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Temperature Programmed Hydrogenation of Toluene

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Abstract Supported Ni, Co, Pt and Ir catalysts were studied by temperature programmed gas phase hydrogenation (TPH) of toluene to evaluate the performance of the catalysts and to obtain information about the applicability of temperature programming to hydrogenation studies. On all catalysts the reaction rate passed through a maximum as the temperature increased. The maximum reaction rate was reached at slightly lower temperatures with the Co catalyst than the Ni, Pt and Ir catalysts. This work demonstrates that TPH is a rapid method for evaluating the performance of hydrogenation catalysts and, combined with temperature programmed desorption, provides information on the reaction mechanism unobtainable from isothermal experiments.

Keywords Temperature programmed hydrogenation · Toluene · Temperature programmed desorption

1 Introduction

Temperature programmed hydrogenation (TPH) is related to thermoanalytical techniques such as temperature programmed reduction (TPR) and temperature programmed desorption (TPD) used for characterisation of gas–solid interactions. TPH can also be regarded as a transient kinetic experiment and utilised for kinetic modelling. Temperature-programmed surface reaction experiments, such as TPH, have been applied for the qualitative evaluation of catalyst performance [1–3], the determination of kinetic parameters [4–7] and the detection of surface species after isothermal reaction [1, 8, 9].

Usually, comparison of the performance of catalysts is a laborious and time-consuming task requiring activity measurements under several sets of process conditions. The greatest benefit of temperature programming over conventional steady-state measurements is the acceleration of the experimental work [1, 3, 10]. Data over a wide temperature range can be collected in one run, which reduces the time required for catalyst screening or kinetic studies.

Heterogeneous hydrogenation of aromatic compounds is a widely used model reaction to gauge the catalytic activity of metals, and as well is of environmental and commercial importance [11]. Most studies concern the hydrogenation of benzene; other aromatics have gained less attention. Many details of the hydrogenation reaction mechanism have been mostly agreed on, including the associative adsorption of the reactive aromatic compound and the dissociative adsorption of hydrogen, the behaviour of apparent reaction orders of reactants as the temperature changes, and the occurrence of a maximum in the hydrogenation rate as a function of temperature [12]. Less clear mechanistic features include the nature of the active site(s) and whether the adsorption of the reactants is competitive or non-competitive.

The emergence of a maximum in the hydrogenation rate as a function of temperature makes the gas-phase hydrogenation of aromatics an especially attractive reaction for TPH studies. We carried out the TPH of toluene for four metal catalysts (Ni, Co, Pt, Ir) identifying their activity between 50 and 200 °C. Three heating rates and one feed composition were employed. The aim was to obtain a qualitative view of the activity pattern and quantitative values for the maximum reaction rates and the temperatures at which these were reached. In addition, details of

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the reaction mechanism were examined through specific TPD experiments with toluene and methylcyclohexane and the Ni/Al_2O_3 catalyst. Finally, the TPH method and its merits and challenges were assessed.

2 Experimental

Temperature programmed gas phase hydrogenations were carried out with an Altamira Instruments Ami-100 unit. The unit includes a quartz glass u-tube which was utilised as a continuous flow reactor. The reactor outflow was analysed with a quadrupole mass spectrometer (Balzers Thermocube or Pfeiffer Vacuum ThermoStar). At the beginning of each experiment, a 10.3% H_2/Ar gas mixture (10 cm^3(NTP) min^{-1}) was fed to the reactor for 4 min to saturate the catalyst surface with hydrogen. The H_2/Ar mixture was then directed through a saturator that contained toluene at 0 °C. The saturated gas stream contained approximately 89 vol% Ar, 10 vol% H_2 and 0.9 vol% toluene (calculated composition). During these initial phases the reactor temperature was kept at 50 °C. After the toluene feed had been on for 6.5 min to saturate the sample surface with toluene, the temperature program was started. In each experiment, the temperature was raised three times at a constant but different rate from 50 to 200 °C. The heating rate was 11.5 °C min^{-1} in the first heating ramp, 6 °C min^{-1} in the second and 18 °C min^{-1} in the third. During cooling between the ramps the H_2/Ar gas stream passed by the saturator so that no toluene was fed to the catalyst. After cooling to 50 °C, the H_2/Ar stream was again directed through the saturator, and after a delay of 6.5 min the next temperature ramp was started. All TPH experiments were carried out at atmospheric pressure.

Three commercial catalysts and one non-commercial catalyst, which was prepared by atomic layer deposition (ALD) [13], were tested. The commercial catalysts were 16.6% Ni/Al_2O_3, 0.33% Pt/Al_2O_3 and 21.5% Co/SiO_2. The ALD catalyst was 0.42% Ir/Al_2O_3. The particle size was 0.2–0.4 mm for the nickel and the cobalt catalysts, 0.2–0.5 mm for the platinum catalyst and 0.15–0.35 mm for the iridium catalyst. For the nickel catalyst the absence of diffusion limitation was checked with a smaller particle size and on the basis of the Weisz–Prater criterion it was concluded that there were no diffusion limitations with any of the catalyst.

The catalyst loading was about 20 mg for the nickel and cobalt catalysts and about 70 mg for the platinum and iridium catalysts. Before the hydrogenation the commercial catalysts were dried in argon stream at 160 °C and reduced at 400 °C with pure hydrogen. The pretreatment for the ALD catalyst included calcination between the drying and reduction steps. The calcination was done at 350 °C with 20% O_2/He. The mass spectrometer was calibrated between the pretreatment and hydrogenation. The m/z values were 91 and 92 for toluene, 55, 83 and 98 for methylcyclohexane (MCH), 2 for H_2 and 20 for Ar. During the calibration the pretreated catalyst was kept under argon flow.

Toluene-TPD and methylcyclohexane-TPD (MCH-TPD) were carried out with the Ami-100 unit for the nickel catalyst. Toluene-TPD was also performed with pure alumina (Akzo 001-1.5E, sieve fraction 0.2–0.4 mm). Adsorption temperature was 50 °C. During the adsorption, an argon flow of 10 cm^3 min^{-1} saturated with a hydrocarbon was directed through the sample. The adsorption was continued until the sample was saturated with the hydrocarbon. After the adsorption, temperature was increased from 50 to 200 °C at a constant rate of 11.5 °C min^{-1}. In toluene-TPD the heating stage was run in one of two different ways: (1) the toluene feed was kept on during the heating or (2) the sample was flushed with Ar for 15 min after adsorption, and during the heating only argon was fed to the sample. MCH-TPD was run only with option 2. The amount of desorbed toluene or MCH was monitored with the mass spectrometer.

The chemicals used were toluene ($\geq$99.5%, AnalytiCals Carlo Erba) and MCH (99%, Sigma–Aldrich). The gases were argon (99.999%), hydrogen (99.999%), 10.3% hydrogen (99.999%) in argon (99.999%) and 20% oxygen (99.999%) in helium (99.99%). All gases were purchased from AGA.

MCH has been reported to be the only hydrogenation product of toluene [12, 14–16]. This was confirmed experimentally with the nickel catalyst by scanning the mass spectrum of the reactor outflow up to m/z 100 (molar mass of MCH is 98). No additional peaks were detected relative to the mass spectra of toluene and MCH. Hydrocarbon mass balances were calculated for each run. The relative errors from −9 to +5% in the hydrocarbon balances were attributed to errors in the analysis or to fluctuations in the feed flow of toluene. Because the mass balances were as accurate with the other catalysts as with the nickel catalyst, it was concluded that MCH was the only product with all the catalysts.

In this study the hydrogenation rate is defined to be equal to the molar outflow of MCH. This was judged to be a reasonable simplification for qualitative analysis of the TPH results although the reactor did not behave as a differential one in all of the experiments. The reaction rates reported in the results and discussion section were calculated directly from the molar outflow of MCH. The temperature of the maximum reaction rate (T_{max}) is defined as the temperature at which the MCH flow reached a maximum. The TPH results were reproducible.

Apparent turnover frequencies (TOF) were calculated on the basis of static hydrogen chemisorption measurements done with Coulter Omnisorp 100CX equipment. Details of these measurements can be found elsewhere [17, 18]. For the nickel, platinum and iridium catalysts the calculation of apparent TOF was based on irreversible hydrogen uptake at 30 °C. For the cobalt catalyst the calculation was based on total hydrogen uptake at 100 °C.

3 Results and Discussion

3.1 Qualitative Characteristics of TPH

All catalysts were active in toluene hydrogenation in the studied temperature and concentration ranges, and methylcyclohexane (MCH) was the only product. The MCH and toluene flows out of the reactor as a function of temperature for each catalyst are presented in Fig. 1. The MCH formation was similar for the four catalysts: when the temperature ramp was started the amount of MCH began to increase, at some point (T_{max}) it reached a maximum, and then it began to decrease, so that at the end of the ramp (T = 200 °C) it was around the same level as at the beginning. The maximum reaction rate (r_{max}) and T_{max} were different for each catalyst. Another direct observation regarding the MCH curves was that a severe deactivation took place in all TPH experiments, as the activity dropped cycle by cycle.

As the temperature ramp began, the amount of toluene in the exit stream increased above the feed level, it then smoothly dropped to a minimum, before increasing again to the feed level. The increase above the feed level is explained by net desorption of toluene: some of the toluene was adsorbed on the catalyst before the ramp at 50 °C and began to desorb as the temperature increased. Owing to the partial overlap of the toluene desorption and the toluene consumption in the surface reaction, the minimum in the toluene curve and the maximum in the MCH curve do not occur simultaneously. The toluene outflow behaved qualitatively the same with the nickel, platinum and iridium catalysts (Fig. 1). With the noble metal catalysts the toluene desorption dominated the outflow curve to such an extent that in the second and third cycles the consumption of toluene on the surface reaction was practically undetectable. With the cobalt catalyst the toluene desorption peaks were not clear, especially in the second and third ramps the amount of toluene in the exit stream appeared to fluctuate more or less randomly. The amount of hydrogen in the exit stream was as expected (not displayed), and the minimum was correlated with the maximum of the MCH curve.

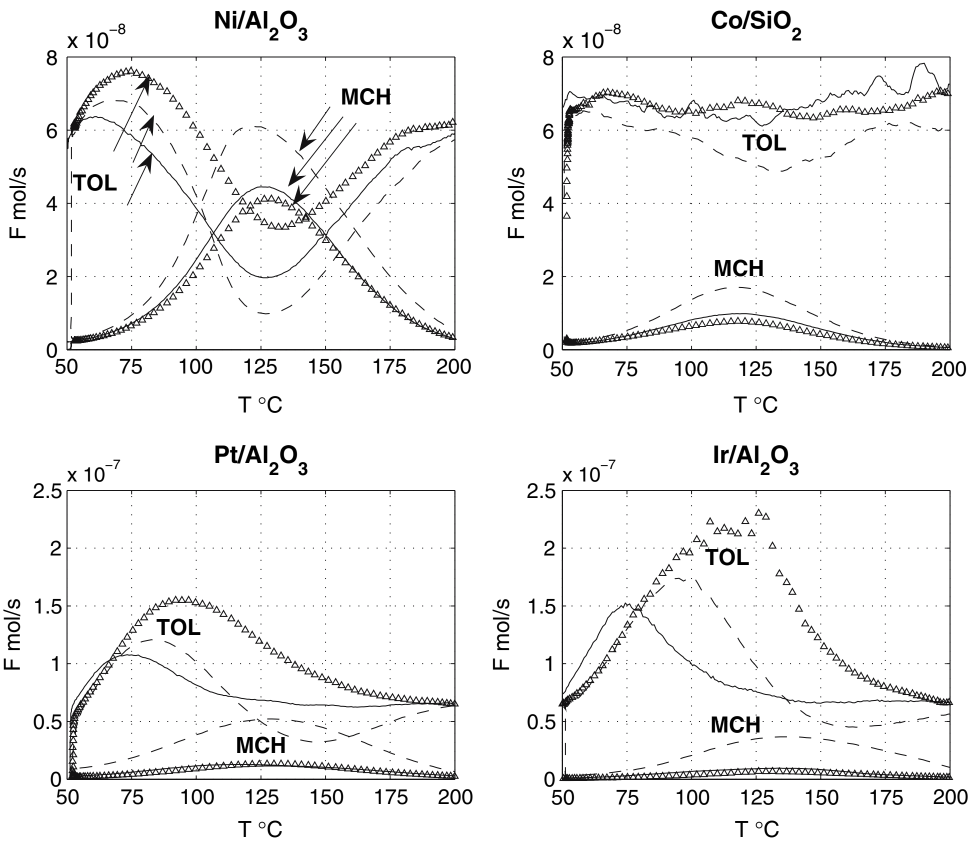

Fig. 1 Amounts of toluene and methylcyclohexane in the exit stream in temperature programmed hydrogenation of toluene. The heating rates in the first (dashed line), second (continuous line) and third (triangles) ramp were 11.5, 6 and 18 °C min^{-1}, respectively

Table 1 Toluene-TPH results in the first heating ramp (11.5 °C/min)

Catalyst	16.6% Ni/Al_2O_3	21.5% Co/SiO_2	0.33% Pt/Al_2O_3	0.42% Ir/Al_2O_3
Catalyst loading (mg)	21	19	67	69
T_{max} (°C)	122	118	129	137
Reaction rate at T_{max} per mass of the catalyst (mol s^{-1} $g_{cat}{}^{-1}$)	3×10^{-6}	9×10^{-7}	8×10^{-7}	5×10^{-7}
Reaction rate at T_{max} per mass of the metal (mol s^{-1} $g_{met}{}^{-1}$)	2×10^{-5}	4×10^{-6}	2×10^{-4}	1×10^{-4}
Apparent TOF at T_{max} (s^{-1})	8×10^{-3}	1×10^{-2}	6×10^{-2}	2×10^{-2}
Hydrogen uptake in static chemisorption (mol H^- atoms/g_{met}); for Co, total; for others, irreversible	2.3×10^{-3}	2.8×10^{-4}	4.2×10^{-3}	6.8×10^{-3}

3.2 Hydrogenation Rate Maximum

Table 1 reports apparent TOF values, and the reaction rates per mass of catalyst and per mass of the metal at T_{max} in the first heating ramp. The hydrogen uptake in the static chemisorption, on the basis of which the apparent TOF values were calculated, is included. The order from the highest to lowest apparent TOF was Pt > Ir > Co > Ni. When the maximum hydrogenation rates per mass of the metal are compared, the order from the most active to the least active catalyst is Pt > Ir > Ni > Co. In a comparison of the reaction rates per total mass of catalyst, the following order of the rates is obtained: Ni > Co > Pt > Ir.

A few points should be kept in mind in considering the r_{max} values. First, with the nickel catalyst the conversion of toluene at r_{max} was very high, and the hydrogenation rate was probably somewhat retarded by the exhaustion of this reactant. Second, the chemisorption measurements for the cobalt catalyst were made at higher temperature than those for the other catalysts and the calculations were based on total instead of irreversible adsorption. This was because the chemisorption of hydrogen on cobalt has been reported to be activated [19, 20] and the evacuation time after the measurement of the total adsorption affected the amount of reversibly adsorbed hydrogen on the Co catalyst [17]. Third, since the deactivation was rapid and extensive and probably not equal on all the samples, the reported values are related to the initial transient in operation and do not describe the characteristic activity in long term operation. Despite the above points, the values obtained for the first-cycle apparent TOF at r_{max} suggest that platinum would be intrinsically the most active hydrogenation catalyst under the applied conditions.

The orders of magnitude of the toluene hydrogenation rates expressed as apparent TOF values agree fairly well with those reported previously for Ni [12, 14], Co [19], Pt [21–23] and Ir [24, 25] catalysts. Direct comparisons are not possible because the reaction rates are sensitive to the reaction conditions. Furthermore, when the deactivation is present even slight differences in the experimental procedure may influence the apparent TOF values. When different samples are to be studied and compared by TPH, it is advantageous to run all the samples with a similar procedure under same process conditions. In this way consistent results are obtained.

3.3 Temperature at Maximum Hydrogenation Rate (T_{max})

As Table 2 indicates, all catalysts had their own characteristic temperature (T_{max}) at which the rate maximum occurred. On average, TPH results showed that the maximum of the hydrogenation rate occurred at somewhat lower temperature for the cobalt catalyst than the other catalysts. In addition, T_{max} values varied from cycle to cycle for all catalysts except the cobalt catalyst for which T_{max} was practically constant.

There are two possible reasons for the shift of T_{max} values from cycle to cycle. Either intrinsic kinetics (energetics) is responsible for the shift of the rate maximum as a function of the heating rate or the deactivation is predominantly involved in shifting T_{max} in sequential runs. It is a typical feature of TPD and TPR techniques that with different heating rates the temperatures of rate maxima vary a little: typically the higher the heating rate the higher the T_{max} [26, 27]. The TPH experiments differed from TPD and TPR experiments in three ways: (1) both reagents were fed continuously during the heating ramps, whereas in TPD (and TPR) the species of interest is present as a batch that is consumed during the temperature ramp, (2) more complex reaction network contributed to the observable MCH production than to simpler desorption and reduction and (3) deactivation was present in TPH.

Table 2 Temperature at maximum reaction rate (T_{max}) in the three heating ramps of toluene-TPH

	16.6% Ni/Al_2O_3	21.5% Co/SiO_2	0.33% Pt/Al_2O_3	0.42% Ir/Al_2O_3
T_{max} (°C)				
1st ramp (11.5 °C/min)	122	118	129	137
2nd ramp (6 °C/min)	126	119	116	134
3rd ramp (18 °C/min)	129	118	130	130

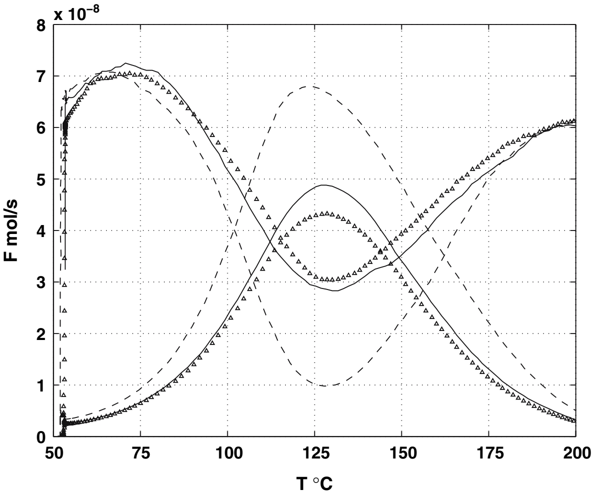

Fig. 2 Amounts of toluene and methylcyclohexane in the exit stream in temperature programmed hydrogenation for 16.6% Ni/Al_2O_3 catalyst with constant heating rate of 11.5 °C min^{-1}. First ramp (dashed line), second ramp (continuous line) and third ramp (triangles)

To distinguish a shift of T_{max} due to heating rate from a possible sift due to deactivation, we performed a three-cycle run with constant heating rate of 11.5 °C min^{-1} with the nickel catalyst. Figure 2 shows the results. The first cycle differed from the rest: T_{max} was lower (122 °C) because the high conversion of toluene around T_{max} started to limit the reaction rate and distorted the curve. In the second and third cycles the T_{max} was constant (128 °C). Thus we concluded that the shift of T_{max} from cycle to cycle is caused by different heating rate, and the deactivation only affects the activity level. This finding allows us to modify the results for the nickel catalyst in Table 2 with the value of T_{max} that is not influenced by the toluene exhaustion (i.e., 128 °C for ramp 11.5 °C/min). Thus, the rule of the higher the heating rate the higher the T_{max} appears to apply for Ni/Al_2O_3 catalyst. In the case of the noble metal catalysts, the T_{max} values of the second and the third cycle do not allow reliable inspection due to the low activity.

In general, the more sensitive T_{max} is to the heating rate, the higher are the energetics related to the rate determining step (rds). Comparison of the T_{max} values for the nickel and cobalt catalysts suggests that the energetics in hydrogenation are more favourable on cobalt than nickel, and possibly the activation energy of the rds is lower for cobalt than for nickel. However, the adsorption characteristics of the reactants are also involved in the determination of the peak position for temperature-programmed surface reactions.

The occurrence of a maximum reaction rate at a certain temperature in the hydrogenation of aromatics has been observed for various metal catalysts and by numerous groups. T_{max} has been observed in steady-state hydrogenation of toluene with Ni/Al_2O_3 catalyst [14] and in TPH of toluene with Co/SiO_2 and Co/Al_2O_3 catalysts [19]. The occurrence of a maximum reaction rate has also been reported in steady-state hydrogenation of toluene for Pt [15, 21, 28, 29] and in TPH of toluene for Ir catalysts supported on alumina and silica–alumina [30]. Under normal reaction conditions the hydrogenation/dehydrogenation equilibrium is completely on the hydrogenation side [12], and thus thermodynamic limitations are ruled out. Keane and Patterson [12] established for the hydrogenation of toluene on Ni/SiO_2 catalyst that the temperature of this reversible rate maximum (T_{max}) increases considerably with partial pressure of hydrogen but it is relatively insensitive to increase in the partial pressure of toluene.

3.4 Deactivation

In addition to the level of maximum activity, TPH data reveals how well the activity is retained. All the tested catalysts deactivated noticeably during TPH. With the nickel and the cobalt catalysts, the maximum hydrogenation rates were 27 and 42% lower in the second heating ramp than in the first. The corresponding values with the platinum and iridium catalysts were 75 and 74%. The noble metal catalysts deactivated clearly faster and more severely than the base metal catalysts.

Because deactivation occurs, the desorption and hydrogenation rates are not the only factors affecting the TPH curves. As mentioned above, however, it seems that deactivation only affects the level of activity and does not cause shifts in the T_{max} (Fig. 2). This implies that deactivation does not cause significant change in the reaction mechanism, but reduces the number of active sites. Others, too, have observed catalyst deactivation in gas phase hydrogenation of toluene. Backman et al. [19], who carried out temperature programmed toluene hydrogenation runs ($100 < T < 200$ °C) with Co catalysts, reported a 40% decrease in the maximum activity between the first and second temperature ramps. Chupin et al. [31] observed 20–30% deactivation in isothermal toluene hydrogenation with Pt/Al_2O_3 catalyst at 110 °C. Cunha and Cruz [24] reported 20–40% deactivation during the first 30 min and slower deactivation thereafter in 2-h toluene hydrogenation with Ir/Al_2O_3 at 60 °C. Cunha and Cruz [24] did not give any explanation for the deactivation, whereas Chupin et al. [31] and Backman et al. [19] attributed it to coking. We assume, as well, that the deactivation observed in our TPH experiments was due to carbonaceous deposits. Temperatures were so low that sintering is unlikely. No deactivation was observed when several adsorption–TPD cycles of toluene were run consecutively, which ruled out the presence of catalyst poisons. Moreover, these adsorption experiments indicate that pure aromatic compound does not cause deactivation to any significant extent under conditions equivalent to those of TPH. Deactivation thus seems to require an introduction of hydrogen. Partially hydrogenated intermediates that remain irreversibly adsorbed on the surface and possibly are polymerized are probably the precursors for coke.

Contrary to our results, some groups have reported no deactivation in the steady-state gas phase hydrogenation of toluene with Ni/Al_2O_3, Ni/SiO_2, Pt/Al_2O_3 and Ir/Al_2O_3 catalysts [12, 14–16]. In these experiments all or most of the deactivation had probably already occurred before the steady state was reached. Additionally, in some of them the hydrogen-to-toluene ratio was clearly higher than ours, which could reduce coke formation.

Lylykangas et al. [17, 18] observed deactivation in liquid-phase hydrogenation of isooctenes with the same Ni, Co and Pt catalysts as used in our study. The Ni catalyst lost 20%, the Co catalyst 45% and the Pt catalyst over 80% of its initial activity during 30 h runs. Thus, despite the different conditions of liquid-phase and gas-phase hydrogenations, there was a similar trend with toluene and isooctenes: the Ni catalyst deactivated least and the Pt catalyst most.

It is not possible on the basis of TPH to draw definitive conclusions about the deactivation behaviour of catalysts in long-term constant temperature hydrogenation. Nevertheless, the optimal reaction temperature should probably not exceed the temperature of the maximum conversion T_{max} in TPH.

3.5 Adsorption and Desorption in Toluene-TPH

As mentioned above, there were clear desorption peaks of toluene at the beginning of TPH with the nickel, platinum and iridium catalysts (Fig. 1). The amounts of toluene desorbed per mass of the metal during the first heating ramp are presented in Table 3. The amount of desorbed toluene was calculated by subtracting the total amount of toluene fed to the reactor during the ramp from the total amounts of toluene and MCH in the exit stream. The results of hydrogen chemisorption are included for comparison.

With the nickel catalyst the desorption peak of toluene in TPH was of moderate size. Less toluene desorbed from the catalyst than hydrogen adsorbed in the static chemisorption. With the platinum and iridium catalysts, in contrast, the amounts of toluene that desorbed during TPH were about 20 times the amounts of hydrogen adsorbed in static chemisorption. This implies that toluene desorbed not only from the platinum and iridium metal but also from the support. Owing to the lower metal contents (0.3–0.5% for noble metals and 16.6% for Ni) and to the consequently larger uncovered area of the support, toluene is able to interact more extensively with the support of the noble metal catalysts than that of the Ni catalyst.

Table 3 Amount of toluene desorbed in the first heating ramp of toluene-TPH

Catalyst	16.6% Ni/Al_2O_3	0.33% Pt/Al_2O_3	0.42% Ir/Al_2O_3
Desorbed toluene ($mol\ g_{met}^{-1}$)	5.2×10^{-4}	9.5×10^{-2}	1.3×10^{-1}
Hydrogen uptake in static chemisorption ($mol\ H^{-}\ atoms\ g_{met}^{-1}$)	2.3×10^{-3}	4.2×10^{-3}	6.8×10^{-3}

3.5.1 *Toluene-TPD Without Reaction*

A TPD experiment was carried out to obtain additional information on the interaction of toluene with the nickel catalyst. The toluene outflow during TPD is presented in Fig. 3. As can be seen, a clear desorption peak emerges in relatively similar temperature range as in TPH experiments with a peak around 80 °C. The net adsorbed and net desorbed amounts of toluene were 1.7×10^{-3} mol g_{met}^{-1}. This value is higher than the corresponding one in Table 3, which is natural because in TPH the surface is occupied also by other species. The amount of toluene adsorbed was so high (1.7×10^{-3} mol g_{met}^{-1} corresponds to 74% of the irreversible static chemisorption of hydrogen) that the exclusive adsorption on nickel metal is practically ruled out.

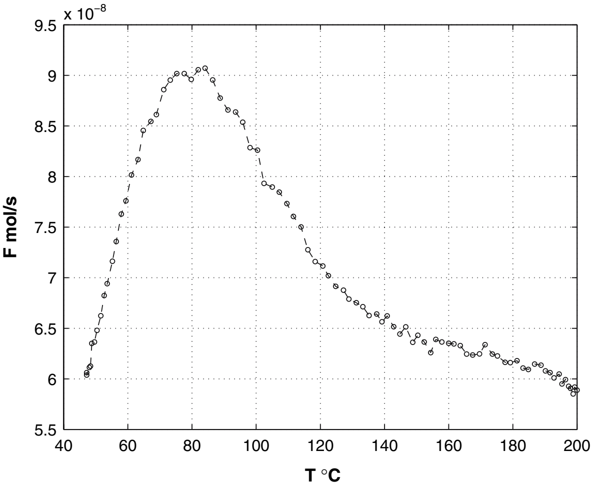

Fig. 3 Toluene-TPD for Ni/Al_2O_3, heating rate 11.5 °C/min

As toluene is known to interact with alumina [32–35], we examined this aspect separately under relevant conditions to determine whether it contributed to the adsorption of toluene on the nickel catalyst and thus to the TPH results. Figure 4 shows the resulting toluene-TPD curve for alumina. Clearly, toluene was able to adsorb on alumina, and it desorbed from the alumina under conditions relevant to TPH experiments. The maximum of desorption was at about 85 °C, close to the desorption peak of toluene for the Ni catalyst. Since toluene-TPD is similar for Ni/Al_2O_3 and pure Al_2O_3, either the major part of the adsorption sites on the catalyst are actually on the support or else toluene has more or less the same propensity for adsorption on nickel metal and on alumina. Gonzalez-Marcos et al. [33] have reported the adsorption entropy and enthalpy values for toluene on alumina ($\Delta S = -35.19$ cal/[mol K] and $\Delta H = -13.75$ kcal/mol), and we applied their values to calculate the adsorption equilibrium constant at different temperatures and resultant surface coverage. Figure 5 shows the equilibrium coverage of toluene in the temperature range from 50 to 200 °C under 0.89 mol% toluene (feed concentration in the TPH experiments). Clear changes in the coverage of toluene are observed up to 130 °C after which the surface is practically empty. These calculated results are in qualitative agreement with our adsorption results.

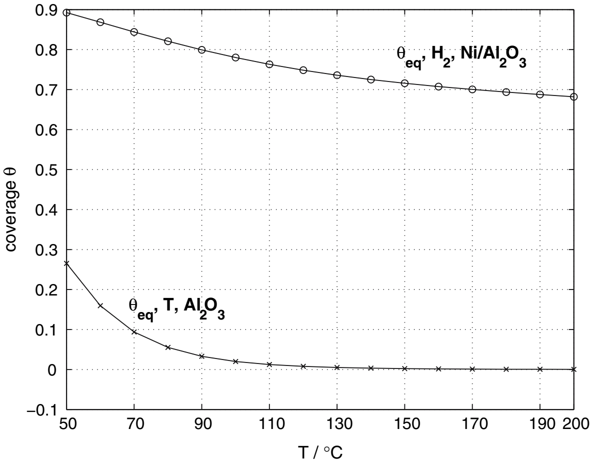

Fig. 5 Equilibrium surface coverage of hydrogen on Ni/Al_2O_3 catalyst, calculation based on Ref. [27], and equilibrium surface coverage of toluene on alumina, calculation based on Ref. [33]

3.5.2 *Interaction of H_2 with Ni/Al_2O_3*

Lindfors and Salmi [14], Rousset et al. [15] and Backman et al. [19] have explained the occurrence of T_{max} in the hydrogenation of aromatics in terms of the desorption of hydrogen: at a certain temperature the increase in the hydrogenation rate constant does not result in increased reaction rate because of decreasing surface coverage of hydrogen. To evaluate the adsorption behaviour of hydrogen in the temperature range of the TPH experiments, we refer to the work of Kanervo et al. [27] in which H_2-TPD was performed for the same nickel catalyst as in this study (Fig. 6). As is readily seen in Fig. 6, hydrogen desorbs in a wide temperature range. The adsorption model reported in Ref. [27] was used to predict the equilibrium coverage of hydrogen in the temperature range from 50 to 200 °C under 10.0 mol% hydrogen. Figure 5 shows how the coverage decreases smoothly from 0.9 to 0.7, and the nickel surface still contains ample amounts of hydrogen at the end temperature of TPH. Thus the adsorption behaviour of hydrogen does not appear to explain the sudden decline of hydrogenation activity after T_{max}.

The toluene-TPD data with the nickel catalyst and pure alumina show that support alumina is involved in toluene

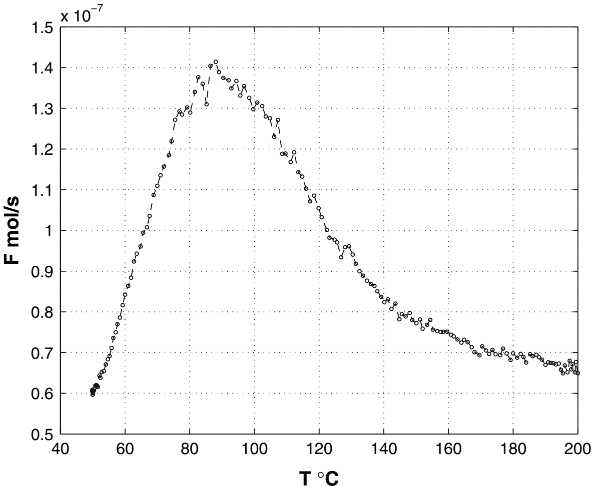

Fig. 4 Toluene-TPD for γ–Al_2O_3, heating rate 11.5 °C/min

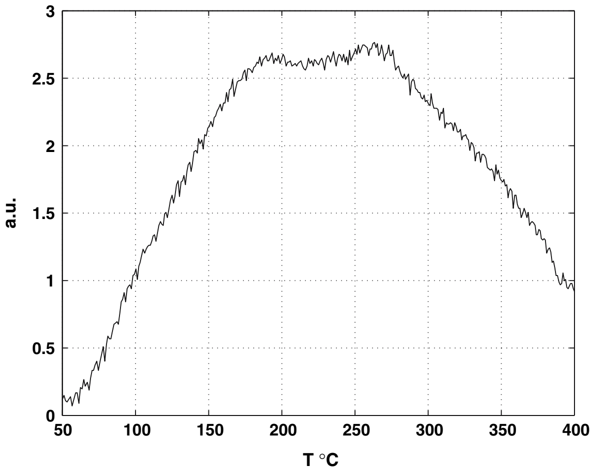

Fig. 6 H_2-TPD for Ni/Al_2O_3 catalyst. Heating rate was 12 °C min^{-1} [27]

adsorption and that the adsorption/desorption behaviour of toluene plays a role in the characteristics of TPH. The emergence of a reversible rate maximum in TPH is probably linked to the escape of aromatic compound from the catalyst rather than to the adsorption characteristics of hydrogen. The role of the support could also explain why adsorption of the aromatic compound and hydrogen has been found to be non-competitive in many gas-phase hydrogenation studies [36–40]. In an isotopic transient hydrogenation of benzene, Mirodatos [41] found that the coverage of surface benzene leading to the formation of cyclohexane is very low (<1% of the exposed metal atoms), and the metal surface is mainly covered with H_2 when Ni catalysts are used. He reported that benzene forms a large reservoir in a loosely adsorbed overlayer above the whole catalyst surface. A slightly different model proposed by Rahaman and Vannice [39] and Lin and Vannice [40] suggests that acid sites on the support in the vicinity of metal particles provide additional adsorption sites for aromatic compounds, which are subsequently hydrogenated by spilled-over hydrogen. Our results imply that the support probably hosts weakly bound toluene species that may feed and enhance the reaction, which means that these species are kinetically relevant. Nevertheless, the catalytic activity is clearly different for each metal since the temperatures of the rate maxima (T_{max}) are metal specific. Thus we conclude that the actual active hydrogenation site is on the metal surface rather than on the support. As suggested by Keane and Pattersson [12], the occurrence of r_{max} could be explained by both the supply and the reactivity of aromatic surface species.

3.5.3 Interaction of MCH with Ni/Al_2O_3

For completeness, the interaction of methylcyclohexane with Ni/Al_2O_3 was examined in a step adsorption experiment shortly followed by a TPD experiment. The TPD results are shown in Fig. 7. The net amount of adsorbed MCH on Ni/Al_2O_3 was of the same order of magnitude as that of toluene, but a little smaller (1.2×10^{-3} mol $g_{met}{}^{-1}$). The interaction of MCH with the nickel catalyst was clearly weaker than the interaction of toluene. This was deduced from the observation that with the same flushing time (15 min) and heating rate (11.5 °C min^{-1}) the response of MCH-TPD ceased earlier than that of T-TPD (in 26 and 32.6 min, respectively). All the adsorbed MCH could probably have been removed from the surface without heating, simply by flushing longer at the adsorption temperature. Product inhibition in hydrogenation is thus highly unlikely, but a minor delay in product desorption can be expected in fast transient experiments.

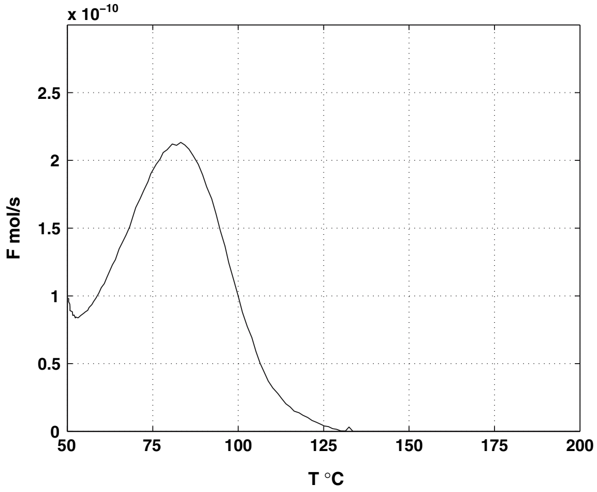

Fig. 7 MCH-TPD for Ni/Al_2O_3 catalyst. Heating rate 11.5 °C min^{-1}

3.6 Summary of the TPH Method

The use of multiple cycle TPH offers several advantages in both catalyst screening and kinetic studies. An overall picture of the catalytic activity as a function of temperature is obtained. In addition, an approximate optimal temperature range is found for each feed composition and catalyst, and the apparent TOF (or otherwise scaled) reaction rate in the optimal range is obtained. Any deactivation is clearly apparent in the TPH results, whereas it may go unnoticed in steady-state experiments. As a transient method, TPH offers rich information for kinetic modelling and kinetic data can be collected more rapidly by TPH than with steady-state experiments. TPH may reveal reaction mechanistic features that are hidden in steady-state data. In this study, for example, the net desorption of toluene from the catalyst at about 70–80 °C in TPH could be related to desorption from the catalyst support. Moreover, since the desorption of surface aromatic species in TPH is followed by a decrease in the hydrogenation activity, these species can be considered as kinetically relevant.

Utilisation of TPH requires careful consideration with regard to performing the experiments and interpreting their results. If catalyst samples are to be compared it is important to standardise the pretreatment and TPH procedure, since results are sensitive to these. It needs to be noted that, besides intrinsic kinetics, reaction rate curve also reflects other things, such as the decay in catalytic activity due to coking. If kinetic modelling is pursued, multiple feed compositions and heating rates are needed, and kinetic interpretation requires dynamic modelling. If long-term operation kinetics is a target of study, a catalyst aged in several heating cycles should be used for measurements.

4 Conclusions

The performance of commercial Ni, Pt and Co catalysts and a non-commercial Ir/Al_2O_3 catalyst was tested in temperature programmed hydrogenation of toluene. With all the catalysts, the hydrogenation rate achieved a maximum at a certain temperature. This maximum was reached at slightly lower temperature with the Co/SiO_2 catalyst than the Ni/Al_2O_3, Pt/Al_2O_3 and Ir/Al_2O_3 catalysts. Highest apparent TOF was obtained with the platinum catalyst, but deactivation was more severe with the platinum and iridium catalysts than the nickel and cobalt catalysts.

Much information about a catalyst can be obtained in single temperature programmed hydrogenation run: activity as a function of temperature, maximum apparent TOF and its temperature, and an overview of deactivation. The temperature programming has potential for reducing the amount of laboratory work in catalyst development, and it could prove useful in discriminating between the activity patterns of catalysts prepared and pretreated by slightly different procedures. To achieve genuinely comparable results for qualitative characterisation, the reaction conditions and the experimental procedure should be carefully standardised.

TPH and TPD experiments with a commercial Ni/Al_2O_3 catalyst resulted in the following observations and conclusions on the reaction mechanism: (1) desorption of toluene starts prior to the hydrogenation rate maximum, (2) a large part of the desorbing toluene probably comes from the support, (3) all the reversibly adsorbed toluene desorbs in the temperature range relevant to TPH, (4) the coverage of chemisorbed hydrogen decreases only moderately during TPH, (5) the product methylcyclohexane interacts weakly with the catalyst. The fifth observation—combined with the fact that the thermodynamics does not favour dehydrogenation—suggests that product inhibition is unlikely. The occurrence of a reversible rate maximum in hydrogenation is governed by the rate constant of the rate determining step together with the availability of the aromatic surface compound.

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