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Kinetic models for catalytic reactions from first principles: benzene hydrogenation

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A fundamental kinetic model was constructed from first principles for the hydrogenation of benzene over a Pt(111) catalyst. Benzene adsorbs at the hollow and the bridge sites of the Pt(111) surface. Benzene at the hollow site is the reactive species, whereas benzene at the bridge site is too strongly bound. Hydrogenation follows a Horiuti–Polanyi mechanism. A reaction path analysis based on quantum chemical density functional theory calculations indicates that the fifth hydrogenation step is the rate determining step with an activation energy of 104 kJ mol^{-1}. From the first principles reaction path analysis, a Langmuir–Hinshelwood–Hougen–Watson rate equation was constructed using first principles kinetic and thermodynamic data. Only the coverage-dependent hydrogen adsorption enthalpy was regressed to accurately (*F* value of 38 500) model laboratory scale data for the hydrogenation of toluene over a Pt–ZSM-22 catalyst. The optimized hydrogen adsorption enthalpy of -68.8 ± 2 kJ mol^{-1} is intermediate between the low and high coverage value of -94.0 and -45.0 kJ mol^{-1} respectively.

1. Introduction

Quality as well as environmental and legal concerns continue to impose stricter limits on the aromatic content of fuels [1]. Hydrocracking of hydrocarbon feedstock for the production of high-quality fuels is perhaps the most important process in petroleum refining. Typical hydrocracking feedstocks contain an important aromatic fraction. An accurate model for the conversion of aromatics is therefore important in the construction of a kinetic model for this process. Hydrocracking is typically carried out over bifunctional transition metal–zeolite catalysts.

As a model system for the hydrogenation of aromatic molecules over the transition metal phase of the hydrocracking catalyst, the hydrogenation of benzene over a Pt(111) surface was investigated from first principles. Many kinetic as well as spectroscopic and surface science studies have been performed for the adsorption and dehydrogenation of different cyclic C6 molecules over Pt(111) (e.g. [2, 3]). Also, some theoretical studies have addressed the adsorption and hydrogenation/dehydrogenation of cyclic hydrocarbons (for an overview, see [3]). Nevertheless, many mechanistic details of benzene hydrogenation are still not well understood. However, these experimental studies provide invaluable input to benchmark and validate the *ab initio* calculations.

The quantum chemical study presented in this paper provides fundamental insight into the reactions that occur on the catalyst surface, which allows postulating a fundamental kinetic reaction mechanism from first principles. The calculations further yield reasonable values for thermodynamic and kinetic parameters. In combination with a limited number of laboratory scale experiments, a fundamental kinetic model is constructed, which can be implemented in mathematical reactor models for the simulation of industrial units.

The main challenge is to bridge the large gap between the molecular level of the quantum chemical calculations and the macroscale of the industrial reactor. To meet this challenge, a systematic approach at different levels was pursued: from the *ab initio* kinetic and thermodynamic parameters, to reaction path analysis and the reaction mechanism, followed by the rate equations and finally a laboratory reactor simulation.

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The approach will be illustrated in this paper for the hydrogenation of aromatic molecules over a Pt–ZSM-22 catalyst.

2. Computional methods

The selection of an adequate quantum chemical method is not an easy task. Studying benzene hydrogenation requires a rather large number of platinum atoms to model the catalyst and platinum is a heavy metal with many electrons for which relativistic effects determine up to 50% of the bond strength. The best *ab initio* method to study this reaction was found to be relativistic density functional theory with the Becke–Perdew (BP86) functional (see, e.g. [4]). Scalar relativistic effects were included through the zero-order regular approximation (ZORA) Hamiltonian [5]. Basis sets were of double-zeta quality and constructed from Slater-type orbitals (STO). The innermost atomic shells were kept frozen and replaced by a fully relativistic core density. The Pt(111) catalyst was modelled by a two-layered Pt_{22} cluster with 14 atoms in the top layer. The Pt–Pt distance was constrained at the bulk value of 277 pm. Adsorption and reaction were studied on the central atoms of the top layer of this cluster. All calculations were carried out using the Amsterdam density functional (ADF2000) computational package [5]. In previous publications we have demonstrated that this approach yields reasonably accurate adsorption energies for benzene [6], 1,4-cyclohexadiene [7] and cyclohexene [8] adsorption on Pt(111), as well as activation energies for cyclohexadiene dehydrogenation [3], both in comparison with fully periodic slab calculations or with known experimental data. The accuracy of density functional theory for the prediction of adsorption energies and activation energies is often stated to be within $20\,\mathrm{kJ\,mol^{-1}}$ of reported experimental values, although relative values are often found to be more accurate [9].

To improve the accuracy of the *ab initio* energy diagram we started from accurate gas-phase standard enthalpies of formation of the intermediates. These were obtained from experimental data or from high-level atom additivity corrected CBS-QB3 [10] calculations. The energy diagram of the adsorbed intermediates was obtained by combining the gas-phase standard enthalpies of formation with adsorption energies from density functional theory. This procedure was shown to improve the accuracy by approximately including thermal and zero-point energy effects [3].

3. Results and discussion

Two objectives were put forward in this study. The first was to construct an adequate kinetic model based on a detailed reaction path analysis using the first principles data. This is a qualitative goal. Second, the kinetic and thermodynamic parameters need to be calculated from first principles with accuracy suitable for kinetic modelling.

Benzene adsorption was studied in great detail, including fully periodic slab calculations [6]. Adsorption energies at the different sites of the Pt(111) surface were calculated. Two sites were found to be important, the hollow and the bridge site (figure 1). Thermodynamic considerations and comparison of the calculated vibrational spectra with experimental data revealed that adsorption at the bridge site is preferred at low coverage, while adsorption at the hollow site becomes more important at higher, catalytically more relevant, coverages. These findings provide new insight into the adsorption of benzene, differing from previous assignments based upon the experimental spectra. The calculated adsorption energies of -102 and $-75\,\mathrm{kJ\,mol^{-1}}$ are in agreement with experimental values. These findings were recently confirmed by Morin *et al.* [11].

Hydrogen adsorption on Pt(111) is strongly coverage dependent [3, 12]. The *ab initio* calculations reproduced the experimental low coverage adsorption enthalpy of $-94.0\,\mathrm{kJ\,mol^{-1}}$. High surface mobility of the hydrogen atom was found [3].

Benzene hydrogenation follows a Horiuti–Polanyi-type mechanism [3]. Hydrogen atoms add sequentially to the adsorbed benzene molecule. Several reaction paths are possible. The questions raised are (i) is there a

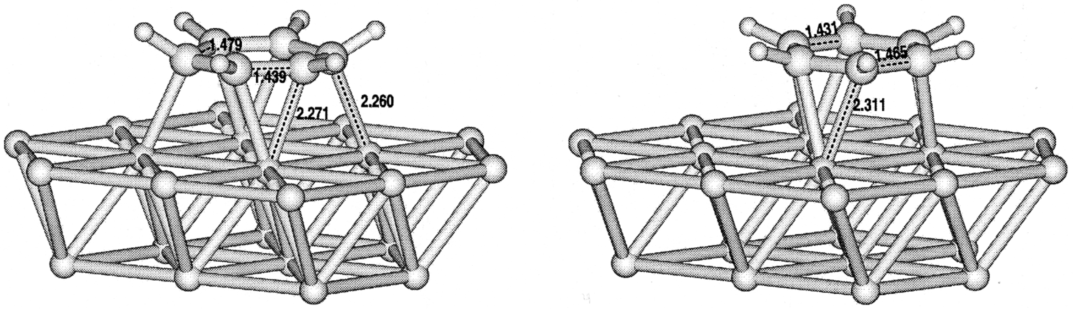

Figure 1. Illustration of benzene adsorbed on the bridge (left) and the hollow (right) site of the Pt_{22} cluster used in this study.

dominant reaction path along which activation energies are lower than along any other or does hydrogen addition occur in a random fashion, (ii) is there a rate-determining step and (iii) is benzene dehydrogenation an important reaction pathway and should it thus be included in the kinetic model?

The hydrogenation of both hollow and bridge bound benzene was studied. It was found that hydrogenation of benzene adsorbed at the hollow site is kinetically and thermodynamically favoured by more than 20 kJ mol^{-1} over hydrogenation of the bridge site adsorbed species [3]. Benzene adsorbed at the bridge site is too strongly bound to be hydrogenated. A similar observation has been made for ethene hydrogenation [13]. Therefore only the hydrogenation product of the benzene adsorbed at the hollow site is considered for addition of the second hydrogen atom. There are five distinct reaction paths for addition of a second hydrogen to this cyclohexadienyl species [3]. Figure 2 illustrates the possible reactions and the corresponding activation and reaction energies. Again a dominant reaction is observed, forming 1,3-dihydrobenzene. The activation energy of the dominant reaction is 19 kJ mol^{-1} lower than the activation energy of any alternative reaction. Also for the addition of the subsequent hydrogen atoms dominant reactions are observed, for which the activation energy is at least 15 kJ mol^{-1} lower than for an alternative addition reaction [14]. As a consequence, there is a dominant reaction path for the hydrogenation of benzene to cyclohexane. The dominant reaction path is shown in bold in figure 3. For the dominant mechanism, hydrogen atoms add sequentially in the meta-position of each other. Addition of hydrogen atoms beyond the third cannot occur in the meta-position for the other hydrogen atoms. Therefore, the corresponding activation energies are significantly higher and the addition of the fifth hydrogen atom is the rate-determining step [14]. Dehydrogenation of benzene was found to be kinetically and thermodynamically unimportant under hydrogenation conditions, due to the high endothermicity of the reaction [3]. The calculated energy diagram also provided an explanation for the experimentally observed dehydrogenation behaviour of 1,3- and 1,4-cyclohexadiene [3]. The difference between the calculated and experimental dehydrogenation activation energies for cyclohexadiene is less than 5 kJ mol^{-1}. The energy profile along the dominant reaction path is shown in figure 4. The energy increases gradually from adsorbed benzene and hydrogen to adsorbed cyclohexane. For comparison the enthalpy diagram along the uncatalysed pathway is also documented. For the latter mechanism the first hydrogenation step is the most difficult one, being endothermic by +122 kJ mol^{-1}. This can be explained by the aromatic stability of benzene. Upon adsorption, benzene loses its aromaticity [3] and the first catalytic hydrogenation step is very similar to the second and third, both thermodynamically and kinetically.

With the knowledge from the *ab initio* reaction path analysis, a simple Langmuir–Hinshelwood–Hougen–Watson (LHHW) model can be constructed with the addition of the fifth hydrogen atom as the rate-determining step. Using standard assumptions, the following rate equation can be derived [14, 15]:

$$R_{\mathrm{AH_6(g)}} = \frac{C_t k_5 \left(\prod_{j=1}^{4} K_j\right) K_A K_{H_2}^{5/2} p_A p_{H_2}^{5/2}}{\left(1 + K_A p_A + (K_{H_2} p_{H_2})^{1/2}\right)^2}. \qquad (1)$$

The *ab initio* activation energies, reaction enthalpies and adsorption enthalpies were introduced in equation (1) to model the hydrogenation of toluene, for which experimental data were obtained by Thybaut *et al.* [15]. Toluene rather than benzene was used for safety reasons. It is assumed that the results of the *ab initio* calculations for benzene can be extrapolated to toluene. The total concentration of active sites was determined experimentally and amounts to 10^{-2} mol kg$_{\mathrm{cat}}^{-1}$ [15]. The pre-exponential factors were obtained from statistical mechanics arguments [16] and are listed in table 1. Whereas before it was assumed intuitively that hydrogen surface species were mobile and that aromatic surface species were immobile [15], the recent *ab initio* calculations indicate that both the aromatic species adsorbed at the hollow site and hydrogen are very mobile on the platinum surface [3, 6]. The values in table 1 correspond to the latter observations.

Next the model predictions of equation (1) were compared with laboratory scale experimental data for toluene hydrogenation over Pt–ZSM-22 [15]. Only the hydrogen adsorption enthalpy, which is known to be strongly coverage dependent, was optimized. As can be seen from table 1, the hydrogen adsorption enthalpy also affects the reaction enthalpy. Regression of the experimental data yields an adequate kinetic model with an F value of 38 500. The optimized value of the hydrogen adsorption enthalpy, -68.8 ± 2.0 kJ mol^{-1}, is intermediate between the low coverage value, -94.0 kJ mol^{-1} and the high coverage value, -45.0 kJ mol^{-1} [12]. Figure 5 shows the parity diagrams for the toluene and methylcyclohexane outlet flow rates.

4. Conclusions

The applicability of quantum chemical calculations for the kinetic modelling of important industrial catalytic reactions was studied. It was illustrated how *ab initio* calculations can be used to gain fundamental insight into the reaction mechanism and to obtain reasonable values for thermodynamic and kinetic parameters for complex

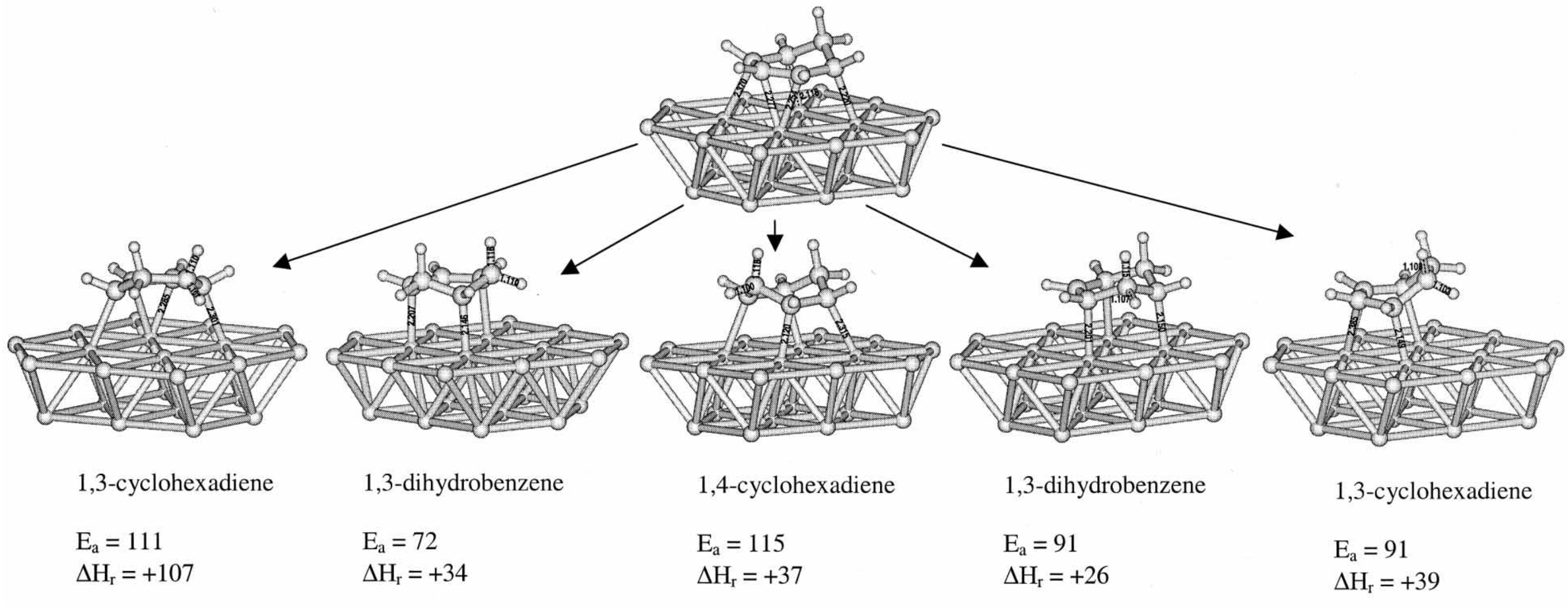

Figure 2. Various possible reactions for the second hydrogenation step. The names of the intermediates, the hydrogenation activation energies and the enthalpies of reaction are reported (kJ mol^{-1}).

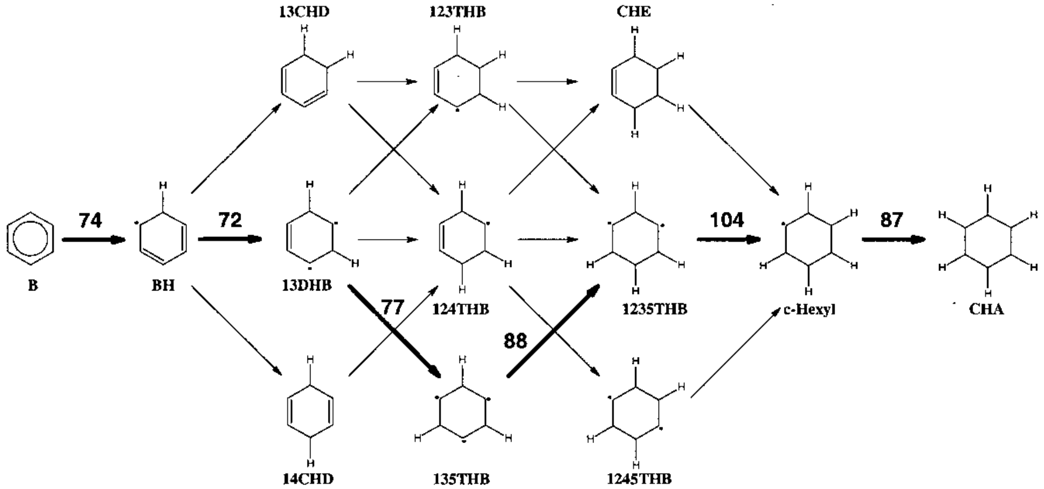

Figure 3. Overview of the different reaction paths for benzene hydrogenation. The dominant reaction path is indicated in bold. The hydrogenation activation energies for every step along the dominant reaction path are indicated (kJ mol^{-1}).

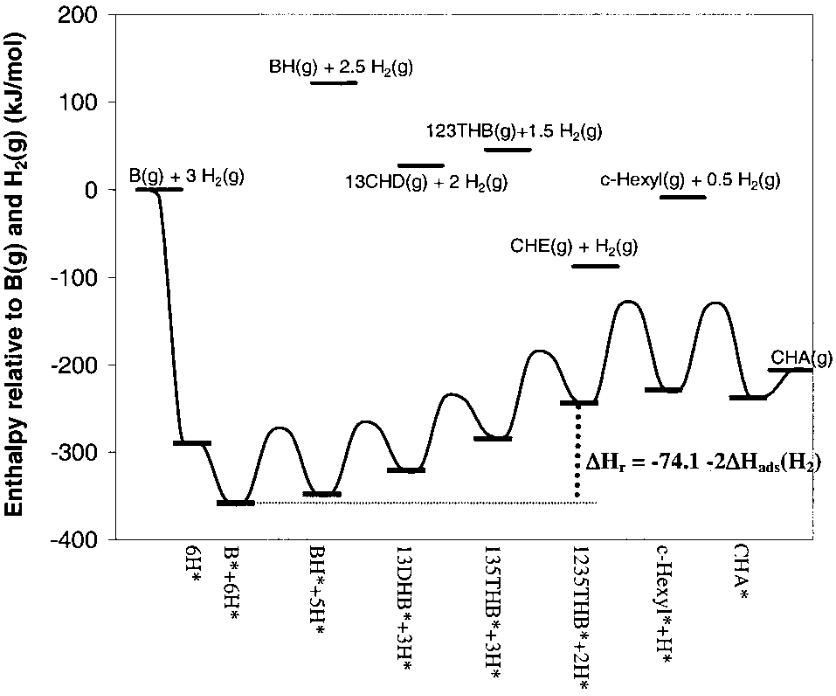

Figure 4. Energy profile along the dominant reaction path of the catalysed reaction and lowest enthalpy diagram for the non-catalysed hydrogenation.

Table 1. First principles kinetic and thermodynamic parameters to be used in the LHHW rate equation (1).

Parameter	Pre-exponential factor	Enthalpy/activation energy/kJ mol^{-1}
C_t	10^{-2} mol kg$_{cat}^{-1}$[15]	–
k_5	10^{12} s^{-1}	103.5 [14]
$\prod_{i=1}^{4} K_i$	10^{-4}	$-74.0 - 2\Delta H_{ads}(H_2)$ [14]
K_A	10^{-10} Pa^{-1}	−70.6 [6]
K_{H_2}	10^{-10} Pa^{-1}	$\Delta H_{ads}(H_2)$

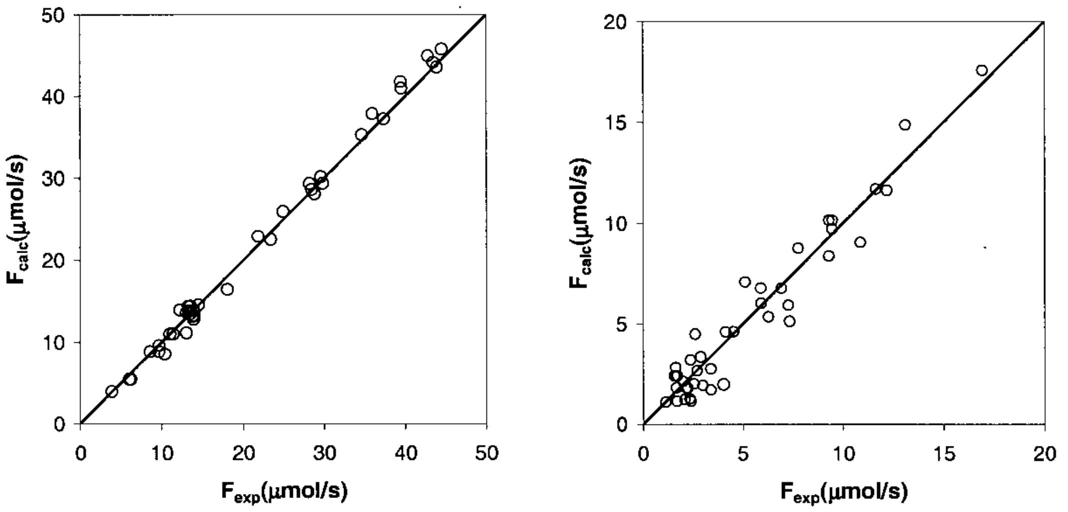

Figure 5. Parity diagrams for the toluene (left) and methylcyclohexane (right) outlet flow rates. Line: experimental data [15]; open circles: model prediction of the first principles kinetic model, equation (1).

catalytic reactions. In combination with a limited number of laboratory scale experiments, a fundamental kinetic model based on elementary reactions can be constructed, which can be implemented in mathematical reactor models for the simulation of industrial units. This approach was illustrated for the hydrogenation of aromatic molecules over a platinum catalyst. From a first principles reaction path analysis a Langmuir–Hinshelwood–Hougen–Watson rate equation was proposed, with the fifth hydrogenation step as rate determining. Using the *ab initio* kinetic and thermodynamic data in combination with only one adjustable parameter, namely the coverage-dependent hydrogen adsorption enthalpy, the proposed kinetic model accurately reproduced laboratory scale experimental data for the hydrogenation of toluene over a Pt–ZSM-5 catalyst.

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