oxygen concentration, which is beneficial for the ST selectivity.²⁵ Remember that CO_x formation requires 6.5–10.5 moles of O₂ per mole of EB, and ST production only requires 0.5. Most of the styrene will be formed just below the top part of the bed that already contains sufficient coke to have full oxygen conversion. However, for coke to form, also O₂ needs to be available. The contributions of these 3 reactions (CO_x, ST, and coke formation) result in an O₂ profile over the reactor like is sketched in Figure 15 and a coke profile over the reactor like in Figure 13, that look very similar when excluding the first part of the bed. More coke will be formed where more oxygen is available. It is also possible that the top sections of the bed are already partly deactivated due to the high coke coverage. The slightly higher temperatures of maximum coke oxidation in the top sections of the bed could indicate this. It is emphasized that these experiments are done in an integral mode and not in a differential mode.

Conclusions

This investigation into the formation of coke and the rate thereof on several catalysts and under different conditions again shows the complexity of the ODH process. Coke is the catalyst for the reaction. Modification of the support material can change the activity and selectivity of the coke, but deactivation is inherent to the ODH reaction, as after initial fast coke formation all samples continuously show a very small, but positive coke build-up with time-on stream as a result of nearly balancing coke formation and gasification rates. The coke

build-up on alumina can be modelled with existing “monolayer-multilayer” models. This shows that the “monolayer” coke amount depends on temperature, where “monolayer” and “multilayer” coke formation are a function of both temperature and O₂:EB feed ratio, 1st and 2nd order, respectively. This work supports the existing correlations:

- The styrene yield shows a linear correlation with the initial coke build-up.
- A higher oxygen partial pressure gives more coke.
- Under operation at full oxygen conversion, a higher temperature will result in less coke without a change in the ODH performance.
- A higher coke loading results in more CO_x.

The amount of coke depends on the temperature, O₂:EB feed ratio, reactant concentrations, *time-on-stream*, and the type of starting material. Furthermore, in integral reactor operation the coverage of coke varies with position in the bed. For an optimal performance in ODH a sufficient but low coverage of coke needs to be available, converting all oxygen at minimal CO₂ formation. This will lead to high temperature and low O₂:EB feed ratios (staged feeding).²⁵ The exact optimal coverage depends on all the above mentioned parameters.

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