

Liquid-Phase Hydrogenation of Naphthalene and Tetralin on Ni/Al₂O₃: Kinetic Modeling

Petri A. Rautanen,^{*,†} Mikko S. Lylykangas, Juhani R. Aittamaa, and A. Outi I. Krause

Helsinki University of Technology, Department of Chemical Technology, P.O. Box 6100, FIN-02015 HUT Helsinki, Finland

The kinetics of the liquid-phase hydrogenation of naphthalene and tetralin (1,2,3,4-tetrahydronaphthalene) in decane was studied on a commercial nickel catalyst at 80–160 °C and 20–40 bar in a CSTR. The proposed kinetic model assumes three adsorption modes (π -, π/σ -, and σ -adsorption), of which two are associative and one is dissociative. The associatively adsorbed aromatic compounds are assumed to be active in hydrogenation, whereas the dissociative adsorption leads to coke formation. Moreover, it is proposed that naphthalene adsorption occurs on a single active site, whereas tetralin adsorption requires an ensemble of Ni atoms. This explains the nonlinear decrease in the tetralin hydrogenation rate with catalyst deactivation, whereas the naphthalene hydrogenation decreases linearly. The proposed reaction and deactivation mechanism is able to describe the main features of the observed kinetics, including the formation of octalins (octahydronaphthalene), changes in the cis-to-trans selectivity of decalin (decahydronaphthalene), and the difference between the naphthalene and tetralin hydrogenation and deactivation rates.

Introduction

Gas-phase hydrogenation of benzene and alkyl-substituted benzene has been frequently studied.^{1–7} Considerably less attention has been paid to liquid-phase hydrogenation, particularly the hydrogenation of polyaromatic compounds. Recently, the reduction of aromatic compounds in fuels and solvents has become important not only in light fractions but also in middle distillates containing significant amounts of polyaromatics.^{8,9} Compliance with future limitations on these compounds will demand the design of new dearomatization units, and for that purpose, a comprehensive understanding of the liquid-phase hydrogenation of heavier compounds (polyaromatics) will be required.

Nickel catalyst is an attractive choice for the hydrogenation of aromatics because of its high hydrogenation activity at low temperatures, which sets it apart from the conventional (sulfided CoMo, NiMo, and NiW) hydrotreating and noble metal catalysts.⁹ Still, no reports on the hydrogenation of polyaromatic compounds on nickel are available, although several mechanisms have been proposed for the hydrogenation of monoaromatic compounds.

In principle, two types of reaction mechanism have been proposed for the hydrogenation of aromatic rings. One model suggests that the hydrogenation of aromatic compounds proceeds through sequential additions of adsorbed hydrogen atoms.^{1–4} The other model suggests the formation of a complex during the first hydrogenation step.^{5–7} This complex consists of adsorbed aromatic compound and hydrogen, together with nickel sites, and it retains its aromatic nature through the second hydrogenation step. Thereafter, the complex is isomer-

ized to a corresponding cyclohexene and further to a fully hydrogenated product. The nature of the adsorbed hydrogen that is active in hydrogenation varies in these models from molecular to atomic; even the Eley–Rideal-type gas-phase addition of hydrogen has been proposed. The divergent views on the rate-determining steps are partly explained by differences in the experimental conditions.

Simple empirical models for reaction and deactivation are sufficient for preliminary reactor and process simulations, but detailed mechanistical models are required for advanced reactor and catalyst design.¹⁰ These models must be based on a thorough understanding of the reactions involved. A proper kinetic model also requires a model for catalyst deactivation, which not only complicates the industrial reactor design but also makes kinetic experiments at the laboratory scale more demanding. The mechanism and rate of deactivation might also be different on these two scales owing to differences in mass transfer and the amounts of impurities in the raw materials. When reaction kinetics defined in the laboratory are applied to industrial-scale reactors, the deactivation kinetics must be evaluated for the conditions of the application, including the purity level of the feed, the solubility of nonreactive compounds, and so on.

In this paper, we propose a rigorous reaction and deactivation mechanism for the liquid-phase hydrogenation of naphthalene and tetralin (1,2,3,4-tetrahydronaphthalene) on a nickel catalyst. The mechanism describes the difference in the measured hydrogenation rates of naphthalene and tetralin, as well as the different deactivation kinetics involved in the hydrogenation. Experimental data obtained in separate hydrogenation studies with naphthalene¹¹ and tetralin¹² were used as a basis for the modeling. The main features of these experiments are summarized below in the Experimental Section.

* Corresponding author. Tel.: +46852065035. Fax: +46852020743. E-mail: petri.rautanen@nynas.com.

[†] Current address: Nynäs Naphthenics, Oljeraffineriet, S-14982 Nynäshamn, Sweden.

Experimental Section

Catalyst and Materials. A commercial nickel-on-alumina (16 wt % Ni) catalyst was reduced in flowing hydrogen at 400 °C. A detailed description of the activation procedure can be found in our earlier report.¹³ Sulfur- and nitrogen-free naphthalene and tetralin in decane were used for the hydrogenation experiments. Oxygen dissolved in the liquid feed during feed-vessel loading was found to have no effect on the catalyst activity. High-purity hydrogen and nitrogen (>99.999%) were used as received.

Apparatus. The hydrogenations of naphthalene and tetralin were performed in a Robinson–Mahoney reactor working in CSTR mode and equipped with static catalyst basket and magnetic stirrer.^{11,12} Continuous gas and liquid feeds were introduced into the isothermally operated reactor, and the mixture of gas and liquid products was withdrawn from the reactor. The products were flashed at room temperature at the reactor pressure, and the liquid product was analyzed with a gas chromatograph with a fused silica capillary column and a flame ionization detector.

Hydrogenation Procedure. Severe catalyst deactivation during the hydrogenation of naphthalene and tetralin suggested the use of an experimental procedure consisting of several stages, each with different reaction conditions (temperature, pressure, and initial concentration of aromatics). The durations of the stages and experiments were varied from 4 to 5.5 and from 30 to 72 h, respectively. The first, last, and every seventh stage was carried out at the reference conditions, i.e., at the same temperature, pressure, and initial concentration of aromatics. Temperature was varied from 80 to 160 °C, the hydrogen pressure from 20 to 40 bar, and the concentration of aromatics from 1 to 15 mol %. The hydrogenation procedure and process parameters are described in more detail in our earlier papers.^{11,12}

Mass-transfer resistance was studied previously in the hydrogenation of toluene.¹³ The same approach was applied during the naphthalene and tetralin hydrogenations because the mass-transfer resistances were expected to be similar. Gas–liquid and liquid–solid mass- and heat-transfer resistance were avoided by adjusting the agitation and catalyst loading. An intraparticle mass-transfer resistance could not be avoided, and it was added to the reactor model in parameter estimation. Intraparticle heat-transfer resistance was estimated to be negligible.^{11–13}

Qualitative Results—Overview

Tetralin is a primary product, and an intermediate, in naphthalene hydrogenation, i.e., naphthalene is first hydrogenated to tetralin, and tetralin is further hydrogenated through $\Delta^{1,9}$ - and $\Delta^{9,10}$ -octalin (octahydronaphthalene) to *cis*- and *trans*-decalin (decahydronaphthalene). The *cis*-to-*trans* ratio was found to be about 1:1 in naphthalene experiments and varied from 0.8:1 to 1.6:1 in tetralin experiments owing to more severe deactivation in the latter case. Indeed, the selectivity of decalin formation was observed to depend on the level of deactivation but only slightly on temperature, pressure, or the initial concentration of aromatics. The conversions of naphthalene and tetralin were always below the thermodynamic equilibrium limits.^{11,12}

Significant catalyst deactivation was observed during the hydrogenation of naphthalene and tetralin even

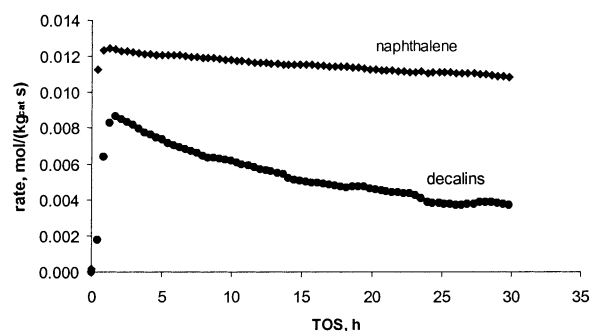


Figure 1. Reaction rate of naphthalene (squares) and formation rate of decalins (circles) at 120 °C, 20 bar, and 5 mol % initial content of naphthalene.

though no impurities were detected.^{11,12} The hydrogen pressure did not have a significant effect on the deactivation, and the temperature dependency of the deactivation was also mild. The deactivation order varied slightly as a function of temperature and was about 0.2 and 1.2 for naphthalene and tetralin, respectively. The difference in the deactivation effects is illustrated in Figure 1: the mild decrease in the rate of naphthalene hydrogenation is almost linear, whereas the rate of decalin formation is more severely inhibited. A similar nonlinear decrease was observed in the rate of tetralin hydrogenation. Thus, sequential reaction steps (each affected by about 0.2-order deactivation) cannot explain the lower deactivation during naphthalene hydrogenation. Rather, the hydrogenations of naphthalene and tetralin must take place through different reaction mechanisms, or their adsorptions onto the catalyst might be different, requiring different amounts of active sites. Furthermore, the hydrogenation of tetralin to decalins was found to be irreversible, but simultaneously some naphthalene formation occurred, even though the experiments were carried out at conditions far below the thermodynamic limit. This, too, points to differences in the hydrogenation mechanisms of naphthalene and tetralin. Reversible hydrogenation of naphthalene and irreversible hydrogenation of monoaromatics have also been reported by other research groups.^{2,6,14,15}

Reaction and Deactivation Mechanism

As noted above, little has been published on naphthalene or tetralin hydrogenation; moreover, no reports appear to exist on the hydrogenation mechanisms of these compounds on nickel. Accordingly, our derivation of the reaction and deactivation mechanism is based on qualitative studies: our previous studies on these compounds,^{11,12} experiments with naphthalene and its intermediates on noble metal catalysts,^{16–19} and studies of monoaromatics on nickel.^{1–7,15,20–25}

Adsorption. Hydrogen adsorbs dissociatively on nickel,^{23,26,27} and weakly bound hydrogen is suggested to take part in the hydrogenation of aromatic rings.^{23,27} In general, hydrogen and aromatic compounds are assumed to adsorb at different sites (noncompetitively) on nickel catalyst. Some authors have nevertheless reported the occurrence of competitive adsorption, typically corresponding to 10–15% of the total hydrogen adsorption.^{22,25} Competitively adsorbed hydrogen is strongly bonded, however, and it presumably does not take part in the hydrogenation.^{23,24,27} In view of these reports, we assumed the adsorption of hydrogen to occur

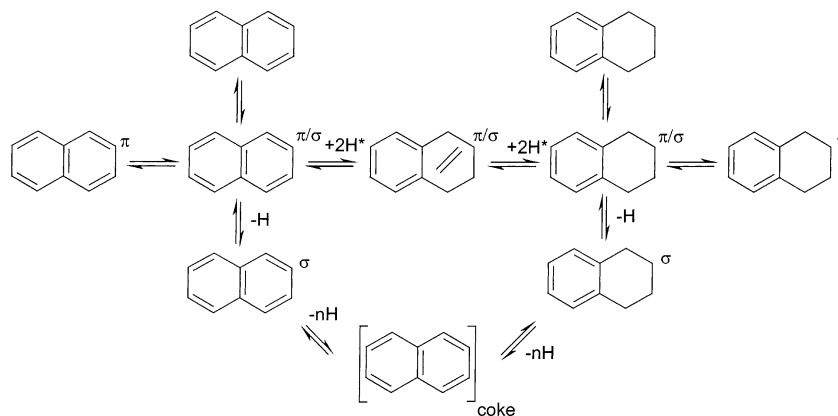
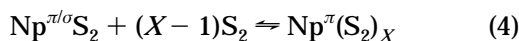
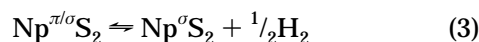
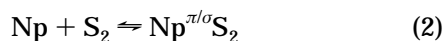


Figure 2. Reaction scheme for the hydrogenation of naphthalene to tetralin.

dissociatively on sites accessible only to hydrogen (S_1).



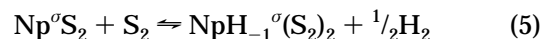
As proposed by Prasad et al.²⁰ and Tjandra and Zaera,²⁸ we assume the existence of three different adsorption forms of aromatic compounds. Naphthalene (represented by Np) and tetralin (represented by T) are assumed to adsorb through a transition state, π/σ complex, that is in equilibrium with π - and σ -bonded forms. Transition and π -bonded forms are associative, whereas the σ -bonded form is dissociative and leads to cleavage of the hydrogen atom from the aromatic ring. The π -bonded form adsorbs horizontally, lying flat on the catalyst surface. The σ -bonded form adsorbs vertically, and the transition form behaves in a manner somewhere between the π - and σ -bonded structures. Different behavior enables high surface coverage of aromatic compounds at high concentrations, as during liquid-phase hydrogenation. The assumption of different adsorption forms is supported by the results of van Meerten et al.²³ and Candy and Fouillox,¹⁵ who observed three different adsorption forms of benzene on nickel, two reactive and one nonreactive. Naphthalene adsorption can now be described by eqs 2–4.



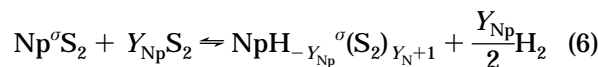
Here, we assume that multiple bonds or an ensemble of Ni atoms (active sites) is needed for the π -adsorption. This assumption is supported by several groups,^{2,6,22,23,25} who have reported that more than one nickel atom is needed for an active adsorption site. Three similar equations can be written for tetralin adsorption.

Deactivation. Because no impurities were detected in the feeds, we assumed that the catalyst deactivation was caused by (1) an inhibition due to dissociatively adsorbed aromatic compounds and (2) a dissociation of these compounds leading to coke formation. Unfortunately, no tools were available to detect or measure coke on the catalyst during the experiments. Adsorbed aromatic compounds were assumed to dissociate to coke through the σ -bonded form (eq 3) and to cause deactivation by occupying active sites. The dissociation would then proceed further and release hydrogen, with adsorbed aromatic compounds occupying additional active

sites through increased bonding. The deactivation was assumed to take place only on S_2 sites, and therefore, hydrogen was assumed to cleave directly without desorption step, as hydrogen adsorption on S_1 sites only was suggested. The first step in naphthalene dissociation (as also in tetralin dissociation) can thus be described by



The second step gives $\text{NpH}_{-2}^{\sigma}(S_2)_3$, the third step gives $\text{NpH}_{-3}^{\sigma}(S_2)_4$, and the Y_{Np} th step leads to



The corresponding steps for tetralin, with four hydrogen atoms removed, would lead to the formation of naphthalene. Indeed, traces of naphthalene were observed in the tetralin hydrogenation experiments¹² during start-up under nitrogen atmosphere and also when the catalyst was severely deactivated. Naphthalene formation during start-up could be explained by high activity of the catalyst, both in hydrogenation and in dehydrogenation, but deactivation should also hinder the dehydrogenation reaction at the end of the experiment. The formation of naphthalene at the end of experiment would thus have to be explained by a parallel formation route (side reaction) that is favored by a high tetralin concentration and a low hydrogenation rate (Figure 2). The reversibly formed hydrogen-deficient compounds (eqs 5 and 6) are probably coke precursors, and the further dissociation and polymerization of these compounds leads, irreversibly, to coke.

Surface Reactions. Naphthalene and tetralin can react through both π/σ - and π -bonded forms, but we suppose that one reaction route dominates under the conditions studied. The dominant adsorption form and reaction route depend on the catalyst (active material and support, catalyst pretreatment, and preparation) and the reaction conditions (temperature, pressure, and concentrations). These factors could explain the great diversity in the reported hydrogenation results for monoaromatic compounds on nickel catalyst.

We propose that naphthalene reacts to tetralin mainly through π/σ -adsorption, forming dihydronaphthalene as an intermediate (see Figure 2). π/σ -adsorption requires just one active site, leading to a linear dependency of active sites and deactivation, in contrast to the nonlinear dependency of π -adsorption, which requires an

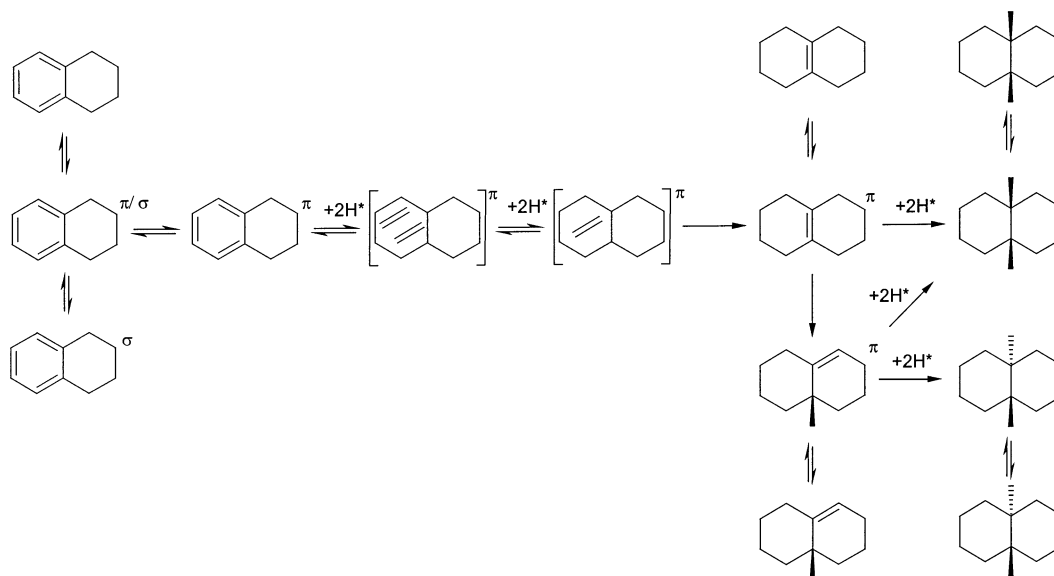
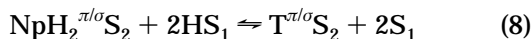
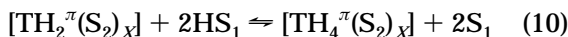
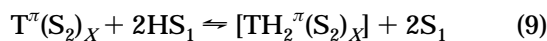


Figure 3. Reaction scheme for the hydrogenation of tetralin to *cis*- and *trans*-decalin.

ensemble of sites (eq 4). We also assume a stepwise addition of two hydrogen atoms



The nonlinear decrease in the rate of hydrogenation of tetralin with decreasing catalyst activity indicates that tetralin hydrogenation requires π -adsorption, where tetralin forms a surface complex with hydrogen and active sites. The complex is proposed to retain its aromatic nature because the formation of hexahydronaphthalene is thermodynamically limited.⁷ Indeed, no traces of hexahydronaphthalene were found among the products.

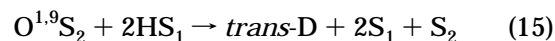
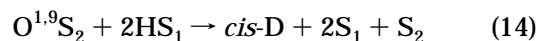
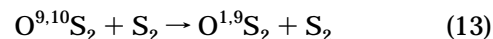
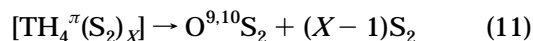


According to our mechanism, the hydrogenation of tetralin should be sensitive to catalyst structure, as several active sites are required, and the hydrogenation of naphthalene should be structure-insensitive. No consensus exists concerning the structure sensitivity of the hydrogenation of aromatic compounds, as is evident in the discussions of Che and Bennett²⁹ and, more recently, Marécot et al.²⁴

The different reaction steps for naphthalene and tetralin hydrogenation can be explained by the difference in aromaticity:^{19,30,31} the π -electron density of the aromatic ring of tetralin is higher than that of naphthalene, and hence, the resonance energy of the aromatic ring is greater in tetralin than in naphthalene.^{19,30} According to our model, the aromaticity of the first ring in naphthalene is so weak that it will react through the transition state (π/σ -adsorption). However, the aromaticity of the remaining ring (tetralin) is much stronger, so this ring requires π -adsorption to be hydrogenated. π -adsorbed tetralin then forms surface complexes, as

presented in eqs 9–10 and in Figure 3, whereas naphthalene is hydrogenated through dihydronaphthalene as illustrated in Figure 2.

The surface complex of tetralin [$TH_4^{\pi}S_2$] is isomerized to $\Delta^{9,10}$ -octalin, which is further hydrogenated to *cis*-decalin or isomerized to $\Delta^{1,9}$ -octalin. Thus, *cis* addition of hydrogen was assumed, leading to the formation of *cis*-decalin from $\Delta^{9,10}$ -octalin and of both *cis*- and *trans*-decalin from $\Delta^{1,9}$ -octalin. These hydrogenation steps must be irreversible because we did not observe any formation of octalins when using *cis*- or *trans*-decalin as the reactant. Nor did we observe any isomerization of decalins, although this has been reported to occur at elevated temperatures.^{14,16,19} We also assumed irreversible isomerization of octalins, as reported by Smith and Burwell.¹⁸ Weitkamp¹⁷ reports that the isomerization of octalins is, in practice, irreversible on noble metal catalysts because of the high hydrogenation rate of $\Delta^{1,9}$ -octalin compared to $\Delta^{9,10}$ -octalin (i.e., $\Delta^{1,9}$ -octalin is hydrogenated to *cis*- and *trans*-decalin rather than being isomerized to $\Delta^{9,10}$ -octalin).¹⁸ The reaction steps from the tetralin surface complex to *cis*- and *trans*-decalin can now be described by the following equations



The isomerization of $\Delta^{9,10}$ -octalin must require an additional active site because deactivation causes changes in the selectivity to octalins. Thus, the formation of $\Delta^{1,9}$ -octalin is more severely affected by deactivation, and as the reaction proceeds, the *cis*-to-*trans* ratio changes as the active sites become blocked with coke or σ -bonded

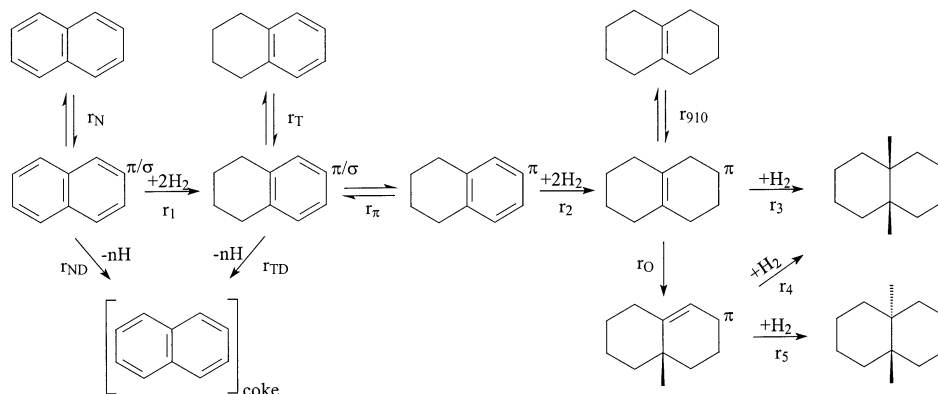
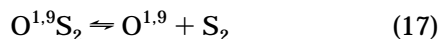
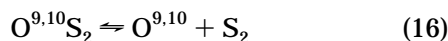


Figure 4. Simplified reaction scheme for naphthalene and tetralin hydrogenation in the kinetic modeling.

aromatics. Octalins were also observed among the products, and their desorption equilibrium can be expressed as



Kinetic Modeling

The estimation of kinetic parameters was performed by minimizing the error of the calculated and experimental mole fractions, which were obtained by adding a kinetic model to a reactor model. The reactor model consisted of dynamic mole balances for the bulk gas and liquid phases and the interior of the catalyst particles. A detailed description of the reactor model can be found elsewhere.¹²

Hydrogenation Kinetics. The kinetic model was based on the proposed reaction schemes (Figures 2 and 3), but with some simplifications made to reduce the number of parameters and avoid excess correlation between parameters. The simplified reaction scheme is depicted in Figure 4. The formation of dihydronaphthalene was excluded because this compound was not detected among the products. The surface coverage of π -adsorbed naphthalene was assumed to be negligible, and the hydrogenation of naphthalene was assumed to proceed only through the π/σ -adsorption state. The hydrogenation of naphthalene was considered irreversible, and the formation of naphthalene through the dissociation of tetralin was also excluded because only minor amounts of naphthalene were observed (<0.17 mol %). The desorption of $\Delta^{1,9}$ -octalin was excluded as well, because only traces of this compound were detected and only in some experiments. Finally, the hydrogenation reactions were assumed to be much faster than the reactor dynamics and thus to be in quasi steady state even though the reactor mole balances were dynamic.

Langmuir adsorption was assumed for reactants and intermediates. Huang and Kang¹⁶ showed that the adsorption of decalins on a Pt catalyst is weak in the presence of naphthalene and tetralin, and on this basis, we assumed that the surface coverage of decalins was negligible. Adsorption of the reactants was assumed to be fast relative to the surface reaction steps. The

adsorption equilibrium of aromatics was then described by eqs 18–20.

$$K_{Np} = \frac{\Theta_{Np}}{\Theta_v c_{Np}} \quad (18)$$

$$K_T = \frac{\Theta_T}{\Theta_v c_T} \quad (19)$$

$$K_\pi = \frac{\Theta_{T,\pi}}{\Theta_v^{X-1} \Theta_T} \quad (20)$$

Noncompetitive dissociative adsorption of hydrogen was assumed, as noted above.

$$K_H = \frac{\Theta_H^2}{\Theta_w^2 c_H} \quad (21)$$

The deactivation mechanism was also simplified. Inhibition of the σ -adsorbed form of naphthalene and tetralin and the formation of coke precursors was combined, and a hydrogen-deficient species (a coke) was assumed to form directly from π/σ -adsorbed aromatics. The average rates of dissociation of naphthalene and tetralin were described by eqs 22 and 23, respectively.

$$r_{NpD} = k_{NpD} \Theta_{Np} \Theta_v^{Y_{N+1}} \quad (22)$$

$$r_{TD} = k_{TD} \Theta_T \Theta_v^{Y_{T+1}} \quad (23)$$

We assumed that coke formation did not have a significant effect on the intraparticle diffusion; that is, pore mouth blockage and pore diameter shrinkage were not considered in the model. The observed deactivation rate describes the loss of active sites rather than the total rate of formation of coke, which is presumed to be formed also on support. Henceforward, the rate of coke accumulation refers to the blockage of active sites. The rate of coke accumulation is equal to the sum of the dissociation rates

$$\Psi \frac{d\Theta_{\text{coke}}}{dt} = r_{TD} + r_{NpD} \quad (24)$$

$$\Theta_{\text{coke}}|_{t=0} = 0 \quad (25)$$

The reaction rates of naphthalene, tetralin, octalins, and hydrogen were derived from the reaction mecha-

nism (Figure 4), assuming a stepwise cis addition of two hydrogen atoms.

$$r_1 = k_1 K_{\text{Np}} K_{\text{H}}^2 c_{\text{Np}} c_{\text{H}}^2 \Theta_{\text{v}} \Theta_{\text{w}}^4 \quad (26)$$

$$r_2 = k_2 K_{\pi} K_{\text{T}} K_{\text{H}}^2 c_{\text{T}} c_{\text{H}}^2 \Theta_{\text{T}} \Theta_{\text{v}}^X \Theta_{\text{w}}^4 \quad (27)$$

$$r_3 = k_3 K_{\text{H}} c_{\text{H}} \Theta_{9,10} \Theta_{\text{w}}^2 \quad (28)$$

$$r_4 = k_4 K_{\text{H}} c_{\text{H}} \Theta_{1,9} \Theta_{\text{w}}^2 \quad (29)$$

$$r_5 = k_5 K_{\text{H}} c_{\text{H}} \Theta_{1,9} \Theta_{\text{w}}^2 \quad (30)$$

$$r_0 = k_0 \Theta_{9,10} \Theta_{\text{v}} \quad (31)$$

Thus, the formation rates of the decalins are given by

$$r_{\text{cis}} = r_3 + r_4 \quad (32)$$

$$r_{\text{trans}} = r_5 \quad (33)$$

The rates of naphthalene and tetralin dissociation, being several orders of magnitude lower than the hydrogenation rates, were excluded from the consumption rates of reactants, which were

$$-r_{\text{Np}} = r_1 \quad (34)$$

$$-r_{\text{T}} = r_{9,10} + r_{\text{cis}} + r_{\text{trans}} \quad (35)$$

$$-r_{\text{H}} = 2(r_1 + r_2) + r_3 + r_4 + r_5 - \frac{Y_{\text{Np}}}{2} r_{\text{NpD}} - \frac{Y_{\text{T}}}{2} r_{\text{TD}} \quad (36)$$

However, because tetralin was an intermediate formed in the hydrogenation of naphthalene, the generation rate for tetralin was obtained from the difference between the desorption and adsorption rates

$$r_{\text{T}} = k_{\text{d}} \Theta_{\text{T}} - k_{\text{a}} c_{\text{T}} \Theta_{\text{v}} \quad (37)$$

As a way to reduce the number of parameters, we applied the quasi-equilibrium approximation for the adsorption of intermediates, i.e., we assumed that the desorption and adsorption rates were significantly higher than their difference (formation of tetralin). The adsorption equilibrium constant could then be used instead of the adsorption and desorption coefficients, and the formation rate of tetralin could be calculated from the mole balance according to

$$r_{\text{T}} = r_1 - (r_{\text{TD}} + r_2) \quad (38)$$

A similar approach was used to calculate the formation rate of $\Delta^{9,10}$ -octalin, which is an intermediate in the hydrogenation of both naphthalene and tetralin

$$r_{9,10} = r_2 - (r_3 + r_0) \quad (39)$$

Surface coverages on the catalyst were solved from rate eqs 26–31 by assuming steady-state conditions for the surface steps. The surface coverages of the reactants were calculated from eqs 18–21. The surface coverage of $\Delta^{9,10}$ -octalin was calculated from the equation

$$\Theta_{9,10} = K_{9,10} c_{9,10} \Theta_{\text{v}} \quad (40)$$

The surface coverage of $\Delta^{1,9}$ -octalin is then given by

$$\Theta_{1,9} = \frac{k_0 K_{9,10} c_{9,10} \Theta_{\text{v}}}{(k_4 + k_5) K_{\text{H}} c_{\text{H}} \Theta_{\text{w}}^2} \quad (41)$$

The sum of the surface coverages describes the site balances

$$\Theta_{\text{v}} + \Theta_{\text{Np}} + \Theta_{\text{T}} + \Theta_{\pi} + \Theta_{9,10} + \Theta_{1,9} + \Theta_{\text{coke}} = 1 \quad (42)$$

$$\Theta_{\text{H}} + \Theta_{\text{w}} = 1 \quad (43)$$

Surface coverages were solved from eqs 18–21, 24, and 40–43, which form a nonlinear equation system. The system was solved numerically (Newton's method) with respect to the number of vacant sites, Θ_{v} . In these equations, the temperature dependency of the rate constants was described by the Arrhenius law and the adsorption coefficients by the van't Hoff equation.

Parameter Estimation. Parameter estimation was performed by minimizing the sum of the errors between the estimated and observed mole fractions for each observation point, $y_i(t_j)$

$$\text{RSS} = \sum_j \sum_i \frac{1}{y_i(t_j)} [y_i(t_j) - y_{i,\text{est}}(t_j)]^2 \quad (44)$$

Equation 44 was minimized with the Levenberg–Marquardt optimization method, with calculations carried out by the in-house optimization program KINFIT.³² A modified Arrhenius law was introduced (eq 45) to minimize the coupling of the rate frequency factors and activation energies ($T_{\text{ref}} = 110$ °C).

$$k = k(T_{\text{ref}}) \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (45)$$

A similar approach was applied to calculate the adsorption parameters.

Simultaneous estimation of the kinetic parameters for the two experimental sets together (naphthalene and tetralin as reactants) did not give a satisfactory results, and the two sets were therefore estimated separately. Unsuccessful simultaneous estimation was most probably caused by the more severe deactivation in tetralin hydrogenation compared to naphthalene hydrogenation. Normalization between the naphthalene and tetralin experiments was also not possible because of the difference in standard stages.

The good fit obtained for naphthalene is illustrated in Figure 5. The estimation results are presented in Tables 1 and 2. The dissociation rate constant for naphthalene, k_{NpD} , is significantly lower than the dissociation rate constant for tetralin, k_{TD} . A difference was also observed between the dissociation rates, r_{NpD} and r_{TD} , which means that the high dissociation rate of tetralin leads to a higher formation rate of hydrogen-deficient species, which occupy the catalyst surface and bring about deactivation.

The parameters of naphthalene dissociation were difficult to identify because of the low deactivation (i.e., dissociation) rate. The degree of dissociation approached zero, indicating that the naphthalene did not dissociate (form coke). This led to an unstable identification of the apparent activation energy of naphthalene dissociation. The dissociation factor, Y_{Np} , and activation energy of dissociation, E_{NpD} , were therefore fixed to zero in order

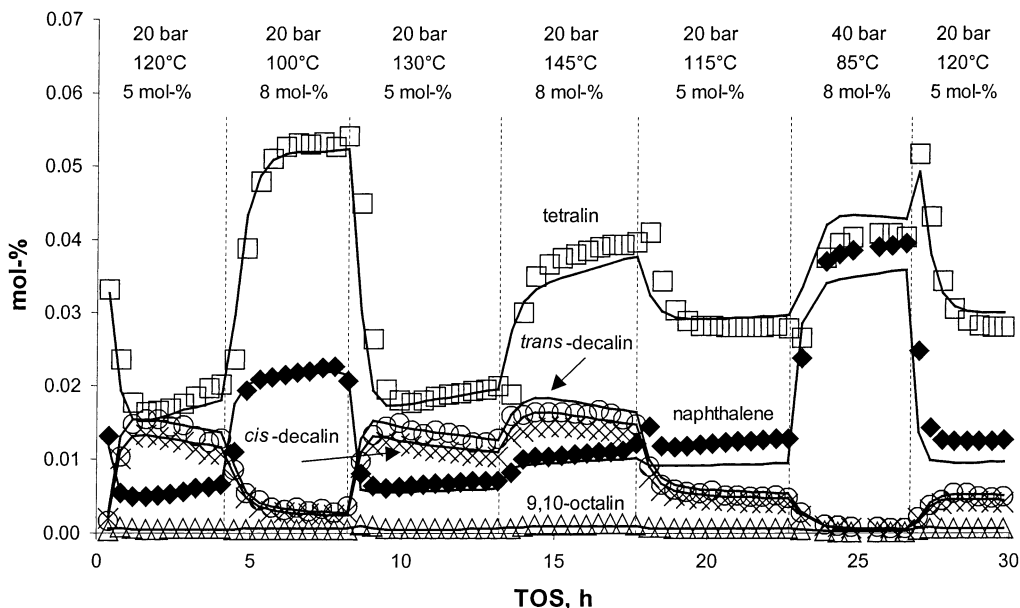


Figure 5. Estimated (lines) and observed (symbols) mole fractions in naphthalene hydrogenation experiment N8.¹¹

Table 1. Parameters of Kinetic Model of Naphthalene Hydrogenation with 95% Confidence Intervals

| Deactivation Kinetics | | | | | |
|--|---|---|---|---|---|
| $k_{\text{NpD}}(T_{\text{ref}}) \times 10^5$ (mol kg _{cat} ⁻¹ s ⁻¹) | E_{NpD} (kJ mol ⁻¹) | Y_{Np} | $k_{\text{TD}}(T_{\text{ref}}) \times 10^5$ (mol kg _{cat} ⁻¹ s ⁻¹) | E_{TD} (kJ mol ⁻¹) | Y_{T} |
| 1.3 ± 0.2 | 0 ^b | 0 ^b | 7.6 ± 3.1 | 68 ± 9 | 3.1 ± 0.2 |
| Hydrogenation Kinetics | | | | | |
| rate parameters | | | | | |
| $k_1(T_{\text{ref}})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_2(T_{\text{ref}})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_3(T_{\text{ref}})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_0(T_{\text{ref}})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_4(T_{\text{ref}})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_5(T_{\text{ref}})$ (mol kg _{cat} ⁻¹ s ⁻¹) |
| 1.4 ± 0.2 | 0.73 ± 0.45 | 0.03 ^a | 3.5 ^a | 130 ^a | 160 ^a |
| E_1 (kJ mol ⁻¹) | E_2 (kJ mol ⁻¹) | E_3 (kJ mol ⁻¹) | E_0 (kJ mol ⁻¹) | E_4 (kJ mol ⁻¹) | E_5 (kJ mol ⁻¹) |
| 90 ± 4 | 99 ± 15 | 140 ± 100 | 66 ^a | 57 ^a | 57 ^a |
| adsorption parameters | | | | | |
| $K_{\text{Np}}(T_{\text{ref}}) \times 10^3$ (m ³ mol ⁻¹) | $K_{\text{T}}(T_{\text{ref}}) \times 10^3$ (m ³ mol ⁻¹) | $K_{\pi}(T_{\text{ref}})$ (m ³ mol ⁻¹) | $K_{9,10}(T_{\text{ref}}) \times 10^3$ (m ³ mol ⁻¹) | $K_{\text{H}}(T_{\text{ref}}) \times 10^3$ (m ³ mol ⁻¹) | |
| 24 ± 3 | 1.7 ± 0.5 | 2.3 ± 2.1 | 3.3 ^a | 22 ± 4 | |
| $-\Delta H_{\text{Np}}$ (kJ mol ⁻¹) | $-\Delta H_{\text{T}}$ (kJ mol ⁻¹) | $-\Delta H_{\pi}$ (kJ mol ⁻¹) | $-\Delta H_{9,10}$ (kJ mol ⁻¹) | $-\Delta H_{\text{H}}$ (kJ mol ⁻¹) | |
| 32 ± 6 | 1 ^a | 15 ^a | 24 ^a | 45 ± 5 | |
| X | | | | | |
| 2.1 ± 0.1 | | | | | |

^a Very large confidence interval. ^b Fixed value.

not to violate the termination conditions (i.e., relative change of parameters less than 1.0×10^{-4} or sum of squares, RSS, less than 1.0×10^{-6}). The temperature dependency of tetralin dissociation was about 68 and 28 kJ/mol during the naphthalene and tetralin hydrogenations, respectively. The average dissociation factor of tetralin, Y_{T} , suggests that tetralin loses about 2–3 hydrogen atoms.

The losses in entropy due to the adsorption during naphthalene hydrogenation were 120, 110, and 150 J/(mol K) for naphthalene, $\Delta^{9,10}$ -octalin, and hydrogen, respectively [calculated from $K_i(T_{\text{ref}})$; see Tables 1 and 2], whereas during tetralin hydrogenation, the loss was 160 J/(mol K) for $\Delta^{9,10}$ -octalin and 140 J/(mol K) for hydrogen. The low content of $\Delta^{9,10}$ -octalin (<0.5%)

caused a large deviation and confidence interval in the adsorption entropy, as well as in other parameters describing $\Delta^{9,10}$ -octalin adsorption and reaction. The change in the entropy of hydrogen, ΔS_{H} , suggests that the adsorbed hydrogen is not mobile on the catalyst, as the gas-phase entropy of hydrogen is close to the adsorption entropy. The losses in entropy of π/σ - and π -bonded tetralin were 55 and 86 J/(mol K), respectively, during naphthalene hydrogenation and 75 and 110 J/(mol K), respectively, during tetralin hydrogenation. Thus, the losses in entropy due to the adsorption of reactive naphthalene and tetralin were very similar.

The adsorption enthalpy of naphthalene was about 32 kJ/mol, whereas the enthalpies of $\Delta^{9,10}$ -octalin were 24 and 43 kJ/mol (in naphthalene and tetralin hydro-

Table 2. Parameters of Kinetic Model of Tetralin Hydrogenation with 95% Confidence Intervals

| Deactivation Kinetics | | | | |
|---|--|---|--|--|
| $k_{TD}(T_{ref}) \times 10^5$ (mol kg _{cat} ⁻¹ s ⁻¹) | E_{TD} (kJ mol ⁻¹) | Y_T | | |
| 6.2 ± 0.4 | 28 ± 5 | 1.9 ± 0.1 | | |
| Hydrogenation Kinetics | | | | |
| $k_2(T_{ref})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_3(T_{ref})$ (mol kg _{cat} ⁻¹ s ⁻¹) | rate parameters $k_0(T_{ref})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_4(T_{ref})$ (mol kg _{cat} ⁻¹ s ⁻¹) | $k_5(T_{ref})$ (mol kg _{cat} ⁻¹ s ⁻¹) |
| 0.90 ± 0.10 | 0.06 ^a | 3.3 ^a | 140 ± 40 | 170 ± 40 |
| E_2 (kJ mol ⁻¹) | E_3 (kJ mol ⁻¹) | E_0 (kJ mol ⁻¹) | E_4 (kJ mol ⁻¹) | E_5 (kJ mol ⁻¹) |
| 92 ± 7 | 120 ± 25 | 63 ± 21 | 56 ± 21 | 63 ± 20 |
| adsorption parameters | | | | |
| $K_T(T_{ref}) \times 10^3$ (m ³ mol ⁻¹) | $K_\pi(T_{ref})$ (m ³ mol ⁻¹) | $K_{9,10}(T_{ref}) \times 10^3$ (m ³ mol ⁻¹) | $K_H(T_{ref}) \times 10^3$ (m ³ mol ⁻¹) | |
| 1.4 ± 0.1 | 3.4 ± 0.2 | 3.0 ^a | 32 ± 2 | |
| $-\Delta H_T$ (kJ mol ⁻¹) | $-\Delta H_\pi$ (kJ mol ⁻¹) | $-\Delta H_{9,10}$ (kJ mol ⁻¹) | $-\Delta H_H$ (kJ mol ⁻¹) | |
| 8 ± 3 | 18 ± 8 | 43 ± 20 | 41 ± 5 | |
| X | | | | |
| 2.7 ± 0.1 | | | | |

^a Very large confidence interval. ^b Fixed value.

genation, respectively). The corresponding values for and π/σ -bonded tetralin were 1 and 8 kJ/mol, and those for π -bonded tetralin were 15 and 18 kJ/mol. The adsorption enthalpy of $\Delta^{9,10}$ -octalin, like the adsorption entropy, exhibited a large deviation and confidence interval, which is an indication of the unstable identification associated with the low content of $\Delta^{9,10}$ -octalin. The reactive compounds had adsorption enthalpies of about 20–30 kJ/mol, indicating energetically weak adsorption with a high surface coverage. However, the adsorption equilibrium coefficient was almost an order of magnitude higher for naphthalene than for tetralin or $\Delta^{9,10}$ -octalin. This difference suggests that naphthalene dominated on the catalyst surface and partly explains the higher rate of naphthalene hydrogenation compared to tetralin hydrogenation. The adsorption enthalpy of hydrogen was 45 kJ/mol in naphthalene and 41 kJ/mol and tetralin hydrogenation, likewise indicating a high surface coverage of naphthalene.³³ The increased solubility of hydrogen at elevated temperatures increases the hydrogenation rate, compensating for the decreased adsorption and resulting in an increasing rate with increasing temperature throughout the studied temperature interval. At still higher temperatures, the hydrogenation rates would clearly start to decrease, which would cause a maximum in the reaction rate, as is widely reported for gas-phase hydrogenations.^{3,4,9}

According to our estimation, π -adsorbed tetralin occupied 2–3 active sites (Tables 1 and 2). This is close to the values reported by Mirodatos et al.,² Myers et al.,³⁴ and Martin and Dalmon,³⁵ but slightly lower than those reported by van Meerten et al.¹ (about 5) and Candy and Fouillox²⁵ (about 6). The active site for the hydrogenation of tetralin requires, therefore, an ensemble of Ni atoms, and tetralin hydrogenation can be considered to be structure-sensitive to very fine nickel particles. This view is consistent with that of Che and

Bennett.²⁹ It also explains the difference between the hydrogenation rates of naphthalene and tetralin: the decrease in the rate of naphthalene hydrogenation is linear, but the decrease in the rate of tetralin hydrogenation to decalins is more severely affected (see Figure 1) because tetralin requires an ensemble of Ni atoms.

As can be seen in Tables 1 and 2, the rate constant for the reaction of naphthalene to tetralin, $k_1(T_{ref})$, is similar in value to the rate constant for the reaction of tetralin to $\Delta^{9,10}$ -octalin, $k_2(T_{ref})$. However, a comparison of the rate constants is not relevant in our case because different types of adsorption are involved and both rate constants, k_1 and k_2 , are lumped factors of at least two reaction steps. It is more useful, therefore, to compare the reaction rates of naphthalene (r_1) and tetralin (r_2). It should be emphasized that the reaction rate of tetralin is more sensitive to deactivation than that of naphthalene, and the ratio of r_1 to r_2 thus increases during the experiment. The ratio was about 2 under the standard conditions at the beginning of experiment and about 5 at the end of the experiment; in between, it varied from 1.5 to 77, depending on the process conditions and was typically about 10. This is slightly lower than the values reported by Cooper and Donniss⁹ and Girgis and Gates¹⁴ for hydrogenation on sulfided catalysts, which ranged from 20 to 40. Similarly, Weitkamp¹⁹ reported a 25 times larger rate for naphthalene than tetralin on noble metal catalysts.

Low temperature favored naphthalene hydrogenation relative to tetralin hydrogenation, largely because of the difference in the activation energies E_{Np} and E_T . These activation energies (Tables 1 and 2) imply that a greater energy barrier has to be overcome to saturate the aromatic ring than to saturate the single double bond (octalin) and also easier hydrogenation of naphthalene to tetralin than of tetralin to octalin. This is consistent with our earlier assumptions: hydrogenation of the first ring of naphthalene occurs more easily than hydrogenation

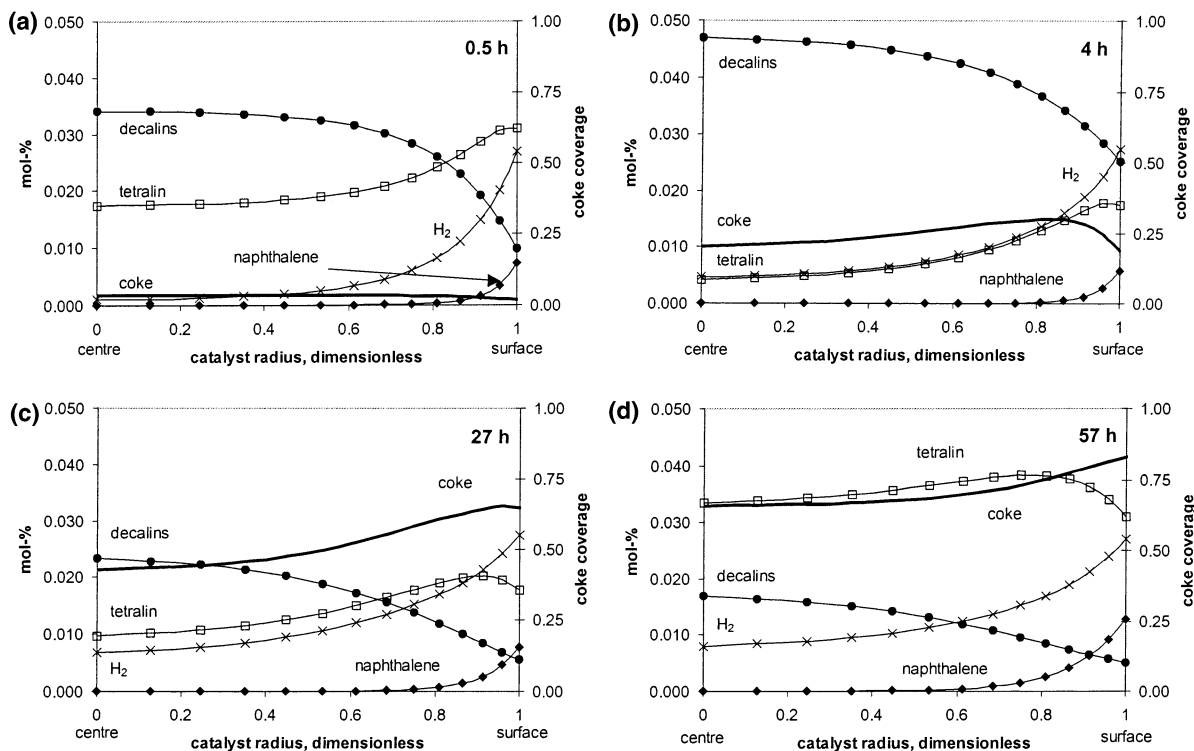


Figure 6. Liquid mole fractions in the catalyst and coke coverage on the catalyst surface calculated for a typical experiment (naphthalene hydrogenation at 120 °C, 20 bar, and 5 mol % initial content of naphthalene) after (a) 0.5, (b) 4, (c) 27, and (d) 57 h.

tion of the second ring (tetralin) because the resonance energy of the first ring is lower.^{30,31}

The hydrogenation rate of $\Delta^{9,10}$ -octalin to *cis*-decalin, r_3 , was 1–3 orders of magnitude lower than the isomerization rate of $\Delta^{9,10}$ -octalin to $\Delta^{1,9}$ -octalin, r_6 , or the hydrogenation rates of $\Delta^{1,9}$ -octalin to *cis*- and *trans*-decalin, r_4 and r_5 . The activation energies of $\Delta^{9,10}$ -octalin hydrogenation, about 140 and 120 kJ/mol in naphthalene and tetralin hydrogenation, respectively (Tables 1 and 2), were much higher than the corresponding activation energies of isomerization, 66 and 63 kJ/mol, or of $\Delta^{1,9}$ -octalin hydrogenation, 57 and 56 kJ/mol to *cis*-decalin and 57 and 63 kJ/mol to *trans*-decalin. Thus, it is easier to isomerize than hydrogenate $\Delta^{9,10}$ -octalin and easier to hydrogenate $\Delta^{1,9}$ - than $\Delta^{9,10}$ -octalin. These findings were in good agreement with our experimental observations¹¹ and the results of Weitkamp¹⁷ and Smith and Burwell.¹⁸

The intraparticle mass-transfer resistance had a significant effect, as seen from Figure 6. The naphthalene was most severely affected, whereas tetralin and hydrogen exhibited milder mass-transfer resistance. Still, no heat-transfer limitations were indicated (according to the modeling) because of the low initial concentration of aromatic compounds. Mass-transfer limitations became milder as the catalyst lost some activity due to coking, and the effectiveness factor with respect to the naphthalene hydrogenation rate, r_1 , increased, typically from about 17 to 35% during a 30-h experiment.

The simulated surface coverage of coke during the standard sequences is illustrated in Figure 6. The coke profile for the catalyst is flat at the beginning of the experiment (Figure 6a) but assumes a parabolic shape at the end of the first standard sequence, after 4 h (Figure 6b). The coke profile becomes linear again at the end of experiment, as seen in Figure 6c and d. The parabolic shape of the coke distribution at 4 h can be

explained in terms of the similar shape for adsorbed tetralin, which, as described above, dissociates and forms coke more readily than naphthalene.

Conclusions

A new reaction and deactivation mechanism was proposed for the hydrogenation of naphthalene and tetralin on a nickel catalyst. The model includes three adsorption modes (π -, π/σ -, and σ -adsorption), of which two are active in hydrogenation and one dissociative, the latter leading to coke formation and catalyst deactivation. Naphthalene is hydrogenated to tetralin through sequential *cis*-addition steps of two dissociatively adsorbed hydrogen atoms. Tetralin forms surface complexes with the adsorbed hydrogen and active sites, and these complexes react to $\Delta^{9,10}$ -octalin, which is either hydrogenated to *cis*-decalin or isomerized to $\Delta^{1,9}$ -octalin. $\Delta^{1,9}$ -Octalin is, in turn, hydrogenated to *cis*- and *trans*-decalin.

The results indicate that catalyst deactivation is caused by tetralin dissociation; the dissociation rate of naphthalene is relatively insignificant. Hydrogenation of π -bonded tetralin requires an ensemble of Ni atoms, so that catalyst deactivation causes a more severe decrease in the hydrogenation rate of tetralin than in the hydrogenation rate of naphthalene.

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Notation

c = concentration, $\text{m}^3 \text{mol}^{-1}$
 E = activation energy, kJ mol^{-1}

ΔH = adsorption enthalpy, kJ mol^{-1}
 k = reaction rate constant, $\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$
 K = adsorption equilibrium constant, mol m^{-3}
 r = reaction rate, $\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$
 R = gas constant, $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$
 ΔS = adsorption entropy, $\text{J mol}^{-1} \text{ K}^{-1}$
 t = time, s
 T = temperature, K
 X = number of active sites occupied by a π -adsorbed compound
 Y = degree of dissociation
 y = liquid mole fraction
 $[]$ = surface complex

Sub- and Superscripts

calc = calculated
 exp = experimental
 H = hydrogen
 i = compound i
 j = discretization piece j
 Np = naphthalene
 T = tetralin
 1,9 = $\Delta^{1,9}$ -octalin
 9,10 = $\Delta^{9,10}$ -octalin

Greek Letters

π = π -adsorbed compound
 π/σ = π/σ -adsorbed (transition-state) compound
 Θ = fraction of vacant sites on the catalyst
 σ = σ -adsorbed compound
 Ψ = adsorption sites for aromatic compounds on catalyst, $\text{mol kg}_{\text{cat}}^{-1}$

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