Description of heterogeneous catalytic ignition using a skeletal reaction kinetic model

PhD thesis abstract

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Introduction

Heterogeneous catalytic combustion is a process where a fuel gets oxidized on the surface of a catalyst via heterogeneous catalytic reactions. Usage of a catalyst enables the oxidation process to take place at low temperature where the homogeneous gas-phase reaction and flame propagation is not possible.

An important field within the study of heterogeneous combustion is the investigation of heterogeneous catalytic ignition. The processes in heterogeneous ignition are basically known, however, their quantitative description is still an active field of research. The literature concerning catalytic ignition can be divided into the following two parts: 1. measurements of the ignition temperature using various catalysts, gas compositions and experimental conditions; 2. calculation of the ignition temperature using reaction kinetic models.

The heterogeneous ignition can be described by the following two basic types of models. The models that use detailed reaction mechanisms attempt to take into consideration all elementary reactions taking place on catalyst surfaces. The other possibility is to describe the surface reactions with a skeletal mechanism, taking into account the rate limiting steps.

The models using a detailed reaction mechanism require quantitative knowledge of the elementary processes taking place on the surface. A considerable part of the information on the elementary surface processes has been determined at low pressure and temperature, and these values are used unchanged in the detailed reaction mechanisms. In the experimental study of the heterogeneous ignition, the usual pressure range is in the order of the atmospheric pressure, and the temperature is above room temperature; therefore, the validity of the data used in the detailed reaction mechanisms may be questionable. The skeletal reaction mechanisms does not require knowledge of all elementary reactions; only the parameters of the rate limiting steps must be determined in the temperature and pressure range relevant to the applied experimental conditions.

Several publications proved that before ignition the catalyst surface is almost completely covered with the dominant surface species. In this case the heterogeneous catalytic ignition temperature is determined (apart from the catalyst and the gas mixture composition) primarily by the rate of the adsorption and desorption processes; the rates of the (rather complex) surface reactions do not play a role. Therefore, the catalytic ignition can be conveniently described using a skeletal mechanism.

César Treviño has investigated the condition of the catalytic ignition in a case when the activation energy required for the ignition was provided by heating up the gas mixture. In that case, without heterogeneous catalytic reactions the steady-state temperature of the surface and that of the gas mixture would be identical (assuming that the heat loss of the catalyst through the sample holder is negligible). The experimentally determined catalytic ignition temperatures available in the literature have usually been measured using another method: instead of the gas mixture the catalyst was heated. In this case, the temperature of the surface and that of the gas cannot be considered equal, even in the absence of catalytic reactions. *The first aim of my research was to develop a model based on a skeletal reaction mechanism that can be used to interpret the experimental ignition temperature data.*

Skeletal reaction mechanisms have already been used to simulate heterogeneous catalytic ignition by several research groups; however, reaction kinetic parameters for these skeletal mechanisms have either been taken from detailed mechanisms or values determined at conditions very different from that of catalytic ignition have been used. Applying a suitable model, the measured ignition temperatures can be used to determine important physical parameters of adsorption and desorption. *The second aim of my research was to apply the model developed in my PhD work to determine the reaction kinetic parameters of the adsorption and desorption processes, which are vital to the catalytic ignition.*

The sensitivity analysis of mathematical models studies the relationships between the parameters and the results of the model, which is important to the application of that kind of models. The parameters of a model can be obtained by fitting the results of the model to the experimental data; however, this kind of determination is only reliable if the model results are sensitive to the determined parameters. *The third aim of my research was to perform sensitivity analysis on the model of the catalytic ignition, and to identify the parameters that can be determined from the measured values with high accuracy.*

Scientific work and results

1. An analytic model, based on a skeletal reaction mechanism, has been created to describe the catalytic ignition. The skeletal mechanism consists of the following reactions:

$$\mathrm{F} + m\ \mathrm{M(a)} \rightleftharpoons m\ \mathrm{F(a)} \tag{R1}$$

$$\mathrm{O_2} + 2\ \mathrm{M(a)} \rightleftharpoons 2\ \mathrm{O(a)} \tag{R2}$$

$$m\ \mathrm{F(a)} + 2\sigma\ \mathrm{O(a)} \rightarrow k\ \mathrm{P(a)} + (m + 2\sigma - k)\ \mathrm{M(a)} \tag{R3}$$

$$\mathrm{P(a)} \rightarrow \mathrm{P} + \mathrm{M(a)} \tag{R4}$$

where F and P denotes gas phase fuel and product molecules, respectively, M(a) is a vacant surface position, (a) indicates adsorbed species on the surface.

1.1. The conditions of the complete surface coverage of the catalyst before ignition has been derived for the possible adsorption reaction orders, both for fuel-covered and for oxygen-covered surfaces.

1.2. The expressions for the overall reaction rate have been derived, taking into account the surface coverage and the temperature dependence of adsorption and desorption rates.

1.3. Analytic expressions have been deduced to describe the conditions for the catalytic ignition temperature, using the heat balance of the catalyst and the Franck-Kamenetskii condition. The parameters of these expressions include the physical parameters describing the adsorption and desorption: the ratio of the adsorption reaction orders of the fuel and of oxygen; the ratio of the zero coverage sticking coefficients of the fuel and of oxygen; the activation energy and the preexponential factor of the desorption of the dominant surface species.

1.4. The approximations applied have been thoroughly examined; the validity range of the model, the possible applications and the limitations were identified.

2. A computer subroutine has been written in FORTRAN to solve the mathematical model numerically. The program uses the utility procedures of CHEMKIN-II, a general-purpose gas kinetics program package, in order to calculate the reaction enthalpies and the transport properties of the gas mixture.

The subroutine has been embedded into three computer programs:

(a) A program that calculates the catalytic ignition temperature as a function of the gas composition, if all parameters are known.

(b) A nonlinear parameter estimation program using Marquardt method. This program can be used to evaluate ignition temperature data published in the literature. It is possible to evaluate several data sets simultaneously, allowing us to distinguish parameters that are shared among the data sets and parameters whose values may depend on the data set.

(c) A suitably modified version of KINAL program package that performs sensitivity analysis and principal component analysis of the sensitivity matrix. This program can be used to identify, which parameters of the model can be determined with a small error limit and independently from the other parameters.

3. Using the skeletal model of the heterogeneous catalytic ignition, published experimental ignition temperature *vs.* gas composition data have been evaluated for polycrystalline platinum catalyst and the following fuels: carbon monoxide, hydrogen, methane, ethylene, propylene.

3.1. Nonlinear parameter estimation has been used to determine the following parameters: the ratio of the adsorption reaction orders of the fuel and of oxygen; the ratio of the zero coverage sticking coefficients of the fuel and of oxygen; and the activation energy and the preexponential factor of the desorption of the dominant surface species. In the case of CO, H_2, C_2H_4 and C_3H_6, the surface is covered by the fuel, therefore, desorption parameters determined refer to these species. In the case of methane, the surface is covered by oxygen atoms, and desorption parameters determined refer to oxygen.

3.2. Principal component analysis of the sensitivity matrix of the model has been performed to examine whether the model parameters are independent of each other. If some of the parameters were not independent, then the fitting equations have been transformed using different combinations of the physical parameters. This way it was possible to get a new fitting expression, containing independent (but not always effective) fitting parameters only. It has been found that the activation energy of desorption is an effective and independent parameter, therefore, its value can be accurately determined. The sticking coefficient and the preexponential factor of desorption were not always independent of each other; however, using a suitable transformation of the fitting equation, the ratio of the sticking coefficients has also been managed to determine independently. The model is quite insensitive to the value of the preexponential factor of desorption, therefore, its fitted value can only be considered as an order-of-magnitude estimation.

3.3. It has been pointed out that the failure to satisfy the assumptions made in the model causes a bias primarily in the value of the preexponential factor, and the determination of the other parameters are not affected.

3.4. The results of the parameter estimation have been summarized in the following table, giving also the confidence interval of the values at a significance level of 95%.

fuel	the determined parameters	
CO	E_D	107.2 ± 12.7 kJ/mol
	$n_{F,A}/n_{O_2,A}$	1.03 ± 0.10
	$S_{F,0}/S_{O_2,0}$	41.2 ± 8.5
H_2	E_D	43.3 ± 5.2 kJ/mol
	$n_{F,A}/n_{O_2,A}$	1.08 ± 0.15
	$S_{F,0}/S_{O_2,0}$	36.7 ± 9.6
C_2H_4	E_D	136 ± 21 kJ/mol
	$n_{F,A}/n_{O_2,A}$	1.0 ± 0.2
	$S_{F,0}/S_{O_2,0}$	15.6 ± 1.9
C_3H_6	E_D	161 ± 53 kJ/mol
	$n_{F,A}/n_{O_2,A}$	1.1 ± 0.3
	$S_{F,0}/S_{O_2,0}$	11.9 ± 1.7
CH_4	E_D (O_2)	190 ± 34 kJ/mol
	$n_{F,A}/n_{O_2,A}$	0.95 ± 0.25
	$S_{F,0}/S_{O_2,0}$	0.169 ± 0.009

3.5. The adsorption and desorption parameters determined during my research have been compared to the available literature data, giving also the methods and conditions of their determination.

Values determined in the thesis	Literature values and their methods of determination		
E_D (CO) = 107.2 ± 12.7 kJ/mol	92 kJ/mol	Ertl, 1977	LEED, 0–300°C, Pt(111),UHV
	105 kJ/mol	Collins, 1976	TPD, 350–600K, UHV
	103 kJ/mol	Chatterjee, 2001	used in a model
E_D (H_2) = 43.3 ± 5.2 kJ/mol	51.3 kJ/mol	Lisowski, 1988	TPD, 250–450K, UHV
	45.0 kJ/mol	Wolf, 1999	used in a model
E_D (C_2H_4) = 136 ± 21 kJ/mol	160 kJ/mol	Spiewak, 1998	microcalorimetry, 303 K
	50.2 kJ/mol	Salmeron, 1982	TPD, 280 K, Pt(111), UHV
	50.2 kJ/mol	Zerkle, 2000	used in a model
E_D (C_3H_6) = 161 ± 53 kJ/mol	72.7 kJ/mol	Tsai, 1997	TPD, 284 K, Pt(111), UHV
	72.7 kJ/mol	Chatterjee, 2001	used in a model
E_D (O_2) = 190 ± 34 kJ/mol	180 kJ/mol	Parker, 1989	TPD, 500–900 K, UHV
	172 kJ/mol	Rinnemo, 1997	used in a model

Values determined in the thesis	Literature values and their methods of determination		
$S_{O_2,0}$ = 0.024 ± 0.004	0.02	Ljungström, 1989	LIF, 1200 K, <1 Torr
	0.05	Collins, 1976	UPS, 650–900 K, UHV
	0.023–0.07	Deutschmann, 1994	used in a model
$S_{H_2,0}$ = 0.88 ± 0.27	0.95	Lisowski, 1988	TPD, 250–450K, UHV
	1.0	Vlachos, 1996	used in a model
$S_{C_2H_4,0}$ = 0.38 ± 0.08	1.0	Tsai, 1997	TPD, 100 K, Pt(111), UHV
	1.0	Wolf, 1999	used in a model
	0.015	Zerkle, 2000	used in a model
$S_{C_3H_6,0}$ = 0.29 ± 0.06	1.0	Tsai, 1997	TPD, 150 K, Pt(111), UHV
	1.0	Chatterjee, 2001	used in a model
$S_{CH_4,0}$ = 0.0041 ± 0.0009	0.01–0.19	Schoofs, 1989	supersonic molecule beam
	0.01	Veser, 1997	used in a model
	0.0006	Aghalayam, 1999	fitted parameter in a model

Possible applications of the results

The heterogeneous catalytic combustion has recently become a widespread technology due to its considerable advantages: it is easier to control, it has low pollutant emission, and the lower temperature reduces the thermal stress to the structural materials. In catalytically stabilized thermal (CST) combustion, the catalyst initiates and stabilizes the gas phase combustion, which is attainable at such a low concentrations that would not enable pure gas-phase combustion. Catalytic partial oxidation of aliphatic hydrocarbons provides valuable chemicals like ethylene or synthesis gas. The catalytic radiant burners implement a relatively new technology; its advantages include that the achievable surface temperature at the same fuel consumption rate can be much higher than with homogeneous reaction only; its application is possible in a broad range of fuel/oxygen ratio; furthermore, the pollutant formation is low. In solid-oxide fuel cells, the reaction rate is increased both on the anode and on the cathode using a catalytically active metal, usually nickel.

The development and design of catalytic reactors necessitates models that are capable to describe surface reaction rates accurately. A difficulty in the application of detailed reaction kinetic models is the lack of reliable kinetic parameters. In this case, either estimated values are used, or the parameter values taken has been determined and are valid at basically different conditions.

The adsorption and desorption parameters, determined in my research by the evaluation of catalytic ignition temperatures, play a significant role in the simulation of catalytic reactors. The application of the newly determined parameters in skeletal models provides physical parameters that are more suitable to describe the adsorption and desorption processes at realistic conditions than the currently used values. This may contribute to a better agreement of the calculated and experimental results, thus it facilitates the further development of technologies that are based on catalytic combustion.

Publications related to the thesis

Articles published in referred journals:

1. T. Perger, T. Kovács, T. Turányi, C. Treviño: Determination of adsorption and desorption parameters from ignition temperature measurements in catalytic combustion systems, *Journal of Physical Chemistry B* **107**, 2262–2274 (2003)
2. T. Perger, T. Kovács, T. Turányi, C. Treviño: Determination of adsorption and desorption parameters of ethene and propene from heterogeneous ignition temperature measurements, *Combustion and Flame* **142**, 107–116 (2005)

Article published in conference proceedings:

1. T. Perger, T. Kovács, T. Turányi, C. Treviño: Determination of adsorption and desorption parameters from heterogeneous ignition temperature measurements, *Proceedings of the 3rd International Mediterranean Combustion Symposium*, 860–870 (2003)

Talks and posters at international conferences:

1. T. Turányi, T. Perger, C. Treviño: Determination of desorption parameters from ignition temperature measurements in catalytic combustion systems (poster), *2nd International Workshop on Combustion Modelling* (Veracruz, Mexico, 2001)

2. T. Perger, T. Kovács, T. Turányi, C. Treviño: Determination of adsorption and desorption parameters from ignition temperature measurements in catalytic combustion systems (poster), *29th International Symposium on Combustion* (Sapporo, Japan, 2002)

3. T. Perger, T. Kovács, T. Turányi, C. Treviño: Determination of adsorption and desorption parameters from ignition temperature measurements using multiple non-linear parameter estimation (poster), *Chemometry '02* (Tata, Hungary, 2002)

4. T. Perger, T. Kovács, T. Turányi, C. Treviño: Determination of adsorption and desorption parameters from heterogeneous ignition temperature measurements (talk), *3rd International Mediterranean Combustion Symposium* (Marrakech, Morocco, 2003)

Other talks:

1. Perger T., Kovács T., Turányi T., C. Treviño: Determination of adsorption and desorption parameters from heterogeneous ignition temperature measurements (in Hungarian), *Meeting of the Reaction Kinetics and Photochemistry Working Committee of the Hungarian Academy of Sciences* (Balatonalmádi, Hungary, 2001)

Other publications

Article published in referred journal:

1. A. Büki, T. Perger, T. Turányi, U. Maas: Repro-modelling based generation of intrinsic low-dimensional manifolds, *Journal of Mathematical Chemistry* **31**, 345–362 (2002)

Article published in conference proceedings:

1. T. Turányi, T. Perger, L. Balázs: Reaction-diffusion modelling of cylindrical halogen lamps, *Schriften des Forschungszentrum Jülich* **15**, 321–324, (2000)

Posters at international conferences:

1. T. Turányi, T. Perger, L. Balázs: Reaction-diffusion modelling of cylindrical halogen lamps (poster), *10th 'High Temperature Materials Chemistry' IUPAC Conference* (Forschungszentrum Jülich, Germany, 2000)

2. T. Perger, I. Gy. Zsély, T. Turányi: Detailed chemical kinetic modelling of the gas-phase processes during straw combustion (poster), *18th International Symposium on Gas Kinetics* (Bristol, UK, 2004)

3. T. Perger, I. Gy. Zsély, T. Turányi: Detailed chemical kinetic modelling of the gas-phase processes during straw combustion (poster), *HCM2006: Hungarian Combustion Meeting* (Szeged, Hungary, 2006)

4. T. Perger, R. Vintan, M. Entfellner, U. Boesl: Laser Mass Spectrometry: Applications for Internal Combustion Engine Diagnostics (poster), *17th International Mass Spectrometry Conference* (Prague, Czech Republic, 2006)

5. R. Vintan, M. Entfellner, T. Perger, U. Boesl: Qualitative and Quantitative Trace Detection of Ammonia: Laser Mass Spectrometry on Hydrogen Engine (poster), *17th International Mass Spectrometry Conference* (Prague, Czech Republic, 2006)

Other talks:

1. T. Perger, T. Turányi, L. Balázs: Reaction kinetic modelling of halogen lamps, *Meeting of the Reaction Kinetics and Photochemistry Working Committee of the Hungarian Academy of Sciences* (Balatonalmádi, Hungary, 1999)