# Compensation behaviour in the hydrogenation of benzene, toluene and o-xylene over Ni/SiO<sub>2</sub>

**Determination of true activation energies** 

## Mark A. Keane<sup>a\*†</sup> and Patricia M. Patterson<sup>b</sup><sup>+</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

<sup>b</sup> Department of Chemistry, York University, North York, Ontario, Canada M3J 1P3

FARADAY

The vapour phase hydrogenation of benzene, toluene and o-xylene has been studied over an Ni/SiO<sub>2</sub> catalyst prepared by homogeneous precipitation/deposition. The hydrogenations were carried out in the absence of diffusion limitations, catalyst deactivation or secondary conversions. Turnover frequencies and reaction probabilities decrease in the order benzene > toluene > o-xylene. The appearance of well defined reversible maxima  $(T_{max})$  in the rate vs. temperature plots is reported and discussed. The reaction orders with respect to the aromatic and hydrogen partial pressures are plotted as a function of temperature. The effect of temperature on the effective surface collisions is also considered. The temperature dependence of the rate constants was fitted to Arrhenius equations and generated positive ( $T \leq T_{max}$ ) and negative ( $T \geq T_{max}$ ) activation energies. The derivation of true activation energies and heats of adsorption from the kinetic data is presented. The turnover frequencies and apparent activation energies obtained in this study are compared to similar and different systems reported in the literature. A compensation effect is established for the experimentally determined or apparent kinetic parameters. The effect is attributed to variations in the temperature dependences of the surface concentration of the reactive aromatic species.

It is now known that high aromatic content in diesel fuels lowers fuel quality and contributes to the formation of undesired emissions in exhaust gases.<sup>1,2</sup> New environmental regulations governing diesel-fuel specifications limit the aromatic content to low levels (not more than 5% by volume) with the result that aromatic reduction has become a key upgrading parameter in processing middle distillates. The chemical kinetics of model heterogeneously catalysed aromatic hydrogenation provide fundamental information which forms the basis for developments in the catalyst and process technologies. With regard to the existing reports on aromatic hydrogenation, benzene has been the overwhelming choice as the model aromatic feed. The hydrogenation kinetics for benzene have been reported for a range of Group 8 metal and metal sulfide catalysts<sup>1</sup> and the catalytic activity has been shown to increase in the following sequence of active metals,<sup>3,4</sup> Co < Ni < Pd  $\leq$  Pt  $\leq$  Ru < Rh. The reaction has been used to probe the activity of a range of unsupported nickel systems<sup>5-15</sup> as well as nickel supported on both amorphous<sup>5,16-30</sup> and zeolite<sup>23,31-40</sup> carriers. Apparent activation energies in the range 25-94 kJ mol<sup>-1</sup> have been reported for the diverse nickel systems.<sup>5-12,16-24,35-37</sup> Rate maxima at 423 K,<sup>29</sup> 453 K<sup>12,13,15,16,18,23,28</sup> and 473 K<sup>37</sup> have been variously quoted. It has been proposed that the saturated product (cyclohexane) inhibits the progress of the reaction,  $^{9,10,12}$  an assertion which has been refuted by a number of workers.<sup>18,21,28,37</sup> Competition on the catalyst surface between benzene and hydrogen has likewise been assumed<sup>17,41</sup> and discounted.<sup>15,28,38,42,43</sup>

The rate of aromatic-ring hydrogenation is influenced by both steric and electronic factors.<sup>1,4,44,45</sup> In general, hydrogenation rates decrease with alkyl substitution and decrease further with an increasing number of such substituents, unless the addition of alkyl groups introduces exceptional strain, in which case the aromatic systems undergo facile saturation.<sup>4</sup> The hydrogenation of toluene has received far less attention than the benzene system and the reported use of nickel catalysts has essentially related activity to electronic structure.<sup>1,14,16,30,46-52</sup> The available activation energies for toluene hydrogenation over Ni/SiO<sub>2</sub> (67 kJ mol<sup>-1</sup>),<sup>16</sup> Ni/K-Y (78 kJ mol<sup>-1</sup>)<sup>46</sup> and Ni/MgO (57 kJ mol<sup>-1</sup>),<sup>51</sup> are at the high end of the range of values quoted for palladium (29–54 kJ mol<sup>-1</sup>)<sup>53,54</sup> and platinum (25–73 kJ mol<sup>-1</sup>)<sup>54–59</sup> based catalysts. The degree of conversion of toluene to methylcyclohexane has been reported to pass through a maximum at 448 K (nickel hydroxide/layer silicate),<sup>50</sup> at 463 K (Pt/Al<sub>2</sub>O<sub>3</sub><sup>55</sup> and Ni/K-Y<sup>46</sup>) and in the range 463–503 K (Ni/MgO).<sup>52</sup> The competitive hydrogenation of toluene and benzene has also been studied<sup>44,60</sup> and the relative adsorption strengths of both aromatic compounds on a range of active surfaces have been reported.<sup>44,46,61–65</sup>

There have been few reports concerning the heterogeneously catalysed hydrogenation of o-xylene in either the liquid or gaseous phase and the reported activity data are generally given in the form of a percentage conversion or a rate relative to the rate of benzene hydrogenation.<sup>1,4,66-70</sup> Rahaman and Vannice<sup>53</sup> have recently provided the first steady-state specific activities and activation energies (31-63 kJ mol<sup>-1</sup>) for a range of palladium catalysts. The overall rate of aromatic hydrogenation has nevertheless established  $^{1,14,44,53,67}$  as decreasing in the been as decreasing in the order, benzene > toluene > o-xylene. Steady-state activity data for the hydrogenation of benzene, toluene and o-xylene over Ni/SiO<sub>2</sub> are presented in this paper and the nature of temperature dependent rate maxima, effective surface collisions and apparent vs. true kinetic parameters are discussed.

#### **Experimental**

#### Catalyst preparation, activation and characterization

The catalyst was prepared by the homogeneous precipitation/ deposition of nickel onto a non-porous microspheroidal Cab-O-Sil 5M silica of surface area 194 m<sup>2</sup> g<sup>-1</sup>. The silica

<sup>†</sup> Present address: Department of Chemical Engineering, The University of Leeds, Leeds, UK LS2 9JT.

<sup>&</sup>lt;sup>‡</sup> Present address: Department of Fuel and Energy, The University of Leeds, Leeds, UK LS2 9JT.

support was washed with triply deionized water and dried in air for 20 h at 375-383 K before use. The precipitation was carried out in a 2 dm<sup>3</sup> three-necked round-bottomed flask fitted with a Citenco motor driven stirrer. A sample of urea (Aldrich Chem. Co., 99 + %) was added to a 1.5 dm<sup>3</sup> aqueous suspension of Cab-O-Sil 5M in nickel nitrate (Aldrich Chem. Co., 99.999%) at 290  $\pm$  2 K, where the molar ratio of the nitrate to urea was 0.36. The suspension was slowly heated under constant agitation (600 rpm) to  $361 \pm 3$  K and held at this temperature for 6 h. Temperature control was maintained using an oil bath equipped with a heating element and mechanical stirrer to ensure good heat transfer. The pH of the suspension was preadjusted (with nitric acid) to 2.8 to prevent premature hydrolysis and the pH was observed to increase to 5.3 on completion of the precipitation step. The suspension was then filtered and the filtrate washed with  $4 \times 400$  cm<sup>3</sup> hot deionized water and air-dried in an oven at 375-383 K for 20 h. The nickel loading was determined by atomic absorption spectrophotometry (Perkin-Elmer 360 AA spectrophotometer) using the experimental procedure described elsewhere.<sup>71</sup> The water content of the catalyst precursor was measured by thermogravimetry.72 The hydrated sample was reduced, without a precalcination step, by heating it in a 150 cm<sup>3</sup> min<sup>-1</sup> stream of hydrogen at a fixed rate of 5 K min<sup>-1</sup> (controlled using Barber–Coleman а temperature programmer) to a final temperature of 773 + 1 K, which was maintained for 18 h. The hydrogen gas (CANOX, 99.9%) was purified by passing it through water (activated molecular sieve type 5A) and oxygen (1% Pd on WO<sub>3</sub>) traps which were connected in series. The temperature-programmed reduction profile was obtained as outlined previously.73 Nickel metal dispersions, before and after the catalysis step, were determined by carbon monoxide chemisorption at 273 K, assuming a stoichiometry of nickel surface atom to adsorbed carbon monoxide of 2:1.74 A detailed description of the experimental procedure involved in the chemisorption measurements is available elsewhere.<sup>71</sup> The amount of CO adsorbed on the anhydrous support was also measured and subtracted from that adsorbed by the catalyst to give the total number of CO molecules adsorbed by the metal component.

#### **Catalytic procedure**

All the catalytic reactions were carried out at atmospheric pressure in a fixed-bed glass reactor (id = 15 mm) over the temperature range 388-523 K. The catalyst was supported on a glass frit and a layer of glass beads above the catalyst bed ensured that the aromatic reactant reached the reaction temperature before contacting the catalyst. The reactor temperature was monitored by a thermocouple inserted in a thermowell within the catalyst bed; reactor temperature was constant to within  $\pm 1$  K. A Sage pump (model 341 B) was used to deliver the aromatic feed, at a fixed rate via a syringe that had been carefully calibrated. The aromatic vapour was carried through the catalyst bed in a stream of purified hydrogen, the flow rate of which was set using Brooks mass flow controllers. The kinetic measurements were made using catalyst samples sieved in the 125-150 µm mesh range, at a space velocity of  $2 \times 10^3$  h<sup>-1</sup> (STP) and at W/F values in the range 42-112 g mol<sup>-1</sup> h where W is the weight of activated catalyst and F is the flow rate of aromatic species. Steady-state conversions were kept below 25 mol% by varying W in order to minimize heat and mass-transfer effects. The possible contribution of external and internal reactant/product diffusion to the overall reaction rate was monitored by (a) varying the W/F value in the overall range 29–192 g mol<sup>-1</sup> h by altering both parameters and (b) using six separate batches of catalyst with particle diameters in the overall range 50-1200  $\mu$ m. The reaction order with respect to hydrogen was determined at a constant aromatic partial pressure of 0.04 atm

(1 atm = 101 325 Pa) where the hydrogen partial pressure was varied from 0.19 to 0.96 atm using purified nitrogen as diluent. The reaction order with respect to the three aromatic species was measured at a constant hydrogen pressure of 0.94 atm where the pressure of each aromatic species was varied in the range 0.01-0.06 atm, again using nitrogen as the make-up gas. The reactor effluent was either sampled on-line via a  $20 \times 10^{-6}$  dm<sup>3</sup> sampling value or was frozen in a dry iceacetone trap for subsequent analysis. Product analysis was made using a Varian 3400 GC chromatograph equipped with a flame ionization detector and employing a 5% Bentone-5% diisodecylphthalate on Chromosorb W and 30% Silicone SF96 on 60/80 mesh acid washed Chromosorb W (6 ft  $\times$  1/8 in) stainless-steel column for the benzene/toluene and o-xylene reactions, respectively; data acquisition and analysis were performed using the GC Star Workstation. The overall level of hydrogenation was converted to mol% hydrogenation using a 20-point calibration plot for each of the aromatic feeds. The benzene, toluene (Aldrich, 99.9 + %) and o-xylene (Lancaster, 99%) reactants were thoroughly degassed by purging with purified helium followed by a series of freeze-pump-thaw cycles and were stored over activated molecular sieve type 5A.

### **Results and Discussion**

The pertinent physical characteristics of the catalyst precursor and activated material are given in Table 1. It has been shown elsewhere<sup>73</sup> that Ni/SiO<sub>2</sub> precursors prepared by homogeneous precipitation/deposition exhibit stronger nickel-support interactions than samples prepared by impregnation and the metallic phase generated after reduction of the former is present as smaller crystallites with a narrower size distribution. The temperature-programmed reduction profile for the 1.5 wt.% Ni/SiO<sub>2</sub> sample is characterized by a broad peak with maximum intensity at 850 K and an ill-defined peak at 580 K. The low-temperature peak arises at a slightly higher temperature than that recorded for unsupported NiO (565 K) and can be attributed to the reduction of a precipitated hydroxide species which interacts weakly with the support. The bulk of the hydrogen consumption occurs at the higher temperature and must result from the reduction of nickel hydroxysilicate which has been shown to form on catalysts prepared by precipitation/deposition.<sup>75,76</sup> Note that the total hydrogen consumption exceeds the theoretical value for a complete reduction of the nickel content; the excess hydrogen may be due to a spillover from the nickel metal and is held on the support. Nickel metal dispersion was obtained from CO chemisorption and is expressed as  $(Ni_{surface}/Ni_{total}) \times 100\%$ ; CO uptake was reproducible to better than  $\pm 3\%$ . The supported-nickel particle size was determined from the dispersion measurement according to the relationship<sup>77</sup> d = 101/D, where D is the dispersion or percentage of exposed nickel atoms and d is the surface-weighted average crystallite diameter assuming (spherical) particles  $\leq 1$  nm to be 100% dispersed. A value of 0.633 nm<sup>2</sup> for the average surface nickel

 Table 1
 Physical characteristics of the catalyst precursor and the activated material

support	Cab-O-Sil 5M SiO <sub>2</sub> (194 m <sup>2</sup> g <sup>-1</sup> )	
precursor Ni (wt %)	15	
$H_2O$ (wt. %)	0.6	
activated catalyst		
Tree /K	850	
H <sub>2</sub> consumption/ $10^{-3}$ dm <sup>3</sup> g <sup>-1</sup>	7	
Ni <sup>o</sup> dispersion (%)	73	
<i>d<sup>b</sup></i> /nm	1.4	
$S_{\rm Ni0}/m^2 g^{-1}$	74	

<sup>a</sup> Temperature corresponding to the maximum in  $H_2$  consumption.<sup>73</sup>

<sup>b</sup> Surface-weighted average crystallite diameter.

atom<sup>78</sup> was used in calculating the surface area of the supported nickel metal.

The hydrogenation of benzene and toluene over Ni/SiO<sub>2</sub> yielded the respective saturated cycloalkanes, cyclohexane and methylcyclohexane, as the only detected products. The reduction of o-xylene produced both the cis- and trans- forms of 1,2-dimethylcyclohexane but the isomerization of o-xylene to *m*-xylene which has been reported for palladium systems<sup>53</sup> was not observed in this study. Passage of each aromatic species in a stream of hydrogen over the silica support (in the absence of nickel) did not result in any measurable degree of hydrogenation. At temperatures in excess of 523 K the aromatic feed began to undergo partial hydrogenolysis with the result that this investigation has been limited to temperatures  $\leq$  523 K. All the activity data (reproducible to better than  $\pm$ 5%) presented in this paper were obtained at steady state and represent the average of at least five separate test samples. The experimental conditions were chosen so that the reaction rate was not influenced by external or internal diffusion. The possible contribution of external diffusion was monitored by independently varying W and F and establishing that the measured rate was constant at a constant value of W/F. A representative case is illustrated in Fig. 1 where hydrogenation rates (R) of  $3 \times 10^{-4}$  and  $8 \times 10^{-4}$  mol h<sup>-1</sup> obtained using three toluene feed rates correspond to W/F values of  $42 \pm 1$ and  $112 \pm 2$  g mol<sup>-1</sup> h, respectively. The reactor was clearly operating with negligible external diffusion retardation within these W/F values which represent the limits within which the kinetic measurements were made. In a separate set of experiments the role of intraparticle diffusion was probed by varying the catalyst particle size while maintaining W/F constant and representative data are presented in the insert to Fig. 1. The rate of hydrogenation was essentially independent of particle size in the range 50-300 µm but was markedly lower for catalyst particles greater than 800 µm wherein the reaction was controlled to an appreciable degree by transport limitations. There are, however, negligible internal diffusion constraints in the intermediate 125-150 µm mesh range which was chosen for the subsequent kinetic studies. In addition, values of the Weisz criterion<sup>79</sup> were below  $4 \times 10^{-5}$  which again demonstrates that the rates are free from diffusional limitations under the chosen experimental conditions.

The experimentally determined turnover frequencies (TOF), the number of molecules converted per metal site per second, of the three reactants are plotted as a function of reaction temperature in Fig. 2. Ascending and subsequent descending temperature sequences over the entire temperature interval were used to verify maintenance of activity. The TOF of toluene and o-xylene relative to that of benzene at representa-

F2

F3

1.0

3x10-4

0.75

18

12

6

0

0

8x10<sup>-4</sup>

0.25

0<sup>4</sup> R/mol h<sup>-1</sup>



0.50

W/g



Fig. 2 Variation of the experimentally determined TOF of benzene ( $\blacktriangle$ ), toluene ( $\bigoplus$ ) and *o*-xylene ( $\blacksquare$ ) with temperature at  $P_A = 0.04$  atm and  $P_{H_2} = 0.96$  atm

tive temperatures are given in Table 2. The reaction probability (RP) defined below

$$RP = \frac{\text{rate of formation of product molecules}}{\text{rate of incidence of reactant molecules}}$$
(1)

was obtained by dividing each TOF by the rate of molecular incidence, Z (collisions per unit time per unit area), where Z is obtained from the kinetic theory expression

$$Z = \frac{P}{(2\pi m k T)^{1/2}}$$
 (2)

where P and m represent the partial pressure and mass of the gaseous aromatic species, respectively, T is the reaction temperature and k the Boltzmann constant. The reaction probability reveals the overall efficiency of the catalytic process and the values corresponding to the data presented in Fig. 2 lie within the extremes  $2 \times 10^{-11} - 4 \times 10^{-10}$ . Somorjai<sup>80</sup> has recently tabulated benzene hydrogenation probabilities which were calculated for a particular temperature from data available in the literature  $^{16-18,22,24,26,27}$  and gave values in the range  $4 \times 10^{-11} - 2 \times 10^{-8}$ . The reaction probabilities generated in this study are at the lower end of the above range but it should be noted that the values refer to all three aromatic feeds and extend over the temperature interval  $388 \leq T/$  $K \leq 523$  which encompasses the region of decreasing rates as illustrated in Fig. 2. Under steady-state conditions the reported TOF of benzene, toluene and o-xylene at 413 K over palladium catalysts<sup>53</sup> are from 12 to 330, 6 to 80 and 1.4 to 11 times greater, respectively, than those observed in this study. In addition, the TOF of toluene on platinum catalysts has been reported to be up to 40 times higher than on palladium systems.<sup>81</sup> The inferred order of increasing aromatic ring hydrogenation activity, Ni < Pd < Pt, is in agreement with published observations.3,4

The TOF of aromatic molecules increased, over the entire temperature range studied, in the order o-xylene < toluene < benzene. The addition of methyl group(s) to the aromatic ring has likewise been found to decrease the catalytic

**Table 2** Temperature dependence of the experimentally determined TOF of toluene and *o*-xylene relative to the TOF of benzene at  $P_A = 0.04$  atm and  $P_{H_2} = 0.96$  atm

T/K	$\mathrm{TOF}_{\mathrm{toluene}}/\mathrm{TOF}_{\mathrm{benzene}}$	$\text{TOF}_{o-xylene}/\text{TOF}_{benzene}$
393	0.49	0.34
413	0.74	0.51
443	0.84	0.69
473	0.73	0.37
503	0.59	0.25
523	0.49	0.19

activity over supported platinum,<sup>56-58,81</sup> palladium,<sup>53,57,81</sup> rhodium and cobalt<sup>48</sup> systems. It is generally accepted that the presence of methyl substituents on the benzene ring stabilizes the adsorbed  $\pi$ -complex with the resultant introduction of a higher energy barrier for aromatic-ring hydrogenation. The rate of toluene hydrogenation has been reported to be 0.25–0.5<sup>81</sup> and 0.4–0.8<sup>56,57</sup> times that of benzene over palladium and platinum catalysts, respectively. Relative rate ratios for benzene : toluene : *o*-xylene of 1:1.6:1.7,<sup>1</sup> 1:0.77:0.16,<sup>14</sup> 1:0.63:0.11<sup>53</sup> and 1:0.62:0.32<sup>67</sup> have also been quoted. Some authors<sup>82,83</sup> have published relative rates which obey the relationship

$$R_n = R_0 2^{-n} \tag{3}$$

where  $R_0$  is the rate of benzene hydrogenation and  $R_n$  is the rate of hydrogenation of the benzene derivative containing nmethyl groups. All the results cited above refer to a particular reaction temperature but, as shown in Table 2, the relative TOF obtained in this study vary considerably with temperature and the simplistic relationship given above certainly does not hold. A feature of the three plots shown in Fig. 2 is the presence of a reversible maximum at a particular temperature (T<sub>max</sub>), i.e. 473 K for benzene, 463 K for toluene and 453 K for o-xylene. Such maxima may be explained by catalyst poisoning or the influence of diffusion or thermodynamic limitations. In this study, each maximum could be traversed from either the high- or low-temperature side without any loss in activity; this negates the possibility of catalyst deactivation. The catalytic reactor has been shown to operate in the differential mode and the degree of aromatic conversion was far from equilibrium levels. The possibility of nickel crystallite growth during catalysis may also be discounted as the metal dispersion before and after catalyst use was the same. The existence of a temperature-related hydrogenation activity maximum has been ascribed in the case of Ni/Y zeolites<sup>37,46</sup> to a decrease in the surface coverage by the aromatic species with increasing temperature, which at some point results in a decrease in the reaction probability. The surface conditions which prevail during hydrogenation were probed by considering the following three pretreatments: (a) pre-contacting the catalyst which had been swept with nitrogen (400 cm<sup>3</sup> min<sup>-1</sup>) at 723 K for 24 h with a stream (50 cm<sup>3</sup> min<sup>-1</sup> for 1 h) of hydrogen prior to the introduction of the standard reactant feed ( $P_A = 0.96$  atm,  $P_{H_2} = 0.04$  atm); (b) pre-contacting the nitrogen-swept catalyst with the aromatic species  $(3 \times 10^{-3})$ moles) prior to the introduction of the standard feed; (c) passage of the standard feed over the catalyst, which had been purged in nitrogen, without any pretreatment. The degree of hydrogenation of the aromatic component which was obtained by sampling the gas downstream of the catalyst bed 10 min after the introduction of the standard feed, was the same (within experimental error) for the three cases (a)-(c). Pre-adsorption of either reactant on the catalyst before introduction of both reactants had no effect on the progress of the reaction which suggests a non-competitive adsorption of hydrogen and aromatic species under reaction conditions. Benzene is known to be adsorbed on nickel via  $\pi$ -bond interactions in which the ring lies parallel to the active surface.<sup>62,84,85</sup> Toluene is known to be adsorbed in a similar fashion where the C-H and C-CH<sub>3</sub> bonds bend away from the surface.<sup>62</sup> To the best of our knowledge, no spectroscopic study of o-xylene adsorption on metals has been published. It has been shown<sup>46,62-65</sup> in a number of instances that toluene interacts more strongly than benzene with a range of metal surfaces. In general, the strength of adsorption may be considered to increase with increasing methyl substitution owing to the stronger donation from the  $\pi$ -electron cloud to the metal as a result of increasing electron ring density.<sup>64,86</sup> From a consideration of adsorption strength, the order of increasing  $T_{\rm max}$  should be the opposite to that observed, *i.e.* the stronger

interaction of o-xylene with the catalyst should necessitate a higher temperature to lower the surface coverage to the limiting value where reaction probability drops. Vannice and coworkers also observed a lower  $T_{max}$  for toluene compared to that for benzene hydrogenation over both palladium<sup>53</sup> and platinum<sup>87</sup> catalysts. The possible contribution of the reverse, dehydrogenation, reaction to the observed maxima in hydrogenation rates was investigated by passing each of the saturated cycloalkanes over the activated catalyst; there was no measurable conversion of the saturated feed at  $T \leq 493$  K. By eliminating the above possible causes it is reasonable to attribute the existence of  $T_{max}$  to adsorption-desorption phenomena as it has been demonstrated elsewhere that benzene and toluene interactions with the active surface decrease with increasing temperature.<sup>61,88</sup> It is proposed that the adsorbed aromatic species is present as a reactive and unreactive species and the surface coverage by the reactive form governs the rate of formation of the saturated product. The temperature dependence of TOF, shown in Fig. 2, must then mirror the temperature dependence of surface formation of the reactive species. The critical loss of this reactive form occurs at decreasing temperatures with increasing methyl substitution. An in situ spectroscopic study of the surface species present under actual catalytic conditions would certainly provide a valuable insight into the surface phenomena that result in the occurrence of  $T_{max}$ . It has been speculated that benzene is not solely adsorbed on metals as a  $\pi$ -complex but that the  $\pi$ bonded species exists in equilibrium with  $\sigma$ - and  $\pi/\sigma$ - bonded species.<sup>22,88-90</sup> The  $\sigma$ -bonded species, although reactive in exchange reactions, may inhibit hydrogenation by competitive adsorption.<sup>22,91</sup> If such  $\sigma$ -bonding occurs during the chemisorption of toluene and o-xylene the temperature-related maxima in activity may be due to an increase in the relative coverage by an unproductive  $\sigma$ -species. Furthermore, the introduction of a steric factor due to the presence of methyl substituent(s) may favour a non-planar orientation of the aromatic nucleus relative to the metal surface with a consequent greater likelihood of  $\sigma$ -bonding.

The kinetics of the reaction may be represented by the power equation

$$TOF = k P_A^m P_{H_2}^n \tag{4}$$

where k represents the rate constant,  $P_A$  and  $P_{H_2}$  the partial pressure of the aromatic species and hydrogen and m and n the orders of the reaction with respect to the aromatic species and hydrogen partial pressures, respectively. The reaction orders were determined by means of logarithmic plots where, for instance, at constant reaction temperature and  $P_{H_2}$ 

$$\log \text{TOF} = \log(kP_{\text{H}_2}^n) + m \log P_{\text{A}}$$
(5)

and plots of log TOF vs. log  $P_A$  yield m. Representative logarithmic plots depicting the variation of TOF with  $P_{toluene}$ at various temperatures are shown in Fig. 3(a) while the dependence of TOF on the partial pressure of the three aromatic compounds at 443 K is illustrated in Fig. 3(b). The orders with respect to aromatic pressure derived from the experimental data are plotted as a function of temperature in Fig. 4 where the error bars represent 95% confidence limits of the regressed reaction orders. The value of m increased from 0 to 0.5 as the temperature was raised from 388 to 523 K. A variety of empirical correlations for benzene hydrogenation on nickel films, nickel powder and nickel supported on alumina, silica and silica/alumina have been reported where a nearzero order in benzene pressure has been quoted, <sup>5,9,10,12,17,20,21,23,24,42,92,93</sup> in some cases increasing from a low value of 0.1-0.3 at temperatures below 373 K to ca. 0.5 at  $423 \leq T/K \leq 473.^{9,18,25,28,31,42}$  The authors could find no documented temperature dependence of reaction orders in toluene or o-xylene hydrogenations on comparable nickel/amorphous carrier systems. The near-zero-order depen-



**Fig. 3** (a) TOF of toluene as a function of  $P_{\text{toluene}}$  at 413 ( $\blacktriangle$ ), 443 ( $\bigcirc$ ), 473 ( $\blacksquare$ ) and 503 K ( $\diamondsuit$ ) and (b) TOF of benzene ( $\blacktriangle$ ), toluene ( $\bigcirc$ ) and *o*-xylene ( $\blacksquare$ ) as a function of  $P_A$  at 443 K

dence on all three aromatic compounds observed in this study where m < 0.1 at  $T \le 423$  K is consistent with a high surface coverage by the aromatic species. The increase in the reaction order with increasing temperature suggests that the surface coverage is depleted by a temperature induced desorption of the reactive form of aromatic. The order of increasing value of m, o-xylene < toluene < benzene, which was maintained over the entire temperature interval is diagnostic of a decreasing strength of interaction with the catalyst which agrees with the earlier arguments. The reaction order with respect to hydrogen was determined by varying the partial pressure of hydrogen at constant  $P_A$  employing nitrogen as diluent and representative logarithmic plots are shown in Fig. 5 for the hydrogenation of toluene. At temperatures below 373 K, reaction orders with respect to hydrogen in the range  $0.5-0.7^{5,6,9,10,12,13,17,18,20,24,29,42}$  have been reported for the hydrogenation of benzene over nickel catalysts, increasing with increasing temperature to a value of  $1.0-2.5^{9,12,18,27,42,92,94}$  and ultimately reaching a value of 3 at 473 K.<sup>23,25</sup> In this study, the values of n increased from 0.7 to 2.3 with increasing temperature, as shown in Fig. 6. Although the three hydrocarbons exhibit different degrees of interaction with the catalyst the reaction order in hydrogen was essentially the same for the three systems which concurs with a



**Fig. 4** Dependence of the reaction order (m) with respect to  $P_{\text{benzene}}$ ( $\triangle$ ),  $P_{\text{toluene}}$  ( $\bigcirc$ ) and  $P_{o-xy|\text{ene}}$  ( $\bigcirc$ ) on the reaction temperature: the error bars correspond to 95% confidence limits



Fig. 5 TOF of toluene as a function of  $P_{\text{H}_2}$  at 413 ( $\blacktriangle$ ), 443 ( $\bigcirc$ ), 473 ( $\blacksquare$ ) and 503 K ( $\diamondsuit$ )

non-competitive adsorption of the reactants during catalysis. The observed dependences of the reaction orders with temperature strongly suggest that the effective values of the concentration of reactants, represented by  $P_A^m$  and  $P_{H_2}^n$ , vary across the temperature interval employed in this study. Equations of general applicability which express such changes are not readily formulated;95 however, approximate relationships may be acceptable, within the stated experimental regime, as a means of providing a semi-quantitative description of the conditions that prevail on the catalyst surface during the reaction. Assuming that  $\theta_A \propto P_A^m$  and  $\theta_{H_2} \propto P_{H_2}^n$ , the variation of the surface coverage  $(\theta)$  by the aromatic and hydrogen reactants may be approximated by the temperature dependence of the experimentally determined  $P_A^m$  and  $P_{H_2}^n$  values and these relationships are plotted in Fig. 7. The influence of increasing temperature on  $P_A^m$  and by inference on the fractional surface coverage is considerable. The values of  $P_{H_2}^n$  are, however, largely unaffected by temperature. It may be concluded that, under reaction conditions, the reactive aromatic species is adsorbed as a  $\pi$ -complex at site S, adsorption is reversible, surface coverage depends on the reaction temperature and the changes in concentration of surface aromatic species are reflected in the value of m. Hydrogen can be considered to be adsorbed on separate sites, S', where the surface coverage is largely temperature-invariant and independent of the nature of the aromatic species. The observed variation in TOF with temperature must then be due predominantly to the availability of surface aromatic species.

The rate constants  $(k/s^{-1})$  for the three reactions were calculated using eqn. (4) and the experimental Arrhenius relationships are illustrated in Fig. 8. The computed, with 95% con-



Fig. 6 Temperature dependence of the reaction order (*n*) with respect to  $P_{H_2}$  in the hydrogenation of benzene ( $\blacktriangle$ ), toluene ( $\bigcirc$ ) and *o*-xylene ( $\blacksquare$ ): the error bars correspond to 95% confidence limits



**Fig.** 7 Variation with temperature of  $P_{H_2}^n$  (\*) and  $P_A^m$  where A represents benzene ( $\blacktriangle$ ), toluene ( $\bigoplus$ ) and *o*-xylene ( $\blacksquare$ ):  $P_A = 0.04$  atm;  $P_{H_2} = 0.96$  atm

fidence limits, activation energies  $(E_{app})$  and temperatureindependent pre-exponential factors  $(A_{app})$  are given in Table 3 where

$$k = A_{\rm app} \exp(-E_{\rm app}/RT) \tag{6}$$

The value of 49.2 kJ mol<sup>-1</sup> obtained in this study for  $E_{app}$  for the hydrogenation of benzene may be inserted into the array of literature values that were given in the Introduction, the value of 63.6 kJ mol<sup>-1</sup> for the toluene reaction supplements the meagre published data while the value of  $73.4 \text{ kJ} \text{ mol}^{-1}$ for the reduction of o-xylene represents the first value for a nickel catalyst. The series of increasing activation energies, benzene < toluene < o-xylene, mirrors the observed order of decreasing TOF. The temperature dependence of the rate constants at  $T \ge T_{max}$  also obeys the Arrhenius relationship and yields the negative activation energies which are also included in Table 3. A negative activation energy of -92 kJ mol<sup>-1</sup>  $(488 \le T/K \le 553)$  has been reported<sup>25</sup> for the hydrogenation of benzene over an Ni/ZnO catalyst operating in a continuous circulation system and was attributed to the kinetics of the reverse reaction. The activation energies obtained from the relationship between the experimentally obtained rate con-



**Fig. 8** Apparent Arrhenius plots for the hydrogenation of benzene  $(\blacktriangle)$ , toluene  $(\bigcirc)$  and *o*-xylene  $(\bigcirc)$ 

 Table 3
 Kinetic data obtained from the Arrhenius relationships

aromatic feed	T/K	$A_{app}/s^{-1}$	$E_{app}^{a}/kJ \text{ mol}^{-1}$
benzene	393-473	$8 \times 10^3$	$49.2 \pm 2.0$
	473-523	$3 \times 10^{-6}$	$-35.9 \pm 2.3$
toluene	388-463	$3 \times 10^{5}$	$63.6 \pm 2.9$
	463-523	$7 \times 10^{-8}$	$-48.6 \pm 2.9$
o-xylene	393-453	$4 \times 10^{6}$	$73.4 \pm 3.8$
•	453-523	$2 \times 10^{-9}$	$-60.5 \pm 3.0$

<sup>a</sup> 95% confidence limits.

1418 J. Chem. Soc., Faraday Trans., 1996, Vol. 92

stants and temperature are, by convention, termed apparent activation energies, as the surface coverage by the aromatic species does not remain constant throughout the temperature range studied. If the entire temperature effect acts solely on the rate constant then a true activation energy ( $E_{\rm true}$ ) may be derived from the Arrhenius plot. The true activation energy is obtained by adding the enthalpy of adsorption as a positive quantity to the apparent activation energy,<sup>24,96,97</sup>

$$E_{\rm true} = E_{\rm app} - \Delta_{\rm ads} H \tag{7}$$

Chemisorption is always exothermic with the result that  $\Delta_{ads} H$  is negative for the system and  $-\Delta_{ads} H$  has a positive value. The process of chemisorption also has a rate coefficient  $(k_{ads})$ 

$$k_{\rm ads} = \sigma Z \, \exp(-E_{\rm ads}/RT) \tag{8}$$

where  $E_{ads}$  is the activation energy for chemisorption,  $\sigma$  is the sticking probability or fraction of collisions that leads to adsorption and Z is the number of collisions per unit area per unit time. This equation, based on collision theory, is analogous to eqn. (6). Desorption is an activated process since the minimum  $E_{des}$  is that equal to  $\Delta_{ads} H$ , where<sup>83,98,99</sup>

$$E_{\rm des} - E_{\rm ads} = \Delta_{\rm ads} H \tag{9}$$

The three catalytic aromatic hydrogenations reported in this study were conducted in the absence of (a) diffusion/mass transport effects, (b) rate inhibition by the products and (c) secondary reactions and, as such, may be considered to be surface controlled where the overall reaction rate is governed solely by the extent of adsorption/desorption of the reactive species. The activation energies obtained over the temperature ranges corresponding to increasing and decreasing rate constants are essentially equivalent to  $E_{ads}$  and  $E_{des}$ , respectively. Taking each set of experimentally evaluated activation energies, values of  $\Delta_{ads} H$  and  $E_{true}$  for the three cases were obtained from a combination of eqn. (7) and (9) and are given in Table 4 together with 95% confidence limits. In two previously published studies the kinetics of benzene<sup>37</sup> and toluene<sup>46</sup> hydrogenation over an Ni/K-Y catalyst of similar metal loading (2.2 wt% Ni) were presented and the activation energies which were reported are included in Table 4. The rates of benzene and toluene hydrogenation passed through maxima at 473 and 463 K, respectively, as observed in this study. The variation of rate constant with temperature where  $T \ge T_{\text{max}}$  also obeyed the Arrhenius relationship and negative values of  $-11.5 \pm 1.7 \text{ kJ mol}^{-1}$  (473  $\leq T/K \leq 523$ ) and  $-22.9 \text{ kJ mol}^{-1}$  (463  $\leq T/K \leq 523$ ) were recorded for benzene and toluene, respectively. It can be seen that the positive  $E_{app}$  values for the zeolite and silica systems differ by more than the possible overlap of values when the 95% confidence limits are taken into account. However, the values of  $E_{\rm true}$  certainly agree within the stated margin of error. The differences in  $E_{app}$  arise from differences in  $\Delta_{ads} H$ , which may be attributed to a support effect, either in terms of a direct contribution to the chemisorption step or to an interaction

**Table 4** Values of  $E_{app}$ ,  $\Delta_{ads}H$  and  $E_{true}$  with 95% confidence limits obtained from the Arrhenius relationships shown in Fig. 8

aromatic feed	$E_{app}/kJ \text{ mol}^{-1}$	$\Delta_{ads} H/kJ \text{ mol}^{-1}$	E <sub>true</sub> /kJ mol <sup>-1</sup>
Ni/SiO,			
benzene	$49.2 \pm 2.0$	$-85.1 \pm 3.1$	134.3 ± 3.7
toluene	$63.6 \pm 2.9$	$-112.2 \pm 4.1$	$175.8 \pm 5.0$
o-xylene	$73.4 \pm 3.8$	$-133.9 \pm 4.8$	$207.3 \pm 6.1$
Ni/K-Y			
benzene <sup>a</sup>	$59.5 \pm 4.0$	$-71.0 \pm 4.4$	130.5 ± 6.0
toluene <sup>b</sup>	78.2 ± 4.3	$-101.1 \pm 5.0$	179.3 ± 6.6

<sup>*a*</sup>  $E_{app}$  for T = 403-473 K.<sup>37</sup> <sup>*b*</sup>  $E_{app}$  for T = 403-463 K.<sup>46</sup>

It is often observed that, when either the same reaction is studied on a series of different catalysts or a series of related reactions is studied on the same catalyst, a relationship exists between the values of the apparent activation energies and the pre-exponential factors. This takes the form

$$\ln A_{\rm app} = eE_{\rm app} + B \tag{10}$$

where e and B are constants, termed 'compensation' factors. The above relationship implies that an increase in  $\ln A_{app}$ which should increase the reaction rate is accompanied or compensated by an increase in  $E_{app}$  which results in a decrease in reaction rate. Galwey,<sup>95,100</sup> in particular, has recorded the various compensation relationships reported in the literature and has stressed the significance of experimental error and the accuracy of the data fit to an overall obedience of eqn. (10). The pre-exponential factors  $(A_{app})$  obtained in this study are plotted against the corresponding activation energies in Fig. 9. It can be seen that the linear relationship (correlation coefficient = 0.9997) holds true for the three sets of positive and negative activation energies where e = 0.262 + 0.009 mol  $kJ^{-1}$  and  $B = -3.872 \pm 0.487 \text{ s}^{-1}$ . This paper represents the first report of the compensation effect (CE) criteria being met by negative activation energies. The previously reported data for the Ni/K-Y system  $^{37,46}$  are also included in Fig. 9 and likewise show a consistency with eqn. (10). A true compensation effect is established if a single point of concurrence appears in the Arrhenius plots.<sup>80,83,95,100-102</sup> The temperature corresponding to such a point, the isokinetic temperature  $(T_{iso})$  is obtained from

$$T_{\rm iso} = \frac{1}{eR} \tag{11}$$

n

80

where *e* is the slope of the compensation plot and *R* is the gas constant; the calculated value of  $T_{iso}$  is  $458 \pm 13$  K. The experimentally determined rate constants at 453 K give the ratios  $k_{benzene}$ :  $k_{toluene}$ :  $k_{o-xylene} = 1:0.93:0.95$ . The agreement between the calculated and experimental  $T_{iso}$  values is satisfactory and confirms that the attribution of a compensation effect to the hydrogenation of the three aromatic compounds over Ni/SiO<sub>2</sub> is justified. The error margin in the calculated  $T_{iso}$  reflects the critical nature of the goodness of the fit to any data set when applied to a discussion of the compensation effect as has been argued elsewhere.<sup>95,100-104</sup> The actual source of the compensation effect is still a matter of some debate and the validity of the effect as a kinetic observation and not merely an experimental artifact remains open to ques-

17

7

-3

-13

-23

-60

In A<sub>app</sub>/s

 $E_{app}/kJ \text{ mol}^{-1}$ Fig. 9 Compensation plot for the hydrogenation of benzene ( $\triangle$ ,  $\triangle$ ), toluene ( $\bigcirc$ ,  $\bigcirc$ ) and o-xylene ( $\blacksquare$ ,  $\square$ ) over Ni/SiO<sub>2</sub> at W/F = 61 g mol<sup>-1</sup> h where the equation of the fitted line is ln  $A_{app} = (0.262 \pm 0.009)E_{app} - 3.872 \pm 0.487$ . In  $A_{app}$  vs.  $E_{app}$  data for the hydrogenation of benzene ( $\diamondsuit$ ,  $\diamondsuit$ )<sup>37</sup> and toluene ( $\bigstar$ ,  $\backsim$ )<sup>46</sup> over Ni/K-Y; the error bars correspond to 95% confidence limits.

10

45

-25

tion. Nevertheless, reports of compensation behaviour appear as a direct consequence of kinetic studies concerned with reactions proceeding at comparable rates and over similar temperature ranges. The compensation effect has, however, been rationalized in terms of an energetically heterogeneous catalyst surface, enthalpy/entropy effects and changes in the energy levels of the transition state or in the surface concentration of active sites with temperature.95 In particular, surface heterogeneity, in one form or other, and the occurrence of two or more concurrent reactions have been most frequently proposed as explanations. The dilute nickel catalyst prepared by homogeneous precipitation/deposition is characterized<sup>73</sup> by a uniform dispersion of small metal particles (<2 nm) which are stable during catalysis and may be considered to possess a high degree of surface homogeneity where the adsorption energy of each active site is the same. The only reaction which takes place under the stated conditions is aromatic-ring hydrogenation, which may be assumed to proceed on the same reaction sites, regardless of the presence or absence of methyl substituents, where the reaction rate is governed by variations in surface concentrations. The extension in this study of the compensation effect to negative activation energies suggests the involvement of adsorption/desorption effects. The CE is obeyed by the experimentally determined or apparent A or E values which do not represent the frequency of occurrence or the energy requirements of the surface reactions because the concentration of the surface reactants varies across the temperature interval studied. The true pre-exponential factor, corresponding to the true activation energy, must take account of both the probability of collision between the two reactants and the change in the surface concentration with temperature. A modified Arrhenius equation, based on collision theory

$$k = \sigma Z \, \exp(-E_{\rm true}/RT) \tag{12}$$

describes the true temperature dependence of the rate constant where  $E_{true}$  refers to the rate-determining step and the term  $\sigma Z$  makes due allowance for variations with temperature in the probability of surface collisions. Values of  $\sigma Z$  were calculated using eqn. (12), inserting the experimentally determined rate constants  $(k_{app})$  over the temperature range of this study. The relationship between  $\sigma Z$  and T, shown in Fig. 10, is linear and the decrease in collision probability with temperature is diagnostic of increasing desorption of reactive aromatic from the surface. A plot of  $\ln (k_{app}/\sigma Z)$  vs. 1/T gives the slope  $-E_{true}/R$  according to eqn. (12). Three plots were generated accordingly using the calculated values of  $E_{true}$  for each process over the experimental temperature interval and are shown in Fig. 11. Each plot exhibits excellent linearity, demonstrating true Arrhenius behaviour and the ratio  $k_{app}/\sigma Z$ is essentially equivalent to  $k_{true}/A_{true}$ .

It may be tacitly assumed, as the compensation effect holds, that the rate-determining step in the true surface reaction is



**Fig. 10** Temperature dependence of  $\ln \sigma Z$  for the hydrogenation of benzene ( $\blacktriangle$ ), toluene ( $\bigcirc$ ) and *o*-xylene ( $\blacksquare$ )



Fig. 11 True Arrhenius plots for the hydrogenation of benzene ( $\blacktriangle$ , solid line), toluene ( $\blacklozenge$ , dashed line) and *o*-xylene ( $\blacksquare$ , dotted line)

the same for the three processes. If the surface reaction proceeds with the stepwise addition of hydrogen atoms to the adsorbed aromatic species, the rate-determining step must then be represented by one of these stepwise additions. The hydrogenation of benzene has been viewed as occurring via simultaneous<sup>9,11</sup> or sequential addition of hydrogen atoms to the adsorbed aromatic species where no rate-determining step is apparent<sup>42,43</sup> or where the addition of the first/ second<sup>22,53,55</sup> or the sixth<sup>22</sup> hydrogen atom is the slow step. Vannice and co-workers<sup>53,87</sup> have provided persuasive evidence that the addition of the first hydrogen atom to the aromatic species when adsorbed on platinum and palladium catalysts is rate determining, an assertion that has found support in recent data reported by Tétényi<sup>105</sup> for the hydrogenation of benzene on platinum black. Certainly, the destabilization of the resonance energy that is initiated by the addition of the first hydrogen atom should be energetically demanding. The observed increase in activation energy with increasing resonance energy of the aromatic nucleus is consistent with such a mechanism. The identification of an exclusive rate-limiting step is beyond the scope of this report. Nevertheless, the data presented in Fig. 11 illustrate the dependence of the rate constant of the true surface reaction on temperature. While the apparent Arrhenius relationships exhibit a common isokinetic temperature (Fig. 8), the true Arrhenius plots do not possess a single point of concurrence. Therefore, the principal criterion for compensation behaviour is not met in the latter case. The compensation effect can be said to be a direct result of apparent kinetic measurements which neglect the underlying adsorption phenomena.

# Conclusion

The principal findings reported herein may be summarized thus: (i) Under steady-state conditions and in the absence of diffusional constraints TOF and RP increase in the order oxylene < toluene < benzene over the temperature range  $388 \leq T/K \leq 523$ . (ii) A reversible  $T_{max}$  which was observed to decrease in the sequence benzene > toluene > o-xylene is attributed to a critical loss of the reactive aromatic species from the surface. (iii) The reaction orders with respect to the aromatic and hydrogen partial pressures increase with increasing temperature from 0 to 0.5 and 0.7 to 2.3, respectively, where a non-competitive adsorption of the reactants occurs on the surface. (iv) The variation of rate constant with temperature yields both positive and negative activation energies. Taking the reaction energies to be equivalent to the chemisorption energies, values of  $\Delta_{ads} H$  were evaluated where the enthalpy of adsorption increases with increasing methyl substitution. (v) Values of  $E_{true}$ , obtained by adding  $\Delta_{ads} H$  as a positive quantity to  $E_{app}$ , reflect an increase in aromatic-ring stability with methyl substitution. While the  $E_{app}$  values for

benzene and toluene hydrogenation over Ni/SiO<sub>2</sub> differ, beyond experimental error, from those recorded for Ni/K-Y the values of  $E_{true}$  that were obtained are in agreement. (vi) A compensation effect has been observed for the relationship between  $\ln A_{app}$  and  $E_{app}$  with a  $T_{iso} = 458 \pm 13$  K. It is concluded that  $A_{app}$  and  $E_{app}$  are composite terms which incorporate contributions due to the temperature dependence of the surface concentration of the reactive species.

#### References

- 1 A. Stanislaus and B. H. Cooper, Catal. Rev.-Sci. Eng., 1994, 36, 75.
- 2 M. J. Ledoux, K. Kippelen, G. Mare, G. Szabo, J. Goupyl and O. Krause, *Bull. Soc. Chim. Belg.*, 1991, **100**, 873.
- 3 H. Greenfield, Ann. N.Y. Acad. Sci., 1973, 214, 233.
- 4 P. N. Rylander, *Hydrogenation Methods*, Academic Press, London, 1985.
- 5 J. W. E. Coenen and R. Z. C. van Meerten, in Proceedings of the 5th International Congress on Catalysis, ed. J. W. Hightower, North-Holland, Amsterdam, 1973, p. 671.
- 6 W. M. Madden and C. Kemball, J. Chem. Soc., 1961, 54, 302.
- 7 J. R. Anderson, Aust. J. Chem., 1957, 10, 409.
- 8 G. D. Lyubarskii, L. I. Ivanooskaya and G. G. Isaeva, Kinet. Katal., 1960, 1, 235.
- 9 J. E. Germain, R. Maurel, Y. Bourgeois and R. Sinn, J. Chim. Phys., 1963, 38, 1219.
- 10 K. P. Roethe, A. Roethe, B. Rosahl and D. Gelbin, Ing. Tech., 1970, 42, 805.
- 11 L. N. Canjar and F. S. Manning, J. Appl. Chem., 1962, 12, 73.
- 12 J. Nicolai, R. Martin and J. C. Jungers, Bull. Soc. Chim. Belg., 1948, 57, 555.
- 13 O. Beeck and A. W. Ritchie, Discuss. Faraday Soc., 1950, 8, 159.
- 14 B. Wauquier and J. C. Jungers, Bull. Soc. Chim. France, 1957, 1280.
- 15 C. Herbo, Bull. Soc. Chim. Belg., 1941, 50, 257.
- 16 R. A. Ross, G. D. Martin and W. G. Cook, Ind. Eng. Chem. Prod. Res. Dev., 1975, 14, 151.
- 17 P. C. Aben, J. C. Platteeuw and B. Southame, in *Proceedings of the 4th International Congress on Catalysis*, ed. J. W. Hightower, North-Holland, Amsterdam, 1969, p. 543.
- 18 R. Z. C. van Meerten and J. W. E. Coenen, J. Catal., 1975, 37, 37.
- 19 W. F. Taylor, J. Catal., 1967, 9, 99.
- 20 G. M. Dixon and K. Singh, Trans. Faraday Soc., 1969, 65, 1128.
- 21 K. P. G. Kehoe and J. B. Butt, J. Appl. Chem. Technol., 1972, 22, 23.
- 22 K. H. V. Prasad, K. B. S. Prasad, M. M. Mallikarjunan and R. Vaidyeswaren, J. Catal., 1983, 84, 65.
- 23 W. F. Taylor, D. J. C. Yates and J. H. Sinfelt, J. Phys. Chem., 1964, 68, 2962.
- 24 C. Mirodatos, J. A. Delmon and G. A. Martin, J. Catal., 1987, 105, 405.
- 25 N. E. Zlotina and S. L. Kiperman, Kinet. Katal., 1967, 8, 337.
- 26 R. Z. C. van Meerten, A. C. M. Verhaak and J. W. E. Coenen, J. Catal., 1976, 44, 217.
- 27 M. S. Borisova, V. A. Dzisko and Yu. O. Bulgakova, *Kinet. Katal.*, 1971, **12**, 344.
- 28 H. A. Franco and M. J. Philips, J. Catal., 1980, 63, 346.
- 29 G. A. Martin and J. A. Delmon, J. Catal., 1982, 75, 233.
- 30 H. Fujie, K. Mori, K. Tamura, S. Okada, S. Matsuoka and H. Matsuoka, Chem. Lett., 1982, 1449.
- 31 K. G. Ione, V. N. Rommanikov, A. A. Davidov and L. B. Orlova, J. Catal., 1979, 57, 126.
- 32 V. Kanazirev, V. Penchev, C. Minchev, U. Ohlerich and F. Schmidt, in *Structure and Reactivity of Zeolites*, ed. P. A. Jacobs, Elsevier, Amsterdam, 1984, p. 329.
- 33 P. N. Galich, V. S. Gutyra and A. A. Gallinski, in Proceedings of the 5th International Conference on Zeolites ed. L. V. C. Rees, Heyden, London, 1980, p. 661.
- 34 L. Daza, B. Pawelec, J. A. Anderson and J. L. G. Fierro, Appl. Catal. A: General, 1992, 87, 145.
- 35 M. Suzuki, K. Tsutsumi and H. Takahashi, Zeolites, 1982, 2, 51.
- 36 M. Briend-Faure, M. F. Guilleux, J. Jeanjean, D. Delafosse, G. Djega Mariadassou and M. Bureau Tardy, Acta Phys. Chem. (Szeged), 1978, 24, 99.
- 37 B. Coughlan and M. A. Keane, Zeolites, 1991, 11, 12.
- 38 B. Coughlan and M. A. Keane, Zeolites, 1991, 11, 483.
- 39 B. Coughlan and M. A. Keane, J. Mol. Catal., 1990, 63, 193.
- 40 B. Coughlan and M. A. Keane, J. Mol. Catal., 1992, 71, 93.

- 41 R. L. Motard, R. F. Burke, L. N. Canjar and R. B. Beckmann, J. Appl. Chem., 1957, 7, 1.
- Yu. S. Snagovskii, G. D. Lyubarskii and G. M. Ostrovskii, 42 Kinet. Katal., 1966, 7, 232.
- R. Z. C. van Meerten and J. W. E. Coenen, J. Catal., 1977, 46, 43
- L. Červený and V. Růžička, Catal. Rev.-Sci. Eng., 1982, 24, 503. A. P. G. Kieboom and F. van Rantwijk, Hydrogenation and 44 45
- Hydrogenolysis in Synthetic Organic Chemistry, Delft University Press, Delft, 1977. 46 B. Coughlan and M. A. Keane, Catal. Lett., 1990, 5, 101.
- L. M. Marmaladze, N. V. Nekrasov, B. S. Gudkov and S. Kiper-47 man, Acta Chim. Acad. Sci. Hung., 1977, 92, 73.
- J. Völter, M. Hermann and K. Heise, J. Catal., 1968, 12, 307. 48
- 49 F. Hartog and P. Zwietering, J. Catal., 1963, 2, 79.
- 50 K. Ohtsuka and J. Koga, J. Chem. Lett., 1992, 2073.
- 51 J. Völter, J. Catal., 1964, 3, 297.
- K. Matsuo and K. J. Klabunde, J. Catal., 1982, 73, 216. 52
- 53 M. V. Rahaman and M. A. Vannice, J. Catal., 1991, 127, 251; 1991, **127**, 267.
- J. M. Orozco and G. Webb, Appl. Catal., 1983, 6, 67. 54
- 55 S. Zrnčević and D. Rušić, Chem. Eng. Sci., 1988, 43, 763.
- 56 R. Gomez, G. Del Angel, C. Damian and G. Corro, React. Kinet. Catal. Lett., 1979, 11, 137. G. Lietz and J. Völter, J. Catal., 1976, 45, 121.
- P. Rabette, A. M. Deane, A. J. Tench and M. Che, Chem. Phys. 58 Lett., 1979, 60, 348.
- 59 J. Bandiera and P. Meriaudeau, React. Kinet. Catal. Lett., 1988, 37, 373.
- M. A. Keane, Ind. J. Technol., 1992, 30, 51.
- B. Coughlan and M. A. Keane, J. Chem. Soc., Faraday Trans., 61 1990, 86, 3961.
- C. Minot and P. Gallezot, J. Catal., 1990, 123, 34. 62
- C. M. Friend and E. L. Muetterties, J. Phys. Chem., 1987, 91, 63 389
- 64 M. Abon, J. C. Bertolini, J. Bily, J. Massardier and B. Tardy, Surf. Sci., 1985, 162, 395.
- 65 C. L. Lau and R. G. Snyder, Spectrochim. Acta., 1971, 27, 2073.
- Ch. P. Rader and H. A. Smith, J. Am. Chem. Soc., 1962, 84, 66 1443.
- 67 H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 1945, 67, 279.
- N. Najemnik and M. Zdrazil, Collect. Czech. Chem. Commun., 68 1976, 41, 2895.
- 69 M. Armendia, V. Borau, C. Jimenez and J. M. Marinas, Bull. Soc. Chim. Belg., 1982, 91, 743.
- S. Siegel, Adv. Catal., 1966, 16, 123. 70
- 71 M. A. Keane and G. Webb, J. Catal., 1992, 136, 1.
- 72 B. Coughlan and M. A. Keane, J. Catal., 1990, 123, 364.
- 73 M. A. Keane, Can. J. Chem., 1994, 72, 372.
- 74 W. Romanowski, Highly Dispersed Metals as Adsorbents, Wiley, New York, 1987, p. 171.

- 75 J. W. E. Coenen, Appl. Catal., 1989, 54, 65.
- M. Montes, C. Pennemann de Bosscheyde, B. K. Hodnett, F. 76 Delannay, P. Grange and B. Delmon, Appl. Catal., 1984, 12, 309.
- 77 J. S. Smith, P. A. Thrower and M. A. Vannice, J. Catal., 1981, 68, 270.
- J. W. E. Coenen, Appl. Catal., 1991, 75, 193. 78
- P. B. Weisz, Z. Phys. Chem. (Frankfurt am Main), 1957, 11, 1. 79
- 80 G. A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.
- S. D. Lin and M. A. Vannice, in Proceedings of the 10th International Congress on Catalysis, ed. L. Guczi, F. Solymosi and P. Tetenyi, Elsevier, 1993, p. 861.
- G. Gilman and G. Cohn, Adv. Catal., 1957, 9, 733. 82
- 83 G. C. Bond, Catalysis by Metals, Academic Press, London, 1962.
- 84 J. Candy and P. Foilloux, J. Catal., 1975, 38, 110.
- A. J. Renouprez and G. Clagnet, J. Catal., 1982, 74, 296. 85
- M. C. Tsai and E. L. Muetterties, J. Am. Chem. Soc., 1992, 104, 86 2543.
- 87 S. D. Lin and M. A. Vannice, J. Catal., 1993, 143, 554; 1993, 143, 563.
- P. Tétényi and L. Barbenics, J. Catal., 1967, 8, 215; 1970, 17, 35. 88 M. R. Churchill and R. Mason, Proc. R. Soc. Ser. A, 1966, 192, 89
- 61.
- J. M. Basset, G. Dalmai-Imelik, M. Primet and R. Martin, J. Catal., 1975, 37, 22. 90
- J. R. Anderson and C. Kemball, Adv. Catal., 1957, 9, 51. 91
- W. F. Taylor and H. K. Staffin, Trans. Faraday Soc., 1967, 63, 92 2309.
- 93 R. Z. C. van Meerten, A. Morales, J. Barbier and R. Maurel, J. Catal., 1979, 58, 43.
- R. A. Ross and B. G. Walsh, J. Appl. Chem., 1961, 11, 469. 94
- 95 A. K. Galwey, Adv. Catal., 1977, 26, 247
- G. A. Martin, J. Catal., 1979, 60, 345. 96
- 97 A. Frennet, G. Lienard, A. Crucq and L. Degols, J. Catal., 1978, 53, 150.
- 98 P. G. Ashmore, Catalysis and Inhibition of Chemical Reactions, Butterworths, London, 1963.
- A. W. Adamson, Physical Chemistry of Surfaces, Wiley, New 99 York, 5th edn., 1990.
- 100 A. K. Galwey and M. E. Brown, J. Catal., 1979, 60, 335.
- 101 R. K. Agrawal, J. Therm. Anal., 1986, 31, 73; 1989, 35, 73.
- O. Exner, Collect. Czech. Chem. Commun., 1973, 38, 1425. 102
- A. Corma, F. Llopis, J. B. Mouton and S. Weller, J. Catal., 1993, 142, 97; 1994, 148, 415. 103
- A. Palermo, M. P. Suárez and C. M. Aldao, J. Catal., 1994, 148, 104 413.
- P. Tétényi, J. Catal., 1994, 147, 601. 105

Paper 5/06436H: Received 29th September, 1995