

*Juha Ahola*

REACTION KINETICS AND  
REACTOR MODELLING  
IN THE DESIGN OF  
CATALYTIC REACTORS FOR  
AUTOMOTIVE EXHAUST  
GAS ABATEMENT

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## **Ahola, Juha, Reaction kinetics and reactor modelling in the design of catalytic reactors for automotive exhaust gas abatement**

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### ***Abstract***

The tightening environmental legislation and technological development in automotive engineering form a challenge in reactor design of catalytic reactors for automotive exhaust gas abatement. The catalytic reactor is the heart of the exhaust aftertreatment processes, but it can be seen also just as one subsidiary part of vehicles.

The aim of this work is to reveal applicable kinetic models to predict behaviour of the particular catalysts and to establish guidelines for modelling procedures and experimentation facilitating catalytic reactor design, especially in the field of automotive exhaust gas abatement.

The studies in this thesis include catalyst kinetics with synthetic exhaust gas composition in stoichiometric and net oxidative conditions, DRIFT measurements, and the warm-up of three-way catalysts in real conditions.

Knowledge on surface concentrations facilitates kinetic model construction and discrimination. For example, identification of even semi-quantitative surface concentrations may lead to a successful falsification of incorrect kinetic model candidates. Especially, that is clearly seen in cases where models predict the same kind of gas phase behaviour but different kinds of surface concentration profiles.

The transient kinetic experiments could give a hint on predominant reaction mechanism, support quantifying of the adsorption capacity and reveal the impact of surface phenomena on reactor dynamics.

The level of model complexity should be adapted depending on the purpose of the model. For example, it is mostly convenient for reactor design purposes to perceive only one type of active sites even in a case of mechanical mixture of different catalytic materials; whereas the optimisation of catalyst content demands the management of every prominent site type separately. Or, when a catalytic material has been selected, the stationary kinetic model is, in most cases, adequate for the catalytic converter design and structural optimization for warm-up conditions.

*Keywords:* catalyst, chemical reactors, modelling, reaction kinetics



*Dedicated to my grandfather Juho Pihlanen*





## Preface

This work was carried out in the Department of Process and Environmental Engineering at the University of Oulu in the past decade.

I wish to express my thanks to my supervisors Prof. Juha Tanskanen for advises and encouragement to complete my thesis, and Emer. Prof. Veikko Pohjola for instigation to unprejudiced and systemic way of thinking.

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Oulunsalo, January 2009

Juha Ahola



## List of symbols and abbreviations

$A_i$	Cross-sectional area of phase $i$ , $m^2$
$\mathbf{A}$	Stoichiometric matrix, dimensionless
$c$	Concentration, $mol/m^3$
$\hat{C}_{p,i}$	Specific heat capacity, $J/(kg\ K)$
$D$	Effective axial dispersion coefficient, $m^2/s$
$D_h$	Hydraulic diameter, $m$
$E$	Effective axial thermal dispersion coefficient, $m^2/s$
$h$	Heat transfer coefficient, $W/(m^2K)$
$\Delta H_r$	Reaction enthalpy, $J/mol$
$k_i$	Kinetic rate parameter, case dependent
$K_i$	Equilibrium constant, depend on case
$L$	Length, $m$
$m_{cat}$	Mass of catalyst, $kg$
$p_i$	Partial pressure, $Pa$
$\mathbf{r}$	Reaction rate vector, $mol/m^3s$
$t$	Time, $s$
$T$	Temperature, $K$
$\bar{u}$	Average flow rate, $m/s$
$v$	Linear velocity, $m/s$
$V_g$	Gas phase volume of reactor, $m^3$
$\mathbf{y}_g$	Gas phase molar fraction vector, dimensionless
$z$	Dimensionless length of reactor, dimensionless
$\alpha_T$	Molecular thermal diffusion coefficient, $m^2/s$
$\lambda_s$	Heat conductivity of solid, $W/(m\ K)$
$\theta_i$	Surface coverage, dimensionless
$\rho_i$	Density, $kg/m^3$
BET	Brunauer-Emmet-Teller
DRIFT	Diffuse Reflectance Infrared Fourier Transform
ER	Eley-Rideal
FTIR	Fourier Transform Infrared
FTP	Federal Test Procedure
HC	Hydrocarbon

HCHO	Formaldehyde
HC-SCR	Hydrocarbon Selective Catalytic Reduction
LLHW	Langmuir-Hinshelwood-Hougen-Watson
NEDC	New European Driving Cycle
NMHC	Non-Methane Hydrocarbon
NMOG	Non-Methane Organic Gas
OSC	Oxygen Storage Component
PGM	Platinum Group Metal
PM	Particulate Matter
SOF	Soluble Organic Fraction
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
TPSR	Temperature Programmed Surface Reaction
TWC	Three-Way Catalyst

## List of original papers

This thesis includes the following original publications:

- I Maunula T, Ahola J, Salmi T, Haario H, Härkönen M, Luoma M & Pohjola VJ (1997) Investigation of CO oxidation and NO reduction on three-way monolith catalysts with transient response techniques. *Applied Catalysis B: Environmental* 12: 287–308.
- II Maunula T, Ahola J & Hamada H (2000) Reaction mechanism and kinetics of NO<sub>x</sub> reduction by propene on CoO<sub>x</sub>/alumina catalysts in lean conditions. *Applied Catalysis B: Environmental* 26: 173–192.
- III Ahola J, Huuhtanen M & Keiski LR (2003) Integration of in situ FTIR studies and catalyst activity measurements in reaction kinetic analysis. *Ind Eng Chem Res* 42: 2756–2766.
- IV Ahola J, Kangas J, Maunula T & Tanskanen J (2003) Optimisation of automotive catalytic converter warm-up: Tackling by guidance of reactor modelling. *Computer-aided chemical engineering* 14: 539–544.
- V Maunula T, Ahola J & Hamada H (2006) Reaction mechanism and kinetics of NO<sub>x</sub> reduction by methane on In/ZSM-5 under lean conditions. *Applied Catalysis B: Environmental* 64: 13–24.
- VI Maunula T, Ahola J & Hamada H (2007) Reaction mechanism and microkinetic model for the binary catalyst combination of In/ZSM-5 and Pt/Al<sub>2</sub>O<sub>3</sub> for NO<sub>x</sub> reduction by methane under lean conditions. *Ind Eng Chem Res* 46: 2715–2725.

In paper I the experiments and data analyses were the author's contribution and the manuscript was written in close collaboration with the first author. In papers II, V and VI the author's contribution was the modelling work including model construction and writing in manuscripts. In paper III experimental design and modelling, including interpretation of results, were the author's contribution and the manuscript was written in collaboration with the co-authors. In paper IV the author's contribution was interpretations of the results. The model construction was performed together with second author and the manuscript was written in collaboration with the co-authors.



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# 1 Introduction

The tightening environmental legislation and technological development in automotive engineering form a challenge in reactor design of catalytic reactors for automotive exhaust gas abatement. The catalytic reactor is the heart of the exhaust aftertreatment processes, but it can be seen also just as one subsidiary part of vehicles.

The aim of this work is to reveal applicable kinetic models to predict the behaviour of the particular catalysts and to establish guidelines for modelling procedures and experimentation, thus facilitating catalytic reactor design especially in field of automotive exhaust gas abatement.

## 1.1 Legislation

The legislation differs in every traditional market area, i.e., US, EU and Japan. The common trend is tightening NO<sub>x</sub> emission limits and introducing the limits for particulate matter.

EU emission standards are shown in Table 1. EURO 5 and EURO 6 tiers limit non-methane hydrocarbons into 0.068 g/km for gasoline engines in addition to total hydrocarbon limit shown in the table. All years listed in Tables 1-4 below refer to new type approvals. The trend in EU emission regulations is tightening NO<sub>x</sub> limits and particulate matter in the near future.

**Table 1. EU emission standards for passenger cars in NEDC test (Dieselnet 2008a).**

Standard	Year	CO g/km	HC g/km	HC+NO <sub>x</sub> g/km	NO <sub>x</sub> g/km	PM g/km
Diesel						
Euro 3	2000	0.64	-	0.56	0.5	0.05
Euro 4	2005	0.5	-	0.3	0.25	0.025
Euro 5	2009	0.5	-	0.23	0.18	0.005
Euro 6	2014	0.5	-	0.17	0.08	0.005
Gasoline						
Euro 3	2000	2.3	0.2	-	0.15	-
Euro 4	2005	1.0	0.1	-	0.08	-
Euro 5	2009	1.0	0.1	-	0.06	0.005
Euro 6	2014	1.0	0.1	-	0.06	0.005

Selected US emission standards are shown in Table 2. In addition to these standards, the passenger cars shall meet the supplemental exhaust emission standards in US06 and SV03 driving cycles in which emissions is measured during mimicking aggressive highway driving and urban driving emissions while the vehicle’s air conditioning system is operating. In these tests, the limits are set only for CO and NMHC+NO<sub>x</sub> emissions.

**Table 2. US emission standards for passenger car in full useful lifetime (Dieselnet 2008b).**

Standard	Cycle	CO g/mi	NMOG g/mi	HCHO g/mi	NO <sub>x</sub> g/mi	PM g/mi
Tier 1 diesel	FTP-75	4.2	0.31	-	1.25	0.1
Tier 1 gasoline	FTP-75	4.2	0.31	-	0.6	0.1
Tier 2 bin 5	FTP-75	4.2	0.09	0.018	0.07	0.01

The environmental legislation which defines the emission limits in Japan includes several acts. The most prominent laws are “*Law Concerning Special Measures to Reduce the Total Amount of Nitrogen Oxides and Particulate Matter Emitted from Motor Vehicles in Specified Areas*” and “*Tokyo Diesel Retrofit Program*”. Japanese emission standards for diesel passenger cars are summarised in Table 3.

**Table 3. Japanese emission standards for diesel passenger cars (Dieselnet 2008c).**

Test mode	Year	CO g/km	HC g/km	NMHC g/km	NO <sub>x</sub> g/km	PM g/km
10-15 mode	2002	0.63	0.12	-	0.28	0.052
JC08	2005	0.63	-	0.024	0.14	0.013
JC08	2009	0.63	-	0.024	0.08	0.005

In the other market areas, the European or US standards have been adopted. In American continents the US standards are widely applied. Australia accepts concurrently European, US and Japanese emission standards. On the Asian continent, the basis of legislation is mostly based on EU standards. For example, China has adopted the European Union standards concerning the legislation. However, the legislation tightening has been delayed compared to European one as shown in Table 4.

**Table 4. Emission standards for passenger car in China (Dieselnet 2008b).**

Standard	Date	Region
Euro 1	01/2000	Nationwide
Euro 2	08/2002	Beijing
	03/2003	Shanghai
	09/2003 (diesel)	Nationwide
	07/2004 (gasoline)	
Euro 3	12/2005	Beijing
	10/2006	Guangzhou
	01/2007	Shanghai
	07/2007	Nationwide
Euro 4	01/2007 (diesel)	Beijing
	03/2008 (gasoline)	
	07/2010	Nationwide

The emission standards vary between different regions. The emission valuation is not the only difference between the standards, but also remarkable differences exist in the driving cycles, in which the emission measurements are carried out. One cycle stresses the warm-up phase, others the non-steady urban driving, while some other cycle stresses high-speed extra-urban driving conditions more than the other ones. Thus, the emission limits demanded in different regions are not directly comparable.

This induces challenges to the emission control system and, in particular, to design and optimise the catalytic converter. It does not matter whether the strategy is to meet the regulations based on different standard simultaneously or to tailor the emission control system depending on the market area.

## 1.2 Abatement technologies

To meet the environmental requirements both advanced engine technology and aftertreatment of emissions are demanded.

The three-way catalytic converters have been used for decades in the aftertreatment of the spark engine emission. The method converts simultaneously carbon monoxide, hydrocarbons and nitrogen oxides to less harmful compounds. The method demands a motor control system to keep the redox ratio of exhaust

gas in stoichiometric condition at least as short term average. Most HC emissions are emitted before the TWC reaches the light-off temperature because of low activity of TWC in low temperature. To overcome this problem, close coupled catalysts and advanced catalyst formulations were introduced. It was recognized that segregating a portion of the Pd from ceria produced better low-temperature performance. This led to the deployment of the noble metals in different layers or on different support particles within a single washcoat layer. (Twigg 2007, Kašpar *et al.* 2003, Gandhi, Graham & McCabe 2003, Farrauto & Heck 1999)

Lean-burn gasoline engines have been introduced to enhance the fuel economy and to reduce the carbon dioxide emission. In these engines the carbon monoxide and hydrocarbon emissions are easy to treat, but new technologies were necessitated to handle NO<sub>x</sub> emissions. An acceptable solution is periodically operated NO<sub>x</sub>-traps in which earth alkaline metals, e.g. barium and strontium, are added as oxides to trap NO<sub>2</sub> as metal nitrates. Thus, the NO must first be converted to NO<sub>2</sub> in the lean operation. After every certain time period, a short fuel pulse is injected into the exhaust gas stream, which reduces the trapped NO<sub>x</sub>. The material is regenerated to carbonate and oxide forms, which has the ability to trap NO<sub>2</sub>-molecules again. The trap becomes less effective for NO<sub>2</sub> adsorption due to poisoning by the SO<sub>2</sub> even in relative low sulphur content of exhaust gas. Periodical desulphating shall be carried out, e.g. at a high temperature and with a rich air to fuel ratio to remove the adsorbed sulphur oxides. (Twigg 2007, Heck & Farrauto 2001)

The selective catalytic reduction (SCR) has been used to reduce NO<sub>x</sub> emissions of heavy duty diesel engines. The method is adopted from emission control of stationary sources where ammonia is the most typical reducing agent. In heavy duty vehicle applications, urea is used as a stored reducing agent whereas the ammonia is the primary reductant formed from urea within aftertreatment. The SCR-method is also coming to the aftertreatment method for diesel engines powered passenger cars. For these applications, hydrocarbons could be a more convenient reducing agent than nitrogen containing reductants. The most convenient aftertreatment process would be generated if the fuel itself is the reducing agent. (Twigg 2007, Ciardelli *et. al* 2007)

The very low exhaust gas temperature in diesel engines together with SO<sub>2</sub> in the exhaust gas makes catalytic oxidation of HC and CO a challenging task. Platinum-based catalysts incorporating zeolites are used to oxidise CO and HC. The zeolites function by adsorbing HC at low temperatures. At higher

temperatures, the HC is desorbed from the zeolite and oxidised over the platinum catalyst sites. (Twigg 2007)

The non-gaseous diesel emissions are grouped into three categories: soluble organic fraction (SOF), sulphate and soot. Recently, tremendous advances were made in the fuelling and combustion processes of modern high-speed diesel engines used in passenger cars, e.g. high pressure common rail injection, an increased number of smaller injection nozzles, and multiple injections. Nevertheless, there are still concerns about the possible health effects of diesel PM. Removal of the liquid fraction of PM is generally achieved by an oxidation catalyst. Fortunately, the larger hydrocarbon molecules that make up the SOF are more easily oxidised, with a proper catalyst, at low temperatures than the lower molecular weight hydrocarbons present as gases. Removal of soot may be achieved by means of filtration. The most satisfactory means of removing trapped PM is to oxidise it to CO<sub>2</sub> and water. Under conditions prevailing on heavy-duty diesel vehicles, it is possible to use a process that continually oxidises trapped PM. The exhaust gas temperature of diesel passenger cars is rarely high enough to combust PM. Thus, the key to employing filters on diesel cars is to boost the exhaust gas temperature to the level where the soot burns. (Twigg 2007, Kašpar *et al.* 2003, Heck & Farrauto 2001, Farrauto & Heck 1999)

Biofuels can play an important role in addressing the CO<sub>2</sub> emissions of transport as well as dependency on crude oil. Various routes have good potential to produce biofuels. Examples are ethanol produced from lignocellulosic biomass or sugar and starch crops, biodiesel produced from lignocellulosic biomass via gasification and chemical synthesis or direct liquefaction and biodiesel produced via esterification of vegetable oils. (Hamelinck & Faaij 2006) Hydrocarbon distribution as well as minor impurities of biofuels typically differ from crude oil based fuels and further more the content of engine-out emission. This induces a challenge to design the aftertreatment system in such a way that tailpipe emissions are still acceptable despite the use of alternative fuels. The engine-out acetaldehyde emissions on gasoline engines increases as the proportion of ethanol increases, whereas the emissions of other carbonyls mainly decrease (Pang *et al.* 2008, He *et al.* 2003, Magnusson *et al.* 2002). A Pt/Rh based catalyst are effective in converting acetaldehyde emission compared to conversion of unburned ethanol and can keep the tailpipe acetaldehyde emissions low except in a few operation conditions (He *et al.* 2003). Thus, the conversion and selectivity of ethanol on a catalytic converter may play the main role in the aftertreatment design.

Nowadays, various methods to meet the present and known future regulations are available. While strategies for lean-burn gasoline and diesel have been substantially developed over the past 10–15 years, the underlying technologies are immature compared with that of the TWC. The challenge is to develop a more effective, durable and cost-efficient commercial application based on these methods. Alternative fuels, health effects of presently unregulated emissions especially in urban environment, not forgetting CO<sub>2</sub> efficiency, may establish new demands on emission control.

### **1.3 Reactor design**

The design of catalytic reactors needs information on chemical reactions themselves, hydrodynamics as well as heat and mass transfer. A crucial part of the reactor design is the catalytic material design. The reaction mechanism and detailed kinetic information facilitate the catalyst selection. It is possible to complete the reactor design without detailed kinetics, for example, just with experimentation or with guidance of empirical model on the overall reaction. However if more detailed information is available, it is beneficial to apply that to the reactor design and optimisation. As long as the task only involves developing a catalyst for an existing process, the problem is straightforward because it consists of optimisation of the catalyst characteristics for known operation conditions. The problem is more complicated when developing a new process because process concepts should be associated with each catalytic formula, and chosen the catalyst will correspond to the economic optimum for the catalytic process as a whole. (Le Page *et al.* 1987, Froment & Bischoff 1990)

In environmental applications, there are only limited, if any, opportunities to affect on the raw material, i.e. emission flow fed to treatment process, in contrast to industrial applications where selection of raw material is an intimate part of process design. In addition, composition of emissions is typically complicated and, especially in the case of vehicle exhaust gases, the composition as well as the flow rate and temperature are time dependent. Moreover, these properties vary between vehicles depending onto the manufacturer, model year and model variant.

Instead of conventional multi-tubular or packed bed reactors, structured reactors, namely monoliths, have mostly been applied in exhaust purification. The use of monoliths as catalytic reactors in exhaust gas abatement applications focuses mainly on importance of a low pressure drop. In addition, monolith

reactors can be considered as adiabatic for most practical purposes. In automotive exhaust gas abatement, adiabatic behaviour is even stimulated by insulation of the reactor wall to promote a fast light-off after a cold engine start. (Hoebink & Marin 1998)

The modelling is one tool for reducing the time period of design cycles and design costs. The increasing possibilities of computers have led to an extensive exploration in the reactor design. Models now range from the very simple ones that could be handled several decades ago to some very sophisticated ones presented in the last decade. A required degree of sophistication depends firstly on the process, that is, on the reaction scheme and on its sensitivity to perturbations in the operation conditions. Of equal importance, however, is the degree of accuracy with which the kinetic and transport parameters are known. Obviously, the numbers will be no better than the physical insights that generated them. (Nauman 1987, Froment & Bischoff 1990)

The same tendency can be seen on exhaust gas catalysis. The importance of the catalytic converter modelling is well recognised in the literature (Koltsakis, Konstantinidis & Stamatelos 1997, Koltsakis & Stamateos 1999, Lacin & Hayes 2000). Avoiding unnecessary complexity is also recognised, e.g. Silva *et al.* (2006). In most classical reactor modelling works reported, the gas phase is one-dimensional either operating in dynamic state (Lacin & Zhuang 2000, Mukadi & Hayes 2002) or in steady-state conditions (Hoebink *et al.* 2000; Massing *et al.* 2000, Siemund *et al.* 1996). The flow is commonly assumed to follow the plug flow pattern. When a two-dimensional gas phase model has been adopted, a steady-state has typically been assumed (Hayes & Kolaczkowski 1994, Koltsakis *et al.* 1997). However, Mukadi & Hayes (2002) have published a paper, where transient surface reaction and dynamic pore diffusion are included in a catalytic converter model. The solid phase has been assumed to be in the steady-state in some models (e.g. Siemund *et al.* 1996), but in the majority of cases heat accumulation has been taken into account. Typically diffusion limitations have been included by lumping pore diffusion with the chemical kinetics and approximating film diffusion from the flow pattern based correlations. In the modelling of TWC, surface reactions have usually been assumed to be at a steady-state (Massing *et al.* 2000; Hayes & Kolaczkowski 1994) except for the unsteady storage of oxygen (Koltsakis & Stamatelos 1999). Depcik & Assanis (2005) conclude in their recently published review that classical models with a simplified representation of the fluid flow have proven their effectiveness in designing catalyst systems.





## 2 Conceptual model of heterogeneous catalysts

In chemical reaction engineering, a catalytic surface is usually assumed to be a pseudo-homogeneous mixture of vacant active sites and adsorbed surface complexes, where the adsorbed particles lost their memory about the site of contact. The effect of that is equivalent to assuming a rapid surface diffusion. When surface diffusion is finite, the distribution of coverage becomes significant. The other extreme situation is immobile particles, where molecules communicate only with their neighbour molecules without any possibility to travel on the surface.

Non-uniformities, such as add-atoms and terraces, are encountered on the catalytic surface. In the supported catalyst, atoms in a cluster-support interface induce non-uniformity, and cluster size affects the catalytic activity. In addition, several types of adsorption sites, e.g., top, hollow and bridge, exist even in low index surface (Lynch & Hu 2000). However, phenomena and behaviour of material caused by a non-ideal surface are not usually taken explicitly into account in the field of chemical reaction engineering even though it is known that these phenomena occur in the process interior and effects of them are detected. This common procedure is used to keep the model solvable and avoid situations where the values of the parameters are not obtainable or are impossible to estimate. When both the functional forms and the parameter values of relations can be constructed by the guidance of molecular level information, a credible model, with even less number of adjustable parameters, can be achieved. However, nowadays experimental and computational molecular level methods give valuable support to the selection of the model structures and good initial guesses for them, rather than ‘correct’ kinetic models for real catalytic processes.

The process described here is a catalytic converter for abating exhaust pollutants of vehicles. The purpose of the process is to reduce nitrogen oxides and to oxidise carbon monoxide and hydrocarbons to less harmful materials: nitrogen, carbon dioxide and water. The performance of the process is evaluated against its purpose. Ultimate performance criteria are appointed by the legislations.

The most primitive description of a process structure is the single node model, which consists of one process block with an inlet and outlet stream. Frequently that is not enough and model is detailed down. (Douglas 1988, Pohjola 2003) In exhaust gas abatement, the reactor itself is connected to the manifold with the front and end cones resulting in a three-node model. The cones are

required parts in the model only if their effects on flow distribution into reactor and backpressure of the process shall be taken account. The reactor is further disaggregated into individual channels presenting a honeycomb structure in the converter. The walls between the channels are typically ceramic or metallic. The only properties of the wall which are needed in process state modelling are heat capacity, heat conductivity and non-permeability, i.e. unlike energy flow the material flow through the wall is absent. On the macroscopic level, the structure is identical between the channels, but the state depends on flow distribution at the front cone and energy interaction with the other channels as well as the outer mantle of the reactor. When inputs to the channels are identical and the heat conductivity through the solid boundaries is large (infinity) or very small (zero), the state distribution is equal in each channel and thus, only one of them is needed to be considered in modelling.

Phenomena taking place in the channel are heat transfer, mass transfer and chemical reaction. Chemical reaction can be disaggregated into adsorption, surface reaction and desorption, or to overall reactions, such as CO oxidation, HC oxidation and NO reduction. These composite reactions disaggregate further to elementary reactions.

The material in the channel shall also be described in more detail. Further disaggregation of a channel is always possible, but it is more convenient to advance in the unit structural dimension. The material can be disaggregated into the 'Pseudo-homogeneous gas', the 'Catalyst surface' and the 'Bulk catalyst'. If mass transfer limitations exist and the film or pore diffusion model is applied, pseudo-homogeneous gas should be disaggregated further into the 'Bulk gas', the 'Gas next to the solid matter' and 'Gas inside pores'. These gas phase materials can be disaggregated into pure components and further to their unit structural parts, molecules. Instead of being pure component nodes, the materials can also be composites. For example, the composite 'Hydrocarbon' includes all different hydrocarbons present in the reactor. Unit structural part of this material is described similarly as pure components. The unit structural parts of the material named 'Hydrocarbon', e.g. called molecule ' $C_nH_m$ ', include the average properties of all different hydrocarbon molecules included in class ' $C_nH_m$ '. Therefore, they are lumped into a pseudospecies, and the use of lumped models has been a common engineering practice of which Okino and Mavrovouniotis (1998) have published a mathematically oriented review.

The 'Catalyst surface' can be disaggregated to 'Active site' and 'Surface complexes'. Another choice is to disaggregate 'Catalyst surface' to 'Platinum

Group Metal clusters' and 'Porous solid'. This may lead to a model that consists of different active sites including their location and relative amount. For example, in a typical three-way catalyst at least two totally different types of active sites can be considered, a platinum group metal cluster site (PGM) and an oxygen storage component site (OSC). These active sites are contacting each other through a solid-solid phase interface. Oxygen on the OSC sites travels by surface diffusion to the interface and reacts with the interface site of the PGM clusters or with a reductant adsorbed on the site. In addition, the reactants in PGM cluster have the ability to diffuse onto the interface.

Selection of active site types depends on the conditions which the model should be able to handle. Typically one type of sites is more active than another, and thus, considering only the most active sites may be reasonable in steady-state modelling. However, this might not be enough in dynamic conditions. In addition to the rate, adsorption capacity is a significant property in dynamic conditions. Thus, a model where one site type is linked to the reaction rate and another type is used to treat the adsorption capacity might be favourable.

## **2.1 Reaction mechanisms**

In automotive exhaust gas catalysis, the most common reactants are carbon monoxide, nitrogen oxides and hydrocarbons. The desired products are carbon dioxide, nitrogen and water. Ammonia, nitric oxide and partially oxidised hydrocarbons, e.g. alcohols and carbonyls, are able to exist as reactants or by-products.

The surface reaction takes place by either the Langmuir-Hinshelwood-Hougen-Watson or the Eley-Rideal mechanism. In automotive exhaust gas catalysis, the LHHW-type mechanisms are mostly proposed to be predominant, but in some cases the ER-type mechanism has at least a minor effect. The catalytic cycle consists of adsorption of one or more reactants onto the surface, manoeuvres of molecules on the surface and desorption of products from the surface. In addition to the heterogeneous catalytic reactions, homogeneous gas phase reactions can take place at a significant rate at the highest temperatures present in exhaust gas abatement reactors.

### 2.1.1 Adsorption onto the surface

The following adsorption phases are self-evident:



Dissociative adsorption of oxygen has commonly been proposed as:



Hydrocarbon adsorption is possible onto the metallic and oxidised noble metal site. For propylene and methane this results in the following adsorption phases:



Adsorption of reaction products, such as  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , on a noble metal surface is typically not considered even though  $\text{CO}_2$  and  $\text{H}_2\text{O}$  have the ability to stay on the surface at least as carbonate and hydroxyl complexes, respectively. Whereas, adsorption of by-products  $\text{N}_2\text{O}$  and  $\text{NO}_2$



frequently have been taken into account.

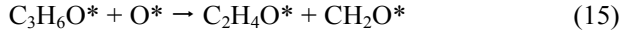
### 2.1.2 Reactions with oxygen

Total oxidation of carbon monoxide, hydrocarbons and hydrogen are the most common reactions with oxygen on the automotive exhaust gas catalysts. In hydrocarbon oxidation, carbon monoxide is formed in certain conditions as a by-product. In addition, oxidation of nitrogen oxide to nitrogen dioxide is possible in net oxidising conditions. Small amount of partially oxidised hydrocarbon derivatives also might possibly form.

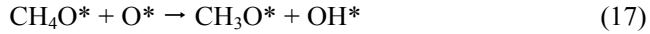
The direct oxidation of small surface complexes, i.e.,  $\text{CO}^*$ ,  $\text{NO}^*$  and  $\text{H}^*$ , are straightforward:



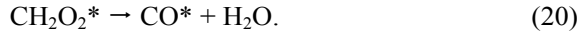
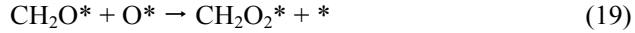
The oxidation of hydrocarbons is obviously a complicated set of reaction routes which shall be heavily simplified for chemical reaction kinetic modelling purposes. The most common reaction phases are breakage of the carbon-carbon bond, the split of a hydrogen atom and substitution or addition of oxygen. In Papers II and V, oxygen assistant cracking and partial oxidation was proposed. Cracking steps are as follows:



and partial oxidation in surface is as follows:



following in later case with

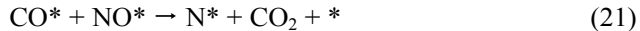


In a similar way, the formation of the peroxy radicals, e.g.  $\text{CH}_3\text{O}_2$ , is possible.

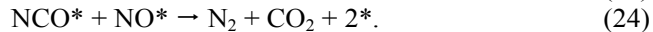
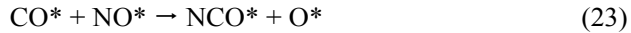
### 2.1.3 NO reduction

The desired product from NO reduction is gaseous nitrogen, but nitrous oxide also commonly forms. In addition, ammonia could be formed in a poorly operated catalyst if a hydrogen source exists.

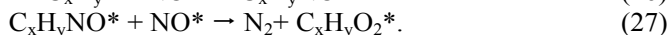
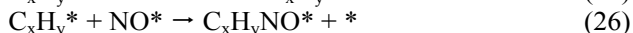
The NO is proposed to react via different kinds of reaction routes which can be classified as regenerative or bimolecular. A bimolecular reaction with CO as a reductant can be written as follows:



or

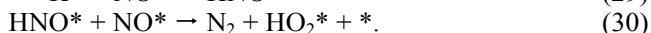


When hydrocarbon acts as reductant, it can analogically be written as follows:



However, in the case of hydrocarbons the completed reaction chain is more complicated including, e.g. cracking, partial oxidation and dehydrogenation as well as reaction phases where different kinds of nitrogen containing hydrocarbon complexes (e.g. nitro-hydrocarbons) exist on the surface.

When hydrogen acts as reductant, it can analogically be written as follows:

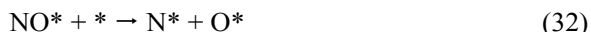


However, instead of the formation of an adsorbed hydroperoxyl radical in net reducing conditions, the reaction of HNO\* with adsorbed hydrogen



proposed in Paper I is more convenient.

Another possible group is regenerative mechanisms in which the reductant just regenerates the catalytic surface by cleaning off the oxygen atoms stuck on surface. The NO reduces by dissociation



or via a route where two adsorbed NO species react, e.g.



The surface oxygen reacts with a reductant in some of the routes described above as reactions with oxygen adsorbed from the gas phase.

## 2.2 Kinetic models

In this work, kinetic models were created for two different conditions, near stoichiometric redox ratio and net oxidative conditions. Mostly kinetic models are based on a particular mechanism, but only once (Paper IV) was the empirical model applied. However, the reaction rate equation is also in this case rational function instead of usual power law expression.

The reactions in exhaust gas catalysts were proposed to occur via Langmuir-Hinshelwood-Hougen-Watson type mechanisms as shown above. Thus, mechanism based reaction rate equations are rational functions. For example, in Paper V the reaction rate equation for gaseous nitrogen formation was given as

$$\frac{\partial p_{N_2}}{\partial t} = \frac{k_{131} p_{NO}^2 p_{CH_4}}{1 + K_{\text{sqrt}O_2} p_{O_2}^{1/2} + K_{NO_2}^{eq} p_{NO_2}}. \quad (36)$$

Reaction rate equations are based on certain assumptions. The first assumption is the proposed reaction mechanism itself. In the second phase, the equilibrium reaction steps are assumed. Typically, some or all adsorption steps are proposed to be in quasi-equilibrium. A more detailed description is provided in Paper III together with the derivation of the rate equations in the appendices.

It is convenient to reparameterise the kinetic model in such way that the new parameter's values are easier to identify. In addition, the standard reparameterisation of the Arrhenius equation the rate parameters are lumped. If the lumping decreases the total number of estimated parameters, the operation is model simplification rather than pure reparameterisation. As an example, lumping of parameters, which describe a rate limitation of adsorbed species, simplifies denominator of a reaction rate equation in Paper III:

$$\begin{aligned} \frac{1}{\theta_v} &= 1 + K_{NO} c_{NO} + K_{CO} c_{CO} + \frac{k_{12} K_{CO}}{k_{14}} c_{CO} + \frac{2k_6}{k_7 K_{CO}} \frac{c_{O_2}}{c_{CO}} + \frac{k_{12} K_{NO}}{k_7} c_{NO} + \frac{2k_{22} K_{NO}^2}{k_7 K_{CO}} \frac{c_{NO}^2}{c_{CO}} \\ &= 1 + K_{e1} c_{CO} + K_{e2} \frac{c_{O_2}}{c_{CO}} + K_{e3} c_{NO} + K_{e4} \frac{c_{NO}^2}{c_{CO}}. \end{aligned} \quad (37)$$

Mostly, the simplifications were selected during the parameter estimation. If a parameter is identified as a value near zero and the value of the cost function does not increase significantly with the parameter value of zero, the parameter is ruled out from the model. Unidentified parameters could also be ruled out. However, in these situations it should be examined that values of the parameters are not in wrong magnitude, which may result in a virtual redundancy.

In the stoichiometric condition, reactions in automotive catalysis are virtually irreversible, whereas in net oxidative conditions the equilibrium limitation of NO oxidation to NO<sub>2</sub> is taken into account in most cases.

### 2.3 Reactor models

The real flow pattern in a channel of a catalytic converter is close to a laminar flow. Despite the laminar flow, monolith reactors still may be approached as plug-flow reactors because of the considerable radial diffusion in the narrow channels. Thus, the plug flow model was mostly applied. When external heating was used in experimental equipment, a constant temperature along the length of the reactor was proposed. The reactor model then becomes:

$$v \frac{\partial \mathbf{y}_g}{\partial z} = \frac{m_{cat}}{V_g C_{tot}} \mathbf{A} \mathbf{r} . \quad (38)$$

In Paper IV, where a real converter was simulated, it was applied a model with assuming the plug flow and axial dispersion. Naturally, the temperature profile along the length of the reactor was taken into account. Heat transfer between gas and solid is also a crucial phenomenon in a real catalytic converter. Dynamic mass and energy balance equations for one-channel of the catalytic converter become:

$$\frac{\partial \mathbf{y}_g}{\partial t} = D \frac{\partial^2 \mathbf{y}_g}{\partial z^2} - v \frac{\partial \mathbf{y}_g}{\partial z} + \frac{m_{cat}}{V_g C_{tot}} \mathbf{A} \mathbf{r} , \quad (39)$$

$$\frac{\partial T_g}{\partial t} = E \frac{\partial^2 T_g}{\partial z^2} - v \frac{\partial T_g}{\partial z} + \frac{4h}{D_h \rho_g \hat{C}_{p,g}} (T_s - T_g) , \quad (40)$$

$$\frac{\partial T_s}{\partial t} = \frac{\lambda_s}{\rho_s \hat{C}_{p,s}} \frac{\partial^2 T_s}{\partial z^2} - \frac{4hA_g}{D_h A_s \rho_s \hat{C}_{p,s}} (T_s - T_g) - \frac{1}{A_s L \rho_s \hat{C}_{p,s}} \sum_{i=1}^n (\Delta H_r)_i r_i . \quad (41)$$

It can be seen in these model equations that the reactor is proposed to be adiabatic, i.e. the heat flux through heat insulation between the honeycomb and outer mantle is insignificant.

Numerical values of the parameters can be approximated from empirical, semi-empirical or first principles based correlations for transport phenomena. For example, the effective axial dispersion coefficients ( $D$ ) and effective axial thermal dispersion coefficient ( $E$ ) were obtained in Paper IV from analogous correlations (Nauman, 1987)

$$D = D_i + \frac{\bar{u}^2 D_h^2}{192 D_i} \quad \text{and} \quad E = \alpha_T + \frac{\bar{u}^2 D_h^2}{192 \alpha_T} , \quad (42)$$



where the diffusion coefficients ( $D_i$ ) were estimated by the Slattery-Bird equation for the binary diffusion coefficients (Bird *et al.* 1960).

In stoichiometric conditions, all the main reactions achieve maximum conversion approximately at the same temperature region, and selectivity does not change after the maximum conversion has been achieved. The domain bound restriction of zero concentration could be taken into account in a rough way, such as by defining a small positive number as concentration bound, below which the value zero is given for reaction rates.

In net oxidative conditions the selectivity between NO and O<sub>2</sub> changes even above the temperature in which the maximum conversion of hydrocarbon is achieved. In these conditions, the handling of domain bound restrictions with an immediate substitute zero for the actual reaction rate, as described above, is not adequate. If a fixed non-zero tolerance value is applied on the domain bound, the problem is to find such a value which is high enough to keep concentrations in the domain and low enough to allow the simulation of selectivity changes in conditions with a high reaction rate and a low hydrocarbon concentration. Thus, an exponential cost function was applied as a domain bound restrictor in these kinds of situations.



### **3 Experimental**

Different types of experimental data have been exploited during the model construction and its performance evaluation. Particularly, bench scale converter experiments by using synthetic exhaust gas streams, full-scale experiments where the converter is mounted on the exhaust gas stream of an engine, and the New European Driving Cycle (NEDC) vehicle tests have been carried out.

Transient kinetic experiments were applied to get guidelines for mechanisms in which reactions occur. In addition, the adsorption capacity is evaluated by these kinds of experiments.

Stationary mimicking light-off tests are the common experimental procedure in automotive exhaust gas catalyst research. In these experiments the temperature of catalyst is increased at a constant heating rate by an external heat source. The heating rate is selected in such way that the dynamic phenomena of the catalyst are negligible.

DRIFT analysis was performed to give information on surface species existing in the catalyst when reactions occur. Some other surface measurements, such as sorption analysis for the surface area, pore diameter and a metal dispersion measurement, are applied to monitor stability of catalysts during experimental procedures. In addition, catalyst characterisation methods applied to monitor catalyst synthesis were used in Papers II and V. These applications of surface analysis in catalyst synthesis are not in scope of this thesis.

#### **3.1 Stationary kinetic measurements**

The basic tests for the kinetic modelling are stationary kinetic experiments. The experiments were often carried out in successive constant temperatures. Alternatively, the kinetic experiments can be carried out with a slowly increasing temperature ramp if the pseudo-steady-state occurs in such a way that the difference in the state of the surface at a particular temperature between the ramping experiment and during long period in constant temperature is insignificant. Stationary mimicking light-off tests with a continuously increasing temperature ramp are the common experimental procedures in the kinetic study of automotive exhaust gas catalysis in conjunction with the kinetic experiment in a constant temperature continuous reactor (Koltsakis & Stamatelos 1997, Muraki & Zhang 2000). The constant temperature experiments are also potentially unsteady because of aging, poisoning and fooling effects. For example, coking of a catalyst

can block the pores and cover the active sites at a low temperature when hydrocarbons are present. In addition, constant temperature is difficult to maintain in the temperature region where the rate of exothermic reactions rapidly increases. Thus, the temperature ramp experiments are acceptable.

The light-off tests were applied in Papers III and IV. Kinetic measurement at a constant temperature was applied in Papers II, V and VI. In Paper III, this kind of test was applied in addition to the light-off tests with a continuously increasing temperature ramp. The main composition analyser in Papers II, V and VI was gas chromatography. In addition, a chemiluminescence NO<sub>x</sub>/NO analyser was in use. In Paper III, the multi-component, FTIR gas analyser, was used as a main detector improved with a paramagnetic oxygen analyser.

### **3.2 Transient technique**

Several transient techniques are widely applied, for example, step (Kobayashi 1982a), pulse (Herz & Sell 1985) and cycling feed (Cutlip 1979) experiments. Most often the varying property is concentration, but pressure or temperature variation can also be used as input. In addition, a separate group of transient techniques include temperature programmed experiments, such as temperature programmed desorption (TPD), temperature programmed reduction (TPR), temperature programmed oxidation (TPO) and temperature programmed surface reaction (TPSR) (Falconer & Schwarz 1983). Isotope exchange experiments are a special case of transient techniques (Efstathiou & Verykios 1997).

In this study (Paper I), step-response type transient experiments were carried out. The responses were detected by a quadrupole type mass-spectrometer (Balzers GAM 420) with a secondary electron multiplier used as the detector. The data was collected in 0.5 second intervals. Transient kinetic experiments were applied to acquire guidelines for reaction mechanisms.

### **3.3 Surface measurements**

Surface area and pore size distribution measurements were performed by nitrogen sorption applying BET adsorption isotherm in calculation. The metal dispersion measurement was performed by a chemisorption analysis applying CO or H<sub>2</sub> as the adsorbant.

DRIFT analyses were performed in an environmental chamber in which the composition of gas mixture and temperature could be varied. Both static cell

experiments and the experiment in the flow through cell conditions were applied. Most tight interpretation of DRIFT analysis is carried out in Paper III.

### **3.4 Engine and vehicle tests**

Full-scale laboratory experiments, where the converter is mounted on the exhaust gas stream of an engine and vehicle tests on roller dynamometer test bench, are also used in the exhaust gas catalyst design. On-road vehicle tests can be carried out, but these are even more expensive than engine bench and dynamometer tests. Thus, they are rarely applied except in the final commissioning phase.

In this study (Paper IV), the engine bench test with full scale converters and vehicle dynamometer tests according to the New European Driving Cycle (NEDC) have been carried out. Experimentation measurements are facilitated with a standard emission analysis system supplied by Horiba.

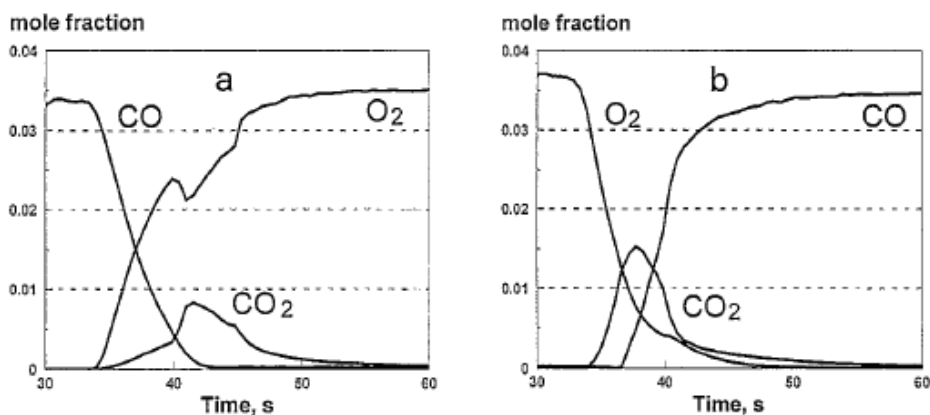


## 4 Results and discussion

### 4.1 Transient kinetic experiments

The transient step response method is applicable to measure the total adsorption capacity of exhaust gas catalysts. The measurement of the oxygen storage capacity (adsorption capacity) using this method is straightforward and most practical. The experiments revealed the high adsorption capacities of ceria promoted catalysts, which is due to the adsorbate spillover in intimate noble metal-ceria interactions. When the NO adsorption in a reduced surface is measured, the self-decomposition resulting in the temporary formation of nitrogen and nitrous oxide is taken into account. The nitrogen oxide adsorbs not only in metal surface but also in oxidic support material. During carbon monoxide adsorption, minor amounts of CO<sub>2</sub> are formed except in high temperature.

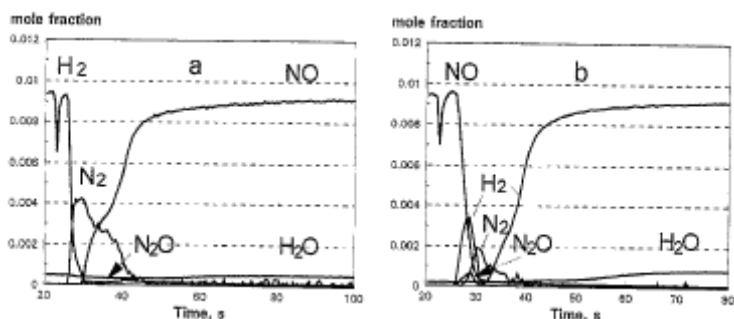
The transient step-response experiments show clearly some inhibition effects of adsorbed components. For example, this is shown in Figure 1.



**Fig. 1. Step response on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at 150 centigrade a) Oxygen after carbon monoxide pre-adsorption b) Carbon monoxide after oxygen pre-adsorption (Paper I).**

When CO is pre-adsorbed to the surface of the alumina-supported catalyst, the formation of CO<sub>2</sub> is delayed when a switch to an oxygen atmosphere is taken place. Whereas when the surface is pre-oxidised, there is not the delay present after a switch to a CO atmosphere. This suggests that adsorbed CO highly restricts the adsorption of oxygen but oxygen does not restrict the adsorption of

CO. Earlier it was found that CO could adsorb to an oxidised metal site (Baraldi *et al.* 1997) or gaseous CO reacts via the Eley-Rideal mechanism with adsorbed oxygen (Su *et al.* 1989). The same kind of unsymmetrical inhibition is found between NO and H<sub>2</sub> (Figure 2), where the restrictive effect of adsorbed NO was seen as a local maximum at the very beginning of H<sub>2</sub> washout function in Figure 2b. However, the absence of a restrictive effect of adsorbed hydrogen can be explained by a significantly higher amount of vacant sites after hydrogen pre-adsorption than after pre-adsorption of the other components studied.



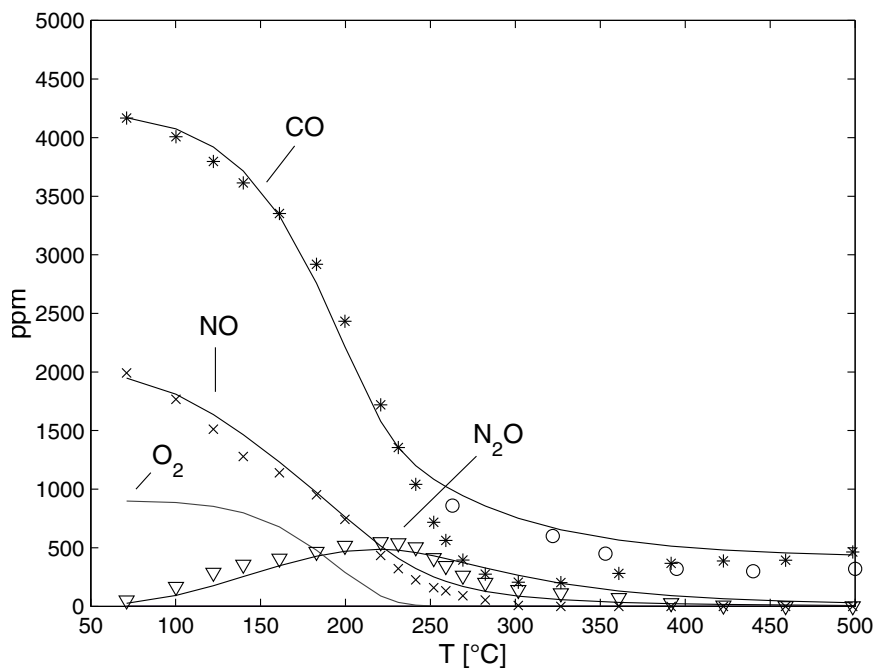
**Fig. 2. Step response on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at 150 centigrade a) Oxygen after carbon monoxide pre-adsorption b) Carbon monoxide after oxygen pre-adsorption (Paper I).**

In falsification and verification of simple mechanistic routes, transient kinetic experiments are powerful tools with a direct classification of responses (Kobayashi 1982a, Kobayashi 1982b) and with simulation support (Salmi 1988). For example, in an experiment reported in Paper I, CO oxidation by ER-type mechanism with adsorbed CO on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst can be ruled out due to the inhibition of adsorbed CO. In addition, the LHHW-type mechanism can be stated as the predominant route, which is based on the overshoot of the product response, when the reactive mixture is used.

In the case of complex kinetics, the transient kinetic experiments give only weak guidance on the mechanistic route. In fact some interpretation can be made. First, a clearly diverged delay is an indication on the formation of different mechanistic steps. However, re-adsorption of product potentially destroys this reasoning. Secondly, a complicated form of response, e.g. dual overshoot or double peak, indicates two or more competitive routes. Finally, the probability evaluation on the ER and LHHW type mechanisms as predominant routes can also be made with complex kinetics.



Adsorption sites, which are kinetically much more active than average and are mostly responsible for catalytic activity, should exist on the surface of the catalyst. On the contrary, another group of surface sites that exist on the surface can be responsible for a large adsorption capacity. The last group can be even catalytically inactive. Isocyanate adsorption into support material was found to induce non-steady behaviour in Paper III. The reactivity of support adsorbed isocyanate itself is relatively low, but acts as a large carbon storage space. In Figure 3, the slow transient behaviour can be seen. There exist notable differences between CO concentrations at real isothermal measurement points and concentrations in corresponding temperatures during temperature ramp with heating rate 10 centigrade per minute at temperature ranging from 250 to 350 centigrade. This evidences that carbon storage takes place during the five minute temperature ramp.



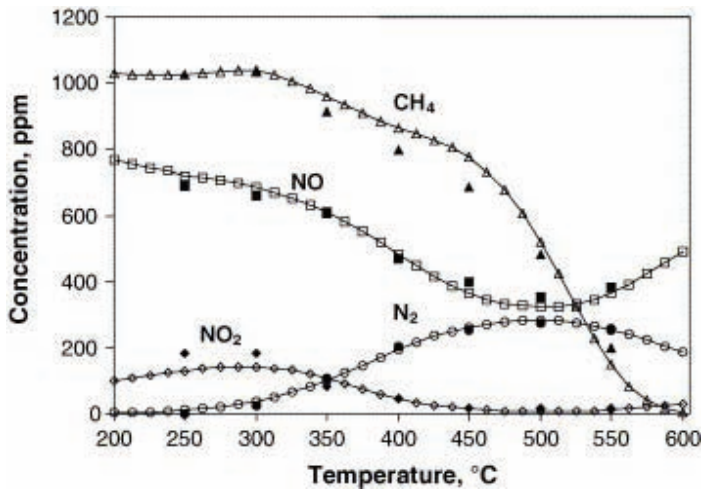
**Fig. 3. Measured CO (\*), NO (x), and N<sub>2</sub>O (∇) concentrations in light-off experiments with regression (solid line) on a direct decomposition model in rich CO+NO+O<sub>2</sub> mixture, where CO concentrations in stationary experiments are marked with O in the figure (Paper III).**

## 4.2 Stationary kinetic experiments

In Papers II, V and VI, the kinetic model for HC-SCR in different catalysts was developed. The  $\text{CoO}_x/\text{alumina}$  and  $\text{In}/\text{ZSM-5}$  catalysts were applied in Papers II and V, respectively. The main focus in Paper VI was on catalyst combination of  $\text{In}/\text{ZSM5}$  and  $\text{Pt}/\text{Al}_2\text{O}_3$ . A wide spectrum of modelling approaches was involved in the parts of research as described below. However, in all cases, the functional form of the reaction rate equation was a rational function.

For the cobalt catalyst (Paper II), the denominator, i.e. inverse of vacant site fraction, includes virtually all adsorption equilibrium constants derived from the proposed mechanism. The parameters were rather well identified, where the values of the adsorption enthalpies were assumed to be zero. Reaction rate constants are also well identified with their temperature dependencies. Exceptionally the minimum value for the  $\text{NO}_2$  formation rate parameter was obtained, but above this value the parameter affects only slightly on the cost function. Thus, its temperature dependence is unclear and the parameter is assumed to be temperature independent.

On the modelling of the  $\text{In}/\text{ZSM-5}$  catalyst (Paper V), there were three main modifications. Firstly, the re-parameter was applied by the lumping of rate and adsorption parameters. In addition, some simplifications of the numerator were made based on a sensitivity analysis. Secondly, the temperature dependence of the adsorption equilibrium parameters was taken into account. Contrary, the denominator was simplified in such a way that only adsorption of oxygen and nitrogen dioxide are effective. Thirdly, the equilibrium constant and reaction enthalpy of  $\text{NO}_2$  formation reaction, which are needed to take account of the equilibrium limitation of  $\text{NO}_2$  formation, were determined by thermodynamic calculations. In Figure 4 an example from the set of experiments fitted by the model is presented. The model has the ability to describe the most prominent features of the experiments.



**Fig. 4. Measured (solid points) and simulated (lines) gas phase compounds in In/ZSM-5 catalyst reactor outlet as a function of temperature (Paper V).**

In Paper VI, an alternative kinetic model for the HC-SCR reaction was presented. The new model is based on a mechanism where ammonium compound ( $H_2N^*$ ) is proposed to be the final reductant instead of amide ( $NCH_2O^*$ ) as proposed in Paper V. The sum of residual squares in the new model is smaller, but visually the fitting is not significantly better. The objective for this modelling work was to study the adequate ways to model the combination of two catalysts. Two different modelling approaches were introduced. In the first approach, the catalyst is handled as a pseudo-homogeneous catalyst with a single type of active sites. In this approach the parameters were simply refitted to data measured over the binary catalyst combination. In the second approach, the kinetic model for reaction in active sites on the  $Pt/Al_2O_3$  catalyst was derived. The model is combined with the reaction kinetic model for the In/ZSM-5 catalyst resulting in a two-site model for binary catalyst combination of these catalytic materials.

Although every parameter was freely adjustable in the estimation, significant changes were found only for three parameters. One of the three parameters is related to  $NO_2$  adsorption. Another one is the  $NO$  adsorption equilibrium constant. The last one is related to a route of surface reactions where  $NO_2$  reacts with partial oxidised hydrocarbon species. The other parameters were unchanged within their trust regions. Thus, according to the modelling, the catalyst combining mostly affects as a change on  $NO_2$  exploitation routes on surface of the Indium catalyst only. The partial oxidation of methane and the formation of

nitrogen-containing carbonaceous intermediates were enhanced by NO<sub>2</sub>, which is a source of reactive oxygen.

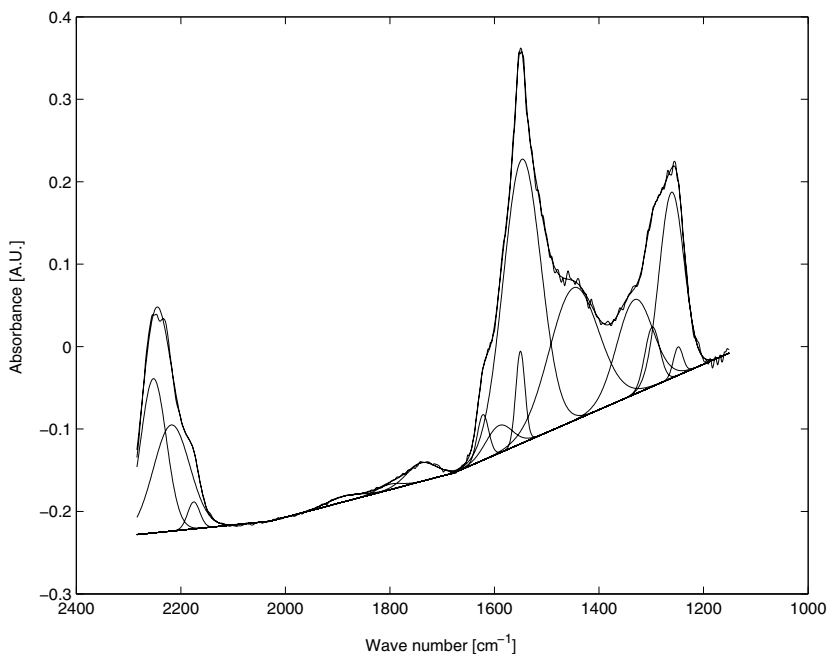
In the two-site model, the model for a pure In/ZSM-5 catalyst with the fitted parameters was used without any changes. The differences between the pure catalyst and binary combination were handled with fitting the parameters of the model for a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst to data measured over a combined catalyst.

A double catalyst model can potentially be applied to optimisation of the mixing ratio at least in a limited region. The pseudo single-site model is valid only with the mixing ratio where data are available. On the contrary, the single-site model could reveal a prevailing reaction mechanism. It is known that the Pt-catalyst effectively produces NO<sub>2</sub> (Mulla *et al.* 2006, Yaying *et al.* 2006). Thus, it was not a surprise that NO<sub>2</sub> related routes were apparently boosted.

Several mechanisms and models can explain the same data. This can be seen in modelling work done in Papers V and VI. The problem is evaluated more systematically in Paper III, in which models based on three different kinds of mechanisms for catalytic reduction of NO with CO were compared. The measurements of gas phase compounds can be equally well explained by the models based on direct decomposition of NO, bimolecular reaction between NO and CO, or reaction with isocyanate as a surface intermediate. The possibilities to utilise surface measurements on the falsification or verification of kinetic models in these kinds of situations are discussed in the next chapter.

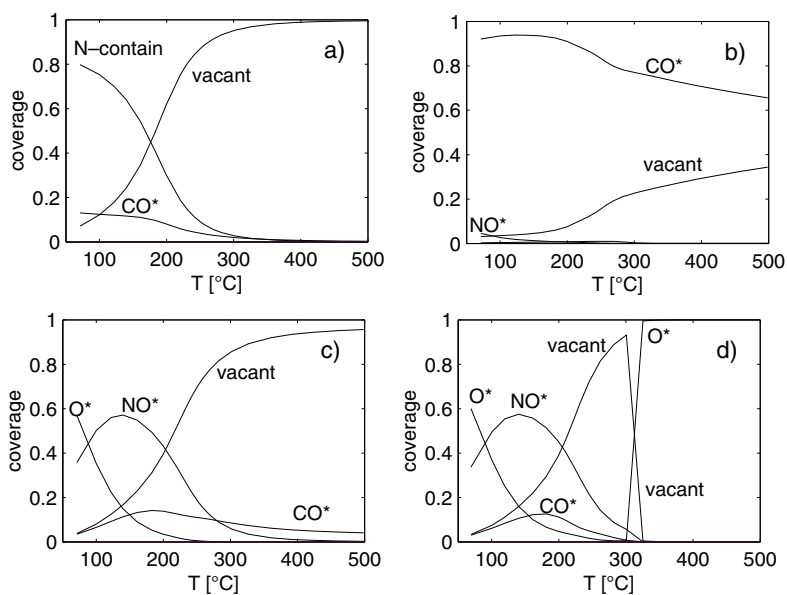
### **4.3 Integration of surface measurements to kinetic experiments**

DRIFT supports the kinetic experiments by giving the knowledge on reaction intermediates on the surface as well as other surface complexes lying there. Semi-quantitative coverage can be treated from DRIFT measurements by a simple empirical de-convolution. An example of the de-convolution is shown in Figure 5.

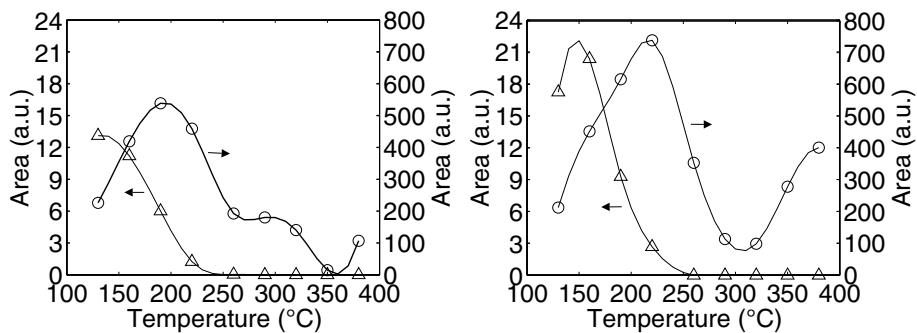


**Fig. 5. DRIFT spectra on rich NO+CO+O<sub>2</sub> mixture at 290°C with de-convolution (Paper III).**

In Paper II, simulated surface coverage (Figure 6) was compared to semi-quantitative adsorption amounts (Figure 7). Based on the comparison, it can be postulated that the bimolecular reaction mechanism is not the main reaction pathway. Whereas, coverage predicted by a direct decomposition reaction (Figure 6c) clearly includes and reaction via isocyanate (Figures 6a) slightly includes the same kinds of features than measured adsorptions (Figures 7a). Thus, the most probable NO reduction route for Pd-containing catalysts occur through direct decomposition steps. The isocyanate measured by DRIFT is mostly adsorbed at the support rather than at platinum metal cluster. However, a minor part of isocyanate might be adsorbed into some kind of active site, but this is hard to detect under high concentration of support adsorbed isocyanate. The isocyanate associated band around 2200 cm<sup>-1</sup> in DRIFT spectra is complex and indicates of more than one type of adsorption sites, but potentially active isocyanate forms can not be distinguish from inactive forms. Thus, the isocyanate route can not be completely ruled out within the limitation of the experimental techniques currently available.



**Fig. 6. Surface coverages on rich CO+NO+O<sub>2</sub> gas mixture predicted by the a) isocyanate based mechanism, b) bimolecular and c) direct decomposition models as well as by the d) lean CO+NO+O<sub>2</sub> mixture predicted by direct decomposition model (Paper III).**



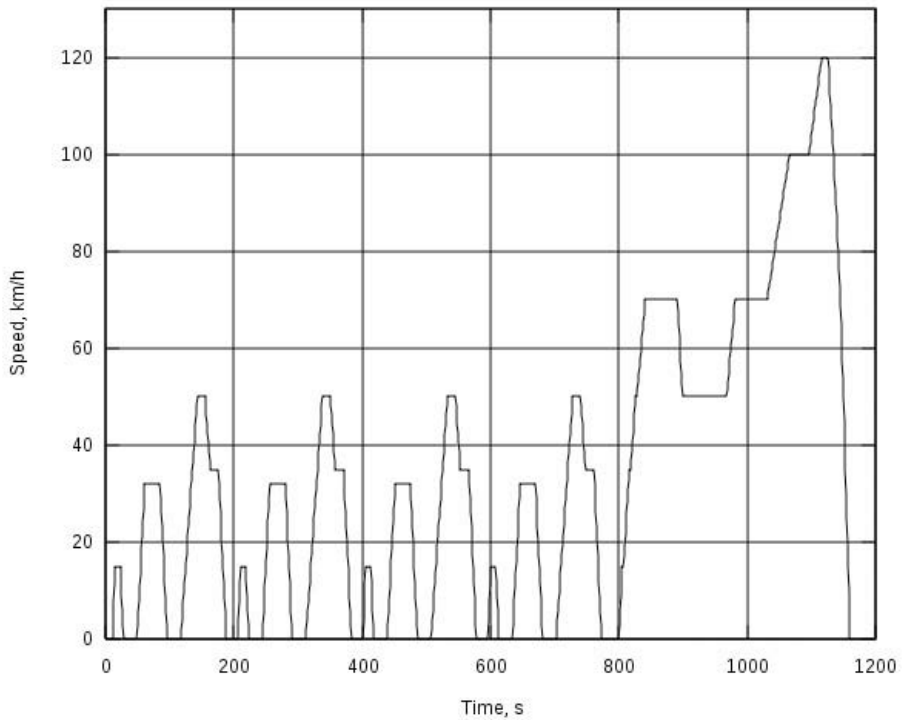
**Fig. 7. Adsorption of NO (O) and CO (Δ) as a function of temperature based on area of de-convoluted bands in a) rich NO+CO+O<sub>2</sub> and b) lean NO+CO+O<sub>2</sub>-conditions (Paper III).**

DRIFT measurements do not give a complete structural guidance for reaction steps, but knowledge on surface concentrations facilitates model construction and discrimination. The other surface measurements performed during this study do not give direct information for reaction kinetic modelling but is applied mainly to detect the stability of a catalyst sample over the experiment sequence.

#### **4.4 Reactor modelling with vehicle and engine test**

In vehicle and engine tests with a full size catalytic converter, several phenomena occur simultaneously in such a way that it is not self-evident which one is dominant. In this study, a rapid warm-up has been selected as the most important design criterion. The mass of active components Pd and Rh (7:1), the thickness of the washcoat and the diameters of the converters were specified to keep constant in the design of the tested prototypes. These selections will give rise to the following features: the prices of the converters are approximately same; pore diffusion does not vary between the converters; and the inlet gas flow distribution is constant in the converter inlet. The thermal mass was found to be the most significant variable in the warm-up of the catalysts. Thus, the heaviest converters have the slowest warm up time, whereas the shortest and lightest converter has the fastest warm-up. However, the design and optimisation is not straightforward. The results on the converter, which was made of thinner metal foil, indicate a disadvantage of fast thermal response. The converter is not only heating up fast but it also cools down fast. In the demonstrative aftertreatment system, the inlet gas temperature is in the catalytic light-off region, i.e. reaction rate is very sensitive to temperature during the warm-up of the catalytic converter. The boosting of exothermic reactions is needed in moving onto the higher operation temperatures. Thus, the converters are sensitive to temperature variations and heat transfer rates.

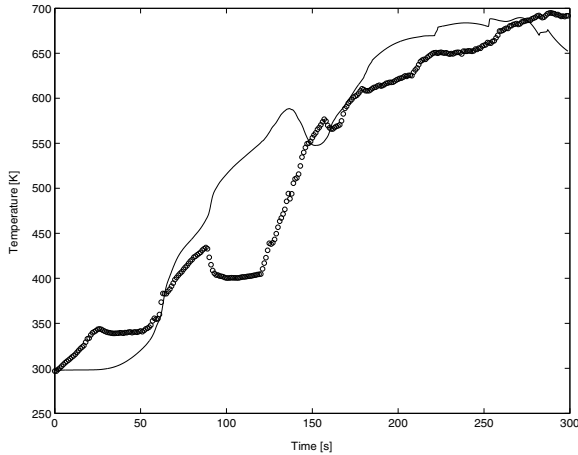
The European legislative test for emissions regulations effective since year 2000 is called NEDC. The test consists of a variable-speed drive in a chassis dynamometer with four repeated ECE 15 driving cycles and the EUDC cycle. The combination of speed profiles is shown in Figure 8.



**Fig. 8. Speed profile during the NEDC vehicle test.**

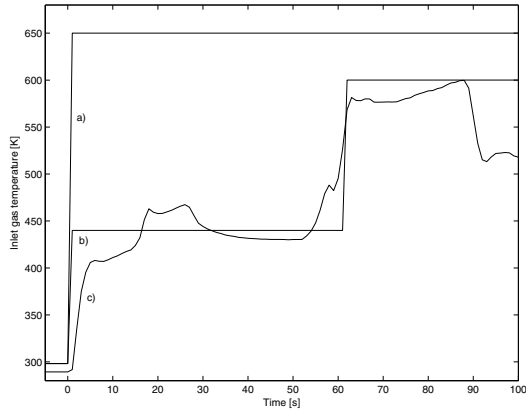
Figure 9 demonstrates that the overall heating rate during NEDC test can be explained by a dynamic reactor model with kinetic rate equations created for a steady-state. The largest differences between measured and predicted temperatures are in time windows from 20 to 50 seconds and from 95 to 120 seconds. The measured outlet temperature within the windows was around 340 K and 400 K, respectively. The 340 K is close to the dew point temperature of 10 per cent water steam (319 K), and the 400 K is close to the normal boiling point of water (373 K). Thus, it was concluded that phase change of water is the phenomenon behind the converter behaviour and difference between prediction and measurements. Effects of the vapour-liquid phase changes on automotive catalytic converter has been recognised earlier, e.g., by Chan & Hoang (1999).





**Fig. 9. Measured (o) and predicted (–) exit temperatures of the exhaust gas from a catalytic converter during first 300 seconds of the NEDC vehicle test.**

Time variation of inlet gas stream conditions differs slightly between individual tests, clearly between vehicle entities and, substantially between vehicle models. In addition, the real gas stream has several input variables that change simultaneously in a complicated way, which may lead to challenging numerical problem and at least increased simulation time. Thus, responses of simplified temperature input functions have been simulated and compared to the measurements. In Figure 10, the evaluated temperature input functions are shown. The measured and predicted light-off period is show in Table 5. The step response, response of double step and response of measured input temperature profile in the NEDC were simulated with the ten reactor prototypes with same catalytic material. The same time variation in inlet gas stream conditions was applied for every reactor in the simulations. The inlet concentrations were kept constant and approximately same as in the engine bench test. The main structural changes between the evaluated reactors were cell density and the thickness of metal foil. Thickness of the washcoat and total amount of platinum group metals in reactors #1 to #8 were kept constant. The mass of PGM in catalysts #9 and #10 was approximately 20 per cent higher than in the other catalysts.



**Fig. 10. Input gas temperature variations used in the simulations: a) step wise, b) double step wise and c) measured profile in the NEDC.**

**Table 5. Time when the converter has achieved 50 per cent conversion in the simulations with different input functions as well as measured ones in NEDC vehicle test.**

Cat #	Stepwise		Double stepwise		Modified NEDC		Measured in NEDC	
	$t_{50,HC}$ [s]	$t_{50,CO}$ [s]	$t_{50,HC}$ [s]	$t_{50,CO}$ [s]	$t_{50,HC}$ [s]	$t_{50,CO}$ [s]	$t_{50,HC}$ [s]	$t_{50,HC}$ [s]
1	16.8	21.3	85	89	93	93	94	90
2	17.2	22	86	90	93	93	93-99	91-95
3	15.5	20.3	84	88	89	93	80	88
4	20.4	26.6	91	96	93	95	95	95
5	27	35.2	100	107	97	106	95	96
6	17	22.4	86	90	93	93	89	91
7	22.2	29.4	94	99	96	99	95	96
8	19.6	26.2	90	95	93	96	95	95
9	12	15.4	79	82	84	92	80	90
10	7.3	9.2	72	74	74	78	73	76

Primarily the moment in which 50 per cent of the conversion over the converter is achieved, i.e. light-off, can be predicted by the model. Despite the potentially unsteady surface coverages, the pseudo steady-state kinetic model has the ability to predict the average behaviour in such a way that thermal effects and the light-off behaviour are reliably predicted. Simplified input functions can be used in rating the converters with different structures. The rating order is approximately the same with every input function. Double stepwise input results in the correct

time scale for the light-off. Obviously the input which is nearest to real one gives the best prediction. However, double stepwise temperature changes give almost as good a prediction as the more complicated patterns and predict distinctly too long warm-up times for the heaviest catalyst (catalyst # 5) constructed of the thickest metal foil. Clearly, the thermal mass has the most significant influence on the catalytic converter warm-up. The heat transfer area between gas and the solid phase has an effect on the warm-up. This is most crucial when the inlet gas temperature is in the catalyst light-off region.



## 5 Conclusions

The catalytic reactions occurring in automotive exhaust gas catalyst are dominantly the LHHW-type which gives rational function type rate equations. In TWC conditions, the main reactions are virtually irreversible; whereas in net lean conditions, the equilibrium limitation of  $\text{NO}_2$  formation should be taken into account. The equilibrium constants can be determined by independent thermodynamic calculations, thus resulting in an asymptotically correct kinetic model.

The kinetic models in the field of chemical engineering are always simplified. The level of complexity should be adapted depending on the purpose of the model. For example, it is mostly convenient, for reactor design purposes, to recognise only one active site type even in the case of mechanical mixture of different catalytic material. The optimisation of catalyst content, however, demands the management of every prominent site separately.

DRIFT analysis integrated with a kinetic experiment gives an added-value to the modelling. Based on combined guidance of DRIFT measurement and kinetic modelling, it was concluded that the most probable NO reduction route over Pd-containing catalyst occurs via a direct decomposition mechanism in which the main role of a reductant is to regenerate the oxygen covered surface. Knowledge concerning surface concentrations facilitates kinetic model construction and discrimination. For example, identification of even semi-quantitative surface concentrations may lead to the successful falsification of incorrect kinetic model candidates. Especially, that is clearly seen in cases where models predict the same kind of gas phase behaviour but different kinds of surface concentration profiles. However, quality activity data are still needed to support the plausible kinetic modelling. In fact, surface measurements bring only limited direct advantage in the creation of kinetic models in the context of chemical engineering.

The transient kinetic experiments could give an indication of the predominant reaction mechanism, to support quantifying of the adsorption capacity and to reveal the impact of surface phenomena on reactor dynamics.

When catalytic material has been selected, the stationary kinetic model is, in most cases, adequate for catalytic converter design and structural optimisation for warm-up conditions. The form of the kinetic model can be an empirical rational function instead of a tightly mechanism-based formulation.

Rounded approximations of time variation of inlet gas stream conditions can be used as model input resulting in a trusted comparison of dynamic behaviour

between examined catalytic reactors with different kind of structures. The presented simplified stimuli are attractive in the preliminary rating of catalytic converters.

Sophisticated models can be reliably solved and surface science methods can be successfully applied, but the workhorse of process design is still the ideal reactor models with stationary kinetics.

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