Virtual control for high conversion of methane over supported Pt

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Abstract

A transient model for oxidation of methane over Pt/Al_2O_3 monolith catalysts has been developed by rigorous consideration of mass- and heat transport and mean-field treatment of the reaction kinetics. By coupling a virtual regulator using the reactant slip, methane or oxygen partial pressures, or oxygen surface coverage as feedback variable(s) as such or in combinations for control of feed composition, the influence of gas composition changes on the methane conversion has been investigated.

Keywords: environmental catalysis; CH_4 oxidation; elementary step model; mean-field kinetics; feedback control; virtual regulator

1. Introduction

The complete oxidation of methane on platinum is of considerable interest because it is one of the generic catalytic reactions [1]. From a practical point of view, catalytic oxidation of methane is of increasing importance in exhaust aftertreatment (emissions from, e.g., natural gas fuelled engines, and homogeneous charge compression ignition and exhaust gas recycling combustion contain methane) as well as energy conversion processes. Although the reaction has attracted attention for decades [1-6], the understanding of elementary key-steps and the corresponding kinetics is still far from complete. Here, on the basis of temperature programmed and pulse-response oxidation experiments with Pt/Al_2O_3 monolith catalysts previously carried out in our laboratory [6], a microkinetic model for simulations of the methane oxidation over alumina supported platinum has been constructed. The present aim is to conceptually use this model to understand the reaction mechanism. Specifically, the influence of changes of inlet gas composition on the conversion of methane has been simulated by coupling the microkinetic model with a virtual regulator for control of the inlet feed composition.

2. Development of the model

To theoretically explore the reaction kinetics of exothermic reactions like oxidation of methane over Pt/Al_2O_3 monolith catalysts, it is essential to consider mass-and heat transport phenomena properly. Here, a model previously developed for simulation of mass-and heat transport during CO oxidation has been employed [7]. The microkinetic model then is based on the mean-field treatment of reaction kinetics. It is mainly founded on the model proposed by Hickman and Schmidt [8]. Herein the surface coverage of different species is calculated by site balance equations based on the reaction steps and corresponding kinetics summarised in Table 1. For example the oxygen coverage is calculated according to $d\theta_O/dt=2r_2-2r_3-r_9-r_{10}-r_{11}-r_{15}+r_{16}$. The model by Hickman and Schmidt was originally derived for steady-state partial oxidation of CH_4 at higher temperatures, i.e., low oxygen coverage, and the oxygen adsorption kinetics was thus considered as non-competitive. Here, instead, competitive oxygen adsorption is employed. Also dissociation of formed CO, CO_2 and H_2O are neglected in the present model. With these modifications, the predicted steady-state conversion of methane and oxygen slip agree relatively well with experiments. However, the transient behaviour, i.e. methane oxidation and oxygen slip during oxygen concentration changes, is relatively poor due to a too rapid poisoning of the platinum surface by either oxygen or carbon depending on the reaction conditions. Based on this observation a step for oxygen storage and release was added. This step can be interpreted as formation and decomposition of platinum oxides and/or other oxygen containing species in the Pt/Al_2O_3 system [9]. With this addition the model can reproduce the experimental data reasonable well also during transients, *cf.* Figure 1, although the dissociation of methane during rich conditions is somewhat underestimated.

Figure 1 demonstrates that the oxidation of methane over Pt/Al_2O_3 is highly sensitive the oxygen coverage, which in turn is a strong function of the gas phase composition. For example at t=25 min where an oxygen pulse is introduced, the outlet methane concentration passes through a minimum indicating temporarily high activity for methane oxidation. After about 2 min of oxygen exposure, the corresponding simulation shows that the majority of the oxygen storage sites are occupied and thus the rate for oxygen storage decreases significantly. Consequently, the oxygen coverage increases which leads to oxygen poisoning and thus low methane oxidation rate (t=27-39 min). It is tempting to interpret this result in terms of possible optimal adsorbate composition which can be approached by transient operation of the gas phase concentrations.

It is instructive to first consider the case where the oxygen pulse duration, and thus also the pulse frequency, is varied. In Table 2, the simulated average methane conversion, here defined as the integrated methane conversion over a period with reproducible responses, corresponding to a simulation series with different fixed time intervals is shown. In this case we have used equally long lean and rich phases. It is clear that the average methane conversion increases as the pulse duration is decreased. For example, for period length of 600 s (i.e., alternating the oxygen feed between 1250 vol.-ppm O_2 for 300 s and no oxygen for the same duration) lead to 42.2% CH_4 conversion while the corresponding case with a period of 20 s results in 89.7% conversion of methane. The improvement originates from that periods corresponding to either high oxygen or carbon coverage (*cf.* t=27-30 and t=31-35 min, respectively, in Figure 1) are shortened and thus the periods with low methane oxidation rate are also shortened leading to increased average CH_4 conversion.

3. Simulations with virtual control

To theoretically explore the influence of transient operation of the gas composition on the methane conversion even further, the model was connected with a virtual regulator to automatically control the oxygen pulse frequency. Here we demonstrate how different parameters like reactant slip, i.e., methane (p_{CH4}) or oxygen (p_{O2}) partial pressures after the catalyst, or the oxygen surface coverage (θ_O) as such or in combinations can be used as feedback variables. The control algorithms were simple in the sense that the feedback variable(s) only triggered switches between two levels of oxygen concentration, i.e., 0 and 1250 vol.-ppm.

In Figure 2 the results from the simulations with p_{O2} as feedback variable are shown. The switches of the oxygen concentration were triggered when the p_{O2} reached either below 50 ppm or above 200 ppm. As can be seen the CH_4 conversion is high, on average of 93.8%. This is, again, thanks to that periods with either too high O or C coverage are suppressed thus facilitating high CH_4 oxidation rate. In fact the low methane oxidation rate during rich periods is completely avoided. In Figure 2, this is observed as only one peak of CH_4 slip per lean-rich cycle. It is clear that the methane conversion can be improved even further simply by using other trigger conditions. For example by restricting the allowed oxygen slip to 50 ppm < p_{O2} < 100 ppm leads to 95.6% methane conversion by increased switching frequency, see Table 2.

Analogously, the oxygen coverage of the active sites can be used as feedback variable. Figure 3 shows the results where $0.1 < \theta_O < 0.6$ was used as trigger conditions (the θ_O refers to the oxygen coverage in the rear part of the monolith catalyst). Although the average methane conversion is high (89.8%), feedback of θ_O is here not as efficient as feedback of p_{O2}. Principally, a well designed regulator based on feedback of θ_O has likely large potential to improve the methane conversion as the methane oxidation rate is strongly dependent on the oxygen coverage. However, as the choice of trigger conditions is critical the present algorithm which is based on information of the θ_O at one position in the catalyst seems too simple to capture the necessary requirements to control the inlet feed as efficiently as in the case of p_{O2} feedback which transfers information on activity of the entire catalyst.

Finally, the use of p_{CH4} as feedback variable with p_{CH4} < 50 ppm as trigger condition resulted in more complex behaviour (Figure 4). The simulation revealed an initiate oxygen storage phase by a relatively long oxygen pulse followed by a phase of increasingly higher frequency of the changes between lean and rich periods (not shown). This resulted in a successive drainage of oxygen in the system, oxygen deficiency, leading to suppressed methane oxidation as a function of time on stream. One strategy to overcome this problem is simply to introduce a longer oxygen pulse after a certain time with low methane conversion. A more attractive strategy, however, is to use complementary triggers. Besides p_{CH4} < 50 ppm the additional condition of $0.1 > \theta_O$ to be fulfilled in the middle of the catalyst monolith was used. This resulted in control sequences with internal variation of pulse duration, mixed long and short pulses, and a relatively high methane conversion.

4. Concluding remarks

A transient model for oxidation of methane over Pt/Al_2O_3 monolith catalysts based on rigorous consideration of mass- and heat transport and mean-field treatment of the reaction kinetics has been developed. By coupling a virtual regulator using the reactant slip (methane or oxygen partial pressures) or oxygen surface coverage as feedback variable(s) as such or in combinations for control of the feed composition, the influence of gas composition changes on the methane conversion has been investigated. The results show that by using a virtual regulator, periods with either too high oxygen or carbon coverage can be avoided thus resulting in improved (average) methane conversion. Generally, the method described here provides opportunities not only to find strategies for improved catalyst efficiency but also to analyse the basic principles and reaction kinetics behind catalytic reactions.

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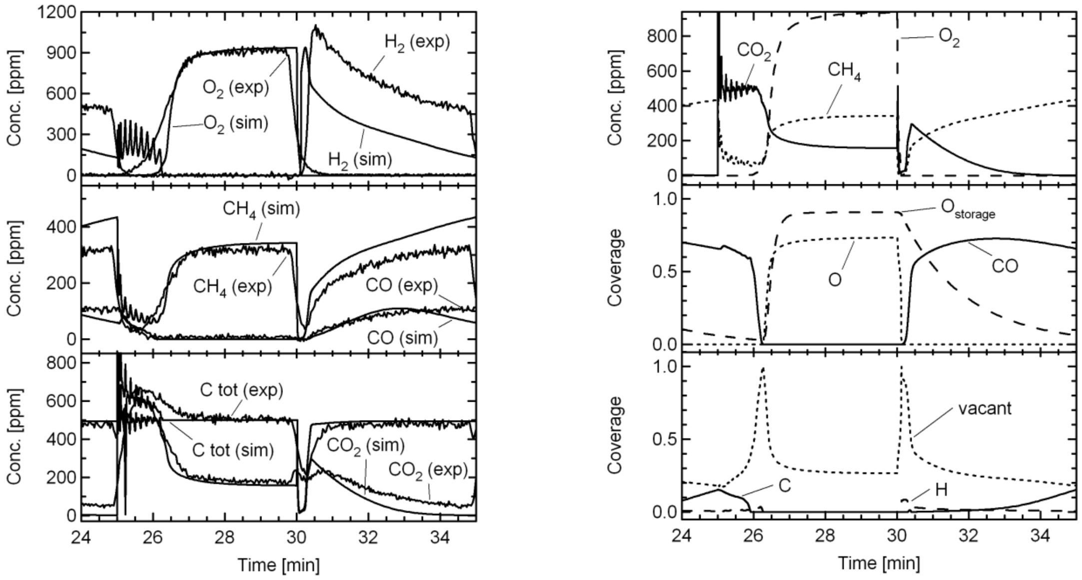

Figure 1. Oxidation of 500 vol. ppm CH_4 over a 5% Pt/Al_2O_3 monolith catalyst while periodically varying the oxygen concentration between 0 vol. ppm (5 min) and 1250 vol. ppm (5 min) at an inlet gas temperature of 673 K. The left panels show the comparison between experiments (exp) and simulation (sim) based while the right panels display solely results from simulations.

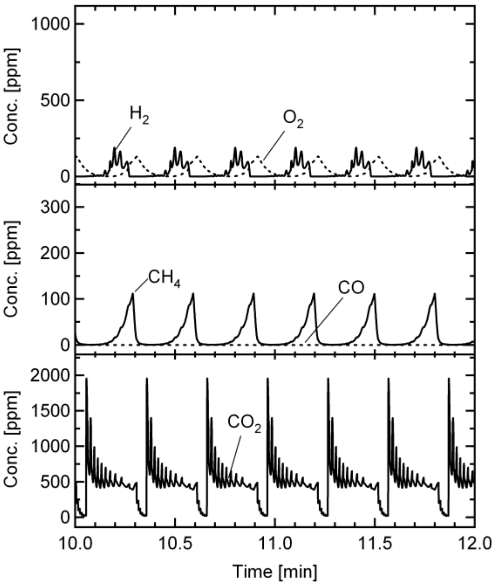

Figure 2. Simulated methane conversion using a virtual regulator to control the feed composition. The oxygen partial pressure in the product stream has been used as feedback variable to control the inlet oxygen pulse frequency.

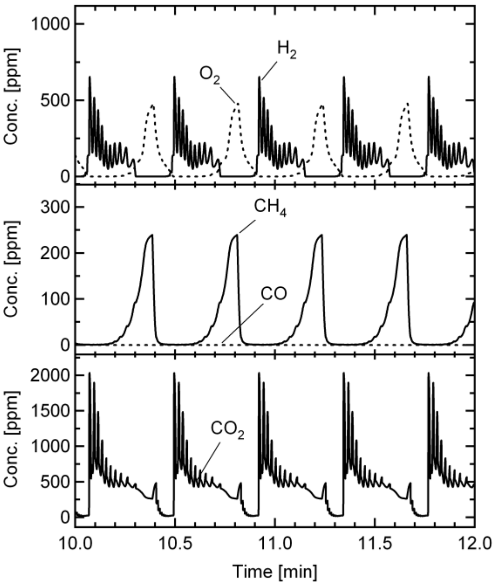

Figure 3. Simulated methane conversion using a virtual regulator to control the feed composition. The oxygen coverage in the rear part of the monolith catalyst has been used as feedback variable to control the inlet oxygen pulse frequency.

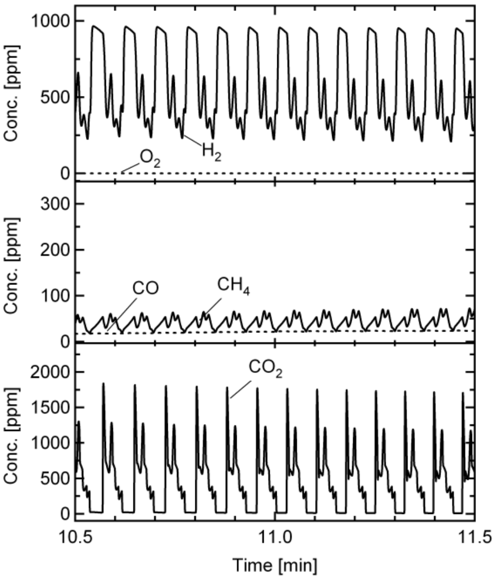

Figure 4. Simulated methane conversion using a virtual regulator to control the feed composition. The methane partial pressure in the product stream has been used as feedback variable to control the inlet oxygen pulse frequency.

Table 1. Summary of elementary steps, kinetic expressions and rate parameters used in the simulations. Rate parameters extracted from Ref. [7] except where indicated.

Reaction	Rate	s^0	v [s^{-1}]	E_a [kJ mol^{-1}]
1. $(CH_4)_{gas} \rightarrow C_{ads} + 4H_{ads}$	$r_1=s^0 p_{CH4}\theta^3$	0.025 (‡)	†	43
2. $(O_2)_{gas} \rightarrow 2O_{ads}$	$r_2=s^0 p_{O2}\theta^2$	0.03 (‡)	†	0
3. $2O_{ads} \rightarrow (O_2)_{gas}$	$r_3=2k_3(\theta_O)^2$	-	6.2e10 (‡)	205
4. $CO_{gas} \rightarrow CO_{ads}$	$r_4=s^0 p_{CO}\theta$	0.84	†	0
5. $CO_{ads} \rightarrow CO_{gas}$	$r_5=k_5\theta_{CO}$	-	1.89e14 (‡)	180 (α=0.33) [10],
6. $(H_2)_{gas} \rightarrow 2H_{ads}$	$r_6=s^0 p_{H2}\theta^2$	0.05	†	0
7. $2H_{ads} \rightarrow (H_2)_{gas}$	$r_7=2k_7(\theta_H)^2$	-	1.71e12 (‡)	75
8. $H_2O_{ads} \rightarrow H_2O_{gas}$	$r_8=k_8\theta_{H2O}$	-	5.24e10 (‡)	45
9. $C_{ads}+O_{ads} \rightarrow CO_{ads}$	$r_9=k_9\theta_C\theta_O$	-	2.03e15 (‡)	63
10. $CO_{ads} + O_{ads} \rightarrow (CO_2)_{gas}$	$r_{10}=k_{10}\theta_{CO}\theta_O$	-	3.93e13 (‡)	100 (α=0.5)
11. $H_{ads} + O_{ads} \rightarrow OH_{ads}$	$r_{11}=k_{11}\theta_H\theta_O$	-	8.79e6 (‡)	9
12. $OH_{ads} \rightarrow H_{ads} + O_{ads}$	$r_{12}=k_{12}\theta_{OH}$	-	7.51e4 (‡)	20
13. $OH_{ads} + H_{ads} \leftrightarrow H_2O_{ads}$	$r_{13}=k_{13}\theta_C\theta_O$	-	3.54e10 (‡)	65
14 $H_2O_{ads} \rightarrow OH_{ads} + H_{ads}$	$r_{14}=k_{14}\theta_{H2O}\theta$	-	2.17e10 (‡)	155
15. $OH_{ads} + OH_{ads} \rightarrow H_2O_{ads} + O_{ads}$	$r_{15}=k_{15}\theta_{OH}\theta_{OH}$	-	4.74e12 (‡)	52
16. $O_{ads} \rightarrow O_{storage}$	$r_{16}=k_{16}\theta_O(1-\theta_{storage})$	-	2.60e1 (‡)	30 (‡)
17. $O_{storage} \rightarrow O_{ads}$	$r_{17}=k_{17}\theta_{storage}$	-	1.13e1 (‡)	40 (‡)

All rates are in monolayers per second with coverages in monolayers. Vacant sites denoted θ and equals $1-\theta_C-\theta_{CO}-\theta_O-\theta_H-\theta_{OH}-\theta_{H2O}$. Rate constants are assumed to have the form $k_i=v_i\exp[-E_{a,i}(1-\alpha_i)/(RT)]$ where v_i and $E_{a,i}$ is, respectively, the frequency factor and activation energy for the ith reaction, R the gas constant and T the absolute temperature. † Adsorption rate expressed according to kinetic gas theory. ‡ This work.

Table 2. Summary of average conversion of methane and average coverage of oxygen for simulations with fixed lean and rich feed compositions and with virtually controlled feed composition.

Fixed variation of feed composition		Virtually controlled feed composition			
(O_2 pressure:time) [ppm:s]	Average CH_4 conversion [%]	(O_2 conc.:time) [ppm:s]	Average CH_4 conversion [%]	Average θ_O (†)	Trigger conditions
(1250:300), (0:300)	42.2	(1250:16.6), (0:4.4)	93.8	0.40	$50\ ppm < p_{O2} < 200\ ppm$
(1250:150), (0:150)	54.1	(1250:15.2), (0:4.0)	95.6	0.40	$50\ ppm < p_{O2} < 100\ ppm$
(1250:75), (0:750)	69.5	(1250:22.8), (0:6.4)	89.8	0.40	$0.1 < \theta_O < 0.6$
(1250:50), (0:50)	76.9	(1250:18.5), (0:6.0)	94.0	0.37	$0.1 < \theta_O < 0.4$
(1250:25), (0:25)	85.0	Decreasing to 2 s	91.2	0.05	$p_{CH4} < 50$ ppm Intermittent 1250 ppm O_2
(1250:10), (0:10)	89.7	Varying between 2 and 15 s	90.8	0.07	$p_{CH4} < 50$ ppm $\theta_O > 0.1$ (‡)

† and ‡ refer to θ_O in the, respectively, rear and middle part of the monolith catalyst.