LIQUID PHASE HYDROGENATION OF AROMATIC COMPOUNDS ON NICKEL CATALYST

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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Chemical Technology for public examination and debate in Auditorium Ke 2 (Komppa-sali) at Helsinki University of Technology (Espoo, Finland) on the 13th of December, 2002, at 13 o'clock.

ABSTRACT

The major applications of aromatic hydrogenation (dearomatisation) are in the production of aromatic-free fuels and solvents. Health risks related to aromatic compounds, such as benzene and some polyaromatic compounds, have encouraged legislators to tighten the restrictions on aromatic content in end products. In diesel fuel, aromatic compounds have the further effect of lowering fuel quality, and they are reported to be responsible for undesired particle emissions in exhaust gases. Indeed, the major remaining concern in regard to exhaust gases is particle emissions, as fuels are already low in sulphur and the emissions of CO, SO_x and NO_x have been significantly reduced.

The aim of the work was, on the basis of experimental data from the liquid phase to develop kinetic and deactivation models of the hydrogenation of aromatic compounds suitable for use in the design and optimisation of hydrogenation reactors operating in the liquid phase. To this end, the hydrogenation of toluene, tetralin, naphthalene and mixtures of these on a commercial nickel catalyst was studied in a continuously working three-phase reactor. These model compounds were chosen to represent monoaromatics (toluene), partly hydrogenated polyaromatics (tetralin) and polyaromatics (naphthalene).

The solvent effect on toluene hydrogenation was studied in cyclohexane, *n*-heptane and isooctane. At low temperatures the hydrogenation rates were similar, but at higher temperature the rate in cyclohexane was significantly lower than the rate in *n*-heptane and isooctane. It was concluded that the difference in the rates at higher temperatures was primarily due to the different solubility of hydrogen. Thus, the matrix effects of all compounds need to be included in the models for reliable parameters and rate expressions to be achieved.

Toluene and tetralin were assumed to form a π-complex with adsorbed hydrogen and surface nickel. Intermediates were presumed to retain their aromatic nature and to react further to corresponding cyclohexenes and thereafter to fully saturated products. The difference between the hydrogenation rates of naphthalene and monoaromatic compounds was explained in terms of adsorption strength and adsorption mode of aromatic compounds. Naphthalene, adsorbing more strongly

than monoaromatic compounds, was proposed to react through π/σ-adsorption rather than π-adsorption.

The kinetic models of toluene, tetralin and naphthalene were successfully applied to the hydrogenation of aromatic mixtures of these compounds. Naphthalene was observed to inhibit the hydrogenation of toluene and tetralin, but toluene and tetralin had no effect on the hydrogenation of naphthalene. The inhibition effect could be explained with the adsorption terms obtained during single component experiments, decreasing in the order naphthalene>>tetralin>toluene. The simulation of the data obtained in the hydrogenation of mixtures with the kinetic models of the single compounds showed that the inhibition effect can successfully be estimated from single compound experiments if well defined adsorption coefficients are available for all compounds.

Severe catalyst deactivation was observed during the work. Coking (formation of hydrogen-deficient species) was assumed to be the cause of this deactivation since no sulphur or nitrogen impurities were detected. Besides increase in the *cis*-to-*trans* ratio, the catalyst deactivation suppressed the hydrogenation of tetralin to decalins relative to the hydrogenation of naphthalene to tetralin. This was explained by the π-adsorption of tetralin, which was proposed to require an ensemble of Ni-atoms, which further on, with deactivation, led to a more severe decrease in the hydrogenation rate of tetralin than in the hydrogenation rate of naphthalene.

PREFACE

Nynäshamn 20 May, 2002

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LIST OF PUBLICATIONS

This thesis is based on the following publications, which are referred to in the text by the corresponding Roman numerals:

I   Rautanen, P.A., Aittamaa, J.R., Krause, A.O.I., Solvent Effect in Liquid Phase Hydrogenation of Toluene, *Ind. Eng. Chem. Res.*, 39 (2000) 4032-4039.

II   Rautanen, P.A., Aittamaa, J.R., Krause, A.O.I., Liquid Phase Hydrogenation of Tetralin on Ni/Al$_2$O$_3$, *Chem. Eng. Sci.*, 56 (2001) 1247-1253.

III   Rautanen, P.A., Lylykangas, M.S., Aittamaa, J.R., Krause, A.O.I., Liquid Phase Hydrogenation of Naphthalene on Ni/Al$_2$O$_3$, *Stud. Surf. Sci. Catal.*, 133 (2001) 309-316.

IV   Lylykangas, M.S., Rautanen, P.A., Aittamaa, J.R., Krause, A.O.I., Liquid-Phase Hydrogenation Kinetics of Multicomponent Aromatic Mixtures on Ni/Al$_2$O$_3$, *Ind. Eng. Chem. Res.*, 41 (2002) 5632-5639.

V   Rautanen, P.A., Lylykangas, M.S., Aittamaa, J.R., Krause, A.O.I., Liquid Phase Hydrogenation of Naphthalene and Tetralin: Kinetic Modelling, *Ind. Eng. Chem. Res.,* 41 (2002) 5966-5975.

Contribution of the author to the publications:

I, II Petri Rautanen drew up the research plan, carried out the experiments, interpreted the results and wrote the manuscript.

III Petri Rautanen drew up the research plan, participated in the experiments, interpreted the results and wrote the manuscript.

IV Petri Rautanen participated in the research planning and contributed to the interpretation of the results and the writing of the manuscript.

V Petri Rautanen participated in the research planning and the experiments and carried out the modelling; he interpreted of the results and wrote the manuscript.

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CONTENTS

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1. INTRODUCTION

Liquid phase hydrogenation covers a huge range of processes, from the hydrogenation of vegetable oils and various sweeteners to hydrocarbons within the petrochemical industry. Even though classified as hydrogenation, all are very different processes, with their own characteristic process solutions. They possess some common features nevertheless, such as mass transfer and reliance on a catalyst. In this work, hydrogenation hereafter refers only to the hydrogenation of aromatic compounds (dearomatisation).

Sabatier and Senderens initiated the study of the hydrogenation of benzene and naphthalene at the turn of the last century. The hydrogenation of naphthalene was of industrial interest, as it was a major component in light fuels.[1] Indeed, fuels and fuel quality have been a major driving force in dearomatisation research throughout, since fuel production has been the major application of aromatic hydrogenation. Non-supported Ni or NiO catalyst was used in the first applications being far less expensive than noble metal catalysts. The discovery of alumina-supported NiMo and CoMo catalysts in the 1950s revolutionised the refining process so that a wider range of crude could be used. Desulphurisation became the major concern, while dearomatisation was of only minor importance.

In the last quarter of 20th century, health risks related to the aromatic compounds in fuels and car exhaust emissions[2-3] (benzene and some polyaromatics) encouraged legislators to tighten the restrictions on aromatic content in fuels. In diesel fuel, aromatic compounds have the further effect of lowering fuel quality,[4] and they are reported to be responsible for undesired particle emissions in exhaust gases.[2-3,5] Indeed the major remaining concern in regard to exhaust gases is particle emissions, as fuels are already low in sulphur, and emissions of CO, SO_x and NO_x have been significantly reduced.[6]

High temperature, high hydrogen pressure and low space velocities are required with sulphided NiMo, CoMo and NiW hydrotreating catalysts to meet the new specifications for diesel fuel.[7] However, increased temperature leads to thermodynamic equilibrium limitation in aromatic conversion[7-8] and high hydrogen pressure and low space velocities are not always economically feasible. The economic constraints can be met by utilising a two-stage process, in which

heteroatom compounds are removed in the first stage with a hydrotreating catalyst and aromatic compounds are hydrogenated in the second stage with a supported noble metal or nickel catalyst.[7-10]

The hydrogenation of monoaromatic compounds, most notably benzene and its derivatives, has been fairly well studied on all sulphided and noble metal catalysts, as well as on nickel. Reports on the hydrogenation of polyaromatic compounds are sparse and concern sulphided and noble metal catalysts. No reports of the hydrogenation of polyaromatic compounds on supported nickel were found, however, even though the nickel catalyst is mentioned[7] as an attractive choice for the second stage of deep hydrotreating owing to the lower operating temperature than for noble metal catalysts. The reduction of polyaromatic compounds is easily achieved but the hydrogenation of monoaromatics is more demanding and, indeed, the challenge created by the proposed future restrictions, especially for diesel fuel, will be the hydrogenation of monoaromatic and partly hydrogenated polyaromatic compounds.

Successful reactor design and process optimisation have depended not only in the achievements in catalysis and engineering but also on the development of research methods that allow adequate reaction rate expressions to be written for the hydrogenation kinetics. Results obtained over the years reveal that the hydrogenation kinetics is most reliably defined in experiments performed under the same conditions of temperature, pressure and concentration as will be used in the process application. Kinetic experiments on hydrogenation are typically performed in the gas phase under atmospheric pressure on Group VIII metal catalysts. The application of these rate models to liquid phase hydrogenation at high pressure is not straightforward, unfortunately.[11] For example, the early work in naphthalene hydrogenation revealed selectivity differences in the liquid and gas phases: liquid phase hydrogenation gave tetralin (tetrahydronaphthalene) and gas phase hydrogenation decalins (decahydronaphthalene) as major product.[12] Furthermore, the effects of solvents and hydrogen solubility are often obscured in the few hydrogenation studies that have been carried out in liquid phase.

The aim of the work was, on the basis of experimental data from the liquid phase, to develop kinetic and deactivation models of the hydrogenation useful for the design and optimisation of hydrogenation reactors operating in the liquid phase. To this end, the liquid phase hydrogenation of toluene (Paper I), tetralin (Papers II and V),

naphthalene (Papers III and V) and mixtures of these (Paper IV) was studied on a commercial nickel catalyst in a continuously working three-phase reactor. These model compounds were chosen to represent monoaromatics (toluene), partly hydrogenated polyaromatics (tetralin) and polyaromatics (naphthalene). The solvent effect on the hydrogenation rate was studied (Paper I) with cyclohexane (representing cycloalkanes), *n*-heptane (representing straight chain alkanes) and isooctane (representing branched alkanes).

2. EXPERIMENTAL

2.1. Catalyst Characterisation

The performances of Group VIII metal catalysts are frequently compared, even though the comparison of catalysts with different active metals and metal loadings is not straightforward. Selectivity, activity and stability vary from metal to metal, and the catalyst support, too, has a pronounced effect on the catalyst performance. Turnover frequency (mole of reacted compound per mole of metal atoms on the catalyst surface vs. time, TOF) is a good tool for comparing the reaction rates on different catalysts.[13]

In this study, a commercial nickel catalyst was used to study the hydrogenation of aromatic compounds. The amount of active sites was determined by characterisation of the catalyst in hydrogen and oxygen chemisorption and in the temperature programmed desorption of hydrogen (TPD). Moreover, the effect of reduction temperature on the properties of the catalyst was studied by chemisorption and by a model reaction (toluene hydrogenation).

2.1.1. Experimental Methods

The catalyst was characterised by H_2 and O_2 volumetric chemisorption in a static system (Coulter OMNISORP 100CX). Samples were dried in helium flow at 110°C for 3 hours and reduced *in situ* in flowing hydrogen, 30 ml_{NTP}/min, at 250-475°C for 2 hours before the hydrogen chemisorption, which was performed at 30°C. The degree of the reduction was measured by oxygen titration at 400°C. It was assumed that the oxidation was complete at 400°C and independent of the reduction temperature.[14]

The amount of active nickel (for the calculation of TOF) and the metal surface area were calculated from the amount of irreversibly adsorbed hydrogen assuming dissociative adsorption. The volume of adsorbed oxygen was calculated in a similar manner to give the degree of the reduction. The obtained values were then used to calculate the metal dispersion on the catalyst using the stoichiometry of 1.0 (H, O/ Ni)[15] for both hydrogen and oxygen atoms.

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Additionally, the catalyst was characterised by temperature programmed desorption of hydrogen (TPD, Altamira Instruments AMI-100). For this, the catalyst sample was dried in argon and reduced in hydrogen at 325°C for two hours, then heated from 30 to 800°C in argon at a rate of 10°C/min. Moisture was removed from the outlet stream with a cold trap (mixture of dry ice and acetone) placed before a thermal conductivity detector.

The effect of catalyst reduction temperature on toluene hydrogenation in isooctane was studied at 100°C and 20 bar in a three-phase reactor. The experimental set-up is described in Paper I.

2.1.2. Catalyst Pre-treatment

As can be seen in the chemisorption results presented in Table 1, the degree of the nickel reduction increases and the dispersion decreases as the reduction temperature is increased. This leads to an optimum in the metal surface area at 375°C. The good agreement between the dispersion of the catalyst reduced at 325°C (23.2% Table 1) and the dispersion calculated from TPD measurements (26.3%) suggests that chemisorption is a valid method for the characterisation.

Table 1. Chemisorption results describing the effect of the reduction temperature on the properties of the nickel catalyst.

Reduction temperature, °C	Metal surface area, m^2/g	Degree of reduction, %	Dispersion, %
250	73	39	28
325	100	64	23
375	111	76	21
400	105	79	20
475	90	84	16

Figure 1 shows TOF and the nickel particle size as a function of reduction temperature for hydrogenation experiments in a three-phase reactor. The results show that the metal particle size increases and the hydrogenation rate obtains approximately constant level with increasing temperature (corresponding to metal particle size larger than 4 nm at temperatures above 325°C). Che and Bennett[16] report similar conclusions with nickel catalyst in their review article.
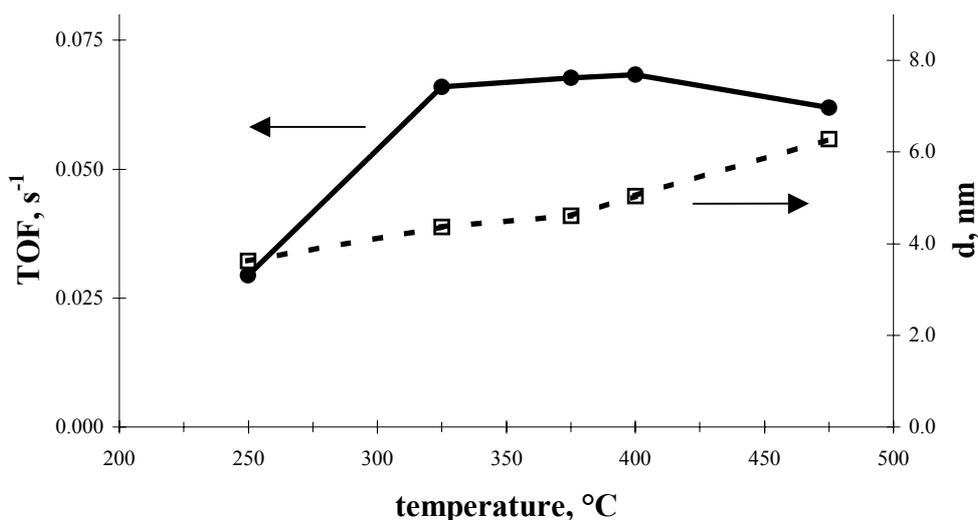
Figure 1. Effect of reduction temperature on toluene hydrogenation rate and nickel particle size.

Catalyst samples of two different lots were used: one lot for the experiments reported in Paper I (results presented in Table 1 and Figure 1) and the other for those reported in Papers II-V. Because the properties of the two lots were slightly different, different reduction temperatures were applied: 325°C for the studies reported in Paper I and 400°C for those reported in Papers II-V. At these temperatures a stable level of hydrogenation was achieved, while excess sintering and other thermal effects were avoided.

2.2. Hydrogenation Procedure

Hydrogenation was performed in a Robinson–Mahoney-type, fixed catalyst basket reactor working isothermally in CSTR mode. The reactor volume was 50 cm^3, and the liquid volume (28.6 cm^3) was determined by the step response method. Liquid products were analysed with a gas chromatograph equipped with fused silica capillary column and flame ionisation detector. A flow scheme of the reactor system is illustrated in Figure 2. A more detailed description of the experimental apparatus can be found in Paper I.

Several start-up procedures were tested, without significant influence on toluene reaction rate. In the final procedure, temperature and pressure were increased under nitrogen atmosphere during the start-up. Temperature was varied from 100 to

200°C for the toluene hydrogenation (Paper I) and from 85 to 160°C for the tetralin and naphthalene hydrogenations (Papers II-V). Hydrogen pressure was 20-40 bar.
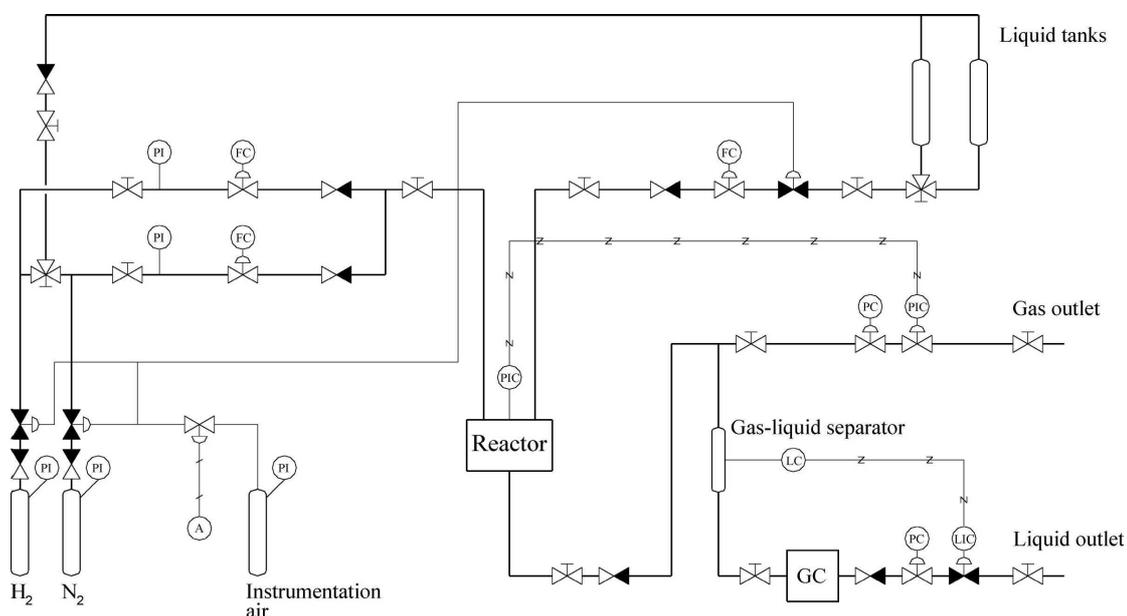
Figure 2. Flow scheme for the reactor system.

Toluene concentration was varied from 15 to 35 mol-% in cyclohexane, *n*-heptane and isooctane (Paper I), tetralin concentration from 5 to 15 mol-% in *n*-decane (Papers II and V), and naphthalene concentration from 1 to 8 mol-% in *n*-decane (Papers III and V). Toluene was varied from 0 to 20, tetralin from 0 to 10 and naphthalene from 0 to 6 mol-% during hydrogenation of the aromatic mixtures (Paper IV). Liquid flow rate was 50 g/h (LHSV about 3.8 h^{-1}) and hydrogen flow 258 cm$^3_{NTP}$ min^{-1}.

In the course of the work, the experimental approach was changed from steady state (Paper I) to dynamic (Papers II-V) in view of the relatively severe catalyst deactivation observed in the hydrogenation of tetralin and naphthalene. One dynamic experiment comprised several stages, under different conditions of temperature, pressure and initial concentration of aromatics. The first, last and every seventh stage were the same (i.e. reference condition) in every experiment to allow normalising of the results and determination of the degree of deactivation. The duration of the stages was varied between 4 and 5.5 hours.

3. KINETIC MODELLING

A continuously stirred tank reactor (CSTR) was used in the experiments. The parameter estimation was performed by minimising the error of calculated and experimental mole fractions, which were obtained by adding a kinetic model to a reactor model. The reactor model included mass balances and mass transfer between phases and within the catalyst particle. Liquid phase concentrations of hydrogen and aromatics were used in the rate expressions to ensure the determination of solvent-independent parameters[17-18] and thus the wider applicability of the models.

3.1. Mass and Heat Transfer

Three-phase systems include mass and heat transfer at gas–liquid and liquid–solid interfaces, through the gas and liquid bulk and within catalyst particles. Kinetic experiments are best performed under conditions free of mass and heat transfer limitations, owing to the difficulties in accurate and reliable determination of mass and heat transfer parameters and concentrations in films and catalyst.

Different experimental approaches[19-23] have been used to detect these mass and heat transfer limitations. Two approaches were applied in this work to determine whether the mass transfer limitations existed: an experimental approach following the guidelines of Satterfield[20] and an approach based on the calculation of mole balances and fluxes over mass transfer films according to the two-film theory (Paper I). The results indicated that neither the gas–liquid nor liquid–solid mass transfer resistance limited the overall hydrogenation rate if agitation and catalyst loading were appropriate. However, the intraparticle mass transfer resistance was significant and could not be avoided with the apparatus employed. A model of intraparticle mass transfer was therefore added to the reactor model.

The experiments were performed isothermally and thus no heat balances were needed for bulk phases. Intraparticle heat transfer resistance was also excluded from the reactor model because the calculated temperature difference inside particles was concluded to be insignificant (Paper I).

3.2. Reactor Model

Different experimental approaches were applied in the course of the work. Both steady state and dynamic experiments were performed, each requiring its own reactor model. The dynamic mole balances (Papers II-V) for the gas and liquid phases are

$$\frac{dn_i^G}{dt} = F_{in,i}^G - V_R N_i a_{GL} - F_{out,i}^G \tag{1}$$

$$\frac{dn_i^L}{dt} = F_{in,i}^L + V_R N_i a_{GL} + m_{cat} r_{app,i} - F_{out,i}^L \tag{2}$$

In steady state, the time-dependent terms are zero (Paper I). Gas and liquid outlet flows were obtained by simulating a P-controller (equation 3) for which the liquid volume was evaluated from a step response experiment.

$$F_{out} = K_p (V_{calc} - V_{exp})^2 \tag{3}$$

The gas–liquid mass transfer was modelled with the two-film theory. Vapour–liquid equilibrium (VLE) constants were calculated by the Soave–Redlich–Kwong equation of state. Coefficients of mass transfer through the gas and liquid films were calculated by the method of Miller[24] (Paper I) or assumed to be high ($\kappa^L a_{GL} = 1.0 \times 10^2$ and $\kappa^G a_{GL} = 1.0 \times 10^4$ s^{-1}) in Papers II-V since the gas–liquid mass transfer resistance was found to be negligible.

The mole balance inside a catalyst particle is

$$\frac{dc_i}{dt} = \frac{D_{eff,i}}{\varepsilon R_p^2} \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{2}{z} \frac{\partial c_i}{\partial z} \right) + \frac{\rho_p}{\varepsilon} r_i \tag{4}$$

The boundary conditions for equation 4 are

$$c_i \big|_{z=1} = c_i^L \qquad \text{at the outer surface of the catalyst and}$$

$$\frac{\partial c_i}{\partial z} \bigg|_{z=0} = 0 \qquad \text{at the centre of the catalyst.}$$

Ordinary (Paper I) and partial (Papers II-V) differential equations for the mass balance inside a catalyst particle were discretised by a 5-point central difference formula. Depending on the steepness of the concentration profiles, an evenly or logarithmically distributed grid was employed. Determination of the mass transfer parameter values for equation 4 is described in Paper I.

The apparent reaction rate for toluene given in Paper I was calculated from the flux at the catalyst surface:

$$r_{app,i} = \frac{3D_{eff,i}}{R_p^2 \rho_p} \frac{\partial c_i}{\partial z}\bigg|_{z=1} \tag{5}$$

This approach cannot be used for consecutive reactions (as in naphthalene hydrogenation), however, since the flux of the intermediate (tetralin) at the surface fails to describe the apparent rate. The better method in this case is to calculate the apparent reaction rate as a sum of the average rates over each discretisation piece:

$$r_{app,i} = \sum_{j=2}^{npp} \frac{r_{i,j} + r_{i,j-1}}{2} \left(z_j^3 - z_{j-1}^3 \right) \tag{6}$$

The steady state model (time-independent terms in equations 1, 2 and 4) was solved with the Newton-Raphson method, while the dynamic model of equations 1, 2 and 4 was solved with the backward difference method. Both models were integrated in the FLOWBAT flowsheet simulator,[25] which included a databank of thermodynamic properties as well as VLE calculation procedures and mathematical solvers.

3.3. Minimisation of Objective Function

The parameter estimation was performed by minimising the sum of errors between the estimated and the observed mole fractions for each observation point, $y_i(t_j)$. Different weight factors, $\omega_i=1$, $1/y_i$ or $1/y_i^2$, were applied during the course of the work.

$$RSS = \sum_j \sum_i \omega_i \left(y_i(t_j) - y_{i,est}(t_j) \right)^2 \tag{7}$$

The square of relative errors ($\omega_i=1/y_i^2$) was used in the modelling of toluene hydrogenation in Paper I. This relative method emphasises the compounds with lowest mole fraction, i.e. the product (methylcyclohexane), because low conversion was used in toluene hydrogenation. The reason for preferring this method is that the relative error of analysis is practically the same for all compounds, which means that the absolute error is smallest for the compound of lowest concentration (methylcyclohexane) and largest for toluene and the solvent.

Very small amounts of some products (close to the detection limit) were present in the product mixture in tetralin and naphthalene hydrogenation. This led to a very large value of the square of the reciprocal, which caused severe numerical problems and forced us to use the absolute errors ($\omega_i=1$) in Papers II-IV and $\omega_i=1/y_i$ in Paper V.

Optimisation was done by the method of Levenberg-Marquard. A local optimum was avoided by using different initial values until parameters converged to similar values.

3.4. Numerical Aspects

Low flow rates ($\sim 10^{-4}$ mol/s) in conjunction with large concentrations ($\sim 10^2$-10^3 mol/m^3) caused numerical problems. These were solved by using mole fractions of bulk phases (Papers I-V) and total mole flow (Paper I) as variables instead of mole flows (Paper I) or concentrations (Papers II-V) of individual components. Relative component concentrations (relative to liquid bulk) inside the catalyst were also used. Furthermore, a summary equation for bulk mole fractions ($\Sigma y_i=1$) was added to the steady state reactor model (Paper I). Abrupt changes in process conditions (dynamic reactor model, Papers II-V) during experiments also caused numerical problems, which were resolved by integrating each sequence (equivalent to one experimental stage, see section 4.1) separately instead of integrating over the whole experiment.

4. RESULTS AND DISCUSSION

4.1. General Features of Hydrogenation Experiments

4.1.1. Intraparticle Mass Transfer Resistance

Typical simulated intraparticle mass transfer profiles are presented in Figure 3 (single component experiments; for mixtures see Paper IV). Comparison of the profiles is complicated by the diversity in experimental conditions, in particular the concentration of the aromatic compound. It seem, however, that, during the hydrogenation of toluene (single component experiment, Paper I), the strong mass transfer resistance, especially at elevated temperatures, $T>150°C$, had an effect on the apparent hydrogen reaction order since the hydrogen concentration was diffusion limited in the catalyst pores. The reaction rate of tetralin decreased significantly due to the strong deactivation, which reduced the effect of diffusion limitations during single compound hydrogenation (Paper II) and encouraged us a simplification of the reactor model to a homogeneous one (no intraparticle diffusion limitations).

Naphthalene hydrogenation was also influenced by the strong diffusion effects (Figure 3c). Here, however, the parameter values of kinetic models were obtained with a reactor model that already took account of the intraparticle mass transfer resistance. Thus, the parameters reported in Papers I and III-V are free from mass transfer effects, whereas the apparent reaction orders in Paper I and the parameters in Paper II might have been affected by the intraparticle mass transfer resistance. The intraparticle mass transfer resistance was not observed to have effect on the selectivity.
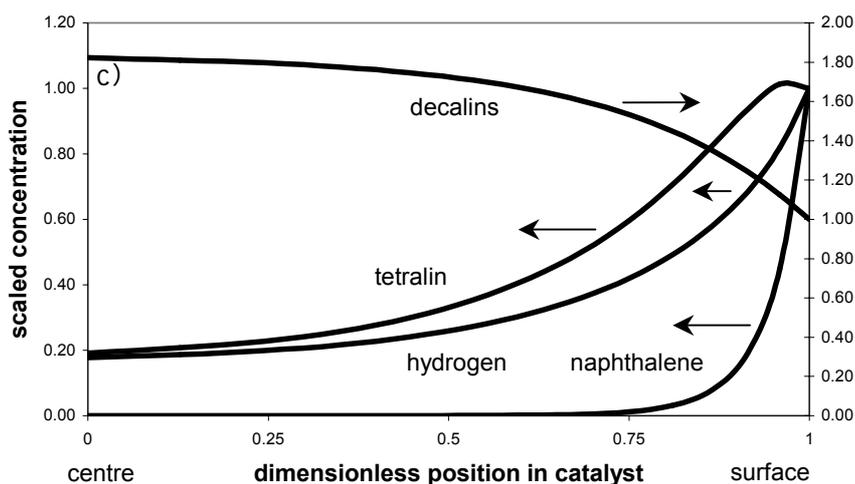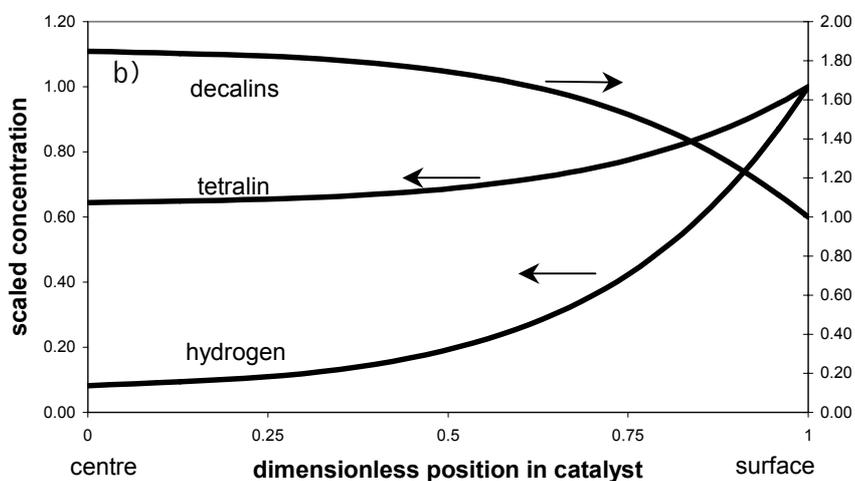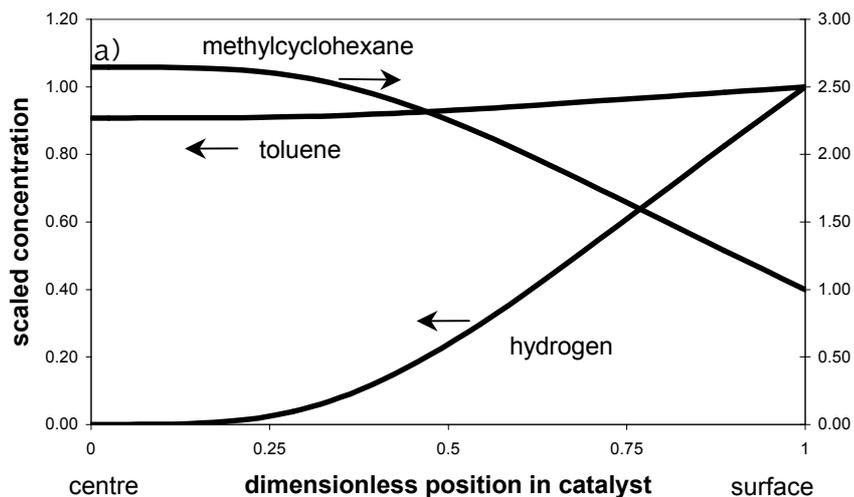
Figure 3. Component mole profiles inside the catalyst particle at 20 bar and a) 125°C, 25 mol-% toluene, b) 115°C, 10 mol-% tetralin and c) 120°C, 5 mol-% naphthalene after about 3 h on stream.

4.1.2. Hydrogenation Kinetics

We did not observe any cycloalkene formation during the hydrogenation of toluene (Papers I and IV). Methylcyclohexane has frequently been reported[26-27] to be the only reaction product in toluene hydrogenation on nickel and our results are in good agreement with that. In contrast, detectable amounts of $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin were formed during the hydrogenation of tetralin and naphthalene (Papers II-IV), as is also reported for the hydrogenation of naphthalene on noble metal catalysts.[28] The ratio of octalins was 4:1 ($\Delta^{9,10}$ to $\Delta^{1,9}$), which is close to the reported[28] thermodynamic equilibrium ratio of these isomers. An additional naphthalene hydrogenation experiment carried out with very low catalyst loading led to a low naphthalene conversion and tetralin as sole product. The experiment showed that tetralin is the primary product or intermediate in the hydrogenation of naphthalene, and no direct conversion of naphthalene to decalins occurs under the conditions studied (Paper III).

In addition to the hydrogenation, dehydrogenation of tetralin to naphthalene took place during the hydrogenation of tetralin, even though the experiments were performed far below the thermodynamic equilibrium (Paper II). The naphthalene formation was independent of temperature and pressure but dependent on the tetralin concentration and the hydrogenation rate. A high tetralin concentration together with a low hydrogenation rate favoured the naphthalene formation. The dehydrogenation was nevertheless a minor reaction and only traces of naphthalene were formed (<0.17 mol-%). Sapre and Gates[29] have reported a similar reversible dehydrogenation–hydrogenation reaction for tetralin and naphthalene on a sulphided CoMo-catalyst.

The apparent reaction order of toluene was close to zero in single component experiments (Paper I). The reaction rates of toluene in cyclohexane, *n*-heptane and isooctane were similar at low temperature but differed at elevated temperatures, in line with the difference in hydrogen solubility in the solvents. The apparent reaction order of hydrogen increased from near zero to one with temperature. No other solvent effects were observed and variation in the toluene hydrogenation rates was explained by the different solubility of hydrogen in the solvents. The results clearly indicate that the matrix effect of all compounds has to be included in the model to achieve reliable parameters and rate expressions with wide range of application.

The application of simple power law models for the hydrogenation of tetralin (Paper II), naphthalene (Paper III) and aromatic mixtures (Paper IV) was complicated by the experimental approach employed in the experiments. The discussion is hereafter based on the reaction orders obtained with the kinetic model (equation 8) used to describe the overall reaction rates (Model II in Paper II).

$$r_i = \frac{k_i \prod_j c_j^{n_j}}{\left(1 + \sum_j \left(K_j c_j\right)^{m_j}\right)^{l_i}} \tag{8}$$

The reaction order for naphthalene was close to 1.6 in single component experiments and 2.1 in mixtures. There are high values compared with the reaction orders on noble metals[30] and sulphided hydrotreating catalysts,[8] probably caused by the low concentration of naphthalene. The reaction order for tetralin was about 0.6 (Paper II), 1.2 (Paper III) and 1.4 (Paper IV) in the tetralin, naphthalene and mixture hydrogenations, respectively. The difference in orders is partly explained by the variation in the concentration of tetralin, but, as noted above, the effect of the mass transfer resistance could not be excluded from the orders presented in Paper II.

4.1.3. Stereochemistry

The *cis*-to-*trans* ratio of decalins increased from about 0.8:1 to 1.2–1.6:1 during the hydrogenation of tetralin (Paper II), but it was virtually constant (about 1:1) during the hydrogenation of naphthalene and aromatic mixture (Paper III-IV), as illustrated in Figure 4. The reaction equilibrium was calculated according to the Gibb's free energy change by the FLOWBAT program.[25] In the studied temperature range of 85–160°C, the thermodynamics favoured the formation of *trans*-decalin: 93.5–96.6% of the total decalins. The observed *cis*-to-*trans* ratio must thus have been governed by kinetic constraints, not by the thermodynamic equilibrium. Changes in the isomer ratio were found to be dependent on the catalyst activity, only slightly dependent on the temperature, and independent of the pressure and the tetralin or naphthalene concentration. Hence, the results show that the precursor of *cis*-decalin is less affected by the deactivation than is the precursor of *trans*-decalin, but the isomer ratio of decalins is virtually independent of the process conditions (temperature, pressure, concentration of aromatics). The observed *cis*-to-*trans* ratio

on nickel catalyst is in good agreement with the results reported in the reviews of Ellis[12] and Berkman *et al.*[1]
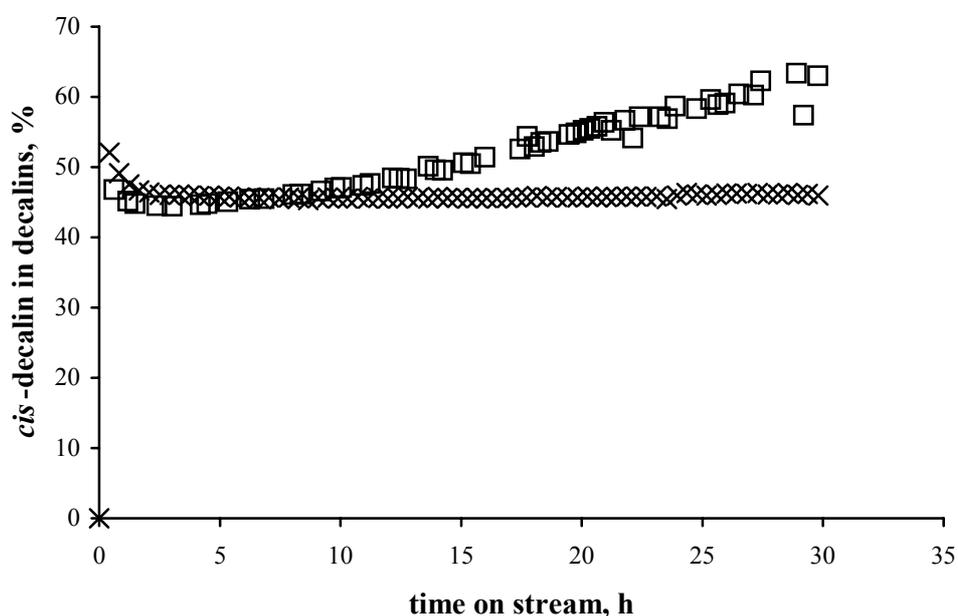
Figure 4. *cis*-Decalin as percentage of total decalin in tetralin hydrogenation (squares) and naphthalene hydrogenation (crosses).

4.1.4. Catalyst Deactivation

Since no deactivation was observed in the toluene hydrogenation (Paper I), it was surprising to observe strong deactivation of the catalyst in the tetralin hydrogenation (Figure 5). Poisoning by impurities was initially assumed. However, the sulphur and nitrogen contents of tetralin and decane were consistently less than 1 mg/kg. Sintering or leaching of nickel was improbable, too, since temperatures used in the hydrogenation were fairly low (<160°C). Similar deactivation was observed during hydrogenation of aromatic mixtures (Paper IV); even toluene hydrogenation was inhibited. In the end, coke formation was assumed to be the main reason for the deactivation.

Moderate deactivation was observed in the naphthalene hydrogenation (Paper III), as illustrated in Figure 5. However, the formation rate of the fully hydrogenated products, the decalins, was more severely inhibited by the deactivation than was the consumption rate of naphthalene. Large differences in the deactivation rates suggest that the hydrogenation of naphthalene and the intermediate (tetralin) may even take place through different reaction steps, or that their adsorption on the catalyst is

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different. It should be emphasised, however, that the content of aromatic compounds in the experiments summarised in Figure 5 is very different: initial content of 5 mol-% with about 90% conversion in naphthalene hydrogenation and initial content of 10 mol-% with about 40% conversion in tetralin hydrogenation. The comparison of the deactivations in naphthalene and tetralin hydrogenation is not straightforward therefore. The deactivation seems nevertheless to be compound dependent, i.e. the formation of coke precursors depends on the nature of the reactive compound. Similar observations have been reported for xylenes.[31]
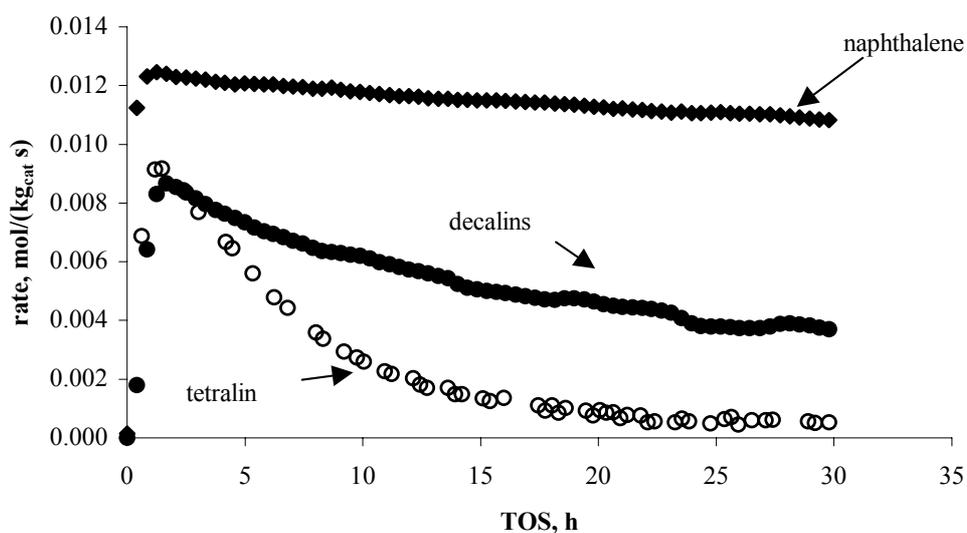
Figure 5. Formation rate of decalins (filled circles) and reaction rates of naphthalene (filled squares) in naphthalene hydrogenation and tetralin (open circles) in tetralin hydrogenation at 20 bar and 120°C.

Initially, the method described by Larsson *et al.*[32] was applied to distinguish between the catalyst deactivation and reaction kinetics. The method calls for an evaluation of the deactivation function before the kinetic modelling. Transient behaviour is included in the deactivation function, and the steady-state assumption is used for the modelling of the reaction kinetics. The step response of the input concentration is used to define the reactor dynamics, which is needed to evaluate the deactivation function.

The evaluation of the deactivation function proved to be very sensitive to variations in the dead-time, and the dead-time varied slightly with temperature, pressure and concentration steps. The activity of the catalyst was assumed to be equal at the

experimental points just before and after each step. In the ideal CSTR, the largest response change is at the beginning, and a small error in the time delay leads to a large inaccuracy in the activity and an unacceptable deviation in the reaction rates.

Since it was not possible to estimate dead-times and responses accurately enough for all combinations of the different steps in our experiments, more conventional methods were, in the end, applied to the modelling of the deactivation and the reaction kinetics: that is, the deactivation parameters were modelled simultaneously with the parameter estimation. A simple decay law[33] was used to estimate the deactivation (Papers I-IV).

$$-\frac{da}{dt} = k_D a^d \qquad\qquad (9)$$

Hydrogen pressure had no effect on the deactivation (Papers II-IV). Temperature dependency of the deactivation (according equation 9) was mild and it was excluded in Papers II and IV and estimated to be below 4 kJ mol^{-1} in Paper III. The deactivation order in the tetralin hydrogenation changed slightly with temperature (Paper II) and was typically about 1.2. The deactivation order in the naphthalene hydrogenation was about 0.2 towards naphthalene and about 1.2 towards tetralin and about 0.9 during hydrogenation of aromatic mixtures.

4.2. Adsorption

4.2.1. Hydrogen

In the studies for Paper I, models corresponding to the dissociative and associative adsorption of hydrogen were applied and compared in the kinetic modelling of toluene hydrogenation, but no significant differences were noticed. Earlier studies on the hydrogenation of aromatic ring on nickel have included both atomic[34-37] and molecular (or two-atomic)[38-39] additions of adsorbed hydrogen. Even though the kinetic modelling did not reveal any significant differences, our assumption is that, under the conditions studied the bond of the hydrogen molecule has to be broken before hydrogenation can take place. The assumption of dissociative adsorption of hydrogen was therefore applied in Papers II-III and V. A factor γ, describing the

number of active sites in hydrogen adsorption, was estimated in Paper IV. Indeed, the estimated value 1.8 supports the assumption that hydrogen undergoes the dissociative adsorption, and chemisorbed H atoms are active species in the hydrogenation.

4.2.2. Aromatic Compounds

We assumed associative adsorption of aromatics (through π–bonding in which the aromatic compound lies parallel to the catalyst surface) in Papers I-IV that is consistent with the reports of benzene adsorption on Group VIII metal catalysts as reviewed by Stanislaus and Cooper.[8] However, several adsorption studies on nickel propose that two or three different adsorption forms of aromatic compound exist simultaneously.[35,40-42] These reports suggest one non-reactive[35,40] and one[35] or two[40] reactive forms (in hydrogenation) of adsorbed aromatic compound. Non-reactive form is frequently proposed to be dissociatively adsorbed (σ-adsorbed), whereas reactive form is related to π-adsorption or to the formation of the π-complex. Based on these observations and proposals of three adsorption forms by Tjandra and Zaera[41] and Prasad *et al.*[43] we described in Paper V a hydrogenation and deactivation mechanism, which includes three different adsorption forms: σ-adsorbed (non-reactive), π-adsorbed (reactive) and π/σ-adsorbed (reactive) forms. We assumed that the aromatic compound adsorbs through π/σ-adsorption form, which is in equilibrium with π- and σ-adsorbed form. Proposed adsorption forms are simplified in Figure 6.
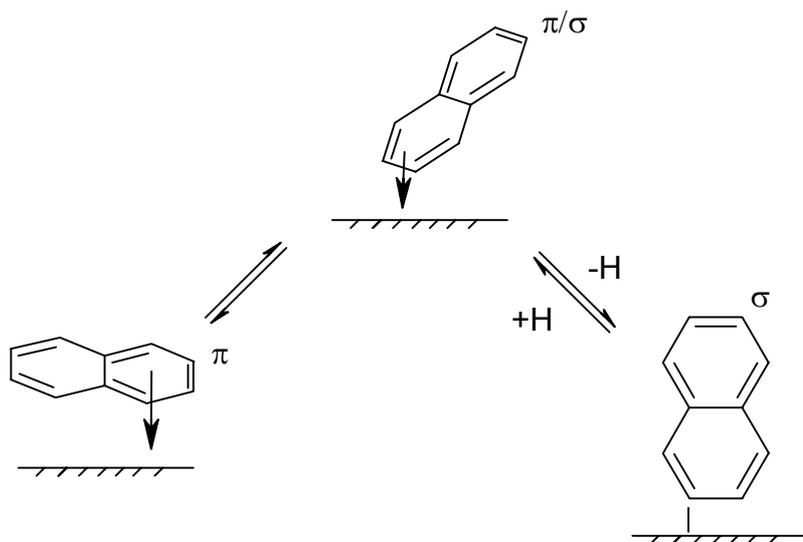
Figure 6. Simplified illustration of proposed adsorption forms of aromatic compounds.

In Paper I we observed that the adsorption equilibrium coefficient for solvent was very low compared to aromatic compounds or hydrogen, and it was therefore assumed zero in the subsequent studies. We also assumed that hydrogenated products desorb immediately from the catalyst which is in agreement with the reported adsorption[41] and hydrogenation[30] studies.

Magnetisation experiments of van Meerten *et al.*,[34] isotopic transient studies of Mirodatos[44] and experiments of Marécot *et al.*[35] have indicated that hydrogen and aromatic compounds (active for the hydrogenation) adsorb onto different active sites on nickel. Nevertheless, both competitive and non-competitive adsorption assumptions have been successfully applied to the kinetic modelling of the hydrogenation of aromatics on nickel.[26-27,45-48] We compared competitive and non-competitive adsorption models in toluene hydrogenation, and found good and almost equal fits (Paper I). Indeed, probably neither of these extremes represents the reality. The large difference in the size of the molecules excludes absolute competition for the active sites; i.e. if large aromatic molecules form a monolayer on the catalyst, there is still space for small hydrogen molecules to adsorb beside them. In Papers II-IV (Model II in Paper II), the hydrogenation rate was modelled with a generalised Langmuir-Hinshelwood type rate expression[11] (equation 8), which indicates the competitive adsorption of aromatic compounds and hydrogen.

A mechanistic hydrogenation model (Model III) described in Paper II includes as well a competitive adsorption approach. However, that model in Paper II gives a higher adsorption term for hydrogen than for tetralin in contradiction with the estimation results of Papers III and IV. Moreover, the results of Marécot et al.[35] and van Meerten et al.[34] suggested that the weakly bound hydrogen (low adsorption term) is active in hydrogenation. It is obvious that kinetic modelling tools can not entirely expose the competitive or non-competitive nature of hydrogen and aromatic compound adsorption, but this requires other experimental methods. In Paper V, we assumed a non-competitive adsorption of hydrogen and aromatic compounds that is in agreement with the adsorption reports of these compounds.[34-35]

Adsorbed aromatic compounds are often reported to occupy multiple vacancies, i.e. an ensemble of active metal atoms.[34,38-39,44,49] In an initial study (Paper I), a model with toluene adsorption on multiple active sites of the catalyst was tested with both dissociative and associative adsorption of hydrogen. The fit was slightly improved (lower residual) relative to the case of toluene adsorption on a single site. However, the confidence intervals for parameter X (number of sites occupied by toluene) were large, indicating an overparameterised model. Accordingly, the adsorption of aromatics on single sites was assumed in Papers II-IV in the form of generalised Langmuir-Hinshelwood rate expression (equation 8). The kinetic model described in Paper V utilised the data from both tetralin (Paper II) and naphthalene (Paper III) hydrogenation studies and therefore, a risk for overparameterisation was lower. Results from Paper V showed that aromatic compound, which adsorbs through an π-adsorption, occupies 2-3 active sites, which is in line with the reported results.[38,42,49] This indicates that the hydrogenation of aromatic compounds is structure sensitive, at least with the π-adsorption. Further on, it is obvious that the ensemble of sites which is active for π-adsorption, requires a specific coordination which leads to a low utilisation of nickel: only small fraction of nickel surface is active in hydrogenation. This is in accordance with the findings of Marécot et al.[35], Mirodatos et al.[38] and van Meerten et al.[34]

4.2.3. Adsorption Parameters

The surface of the catalyst is most probably very crowded in the liquid phase due to the high concentration. Low values for the adsorption enthalpies are then expected,

since enthalpy is reported to decrease with increasing coverage.[50-52] In Paper III, temperature dependency of the adsorption coefficients was estimated according to the equation of van't Hoff: equation 10. In Papers I-II and IV, temperature independent adsorption coefficients were assumed.

$$K_i = e^{\Delta S/R} e^{-\Delta H/RT} \qquad\qquad (10)$$

Estimated values (Paper III) in a semi-empirical model, equation 8 indicate that the adsorption enthalpies are indeed very low, below 9 kJ/mol. In our work, the adsorption coefficients were the most difficult parameters to estimate. In toluene hydrogenation, the adsorption parameter of hydrogen was difficult to identify and it thus had a large confidence interval (Paper I). In tetralin hydrogenation, the hydrogen adsorption parameter was fairly well identified, whereas the adsorption parameters of tetralin and octalin were poorly identified, especially in the semi-empirical models (Paper II). Adsorption enthalpies in Paper V (based on a mechanistic model) were higher, about 25-45 kJ/mol for compounds active in hydrogenation, than in enthalpies in Paper III but indicated still a high surface coverage. The order of adsorption enthalpies was the same: naphthalene had the highest enthalpy of aromatic compounds, followed by tetralin and toluene. This follows the adsorption strengths and reactivities of aromatic compounds in the hydrogenation of mixtures (Paper IV), where competitive adsorption of model compounds with different adsorption strength induced inhibition effect. In mixtures, the most reactive compound, naphthalene, severely reduced the hydrogenation rates of toluene and tetralin, while the rate of naphthalene was little affected by the concentrations of toluene and tetralin. The simulation of the data set of mixtures hydrogenation with the kinetic models of the single compounds (models in Papers I and III) revealed that the inhibition effect can be estimated from the single compound experiments, if all compounds have well defined adsorption coefficients (e.g. Langmuir-Hinshelwood type rate expression).

Entropy loss due to the adsorption showed similar trend, higher values with the mechanistic model (Paper V) compared to the semi-empirical model (Paper III). However, both tetralin and naphthalene had fairly similar adsorption entropy in both cases. The adsorption entropy of hydrogen, 137-150 J/Kmol (the mechanistic model, Paper V) was close to the gas phase entropy indicating that hydrogen is not mobile

on the catalyst. Similar adsorption entropy of hydrogen is reported for the gas phase hydrogenation of benzene[26] and *m*-xylene.[37]

4.3. Hydrogenation and Deactivation Mechanism

4.3.1. Toluene Hydrogenation

The mechanism for the hydrogenation of the monoaromatic ring (i.e benzene or alkylsubstituted benzene) has been widely studied on nickel, and though several different mechanisms have been proposed, no consensus has been found. One mechanism suggested is of Eley-Rideal type, i.e. the aromatic compound adsorbs on the catalyst and reacts in successive steps with gas-phase hydrogen to the corresponding cycloalkane.[53-54] Another mechanism describes the sequential reaction between adsorbed hydrogen and aromatic compound.[27,34,44-45,] Both these reaction mechanisms include cyclohexadiene as an intermediate, even though only cyclohexane and cyclohexene have been reported as products in the hydrogenation of benzene. The formation of cyclohexadiene is thermodynamically unfavourable[55] but has been explained in terms of kinetic coupling,[56] i.e. cyclohexadiene reacts further to cyclohexene much faster than benzene reacts to cyclohexadiene.

Vannice *et al.*[17,57-59] have proposed for hydrogenation on Pt or Pd catalysts a mechanism that consists of sequential addition of dissociatively adsorbed hydrogen atom to associatively adsorbed aromatic compound (benzene/toluene). The addition of the first hydrogen atom is rate determining leading to a non-aromatic intermediate, i.e. aromatic compound looses its aromatic nature during the first addition. They presume non-competitive adsorption of hydrogen and aromatic compound, but a competitive adsorption of concurrently formed hydrogen-deficient phenyl species (inactive in hydrogenation) on the same sites as the aromatic compound.

An alternative mechanism to the three above suggests that the adsorbed aromatic compound forms a complex with the catalyst surface atoms and hydrogen.[60] This complex is isomerised to cycloalkene, so that, the formation of thermodynamically unfavourable cyclohexadiene is not included in the reaction mechanism.[39] A similar mechanism has been successfully applied by Smeds *et al.*[36-37] and Toppinen *et al,*[45,48]

which also encouraged us to apply this mechanism to our model of toluene hydrogenation (Paper I).

4.3.2. Tetralin and Naphthalene Hydrogenation

The mechanistic model in Paper II was based on a reaction scheme, which was closely similar to the scheme proposed by Weitkamp[28] on naphthalene hydrogenation on noble metal catalysts. Otherwise, no mechanistic models of tetralin and naphthalene hydrogenation appear to exist, but some empirical and semi-empirical kinetic models have been reported.[8,30,61] The improved mechanistic model presented in Paper V was based on three adsorption modes of aromatic compounds as described in Chapter 4.2. The π/σ-adsorbed naphthalene was assumed to hydrogenate through dihydronaphthalene to tetralin in consistent with earlier hydrogenation[12,28] and dehydrogenation[62] studies. Unfortunately, we could not identify any dihydronaphthalenes from our product mixture. Early studies of Lush, reviewed by Ellis,[12] support also this assumption. Lush reported that the liquid phase hydrogenation of naphthalene led to a significant decalin yield, whereas the gas phase hydrogenation gave exclusively tetralin as a product. He concluded that this was caused by different adsorption (orientation) of naphthalene on nickel catalyst. Thus, at the gas phase (low concentration, low/ medium coverage) naphthalene has 'room' to adsorb parallel to a catalyst surface (π-adsorption), while naphthalene orientates 'tilted' (π/σ-adsorption, see Figure 6) at the liquid phase (high concentration, crowded surface coverage). Weitkamp[28] suggested also two different adsorption forms of naphthalene, which react with different hydrogenation rates and selectivity.

We assume three adsorption forms also for tetralin but in contrast to naphthalene, only π-adsorbed tetralin was assumed to be hydrogenated. This is explained by the sensitivity toward the deactivation. A linear decrease as a function of time was observed in the hydrogenation rate of naphthalene and non-linear, more severe decrease in tetralin rate. π-Adsorption requires ensemble of active sites and is thus more sensitive for the deactivation. Different reaction steps of naphthalene and tetralin can be explained by the difference in aromaticity.[28,63-64] The π-electron density of the aromatic ring of tetralin is higher than that of naphthalene and hence, the resonance energy of aromatic ring in tetralin is also greater than in naphthalene.

According to our model, the aromaticity of the first ring in naphthalene is so weak that it will react through transition state (π/σ-adsorption) to dihydronaphthalene. However, the aromaticity of the remaining ring (tetralin) is much stronger and requires π-adsorption in order to be hydrogenated.

We proposed (Paper V) that tetralin reacts further to $\Delta^{9,10}$-octalin through a surface π-complex as described for the monoaromatic compounds.[36-37,39] The mechanism excludes then the formation of hexahydronaphthalene even though we proposed in our first papers (Papers II-III) that hexahydronaphthalene could be an intermediate in tetralin hydrogenation to decalins. Weitkamp[28] reported detectable amounts of different isomers of hexahydronaphthalene on platinum but emphasised that this was an intermediate of a minor side reaction because the observed isomers had one double bond in both rings.

We originally proposed a reaction scheme for the hydrogenation of tetralin (Paper II), that included the parallel hydrogenation rate of tetralin (or surface complex) to $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin. The hydrogenation experiment of naphthalene revealed that only *cis*-decalin was observed as the tetralin rate ceased down. This indicates that tetralin reacts to $\Delta^{9,10}$-octalin, which then is hydrogenated to *cis*-decalin or isomerised to $\Delta^{1,9}$-octalin (Papers III-V). $\Delta^{9,10}$-Octalin was assumed to react with two hydrogen atoms (*cis*-addition of hydrogen) to *cis*-decalin or to isomerise to $\Delta^{1,9}$-octalin, which then reacted to *cis*- and *trans*-decalin.

Decalins were not observed to isomerise or dehydrogenate to octalins (Paper III). However, we found reversible hydrogenation–dehydrogenation steps in tetralin hydrogenation, but only as a minor reaction (Paper II). This confirms the different nature of naphthalene and tetralin hydrogenation, as the naphthalene hydrogenation is found reversible and tetralin irreversible.[8,29,61]

4.3.3. Deactivation

The deactivation mechanism (Paper V) was as well based on three adsorption forms of aromatic compounds of which one (σ-adsorption, see Figure 6) leads to the formation of non-reactive compounds (dissociates to coke). σ-Adsorbed benzene is indeed known to act as a poison in hydrogenation reaction and on the other hand, to

form coke on the nickel catalyst.[40-41,65] Our results (Paper V) indicate that naphthalene does not dissociate, whereas tetralin dissociates significantly losing about 2-3 hydrogen atoms.

The change in *cis*-to-*trans* ratio as a function of catalyst activity was explained with the additional active site needed to isomerise $\Delta^{9,10}$-octalin to $\Delta^{1,9}$-octalin (Paper V). This would expound the increased *cis*-content with the decreasing activity.

4.3.4. Model Fit

The recent successful application of kinetic models developed from gas phase experiments of monoaromatic compounds to liquid phase hydrogenation[17,45,48] encouraged us to apply the mechanism derived originally for the gas phase hydrogenation of ethylbenzene[36] to the liquid phase hydrogenation of toluene (Paper I). The kinetic expression based on this model described well the experimental data (Paper I, Figure 9), indicating that mechanisms derived from gas phase experiments can indeed be applied to the liquid phase with reasonable accuracy. However, a better fit was obtained with a model based on the Temkin mechanism[39], which was originally derived for the liquid phase hydrogenation of benzene and toluene. The fairly similar residuals, RSS of both models indicates that more than one kinetic model is able to describe the experimental data, and evaluation of the models should be based on a comparison of parameter values and their significance.

The parameter estimation of tetralin hydrogenation (Paper II) gave similar results as toluene hydrogenation: the fits obtained with a purely empirical power-law model (Model I), a semi-empirical extended power-law model (generalised Langmuir-Hinshelwood, Model II) and a mechanistic model (Model III) were in practice equal (Figure 7). However, the parameter values of the models differed significantly, so that the values of the activation energy and adsorption equilibrium coefficient parameters of the empirical models were physically meaningless, typically insignificant small, whereas parameters with narrow confidence range and physically meaningful values were estimated with the mechanistic model (Model III).

All presented models gave similar residuals and as stated above, the significance of parameters (confidence range and physically meaningful values) was an essential tool in the model evaluation. Moreover, the simulation of aromatic mixture

hydrogenation revealed that the kinetic models of single compound experiments described successfully also the reaction kinetics of mixtures, which indicates a wide applicability of presented models including appropriate adsorption terms.
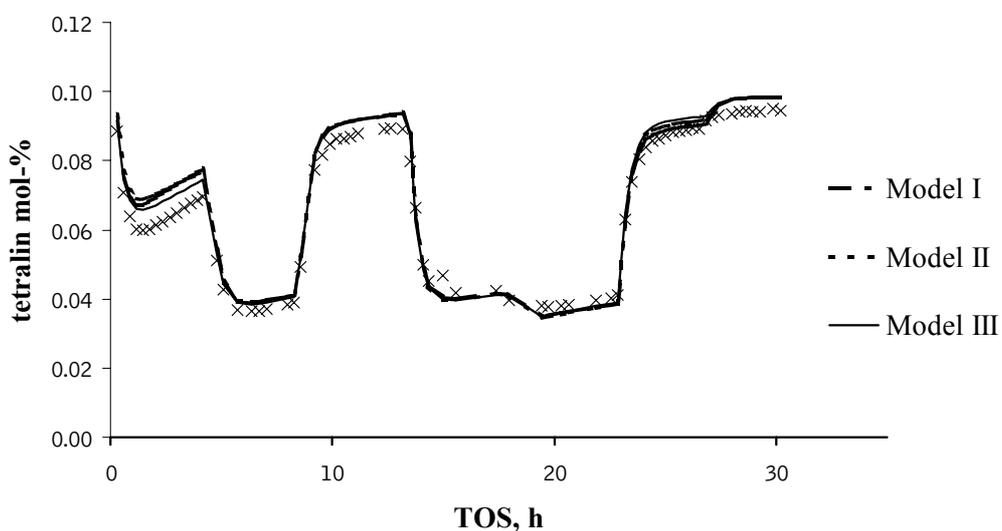

Figure 7. Experimental (crosses) and estimated (lines) mole fraction of tetralin in tetralin hydrogenation: power law (Model I), generalised Langmuir-Hinshelwood (Model II) and mechanistic (Model III) models based on the proposed reaction scheme (Paper II).

5. CONCLUDING REMARKS

The aim of the work was to develop kinetic and deactivation models to describe liquid phase hydrogenation, and to be used these models in process design and optimisation. Therefore, the liquid phase hydrogenation of toluene, tetralin and naphthalene on a commercial nickel catalyst was studied in a three-phase reactor. Despite the hydrogenation kinetic of individual aromatic compounds, also the solvent effect and aromatic mixture hydrogenation were explored.

The solvent effect on toluene hydrogenation was studied in cyclohexane, *n*-heptane and isooctane. Hydrogenation rates were similar at low temperatures, but the rate in cyclohexane was significantly lower than the rate in *n*-heptane and isooctane at higher temperatures. It was concluded that the difference in the hydrogenation rates in the three solvents was primarily due to the different solubility of hydrogen. This clearly indicates that the matrix effect of all compounds has to be included in the model to achieve reliable parameters and rate expressions.

Toluene and tetralin were assumed to form a π-complex with adsorbed hydrogen and surface nickel. Intermediates were presumed to retain their aromatic nature and react further to corresponding cyclohexene and thereon to fully saturated products. The difference between the hydrogenation rates of naphthalene and monoaromatic compounds was explained with adsorption strength and mode. Naphthalene was proposed to adsorb strongest and to react through π/σ-adsorption instead of π-adsorption.

The kinetic models of toluene, tetralin and naphthalene were successfully applied to the hydrogenation of aromatic mixtures of these compounds. Naphthalene was observed to inhibit the rate of toluene and tetralin, whereas toluene and tetralin did not virtually have any affect to the rate of naphthalene. This inhibition effect could be explained with the competitive adsorption and was described in the kinetic model by the adsorption terms obtained during single component experiments decreasing in order naphthalene>>tetralin>toluene. The simulation of the data set of mixtures hydrogenation with the kinetic models of the single compounds revealed that the inhibition effect can be estimated from the single compound experiments, if all compounds have well defined adsorption coefficients.

Severe catalyst deactivation was observed during the course of the work. Coking (or formation of hydrogen-deficient species) was assumed to be the cause of this deactivation since no sulphur or nitrogen impurities were detected. Besides change in the *cis*-to-*trans* ratio, the catalyst deactivation had a lower effect on the hydrogenation of naphthalene to tetralin compared to the hydrogenation of tetralin to decalins. These selectivity changes were explained with the additional sites required by the less favoured reaction steps.

6. NOTATION

a activity

a_{GL} gas–liquid mass transfer area per reactor volume, $m^2\ m^{-3}$

c_i concentration of component i, $mol\ m^{-3}$

d deactivation order

$CSTR$ continuous stirred tank reactor

D_i diffusion coefficient of component i, $m^2\ s^{-1}$

F_i mole flow of component i, $mol\ s^{-1}$

H enthalpy, $kJ\ mol^{-1}$

k_i rate constant of component i, dimension varies according to the model

k_D deactivation rate constant, s^{-1}

K_i adsorption equilibrium coefficient of component i, $m^3\ mol^{-1}$

K_p constant of the P-controller, $mol\ m^{-3}\ s^{-1}$

n_i amount of component i, mol

N_i mole flux of component i, $mol\ m^{-2}\ s^{-1}$

m_{cat} catalyst mass, kg

r_i reaction rate of component i, $mol\ kg_{cat}^{-1}\ s^{-1}$

R catalyst radius, m

RSS residual sum of squares

S entropy, $J\ mol^{-1}\ K^{-1}$

t time, s

TOF turn over frequency, s^{-1}

TPD temperature programmed desorption

V volume, m^3

y_i observed mole fraction of component i

$\hat{y}_i$ estimated mole fraction of component i

z dimensionless position

Greek Letters

ε catalyst porosity

κ_i mass transfer coefficient of component i, $m\ s^{-1}$

ρ density, $kg\ m^{-3}$

ω weight factor

Sub- and Superscripts

app   apparent

calc   calculated (estimated)

eff   effective

exp   experimental

G   gas

L   liquid

p   catalyst particle

R   reactor

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