Single-Event MicroKinetics of Aromatics Hydrogenation on a Pt catalyst

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ABSTRACT

A fundamental single-event microkinetic (SEMK) model for the hydrogenation of aromatic components on a Pt catalyst has been developed. It is based on the Horiuti-Polanyi mechanism considering atomic hydrogen addition steps to the (partially hydrogenated) aromatic species on the catalyst surface. The reaction network used accounts for the position at which the hydrogen atoms are added to the ring. The results from quantum chemical calculations allowed assuming that the kinetic parameters only depend on the degree of saturation of the nearest neighbour carbon atoms of the carbon atom involved in the hydrogen atom addition. The total number of 18 model parameters was reduced to 7 by calculation of the preexponential factors and by accounting for thermodynamic constraints. The model has been regressed to an experimental benzene hydrogenation data set consisting of 43 points measured at temperatures in the range from 423 K to 498 K, benzene inlet partial pressures in the range from 10 kPa to 60 kPa and hydrogen inlet partial pressures from 100 kPa to 600 kPa. The simultaneous estimation of all parameters results in an F-value of 5 103. The coverage dependent chemisorption enthalpy of hydrogen amounts to -60.0 ± 11.3 kJ/mol and corresponds with a surface coverage of 25%. A value of -64.4 ± 6.4 kJ/mol for the chemisorption enthalpy of benzene is estimated. Under typical experimental conditions the surface coverages of the partially hydrogenated species range from 1.2% to 14.7%. The total surface coverage by hydrocarbon species amounts to 60%, without a single dominant surface intermediate. The remaining 15 % of the surface is free.

INTRODUCTION

The hydrogenation of benzene is studied as part of the hydrocracking process. The hydrogenation or saturation of aromatic components is of increasing interest due to the more stringent environmental legislation. Moreover, the removal of aromatic components is benificial for a diesel's quality as the cetane number increases with decreasing aromatic content [1].

The kinetic modeling of aromatic hydrogenation reactions based on steady-state data without in situ characterization of the surface cannot make use of direct information concerning the surface intermediates. This has lead to a variety of possible kinetic models presented for the hydrogenation of aromatic model components. However, recently a reaction path analysis for the catalyzed benzene hydrogenation based on quantum chemical calculations [2] has lead to the construction of more fundamental kinetic models [4][5].

Originally, the SEMK methodology has been applied to thermal [6] and acid catalyzed reactions [7][8]. Recently the methodology has been extended to metal catalyzed reactions using Fischer Tropsch synthesis as example reaction [9]. The current work demonstrates the adequacy of the SEMK methodology for the hydrogenation of aromatic components on a noble metal such as Pt. The model is being validated for benzene hydrogenation and is ready for validation with any other monoaromatic component.

PROCEDURES

The experiments were performed in a gas phase continuous stirred tank reactor at temperatures in the range of 423–498 K, H_2 inlet partial pressures of 100–600 kPa and benzene inlet partial pressures of 10–60 kPa. The total pressure was in the range 1-3 MPa, while space times from 22.5 to 69.2 kg s mol^{-1} have been used. At these conditions intrinsic kinetics are measured since the maximum Weisz moduli obtained amounted to 10^{-2}.

A Levenberg-Marquardt algorithm was used for parameter estimation. An objective function defined as the sum of squared residuals between the observed and calculated outlet cyclohexane flow rates, is minimized. The minimization occurs through adjustment of the model parameter vector **b** which approximates the real parameter vector **β** at the minimal value of the objective function:

$$SSQ = \sum_{j=1}^{nob} (F_{cyclohex} - \hat{F}_{cyclohex})^2 \xrightarrow{b} min$$

The cyclohexane outlet flow rate is calculated by solving the non linear equation:

$$\hat{F}_{mch,j} - \hat{R}_{mch,j} \left(T, p_t, \hat{F}_{mch,j}, F^0_{benzene} \right) W_j = 0$$

i.e., via the mass balance for cyclohexane over the reactor, if the latter is not fed. The cyclohexane net production rate is calculated from the kinetic model, which gives rise to a set of

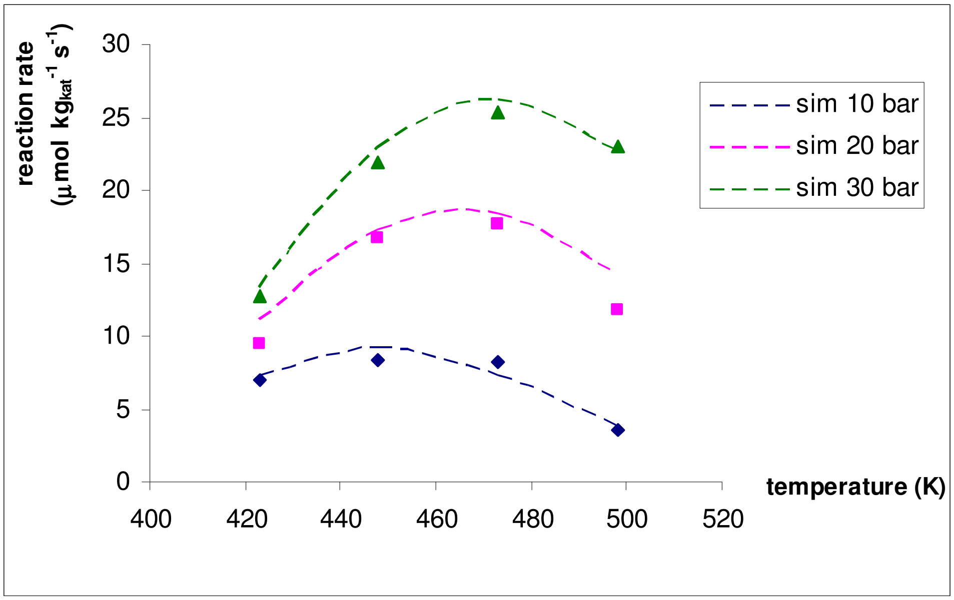

Figure 1 **Temperature effect on the observed hydrogenation rate as a function of the total pressure. (symbols: experimental results; lines: calculated results)**

algebraic equations. These algebraic equations are solved simultaneously with the mass balance equation using a hybrid Powell method [10]. The minimization of the objective function occurs according to the method of Levenberg-Marquardt [11] as implemented in the ODRPACK routine [12].

Quantumchemical calculations were performed using density functional theory. A detailed description of the procedures followed as well as the obtained results can be found in refs. [2][3][5].

EXPERIMENTAL RESULTS

The effect of the operating conditions on the hydrogenation rate is consistent with the literature [4][13]-[16]. The benzene hydrogenation rate shows a maximum as function of the temperature, see Figure 1. At a certain temperature, the increase of the hydrogenation rate coefficient with the temperature is overcompensated by the decrease of the surface concentrations of the partially hydrogenated species. The maximum in the hydrogenation rate with the temperature shifts to higher temperatures if the total pressure is increased. A higher temperature is then necessary to decrease the surface concentrations of the partially hydrogenated species.

An increase in the hydrogen inlet partial pressure enhances the cyclohexane outlet flow rate [4]. The increase in hydrogen inlet partial pressure results in a corresponding increase of the hydrogen surface concentration and, hence, an enhanced cyclohexane outlet flow rate. An opposite effect is observed for the effect of the benzene inlet partial pressure [4]. This can be attributed to a significant increase in surface concentration of partially hydrogenated species

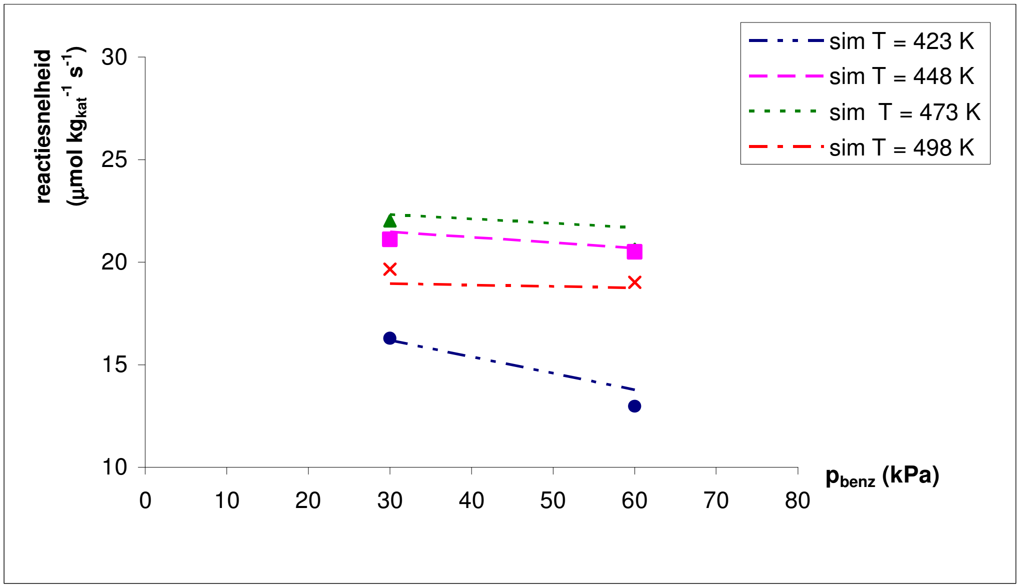

Figure 2 **Benzene inlet partial pressure effect on the observed hydrogenation rate as a function of the temperature. (symbols: experimental results; lines: calculated results)**

hindering the hydrogen chemisorption. The expected increase in hydrogenation because of the higher surface concentrations of the partially hydrogenated intermediates is overcompensated by a corresponding decrease in hydrogen surface concentration. As a result a decrease in hydrogenation rate is observed with increasing benzene inlet partial pressure. The magnitude of the effect decreases with increasing temperature.

HYDROGENATION SINGLE-EVENT MICROKINETICS

MODEL CONSTRUCTION

A characteristic of aromatic hydrogenation kinetic modeling is that many elementary steps occur in the formation of the cycloalkane out of the aromatic component. In steady-state experimentation no direct information is obtained on these reactive intermediates. In order to construct a kinetic model with a reasonable number of adjustable parameters, information with respect to the surface intermediates was obtained from quantum chemical calculations. Activation energies and surface reaction enthalpies for benzene hydrogenation have been assessed using DFT methods [2][3][5]. The number of unsaturated nearest carbon atoms to the carbon atom to which the H-atom is being added was found to be one of the distinctive features between the values obtained for the activation energies and reaction enthalpies of the various H-atom

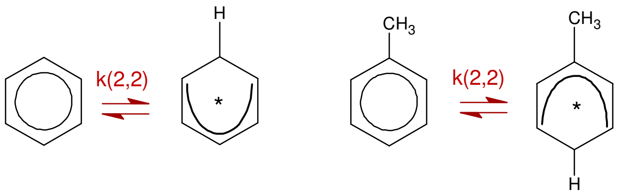

Figure 3 **Symmetry effects in hydrogen atom addition.**

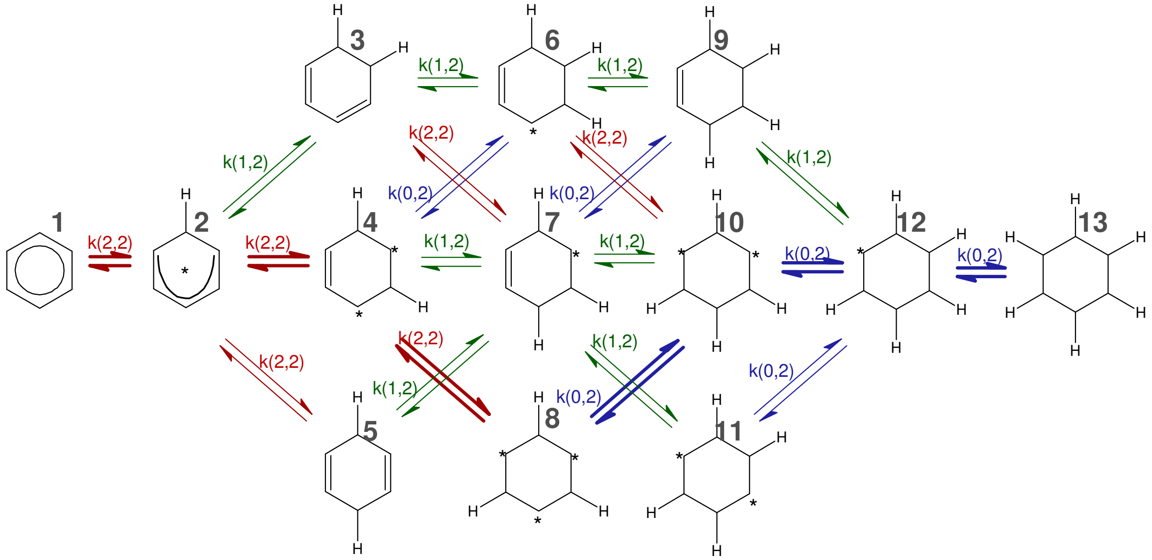

Figure 4 **Benzene hydrogenation reaction network indicating the number of the partially hydrogenated intermediates on the catalyst surface as well as the rate coefficients involved in the various hydrogen atom addition reactions.**

additions. In addition the activation energy and reaction enthalpy of H-addition are also assumed to depend on the secondary or tertiary character of the carbon atom involved. An additional dependence of the rate coefficients is related to symmetry effects. This is illustrated in Figure 3, where the first hydrogen atom addition to benzene can occur in 6 equivalent positions whereas the first hydrogen atom addition to toluene has at most 2 equivalent positions.

Unlike in previous Langmuir-Hinshelwood models [4][5][13]-[16], no dominant reaction path is considered in the current kinetic model. This implies that the entire network has to be considered. The reaction network is generated using a computerized algorithm. A new type of species has been defined as ‘metalrings’ and represents the (partially hydrogenated) aromatic species on the catalyst surface. While for benzene the reaction network is limited to 13 metalrings and 20 H-additions and abstractions, vide Figure 4, its size increases to 40 metalrings and 104 H-additions and abstractions for toluene.

No rate-determining step is assumed. All H-atom additions and abstractions are considered to be non quasi equilibrated. Reactant chemisorption and product desorption was assumed to be quasi equilibrated. The total number of parameters in the model for benzene hydrogenation amounts to 9, i.e., 3 rate coefficients and 3 surface reaction equilibrium coefficients and chemisorption equilibrium coefficients for the aromatic component, the cycloalkane and hydrogen. When accounting for their temperature dependence this number doubles to 18, however, order of magnitude calculations have been performed for the preexponential factors of rate, surface reaction equilibrium and chemisorption coefficients. These calculations were based on reasonable assumptions on the mobility of the species involved in the elementary step considered. E.g., benzene chemisorption was assumed to lead to a significant loss of translational freedom, while the hydrogen mobility on the catalyst surface was assumed to be high. Thermodynamic constraints allow calculating one of the surface reaction enthalpies and one of the chemisorption enthalpies from the remaining parameter values and the overall reaction enthalpy. Hence 7 adjustable parameters remain to be estimated from regression to experimental data.

The main assumptions in the single-event microkinetic model for benzene hydrogenation are summarized below:

1. Competitive dissociative H_2 and molecular benzene chemisorption on identical sites.
2. H_2, benzene and cyclohexane chemisorption are quasi-equilibrated.
3. No dehydrogenated surface species are considered [3].
4. No rate-determining step or dominant reaction path is assumed.
5. Each reaction step of the netwerk is considered to be reversible.
6. The steady state hypothesis is applied for the partially hydrogenated surface intermediates.
7. Rate coefficients for atomic hydrogen addition only depend on the number of unsaturated nearest neighbor carbon atoms with respect to the carbon atom involved in the hydrogen addition.

REGRESSION TO EXPERIMENTAL DATA

Kinetic parameter estimation leads to values which are in agreement with those reported in the literature [4][5][13], i.e., activation energies in the range of 50 to 70 kJ mol^{-1} and surface reaction enthalpies close to 0 kJ mol^{-1}. The benzene chemisorption enthalpy amounted to -64 kJ mol^{-1}, while that of hydrogen amounted to -60 kJ mol^{-1}. The model adequacy is illustrated in the parity diagram for the methylcyclohexane outlet flow rate and in the simulation of the temperature effect on the benzene hydrogenation at various total pressures.

The peculiar temperature effect is related to the evolution of the surface concentrations with the temperature. Benzene and other, partially hydrogenated hydrocarbon intermediates concentrations are high, i.e., occupying more than half of the active sites at lower temperatures but steadily decrease at higher temperatures. Roughly one quarter of the active sites is taken by hydrogen while the remaining fraction is free.

Table 1 **Parameter values for the Single-Event Microkinetic model for benzene hydrogenation on Pt. Values obtained by regression are given with the corresponding 95% confidence interval.**

	(0,2)	(1,2)	(2,2)	C_6H_6	H_2
E_A (kJ/mol)	62.0 ± 2.6	48.1 ± 46.7	66.5 ± 3.3		
ΔH (kJ/mol)	2.3 ± 6.2	4.4 *	6.4 ± 7.2	-64.4 ± 6.4	-60.0 ± 11.3
A	10^{16}	10^{16}	10^{16}		
Exp(ΔS/R)	1	1 *	1	10^{-12}	10^{-11}

* obtained from thermodynamic consistency

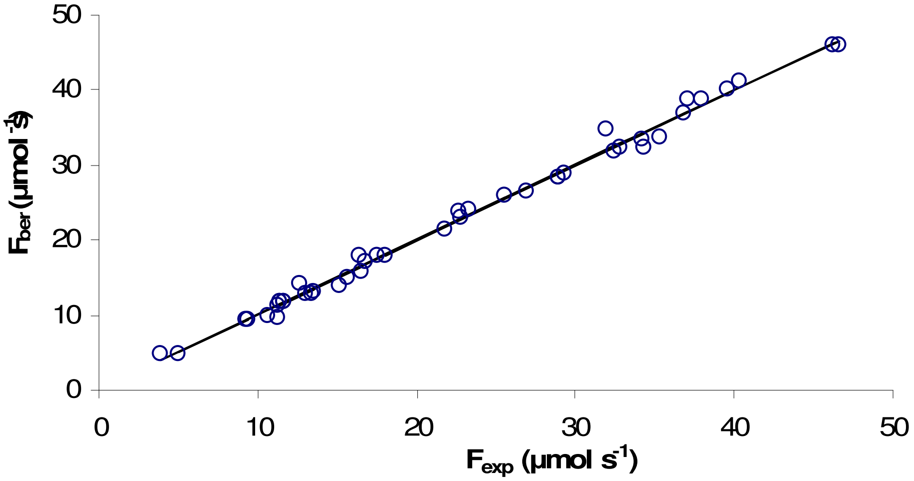

Figure 5 **Parity diagram for the cyclohexane outlet flow rate.**

CONCLUSIONS

The single-event methodology has been successfully extended to metal catalysis. The surface concentrations during benzene hydrogenation determine the experimentally observed effects. Partially hydrogenated intermediates concentrations are high and inhibit the reaction. Relatively high temperatures are required to evacuate these intermediates from the surface and eliminate the inhibitory effect. However, because of the values of the activation energies and chemisorption enthalpies involved in hydrogenation, overall reaction rates decrease at higher temperatures.

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