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A kinetic rate expression for the time-dependent coke formation rate during propane dehydrogenation over a platinum alumina monolithic catalyst

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Abstract

Coke formation rates under propane dehydrogenation reaction conditions on a used monolithic Pt/γ-Al_2O_3 catalyst have been experimentally determined in a thermogravimetric analyser (TGA) as a function of time on stream covering wide temperature and concentration ranges. For relatively short times on stream, especially at low temperatures and low propylene concentrations, a remarkable initial quadratic increase has been observed in the coke formation rates versus time with a high apparent propylene reaction order. After longer times on stream the coke formation rate decreases to a constant residual coke growth above approximately 12 wt.% coke content. The experimental data have been successfully described by a kinetic rate expression based on a mechanistic dual coke growth model. In this model it has been assumed that initially coke precursor is formed via a propylene oligomerisation process, explaining the observed auto-catalysis for short times on stream.

Keywords: Kinetics; Catalyst deactivation; Platinum alumina monolithic catalyst; Coke formation rates

1. Introduction

The strong increase in the demand for lower olefins during the last decade [1] has initiated the development of new alternative processes in addition to traditional petrochemical or refinery processes, where lower olefins are obtained as by-products. The increased availability of lower alkanes resulting from more strict environmental legislation has made dehydrogenation processes economically attractive [2]. Dehydrogenation reactions of lower alkanes are highly endothermic and are carried out at high temperatures because of thermodynamic constraints. At these high temperatures carbonaceous deposits, collectively termed coke, are rapidly formed and as a consequence thereof catalyst deactivation prevails necessitating catalyst regeneration. These difficult process features require dedicated reactor technology.

A novel multifunctional reactor is developed for the non-oxidative propane dehydrogenation. Using a fixed monolithic catalyst as an energy repository, an indirect coupling is achieved between energy necessary for the endothermic propane dehydrogenation and energy released by the combustion with air of the formed coke and added hydrocarbons for overall energy balance. Secondly, recuperative heat exchange is integrated inside the reactor using the concept of reverse flow, i.e. periodic change of the gas flow direction while feeding the reactants without any preheating. In this reaction coupling reverse flow reactor (RCRFR), the propane dehydrogenation reaction, energy supply at high temperatures, catalyst regeneration and recuperative heat

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exchange are all integrated in one apparatus. Information on the total amount of coke deposited on the catalyst and its distribution along the axial coordinate as a function of time at given operating conditions is indispensable for operation and optimisation of this reactor in order to assess the contribution of the combustion of the formed coke relative to the combustion of added hydrocarbons to the total energy supply for the endothermic propane dehydrogenation. Thus, this work focuses on the coke formation rate during propane dehydrogenation. The effect of the coke deposits on the propane dehydrogenation reaction rate was considered separately [3].

Catalyst deactivation during propane dehydrogenation over platinum alumina catalysts has received considerable attention in the past few years [4,5]. However, the research has mainly focussed on the effect of tin addition to platinum catalysts, especially on the extent of reduction of intrinsic catalytic activity caused by the coke deposits. Although the effects of operating conditions have been identified qualitatively, no complete quantitatively predictive time-dependent coke formation rate equation has been published for the propane dehydrogenation over wide temperature and concentration ranges. For the 1-butene dehydrogenation to 1,3-butadiene over a Cr_2O_3/Al_2O_3 catalyst, however, extensive models have been developed describing the time-dependent coke formation rate as a function of the operating conditions [6,7]. The aim of this work is to derive a kinetic rate expression to describe quantitatively the total amount of coke deposits in time on a platinum alumina monolithic catalyst under propane dehydrogenation reaction conditions.

2. Experimental

Experiments were carried out in a TGA operated under differential isothermal reactor conditions at atmospheric pressure. In a quartz tubular reactor a small sample (ca. 5 mm × 5 mm × 2 mm, approximately 80 mg) of a commercial $Pt/\gamma\text{-}Al_2O_3$ monolithic cordierite catalyst, supplied by Engelhard, was connected with a platinum wire to the balance. Using SEM analysis the average channel diameter was determined at 956 μm, the support thickness at 189 μm and the average washcoat thickness at 37 μm (11–89 μm). In the washcoat 1.5 g Pt/l monolith was dispersed. In each experiment the catalyst sample was heated to the desired reaction temperature (600–800°C) under a nitrogen flow. Using a four-way valve a propylene–hydrogen–nitrogen gas mixture was introduced, whose composition and total flow (1–10 $N\,cm^3/s$) was set using mass flow controllers (Brooks). GC analysis of the exit gases confirmed minor conversion of the reactants. After a certain time on stream the four-way valve was switched back to purge the reactor and subsequently air was introduced to regenerate the catalyst sample by combusting the coke deposits. By these repeated alternations between dehydrogenation and combustion reaction conditions coke formation rates were determined on the monolithic sample under reaction conditions analogous to those in an RCRFR. Furthermore, use of the same catalyst sample enables direct comparison of different experiments. Fig. 1 shows the good reproducibility of the experiments except for an experiment starting with a fresh sample, which is probably caused by sintering or permanent destruction of the most active sites or pores by coke deposits during the first few experiments, confirmed by the decrease in BET area (35–16 m^2/g monolith) and increase in average pore diameter (11.2–16.7 nm). The figure confirms absence of further deactivation for coke formation after only a few experiments.

Absence of mass transfer limitations was verified by comparing coke formation rates on the same used monolithic sample for propylene–nitrogen and propylene–helium gas mixtures with equal propylene concentration at high temperatures. Since nearly identical coking rates were obtained mass transfer limitations can safely be excluded.

2.1. Experimental results

Firstly, it has been confirmed that coke deposits during propane dehydrogenation originate almost solely from propylene (see Fig. 1). Furthermore, comparable coke formation rates are obtained for pure propylene on monolith samples with and without platinum dispersed in the washcoat, suggesting that most of the carbonaceous products is formed on acid sites of the $\gamma\text{-}Al_2O_3$ washcoat. The higher coking rates under pure propane atmosphere on the sample with platinum compared to the sample without platinum is probably caused by a small conversion of propane to propylene at the platinum surface sites.

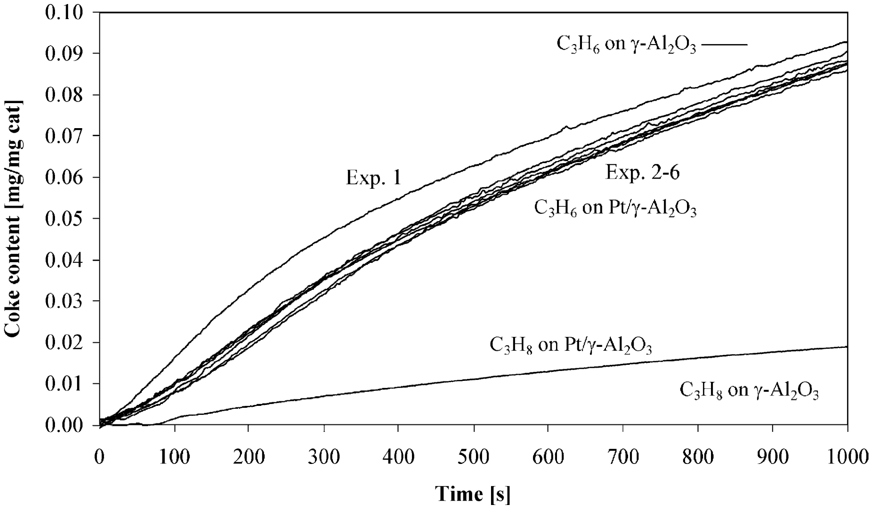

Fig. 1. Coke content versus time for pure propane or propylene on monolithic samples with and without platinum dispersed in the washcoat at 650°C.

Coke formation rates have been determined as a function of time for different propylene–nitrogen and propylene–hydrogen gas mixtures at different temperatures on monolithic samples with platinum dispersed in the washcoat. Some illustrative experimental results of the complex coke formation process are shown in Figs. 2–4 and are shortly described below.

A very strong influence of the reaction temperature has been observed (see Fig. 2). Clearly visible is the marked abrupt decrease in the coking rates when the coke content reaches about 12 wt.% of the total weight of the monolith sample, independent of the reaction temperature. Apparently, the coke formation reaction deactivates itself when the catalyst surface becomes coked after longer times on stream, but a residual coking activity remains. This has also been observed by Dumez and Froment [8] and Peña et al. [7] in their studies on coke formation rates from 1-butene over a Cr_2O_3/γ-Al_2O_3 catalyst, however, with a more gradual deactivation when the coke concentration reached

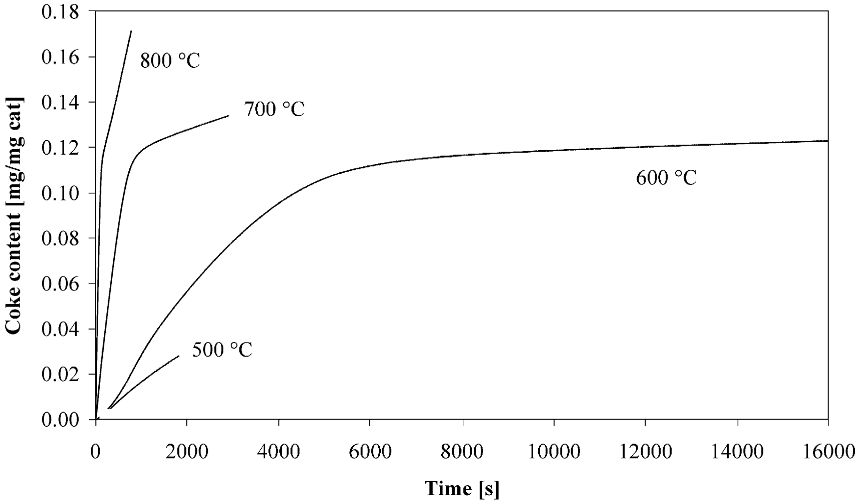

Fig. 2. Coke content versus time for pure propylene feeds at different reactor temperatures.

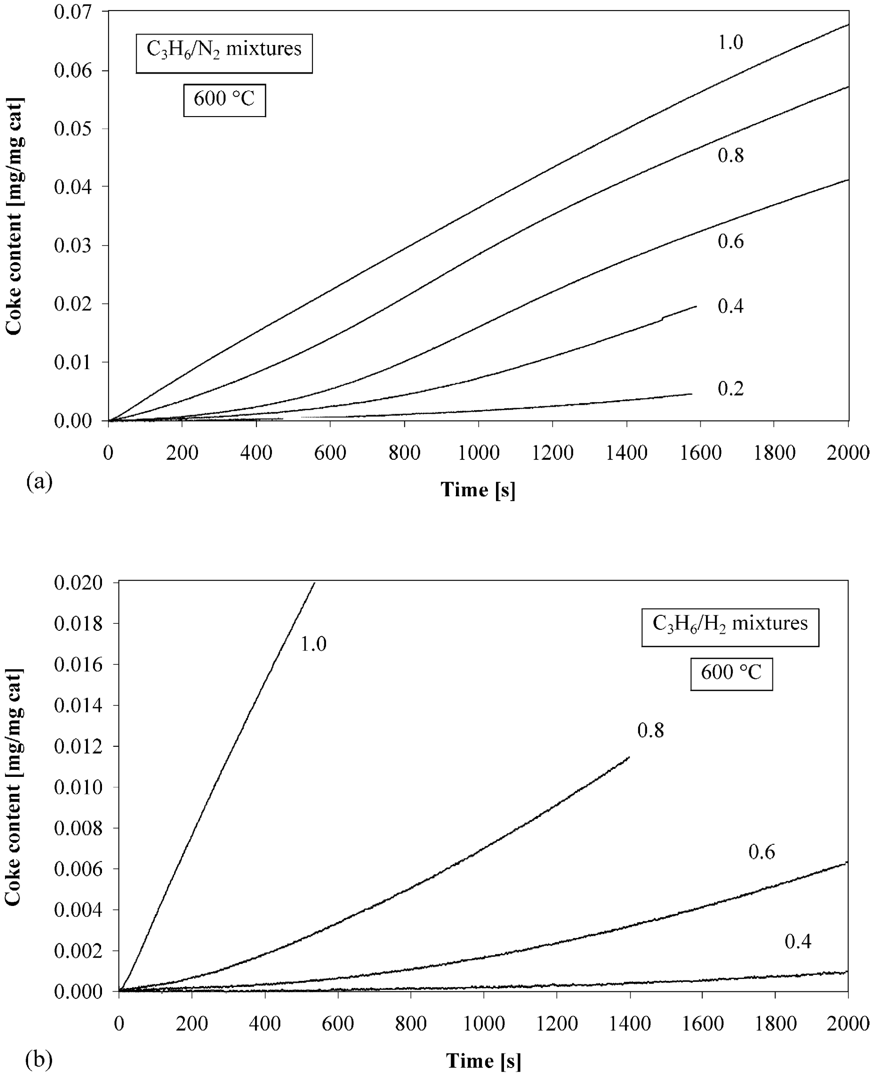

Fig. 3. Coke content versus time as a function of the propylene gas phase mole fraction for propylene–nitrogen (a) and propylene–hydrogen (b) at 600°C.

about 5 wt.%. For relatively long times on stream the coke formation rate has become constant and first order in the propylene gas phase concentration. The hydrogen concentration did not influence the residual coking activity, as also observed by Peña et al. [7].

In Fig. 3 the influence of the propylene concentration in propylene–nitrogen and propylene–hydrogen gas mixtures on the coke formation rates at 600°C is shown. A remarkable increase in the coke formation rates in time can be observed from the increasing slope of the coke content versus time curve, for both propylene–nitrogen and propylene–hydrogen gas mixtures and especially at lower propylene concentrations. An excellent linear regression fit is obtained from the coke content versus time squared. The apparent reaction order of the coking process with respect to the propylene concentration is strikingly high, especially for propylene–hydrogen gas mixtures at relatively short times on stream at lower temperatures.

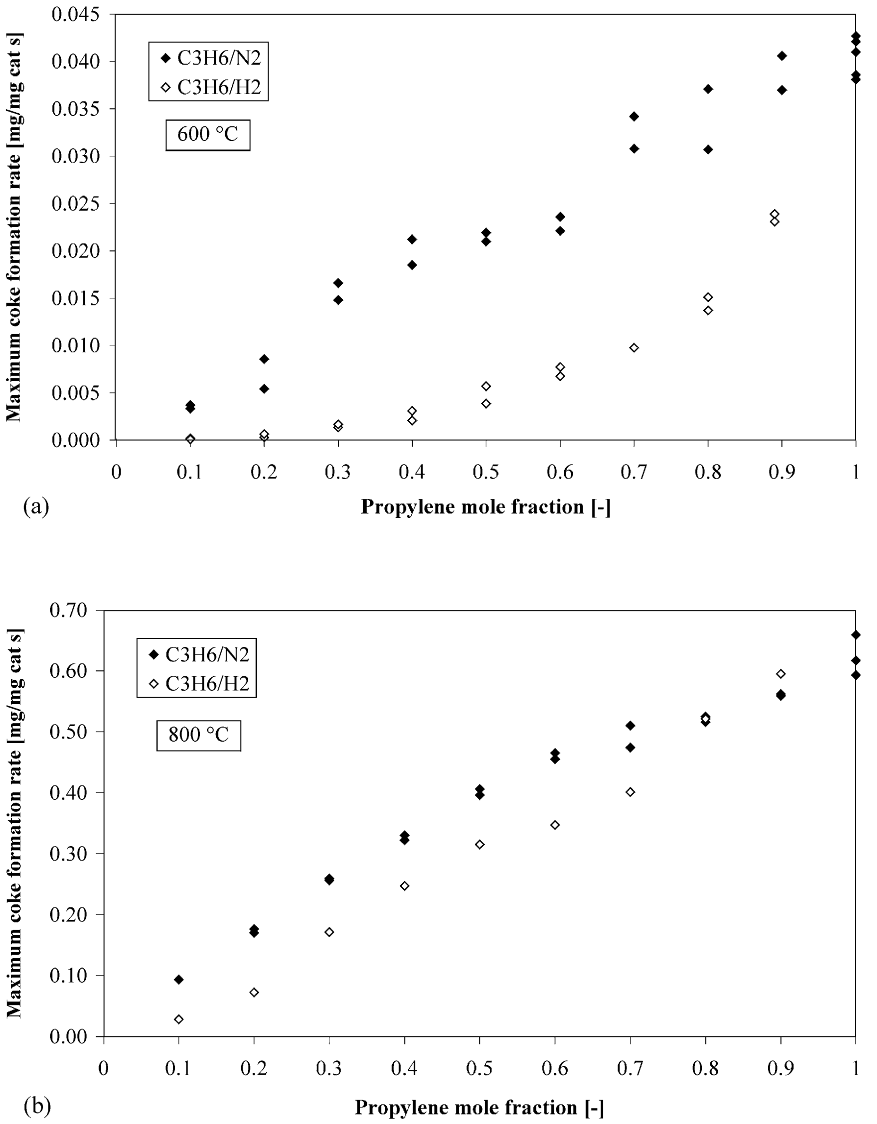

Fig. 4. Maximum coke formation rates versus the gas phase propylene mole fraction for propylene–nitrogen (closed marks) and propylene–hydrogen (open marks) mixtures at 600°C (a) and 800°C (b).

However, the apparent reaction order in the propylene concentration decreases for longer times on stream or with increasing temperature, which corresponds to a higher coking of the catalyst surface. For propylene–hydrogen mixtures the maximum apparent reaction order decreases from as high as 6 at 500 s at 600°C, to 4 at 100 s at 700°C, to 1 at 500 s at 700°C or 50 s at 800°C. Lower reaction orders were found for propylene–nitrogen mixtures, e.g. from 2 at 500 s at 600°C, to 1 at 50 s and 0.7 at 100 s at 600°C, to 0.6 at 50 s at 800°C.

Furthermore, Fig. 3 also clearly shows the very strong influence of the hydrogen concentration on the coking rates. For example, for a 60% propylene–40% nitrogen mixture a coke content of 1.6 wt.% was obtained after 1000 s at 600°C, while for a 60% propylene–40% hydrogen mixture the coke content reached only 0.16 wt.% after 1000 s at 600°C, which is one order of magnitude lower. Also, even small concentrations of hydrogen can suppress the coke formation rates enormously. However, the influence of the hydrogen decreases considerably at higher reaction temperatures as evident from Fig. 4, where the maximum observed coking rates are plotted as a function of the propylene concentration for both propylene–nitrogen and propylene–hydrogen mixtures at different temperatures. Despite the large differences in coking with and without hydrogen at lower temperatures, the maximum coking rates of propylene–hydrogen mixtures approach those of propylene–nitrogen at 800°C.

Finally, it has been tried to regenerate the catalyst by hydrogen treatment. It was not possible to decrease the coke content under a hydrogen atmosphere, not even at 800°C. This is in accordance with findings of Larsson et al. [5].

3. Kinetic model

A kinetic rate expression is developed based on a, as simple as possible, mechanistic model but able to quantitatively describe the above-mentioned experimental observations. The basic assumptions are as follows:

1. All coke deposits originate from propylene; coke formation from propane can be neglected.
2. Most of the coke deposits is formed at acid γ-Al_2O_3 surface sites.
3. The internal catalyst structure is not taken into account, assuming that the smallest pores are blocked in the very early stages of the coke formation process resulting in a negligible amount of coke deposits in these smallest pores [6]. The usefulness of this assumption has also been demonstrated by Peña et al. [7].
4. Following Peña et al. [7] and Marin et al. [6] the marked sudden decrease in the coke formation rate when the coke concentration reaches ca. 12 wt.% is attributed to two different stages in the coke formation process. In the first stage carbonaceous compounds are formed at the catalyst surface from a coke precursor (CP), which originates from adsorbed propylene. These coke deposits are termed monolayer coke, since it is formed directly on the catalyst surface. The second stage consists of growth of these monolayer coke deposits to multilayer coke. The terminology of monolayer and multilayer coke does not necessarily stand for coke growth in layers. The principal difference in these coke formation stages is merely the assumption that monolayer coke (Cm) is formed through reaction of CP with adsorbed propylene, while multilayer coke (CM) is formed via reaction of monolayer coke with propylene directly from the gas phase.
5. Following Marin et al. [6] it is assumed that the formation of CP is the rate determining step in the coke formation process and the CP grows instantaneously to monolayer coke with adsorbed propylene molecules.

Table 1
Proposed coke formation mechanism

Adsorption equilibria	$\frac{1}{2}H_2(g) + S \overset{K_H}{\rightleftarrows} H(s)$
	$C_3H_6(g) + S \overset{K_C}{\rightleftarrows} C_3H_6(s)$
Dimerisation	$C_3H_6(s) + C_3H_6(s) \xrightarrow{k_R} PD$
Coke precursor formation	$PD + C_3H_6(s) \xrightarrow{k_{CP}} CP + S$
	$Cm + C_3H_6(s) \xrightarrow{k_{CP,1}} Cm + CP$
	$Cm + PD \xrightarrow{k_{CP,2}} Cm + CP$
Monolayer coke formation	$CP \rightarrow \cdots \xrightarrow{C_3H_6(s)/PD} \cdots \rightarrow \cdots Cm$
Multilayer coke formation	$Cm + C_3H_6(g) \xrightarrow{k_{CM}} CM$
	$CM + C_3H_6(g) \xrightarrow{k_{CM}} CM$

Table 2
Adsorption and reaction rate constants and their activation energies for the coke formation model in Table 1

Pre-exponential constant	
$K_{C,\infty}$	$1.24 \times 10^{-1}\ m^3\ mol^{-1}$
$K_{H,\infty}$	$1.97 \times 10^{-3}\ m^{1.5}\ mol^{-0.5}$
$K_{r,\infty}$	$3.55 \times 10^{8}\ s^{-1}$
$k_{CP,\infty}$	$6.69 \times 10^{5}\ s^{-1}$
$k_{CP,1,\infty}$	$1.65 \times 10^{0}\ s^{-1}$
$k_{CP,2,\infty}$	$3.32 \times 10^{5}\ s^{-1}$
$k_{CM,\infty}$	$4.30 \times 10^{4}\ m^3\ mol^{-1}\ s^{-1}\ mg\ mg_{cat}^{-1}$
w	$0.12\ mg\ mg_{cat}$
Activation energy	
E_C	$-0.449\ kJ\ mol^{-1}$
E_H	$-47.1\ kJ\ mol^{-1}$
E_R	$186\ kJ\ mol^{-1}$
E_{CP}	$147\ kJ\ mol^{-1}$
$E_{CP,1}$	$46.8\ kJ\ mol^{-1}$
$E_{CP,2}$	$156\ kJ\ mol^{-1}$
E_{CM}	$200\ kJ\ mol^{-1}$

6. The auto-catalytic behaviour of the coke formation process for short times on stream is attributed to the formation of an intermediary product in the formation of CP. From the initial quadratic increase in the coke content versus time it can be concluded that there is only one rate determining intermediary product in the CP formation.
7. Because of the high apparent reaction order in the propylene concentration observed for the coke formation rate for relatively short times on stream, it is tentatively proposed that coke deposits are formed through an oligomerisation process, as proposed by Hamid and Cerouane [9]. From dimerisation of adsorbed propylene an intermediary product is formed, possibly hexene or an even further dehydrogenated or aromatised product. From the reaction of this propylene dimer (PD) with another adsorbed propylene molecule a CP is formed. It is assumed that CPs can also be formed from the reaction of monolayer coke with adsorbed propylene or PD. This last assumption is necessary to describe the very sudden marked transition from primarily monolayer coke formation to only multilayer coke formation for longer times on stream.
8. It is assumed that propylene and hydrogen adsorb competitively at the same surface sites, assuming that hydrogen chemisorbs dissociatively at these surface sites and that the adsorption equilibria are established instantaneously. The decreased influence of the hydrogen concentration at higher temperatures is explained by a decreased hydrogen chemisorption at the catalyst surface sites. Again following Dumez and Froment [8] and Peña et al. [7] it is assumed that the deactivation reaction involves two surface sites, so that CP and monolayer coke occupy two surface sites.

The above outlined coke formation model, obviously a tentatively proposed simplification of the complex coke formation processes, is summarised in Table 1. It is emphasised here that the proposed mechanism aims only at giving information about the reaction rate of the rate determining steps. No details about the precise structure of the species involved and the actual chemical transformations taking place at the catalyst surface are included in this model. All species involved could undergo further reactions, like cracking, dehydrogenation or cyclisation. Even about the order in which these reactions can take place (first dimerisation, then dehydrogenation or the other way around), the proposed mechanism does not give specifics. The assumption in the proposed kinetic model is that the effects of these additional reactions can be lumped in 'overall' reaction rate constants of the rate determining steps. For instance, 'adsorbed propylene' should be considered as a species originating from the adsorption of propylene from the gas phase.

3.1. Coke formation rate equation

The increase in coke content, M_{C}, in time is given by the sum of the monolayer and multilayer coke production rates, thus:

$$\begin{aligned}\frac{\partial M_{\mathrm{C}}}{\partial t} &= \frac{\partial M_{\mathrm{Cm}}}{\partial t} + \frac{\partial M_{\mathrm{Cm}}}{\partial t}\\ &= w\frac{\partial \theta_{\mathrm{Cm}}}{\partial t} + k_{\mathrm{CM}} C_{\mathrm{g,C_3H_6}} \theta_{\mathrm{Cm}}\end{aligned}$$

introducing w as the maximum monolayer coke concentration. The fraction of the total surface sites occupied by PD, θ_{PD}, and monolayer coke, θ_{Cm}, are described by the following balances,

$$\frac{\partial \theta_{\mathrm{PD}}}{\partial t} = k_{\mathrm{R}} \theta_{\mathrm{C_3H_6}}^2 - k_{\mathrm{CP}} \theta_{\mathrm{C_3H_6}} \theta_{\mathrm{PD}} - k_{\mathrm{CP,2}} \theta_{\mathrm{PD}} \theta_{\mathrm{Cm}},$$

$$\begin{aligned}\frac{\partial \theta_{\mathrm{Cm}}}{\partial t} = \frac{\partial \theta_{\mathrm{CP}}}{\partial t} &= k_{\mathrm{CP}} \theta_{\mathrm{C_3H_6}} \theta_{\mathrm{PD}} + k_{\mathrm{CP,1}} \theta_{\mathrm{C_3H_6}} \theta_{\mathrm{Cm}}\\ &\quad + k_{\mathrm{CP,2}} \theta_{\mathrm{PD}} \theta_{\mathrm{Cm}}\end{aligned}$$

and the surface fractions of the free surface sites, θ_{S}, dissociatively chemisorbed hydrogen, θ_{H}, and propylene, $\theta_{\mathrm{C_3H_6}}$, respectively, by the following algebraic equations:

$$\theta_{\mathrm{S}} = \frac{(1 - \theta_{\mathrm{PD}} - \theta_{\mathrm{Cm}})}{1 + K_{\mathrm{H}} C_{\mathrm{g,H_2}}^{1/2} + K_{\mathrm{C}} C_{\mathrm{g,C_3H_6}}},$$

$$\theta_{\mathrm{H}} = \frac{K_{\mathrm{H}} C_{\mathrm{g,H_2}}^{1/2} (1 - \theta_{\mathrm{PD}} - \theta_{\mathrm{Cm}})}{1 + K_{\mathrm{H}} C_{\mathrm{g,H_2}}^{1/2} + K_{\mathrm{C}} C_{\mathrm{g,C_3H_6}}},$$

$$\theta_{\mathrm{C_3H_6}} = \frac{K_{\mathrm{C}} C_{\mathrm{g,C_3H_6}} (1 - \theta_{\mathrm{PD}} - \theta_{\mathrm{Cm}})}{1 + K_{\mathrm{H}} C_{\mathrm{g,H_2}}^{1/2} + K_{\mathrm{C}} C_{\mathrm{g,C_3H_6}}}$$

Initially, the catalyst surface is free of any coke components ($t = 0 : \theta_{\mathrm{PD}} = \theta_{\mathrm{Cm}} = M_{\mathrm{C}} = 0$).

For relatively short times on stream the kinetic rate expression for the coke formation rate can be simpli-

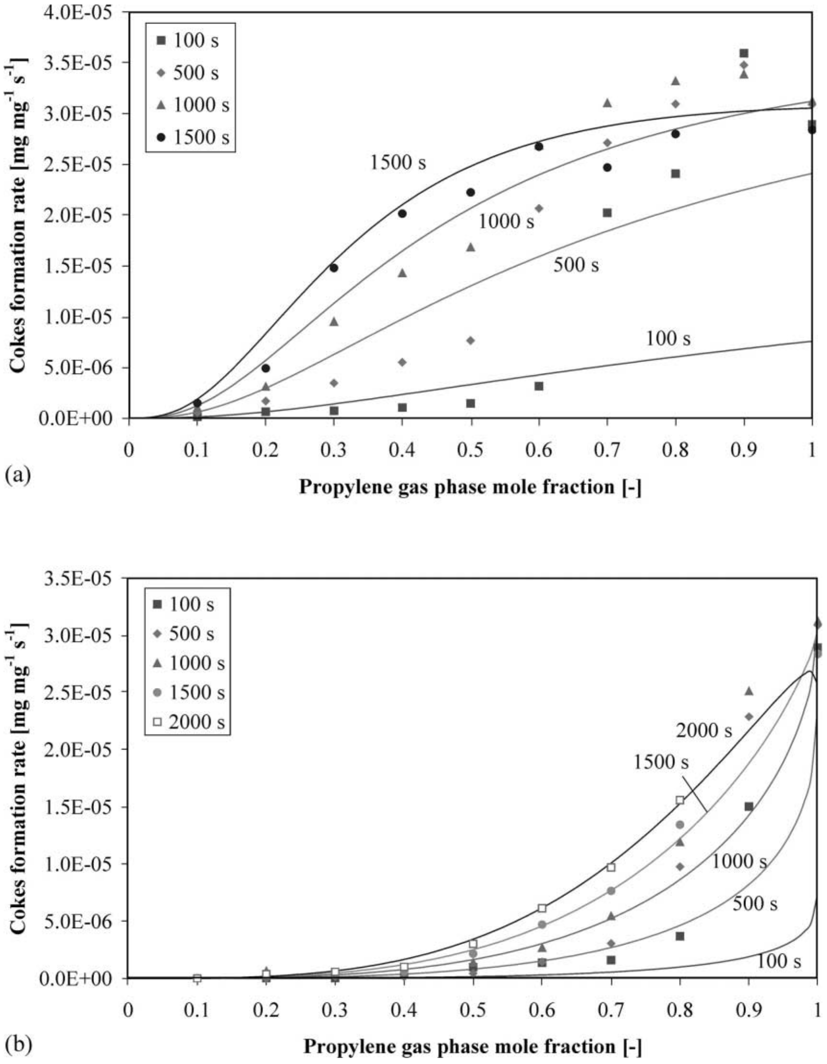

Fig. 5. Comparison of experimentally determined (marks) and theoretically predicted (lines) coke formation rates for propylene–nitrogen (a) and propylene–hydrogen (b) mixtures at 600°C.

fied and solved analytically, giving the following for the coke content as a function of time:

$$M_{\mathrm{C}}(t) = w\left[\frac{k_{\mathrm{R}}\theta^{2}_{\mathrm{C_3H_6},0}t}{1+k_{\mathrm{R}}\theta^{2}_{\mathrm{C_3H_6},0}t} - \frac{1-(1+k_{\mathrm{R}}\theta^{2}_{\mathrm{C_3H_6},0}t)^{-((k_{\mathrm{CP}}/k_{\mathrm{R}}\theta_{\mathrm{C_3H_6},0})-1)}}{(1+k_{\mathrm{R}}\theta^{2}_{\mathrm{C_3H_6},0}t)((k_{\mathrm{CP}}/k_{\mathrm{R}}\theta_{\mathrm{C_3H_6},0})-1)}\right] \approx \frac{1}{2}wk_{\mathrm{R}}k_{\mathrm{CP}}\theta^{3}_{\mathrm{C_3H_6},0}t^{2}$$

where $\theta_{\mathrm{C_3H_6},0}$ denotes the initial propylene surface fraction. A Taylor series expansion of the coke content as a function of time around $t = 0$ shows the experimentally observed second order time dependency of the coke content and the observed high apparent propylene reaction order.

The experimentally determined coke formation rates as a function of time for different propylene–nitrogen and propylene–hydrogen mixtures at different temperatures have been used to fit the adsorption and

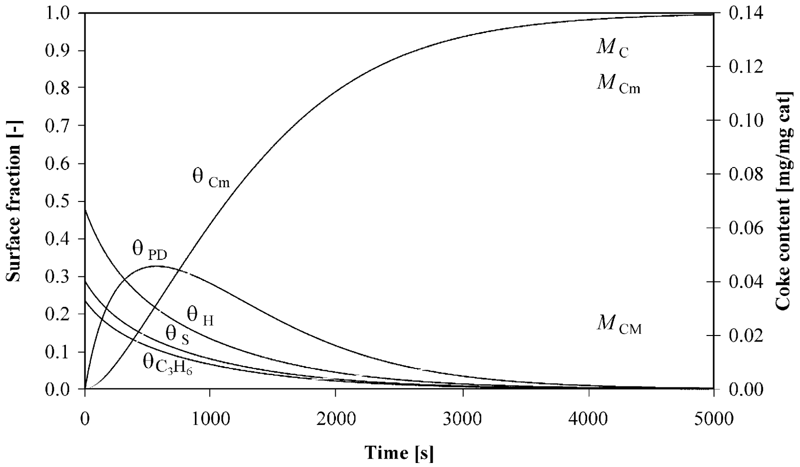

Fig. 6. Model results for the surface fractions and monolayer (M_{Cm}), multilayer (M_{CM}) and total coke content (M_C) for a 50% propylene–50% hydrogen mixture at 600°C.

reaction rate constants in the coke formation model, assuming an Arrhenius-type temperature dependency. The complete set of experimentally determined coke formation rates — not the coke content in order to avoid cumulative errors — at different times on stream and different temperatures has been fitted simultaneously using the multivariable Levenberg–Marquardt algorithm. The maximum monolayer coke concentration has been fixed at 12 wt.% and the pre-exponential multilayer coke formation rate constant $k_{CM,\infty}$ and the multilayer coke formation activation energy E_{CM} has been directly obtained from an Arrhenius plot, using the slope of the coke content versus time curve at large times on stream after the sudden marked decrease in coke formation rate, i.e. for $w > 12$ wt.%. The regression results are presented in Table 2. In Fig. 5 the fitted and experimentally determined coke formation rates at 600°C are plotted as a function of the propylene gas phase mole fraction. Model results for the case of a 50% propylene and 50% hydrogen gas mixture at 600°C are presented in Fig. 6.

4. Conclusions

Experimentally determined coke formation rates as a function of time on stream for propylene–nitrogen and propylene–hydrogen gas mixtures in a TGA over a used Pt/γ-Al_2O_3 monolithic catalyst can be adequately described using a mechanistic dual coke growth model following Peña et al. [7] and Marin et al. [6]. This model has been extended by assuming that the rate determining CP formation initially occurs via propylene oligomerisation. Based on this mechanistic model (see Table 1) a kinetic rate expression has been derived and the adsorption and reaction rate constants and activation energies have been fitted using the Levenberg–Marquardt multivariable algorithm (see Table 2). The kinetic rate expression quantitatively describes the coke formation rates over a wide temperature range (600–800°C) and wide concentration range (at least 0–50% propylene in nitrogen or hydrogen). The model satisfactorily describes the remarkable initial quadratic increase in the coke formation rates versus time (auto-catalysis) with its high apparent propylene reaction order, and the decrease in coke formation rates after longer times on stream (auto-deactivation), with a constant residual coke formation rate when the coke content exceeds 12 wt.%. Also the observed very pronounced influence of the hydrogen concentration is quantitatively captured by the model. The derived kinetic rate expression provides valuable information for the design and optimisation of propane dehydrogenation reactors.

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