



Catalytic partial oxidation of methane on platinum investigated by spatial reactor profiles, spatially resolved spectroscopy, and microkinetic modeling

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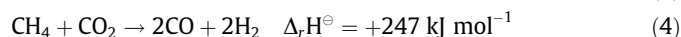
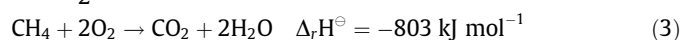
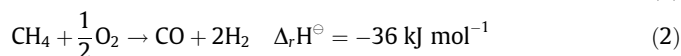
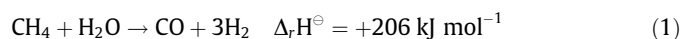
ABSTRACT

Spatially resolved profile measurements, Raman spectroscopy, electron microscopy, and microkinetic modeling have been used to study the catalytic partial oxidation of methane on Pt. The measured species profiles through Pt coated foam catalysts exhibit a two-zone structure: an abrupt change in reaction rates separates the fast exothermic oxidation chemistry at the entrance of the reactor from the slow endothermic reforming chemistry. Spatially resolved Raman spectroscopy and electron microscopy confirm that the position of the mechanistic change could be correlated with Pt transportation and formation of carbonaceous deposits blocking the majority of active Pt sites in the reforming zone. The species profiles were simulated using a pseudo-2D heterogeneous model, which includes heat and mass transport limitations, and two state-of-the-art chemical kinetic mechanisms. Although both mechanisms are in quantitative agreement with the oxygen profiles, the two mechanisms differ substantially in their predictions of the branching ratio between partial and complete oxidation, as well as surface site coverages. The experimentally observed change in reaction rates is attributed to carbon formation, which the mechanisms are unable to reproduce, since they do not include carbon–carbon coupling reactions.

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1. Introduction

Methane steam reforming (Eq. (1)) is currently the dominant technology for synthesis gas production [1]. The process is highly endothermic, and industrial production requires large and capital-intensive operations. Catalytic partial oxidation (CPO) of methane (Eq. (2)) is an attractive alternative, since it is slightly exothermic and considerably faster, with nearly equilibrium yields in synthesis gas within millisecond contact times [2–5], possibly in autothermal operation:



The global mechanism by which methane is oxidized to synthesis gas on noble metal catalysts is frequently debated in the literature. One school of thought suggests that the mechanism must be a two-step process that consists of initially highly exothermic

methane complete oxidation (Eq. (3)) followed by endothermic reforming reactions, i.e. steam (Eq. (1)) and dry reforming (Eq. (4)). The main argument is a commonly observed steep temperature gradient over the catalyst bed [6,7]. Investigations of product selectivities demonstrated that the CO₂ and H₂O selectivity increased with simultaneous synthesis gas loss by either increasing the space velocity or increasing the O₂/CH₄ ratio [7–9]. Additionally, transient experiments did not indicate a direct reaction pathway [10–12]. In contrast, other authors proposed a single step process. Experiments on Pt and Pt/10% Rh meshes and millisecond contact time suggest a direct reaction pathway, as the increasing synthesis gas selectivity with decreasing contact time cannot be explained by the two step mechanism [5,13–15].

Differential reactant conversion can hardly be achieved on autothermally operated performance catalysts such as noble metal coated α -Al₂O₃ foams. If such catalysts are used, transport limitations almost always influence the measured reaction rates, rendering classical kinetic studies nearly impossible. For example, on an 80 ppi Rh coated foam catalyst at 4700 ml min⁻¹ inlet flow rate an O₂ conversion rate of -53 mmol min⁻¹ mm⁻¹ was measured, close to the estimated physical transport limit of -83 mmol min⁻¹ mm⁻¹ [16]. On Pt coated foam catalysts, reaction rates are lower, rendering transport limitations less important. However, even on Pt catalysts, the impact of transport cannot be neglected. Mechanistic conclusions in presence of transport limitations have to be

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Nomenclature

ρ	mass density, kg m^{-3}	z	axial coordinate, m
p	pressure, Pa	S_V	(from μ -CT) geometric foam surface area to total gas-phase volume, m^{-1}
R	ideal gas constant, $8.3144621 \text{ J K}^{-1} \text{ mol}^{-1}$	A	(from μ -CT) geometric surface area of catalyst foam, m^2
T	temperature, K	l	$= \frac{4\epsilon}{S_V}$ characteristic length, m
\bar{W}	$\equiv \sum_k x_k W_k$ average molecular weight, kg kmol^{-1}	δ	$= \frac{D_{O_2 m}}{K_{O_2}}$ boundary layer thickness, m
y_k	mass fraction for species k , $\text{kg}_k \text{ kg}_{\text{tot}}^{-1}$	γ	$= \frac{V_{\text{void}} - V_{\text{bl}}}{V_{\text{void}}}$ volume fraction of bulk gas, $\text{m}^3 \text{ m}^{-3}$
x_k	$= \frac{1}{\sum_j \frac{y_j}{W_j}} \frac{y_k}{W_k}$ mole fraction for species k , $\text{mol}_k \text{ mol}_{\text{tot}}^{-1}$	ϵ	$\equiv \frac{V_{\text{void}}}{V_{\text{total}}}$ foam porosity, with $V_{\text{total}} = V_{\text{void}} + V_{\text{solid}}$
D_{km}	mixture-average diffusion coefficient for species k , $\text{m}^2 \text{ s}^{-1}$	t	time, s
v_z	velocity, m s^{-1}	% ratio	$= \frac{V_{\text{CH}_4}}{2V_{\text{O}_2}}$ ratio between atomic carbon and oxygen in gas feed
μ	average dynamic viscosity, $\text{kg m}^{-1} \text{ s}^{-1}$	κ	extinction coefficient, 2550 m^{-1} [18]
j_k	$= -\rho D_{km} \frac{\epsilon}{\tau} \frac{W_k}{W} \frac{\partial x_k}{\partial z}$ Flux of species k due to molecular diffusion, $\text{kg m}^{-2} \text{ s}^{-1}$	\vec{e}_z	unit vector
W_k	molecular mass of species k , kg kmol^{-1}	f_{active}	ratio of active metal surface area (from H_2 chemisorption) and support surface area (from Kr-BET), $\text{m}^2 \text{ m}^{-2}$
\dot{W}_k	molar rate of production per unit volume of species k by homogeneous chemistry, $\text{mol m}^{-3} \text{ s}^{-1}$	\dot{V}_k	volumetric flow rate of species k , ml min^{-1}
\dot{S}_k	molar rate of production per unit area for species k due to surface chemistry, $\text{mol m}^{-2} \text{ s}^{-1}$	<i>Dimensionless numbers</i>	
τ	tortuosity of the foam, m m^{-1}	R_e	$= \frac{\rho v_z l}{\mu}$
θ_k	site fraction of species k on Pt surface, mol mol^{-1}	S_c	$= \frac{\mu}{\rho D_{km}}$
Γ	surface site density, mol m^{-2}	P_r	$= \frac{\mu c_p}{\lambda}$
σ_k	number of sites occupied by k , mol mol^{-1}	<i>Transport correlations</i>	
h_k	specific enthalpy, J kg^{-1}	S_h	$= 0.045 R_e^{1/2} S_c^{1/3}$
c_p	average heat capacity, $\text{J K}^{-1} \text{ kg}^{-1}$	N_u	$= 0.045 R_e^{1/2} P_r^{1/3}$
λ	average thermal conductivity, $\text{W m}^{-1} \text{ K}^{-1}$		
K_k	$= S_h l^{-1} D_{km}$ mass transfer coefficient, m s^{-1}		
K_T	$= N_u l^{-1} \lambda$ heat transfer coefficient, $\text{W m}^{-2} \text{ K}^{-1}$		

drawn with care. In fact it was shown that the high selectivities to partial oxidation products (H_2 , CO) observed in presence of gas phase O_2 during methane oxidation on Rh catalysts are at least partly due to pronounced film transport limitations and the resulting small O_2 concentration at the Rh surface [17–19]. On the other hand, H_2 and CO selectivities in presence of gas phase oxygen are also not zero even if transport limitations are negligible, as shown by the authors for methane oxidation on Pt foam catalysts [16].

True kinetic control of noble metal catalyzed methane oxidation can only be enforced at high catalyst dilution [20,21] or if specially designed reactors are used [22]. Recently, Igleasia and Neurock published two detailed papers on the mechanism of methane oxidation on supported Pt clusters [20,21]. By combining kinetically well defined experiments on highly diluted catalysts with isotope labeling studies and DFT calculations, many atomistic details about methane oxidation, dry- and steam reforming on Pt nano-particles could be unraveled. Depending on the O_2/CH_4 ratio, four distinct kinetic regimes with corresponding effective rate equations could be discriminated. These regimes differ in their rate limiting steps, most abundant surface intermediates, rate and equilibrium constants.

The present work deals with methane oxidation on Pt coated foam catalysts operated under more application relevant flow and temperature conditions. Sub-millimeter resolution species and temperature profiles can be measured through such foam catalysts via the capillary sampling technique developed by Horn et al. [23]. Reactant conversion and product formation can be followed as a function of position, and the obtained reactor profiles can be used for testing of kinetic models.

Previous work on methane CPO on Rh and Pt supported on ceramic foam monoliths [17,18,23,24] gave clear evidence that both partial and complete methane oxidation proceeds in parallel in a narrow oxidation zone at the entrance of the catalyst foam. This

oxidation zone is followed by a longer endothermic steam reforming zone, and at sufficiently low catalyst temperatures, water gas shift is also observed. Dry reforming does not have a significant impact. The studies found Rh superior in synthesis gas selectivity over Pt [17,24], and no catalyst deactivation was observed over the investigated time period. The high synthesis gas selectivity on the Rh catalyst was investigated by microkinetic modeling with consideration of transport phenomena [18,25].

In the present work methane CPO on Pt coated foam monoliths is investigated. A pseudo-2D heterogeneous reactor model accounting for mass and heat transport has been developed and is combined with two state-of-the-art microkinetic models. The microkinetic models are tested against high resolution spatial reactor profiles. Peculiar features in the species profiles have been investigated by spatially resolved Raman spectroscopy and electron microscopy providing new impulses for model improvements.

2. Experimental

2.1. Catalyst preparation

The catalysts used in this study are Pt coated, cylindrical $\alpha\text{-Al}_2\text{O}_3$ foam monoliths with a pore density of 80 ppi (pores per linear inch). The monoliths (length = 20 mm and diameter = 16.2 mm) were prepared by incipient wetness impregnation with aqueous H_2PtCl_6 as precursor. Prior to impregnation the foam support was cut to the desired length and a centerline channel of 1 mm diameter was drilled through the foam. The foams were washed in acetone in order to remove any residuals from the cooling fluid, then boiled in nitric acid to remove possible metal contaminations from the drilling and confectioning step. Next the support was dried and calcined at 800°C in static air. The impregnation was done in a multi-step approach, in

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