The importance of modifier pH in the generation of enantioselective nickel catalysts

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Enantioselective Ni/SiO_2 catalysts have been prepared by modification with aqueous solutions of (R)-(+)-tartaric acid (TA) and used in the asymmetric hydrogenation of a prochiral β-keto ester (methylacetoacetate) to a β-hydroxy ester ((R)-(−)-methyl-3-hydroxybutyrate). The simultaneous adsorption of TA and corrosive leaching of surface nickel metal are graphically illustrated and the progress of TA buildup on the catalyst surface with the duration of modification is presented. Variations of modifier pH were found to strongly affect the modification process and influence the ultimate hydrogenation rate and enantioselectivity. The surface coverage by TA is correlated to the asymmetric activity and an optimum fractional coverage of 0.2 is identified; at higher coverages modification with basic TA solutions yielded superior enantioselectivities. While TA treatment in basic media was less corrosive, a proportion of the surface enantioselective nickel sites was leached into solution during the hydrogenation step. The difference in the response of nickel precursors, prepared by impregnation and homogeneous precipitation/deposition, to TA treatment is compared and discussed in terms of metal/support interaction.

Keywords: Enantioselective hydrogenation; methylacetoacetate; impregnation; homogeneous precipitation/deposition; tartaric acid adsorption on Ni/SiO_2; nickel leaching

1. Introduction

The widespread use of biologically active compounds in agrochemical and pharmaceutical industries demands the development of new synthetic routes to optically pure products. One possible avenue, the selective production of enantiomers by chiral surfaces, has not as yet been fully explored. Conventional metal catalysts do not possess intrinsic chirality with the result that the bare metal surface generates a racemic product [1–6]. A chiral environment is normally achieved by treating the activated catalyst with an optically pure reagent or catalyst "modifier". Three comprehensive reviews are now available [7–9] in which the various enantioselec-

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tive catalyst systems reported in the literature have been compiled. To date, the asymmetric hydrogenation of β-ketoesters by hydroxy-acid modified nickel catalysts has been the most studied application of asymmetric heterogeneous catalysis. In particular, the enantioselective hydrogenation of methylacetoacetate (MAA) to methyl-3-hydroxybutyrate (MHB) over tartaric acid (TA) modified nickel catalysts has been used as a model system to probe the various experimental parameters affecting the ultimate optical yield [7,10,11].

In the asymmetric conversion of MAA to MHB over TA treated unsupported [1,7,10,13,14,17,18,23,24] and supported [1–4,12,15–17,21,22] nickel systems, the degree of enantiodifferentiation has been shown to be strongly dependent on the modification conditions. The effects of varying the modification time [2,13,14] and temperature [2,7,12,13,15], the modifier concentration [1–3,13,16,17] and the influence of co-modifiers [1–3,7,10,16,21–24] have already been considered. Nevertheless, there is still no consensus of opinion regarding the actual source of the enantiocontrol or the nature of the enantioselective site. Indeed, attempts made to relate optical yield to the surface coverage of modifier have been largely unsuccessful [14,16,24–26]. There is, however, general agreement [1–3,7,10,21,25] that the overall values of enantiomeric excess reflect the relative contribution of the TA modified (selective) sites which promote preferential enantiomer formation and the bare (non-selective) metal sites which catalyse racemic hydrogenation. In this paper the decisive role of pH on the modification process and the ultimate product composition is discussed. Data on the dependence of TA adsorption and nickel leaching on the modifier pH and the sensitivity of the apparent reaction rate to the modification conditions are presented here. The influence of catalyst precursor preparation (deposition versus impregnation) on the modification process is also considered.

2. Experimental

An 11.9% w/w Ni/SiO_2 catalyst was prepared by the homogeneous precipitation/deposition of nickel onto a non-porous microspheroidal Cab-O-Sil 5M silica as described in detail elsewhere [2]. In addition, an 11.6% w/w Ni/Cab-O-Sil 5M silica catalyst was prepared by impregnation to incipient wetness [27]. The hydrated supported precursors (sieved in the mesh range 150–125 μm) were reduced, without a precalcination step, by heating in a 150 $cm^3\ min^{-1}$ stream of purified hydrogen at a fixed rate of 5 K min^{-1} to a final temperature of 723 ± 2 K which was maintained for 18 h. The reduced catalysts were then flushed in a purified stream (200 $cm^3\ min^{-1}$) of nitrogen, cooled to room temperature and contacted with 100 cm^3 (0.02–0.05 mol dm^{-3}) aqueous solutions of TA (pH in the range 1.5–11.8). The resultant solutions were thoroughly purged with nitrogen to remove any entrapped air bubbles. The modification was performed in air with constant agitation (600 rpm) for 2 h at the desired temperature (±2 K). The tartaric acid was of AnalaR grade and the prepared solutions were found to be better than 99% pure by HPLC; the concentrations of the TA solutions used in the modifications were reproducible to within ±1%. After modification, the catalysts were decanted and washed with distilled water (1 × 25 cm^3), methanol (2 × 25 cm^3) and *n*-butanol (2 × 25 cm^3) before being stored in the latter prior to use. Nickel metal dispersions, degree of surface nickel leaching and TA uptake were measured using the published procedures [2].

The liquid phase hydrogenation of MAA (10 cm^3), using *n*-butanol as a solvent (40 cm^3) was carried out at 343 ± 2 K in a 250 cm^3 glass vessel fitted with a condenser, hydrogen inlet and thermocouple well. A 60 cm^3 min^{-1} stream of purified hydrogen was bubbled through the suspension which was kept under constant agitation at 600 rpm. Details of the catalytic apparatus are available elsewhere [2,5]. The extent of hydrogenation was determined by HPLC using a Pirkle type 1A 5μ reversible column (250 × 4.6 mm) with a 10% IPA: 90% *n*-hexane mixture as the mobile phase. The overall degree of hydrogenation was converted to mol% MHB using a 21 point calibration plot; a quadratic equation was used to fit these data to better than ±1%. The combination of bubbling hydrogen at a fixed rate through the thoroughly degassed and agitated catalyst/substrate suspension resulted in conversion levels which were reproducible to ±2%. The extent of nickel leaching during the catalytic step was also monitored by AA spectrophotometry, correcting the calibration curve for the presence of reactant, product and solvent. Optical yields (OY) were determined from measurements of optical rotation (AA-10 Automatic Digital Polarimeter) using the equation

$$\mathrm{OY} = [\alpha]_{\mathrm{D}}^{T}/[\alpha]_{0}^{T} = 100\alpha/[\alpha]_{0}^{T} lc,$$

where $[\alpha]_{\mathrm{D}}^{T}$ is the specific rotation of the product solution measured at the sodium D-line and temperature T (293 ± 3 K), $[\alpha]_{0}^{T}$ is the specific rotation of the pure enantiometer under the same conditions (−22.95° for R-(−)-MHB), α is the measured optical rotation, l is the path length (20 cm) of the cell and c is the solute concentration. Optical rotation versus R-(−)-MHB concentration (in MAA/butanol) data were fitted to a quadratic equation to better than ±2% which was then used to determine the optical yield of the product; optical yields were reproducible to ±4%. In this paper, optical selectivity is expressed in terms of enantiomeric excess (ee) which is defined as

$$\%\mathrm{ee} = 100\{[\text{R-}(-)\text{-MHB}] - [\text{S-}(+)\text{-MHB}]\}/\{[\text{R-}(-)\text{-MHB}] + [\text{S-}(+)\text{-MHB}]\}.$$

3. Results and discussion

Modification of the Ni/SiO_2 catalysts, prepared by impregnation and homogeneous precipitation/deposition (denoted herewith as P/D), with solutions of R-(+)-TA, adjusted to pH 1.5–11.8, yielded R-(−)-MHB as the preferred enantiomeric product; replacement of the modifier by its antipode generated identical values of enantiomeric excess but with a reversal of the sign. Moreover, modification with optically inactive meso- or racemic TA resulted in a virtually racemic (ee < 2%) product mixture. The presence or absence of asymmetric activity in the modified Ni/SiO_2 catalyst therefore depends on the optical purity of the modifier. All the data given in this paper are related to R-(+)-TA modifications. The amount of TA adsorbed as a function of time is plotted in fig. 1 for three representative temperatures where the pH of the modifying solution was preadjusted to the isoelectric point (5.1) for TA. It can be observed that the extent of TA adsorption is both time and temperature dependent. In contrast to the work of Tatsumi [13] (Raney nickel) and of Fish and Ollis [14] (nickel electrodes) where TA adsorption attained equilibrium after 10 min, a more lengthy treatment of the supported catalyst was necessary under the stated experimental conditions. Nevertheless, the time required to achieve the final level of adsorption decreased with increasing temperature. In the absence of any form of agitation, treatment times of up to 5 h were necessary in order to obtain an equivalent uptake of TA. In the case of a calcined (in a 120 cm^3 min^{-1} stream of air at 723 K) unreduced sample, the number of TA molecules adsorbed was less than 6×10^{17} per gram of catalyst which strongly sug-

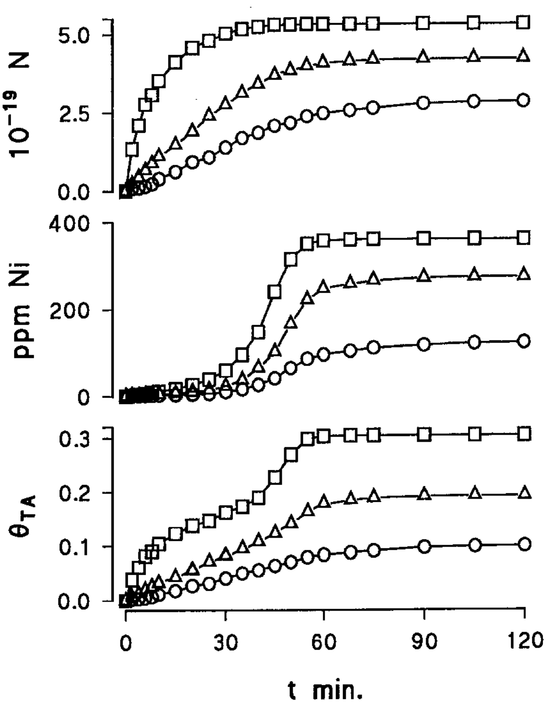

Fig. 1. The variation in the amount of TA adsorbed, the extent of surface nickel metal leaching and the fractional coverage of the 11.9 w/w Ni P/D surface by TA with the duration of modification at 273 K (○), 323 K (△) and 373 K ((□): [TA] = 0.02 mol dm^{-3}; pH = 5.1.

gests that the site for TA adsorption is the supported nickel metal and not the silica carrier or the unreduced nickel cations. It has now been established [1–3,17] that the generation of the enantioselective site is a corrosive process and results in the extraction of nickel atoms from the metal lattice. There is strong spectroscopic evidence [7] to suggest that TA is adsorbed on the metal surface as a carboxylate. In accordance with the work of Sachtler et al. [12,15], TA interacts with the surface nickel to form a nickel tartrate (NiTA) complex, which can either remain on the silica carrier to form a supported selective site or diffuse into solution. The simultaneous adsorption of TA and dissolution of nickel metal is also illustrated in fig. 1. As TA is adsorbed from the liquid to the solid phase, thereby diluting the modifier solution, there is an accompanying removal of nickel from the solid into the liquid phase which, in effect, dilutes the concentration of surface adsorption sites. The concentration of nickel in the modifier only becomes appreciable when the bulk of the TA is adsorbed. The degree of TA coverage (θ_{TA}) on the surface metal is governed by the interplay between the progress of TA adsorption from solution and the extent to which the potential adsorption sites are removed in the corrosive adsorption step. Consequently, the buildup of TA on the surface is a slow process and the ultimate coverage is attained, depending on the modification temperature, at $t_{\mathrm{mod}} > 50$ min.

The influence of modifier pH on the adsorption of R-(+)-TA is illustrated in fig. 2. It can be observed that, for the three representative temperature/TA concentration regimes, the number of TA molecules retained by the catalyst increased as the pH was raised from 1.5 to 6 but decreased at higher pH values. This relationship is in marked contrast to that reported for Raney nickel where TA adsorption decreased continuously with increasing pH over the entire pH range [13,26]. The extent of nickel leaching was observed to decrease with increasing modifier pH. As a consequence of the TA adsorption/Ni dissolution interrelationship and pH dependence, the fractional surface coverage by TA passes through a maximum in the pH range 5–6. The variation of enantioselectivity with pH for the three characterized modification procedures is presented in fig. 3. In the case of the low temperature treatment ($T = 273$ K, [TA] = 0.02 mol dm^{-3}), where the surface coverage by TA was less than 0.1, enantiomeric excess was essentially independent of pH. The two other procedures, which yielded much higher values of θ_{TA}, exhibited maxima in enantiomeric excess in the pH range 9–10, where the enantioselective site can be considered to be a surface nickel sodium tartrate (NiNaTA) complex [13]. In previous studies on a range of catalytic systems, optical yield maxima have been variously reported at pH 3 [1,18], pH 10 [20] and over the range 5–9 [1,15,13,14,26]. Enantioselectivity data obtained from 67 separate catalyst modifications (spanning the pH range 1.5–11.8) are related to modifier coverage in fig. 4. The highest values of enantiomeric excess correspond to a θ_{TA} value of ca. 0.2, regardless of whether the modification was conducted in acidic, neutral or basic media. The existence of a maximum in enantioselectivity at a low surface modifier coverage may be attributed to a "sandwich effect" where both TA and

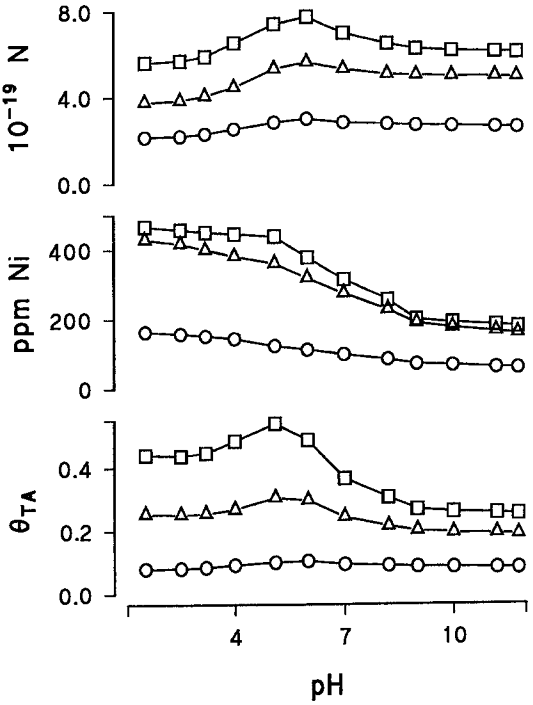

Fig. 2. The effect of the initial modification pH on the amount of TA adsorbed, the extent of surface nickel metal leaching and the fractional coverage of the 11.9 w/w Ni P/D surface by TA: $T_{mod} = 273$ K, [TA] = 0.02 mol dm^{-3}, $t_{mod} = 2$ h (○); $T_{mod} = 373$ K, [TA] = 0.02 mol dm^{-3}, $t_{mod} = 2$ h (△); $T_{mod} = 373$ K, [TA] = 0.05 mol dm^{-3}, $t_{mod} = 2$ h (□).

MAA are co-adsorbed on the catalyst surface as proposed by Gronewegen and Sachtler [28]. In the case of $\theta_{TA} >$ ca. 0.2 there is a crowding effect, where the adsorbed MAA species is "sandwiched" between two TA molecules causing a destructive chemical interference which results in the predominant formation of racemic MHB. Conversely, at $\theta_{TA} <$ ca. 0.2 only a fraction of the adsorbed MAA is sterically influenced while the majority of MAA again undergoes racemic hydrogenation. Accordingly, the optimum TA treatment is one in which the distance between adsorbed TA molecules is large enough to ensure that an adsorbed MAA molecule interacts with only one modifier molecule but small enough to minimize the number of racemic sites. There is a divergence in behaviour between the catalysts modified in acidic and in basic media where $\theta_{TA} >$ ca. 0.3. In the case of the acidic modifications, the measured enantioselectivities decreased steadily with increases in surface coverage, beyond the critical value of 0.2, to values at monolayer coverage which are similar to those observed at very low coverages, i.e. $\theta_{TA} <$ ca. 0.05. At monolayer coverages of TA, the reactant and modifier must interact via the 2-site intermolecular hydrogen bonding scheme, proposed by Harada et al. [24], where MAA remains in the liquid phase. Such a linkage is not as effi-

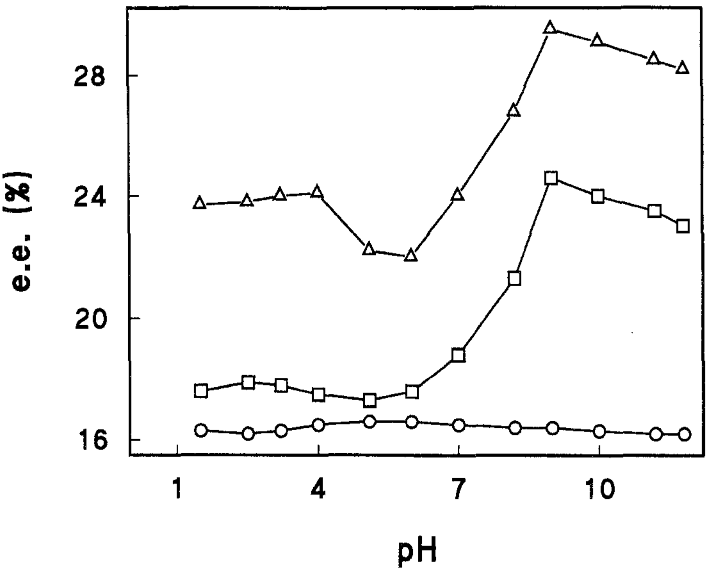

Fig. 3. The dependence of the enantioselectivities exhibited by the 11.9 w/w Ni P/D catalyst on the initial modification pH: T_{mod} = 273 K, [TA] = 0.02 mol dm^{-3}, t_{mod} = 2 h (○); T_{mod} = 373 K, [TA] = 0.02 mol dm^{-3}, t_{mod} = 2 h (△); T_{mod} = 373 K, [TA] = 0.05 mol dm^{-3}, t_{mod} = 2 h (□).

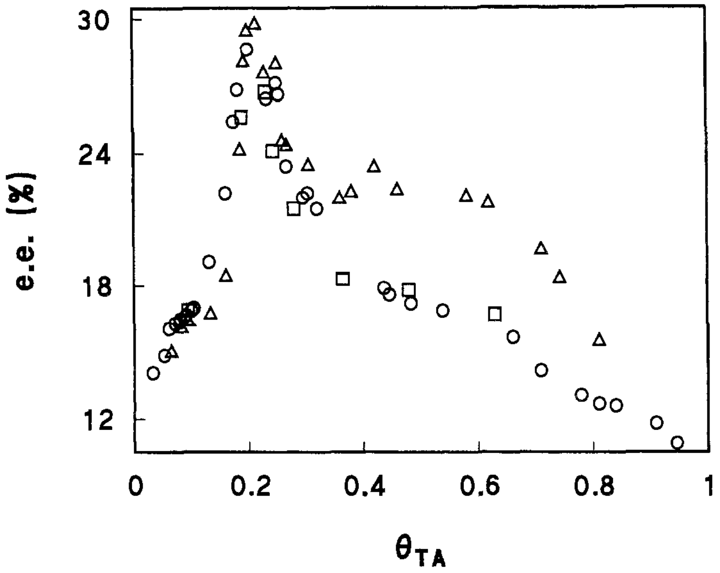

Fig. 4. The relationship between enantiomeric excess and the fractional coverage of the 11.9 w/w Ni P/D surface by TA resulting from a range of modifications conducted in acidic (○), neutral (□) and basic (△) media: $T_{reaction}$ = 343 K; $t_{reaction}$ = 32 h.

cient as the surface co-adsorbed MAA/TA interaction and generates a smaller excess of (R)-(−)-MHB. In contrast to the acid modifications, surfaces with a high coverage of TA (0.3–0.7), generated by treatment in basic media, induce appreciable levels of enantioselectivity (ee>20%). Consequently, where $\theta_{TA} > 0.30$, the highest optical yields are obtained from basic modifier media. Enantiodifferentiation, therefore, depends on both the surface density and nature of the enantioselective site.

It is now well established that Ni/SiO_2 catalysts prepared by impregnation or precipitation/deposition (P/D) exhibit different degrees of interaction between the metal and the support [29–35]. The response of catalyst precursors prepared by these two techniques to TA modification has not yet, to the best of the author's knowledge, been compared. Catalysts prepared by impregnation exhibit weak interactions between the poorly dispersed active phase and the carrier [29,32,33]. In contrast, the P/D procedure has been reported [29–31,34] to yield a uniform dispersion of very small (<6 nm) metal particles. Indeed, from CO chemisorption measurements, the surface weighted average diameters of the nickel crystallites supported on the catalysts used in this study were 2.2 and 11.2 nm, respectively, for the impregnation and P/D techniques. The effects of varying modifier pH on the TA uptake, nickel leaching and overall surface coverage exhibited by the impregnated and P/D catalysts are given in table 1. Under identical conditions, a higher proportion of the initial metal content was leached from the impregnated surface.

Table 1
A comparison of the effects of the initial modification pH on the number of TA molecules adsorbed, the extent of surface nickel leaching and the fractional coverage by TA exhibited by catalyst precursors prepared by impregnation and precipitation/deposition: $t_{mod} = 2$ h; $T_{mod} = 373$ K; [TA] = 0.02 mol dm^{-3}

pH	10^{19} N[a]		% Ni leached[b]		θ_{TA}	
	P/D[c]	I[d]	P/D	I	P/D	I
1.5	3.8	1.1	52	62	0.25	0.45
2.5	3.9	1.2	50	60	0.25	0.46
3.2	4.1	1.4	48	57	0.25	0.49
4.0	4.5	1.6	46	53	0.27	0.53
5.1	5.3	1.9	43	51	0.30	0.58
6.0	5.6	2.0	38	46	0.30	0.57
7.0	5.3	1.8	33	41	0.24	0.43
8.2	5.1	1.7	27	36	0.21	0.37
9.0	5.0	1.6	23	30	0.20	0.32
10.0	5.0	1.5	21	27	0.19	0.29
11.2	5.0	1.5	20	25	0.19	0.28
11.8	4.9	1.5	19	25	0.19	0.28

[a] TA molecules retained by the catalyst.

[b] Percentage of initial metal content leached.

[c] 11.9% w/w Ni/SiO_2 prepared by homogeneous precipitation/deposition.

[d] 11.6% w/w Ni/SiO_2 prepared by impregnation.

The stronger metal/support interactions present in the P/D catalyst must enhance nickel stability as a greater number of TA molecules were adsorbed with less metal dissolution. The degree of dispersion of nickel on the P/D sample (0.4) is considerably greater than that generated on reduction of the impregnated catalyst (0.09) with the result that the number of potential adsorption sites is much higher on the P/D surface. Although the concentration of adsorbed TA is higher on the P/D catalyst the fractional coverage by TA of the impregnated surface is greater at each modifier pH. Both catalytic systems, however, exhibited common trends with regard to increased leaching with decreasing pH and maxima in TA uptake in acidic media. The variations of reaction rate, MAA conversion and enantioselectivity for the same catalyst systems are given in table 2. The catalytic data were obtained under reaction conditions where the contribution of mass transport to the overall reaction rate has been shown to be negligible [6]. Both the apparent reaction rate and the level of MAA conversion were considerably higher for the modified catalysts. This observation is in direct conflict with earlier reports [36–38] where the adsorption of TA on the catalyst surface was viewed as inhibiting hydrogenation activity by occluding part of the active metal. This enhancement of activity may be attributed to an increased concentration of surface adsorbed hydrogen; while the adsorbed TA phase restricts access of the MAA molecules to

Table 2

A comparison of the effects of the initial modification pH on the apparent reaction rate, the degree of MAA conversion to MHB and the enantioselectivity exhibited by catalyst precursors prepared by impregnation and precipitation/deposition: $t_{mod} = 2$ h; $T_{mod} = 373$ K; [TA] = 0.02 mol dm^{-3}; $T_{reaction} = 343$ K

pH	*R*app [a]		MHB [b] (mol%)		ee [b] (%)	
	P/D [c]	I [d]	P/D	I	P/D	I
– [e]	3.4	2.1	75.1	68.3	1	0
1.5	4.0	2.2	76.7	70.0	24	18
2.5	4.1	2.2	77.3	70.4	24	18
3.2	4.4	2.3	78.2	71.0	24	17
4.0	4.9	2.5	79.1	71.3	24	17
5.1	5.2	2.6	79.8	71.6	22	16
6.0	5.2	2.7	80.6	71.7	22	16
7.0	5.3	2.7	82.2	72.4	24	17
8.2	5.8	2.9	86.7	74.1	27	21
9.0	6.0	3.1	87.3	75.3	30	23
10.0	5.7	3.0	87.7	75.6	29	23
11.2	5.6	2.8	88.0	76.0	29	21
11.8	5.6	2.8	88.2	76.0	28	21

[a] Units of *R*app are 10^{-3} mol MAA h^{-1}.
[b] $t = 32$ h.
[c] 11.9% w/w Ni/SiO_2 prepared by homogeneous precipitation/deposition.
[d] 11.6% w/w Ni/SiO_2 prepared by impregnation.
[e] No modification.

the surface metal atoms, hydrogen can readily adsorb on these sites. Consequently, there is a greater "reservoir" of dissociated hydrogen on the modified surface whereas the transport of hydrogen to the unmodified surface is achieved via multilayers of adsorbed MAA [6]. The apparent rate increased for both sets of catalysts with increasing modifier pH and passed through discernible maxima at pH 9; the mol% MHB values were also higher for the basic pH modifications. The hydrogenation of MAA has been shown to be a structure sensitive process in which the apparent rate decreases as the average nickel crystallite size is increased [5]. As a direct consequence, the poorly dispersed impregnated samples exhibited lower apparent rates. Furthermore, it has been demonstrated [2] that the smaller supported nickel metal particles (<2 nm) are preferentially leached during modification. The higher observed rates due to modification in basic media may, in part, be due to the less corrosive nature of the treatment in which a greater proportion of the more active small nickel particles remains on the surface. As described elsewhere [17], the leached nickel species can be recovered and used, in turn, as a heterogeneous asymmetric catalyst to yield activities and selectivities similar to synthesized nickel tartrate. Preliminary studies have since revealed that the reaction proceeds at a much higher apparent rate (0.5 mol MAA h^{-1} g^{-1}) over samples of synthesised NiNaTA than was observed for the prepared NiTA (0.3 mol MAA h^{-1} g^{-1}). The overall higher activities observed for the basic modified catalysts may then arise from the combined action of the very active small (<2 nm) bare nickel particles and the NiNaTA surface complex. Both the impregnated and P/D catalysts exhibited optimum enantioselectivities in the basic pH range. The higher ee values obtained with the P/D sample may be attributed to the less corrosive laydown of TA which results in a higher concentration of the enantioselective site and a fractional surface coverage closer to the optimum value of 0.2, table 1.

To date, the available literature on TA modification of nickel catalysts has tended to relate the extent of catalyst modification solely to the composition of the "pre-modification" solution while the nature of the "post-modifier" has largely been neglected. As shown in table 3, the pH of the post-modifier is higher than that of the preadjusted initial modification pH. Although Wittmann et al. [18] and Smith and Musoiu [39] have observed changes in modifier pH in the course of the TA treatment, no explanation for this phenomenon has been proffered. Addition of NiTA, NaTA and NiNaTA to the original TA solution had no effect on the pH. The increase in pH must be due to the progressive adsorption of TA during modification which essentially dilutes the liquid phase and the pH value at the completion of modification depends on the initial concentration of TA and the combined effect of the degree of dilution of the liquid phase TA and the volume and concentration of NaOH initially added to set the pH. Under basic conditions, where the volume of NaOH initially added is greater, the TA reagent does not interact with the surface nickel metal to the same extent with the result that there is virtually no change in pH throughout the course of modifications in the initial pH range 9–11.8. As discussed, there is a dynamic equilibrium between the adsorbed and dissolved

Table 3
The effect of the initial modification pH and the accompanying change in pH on the extent of surface nickel leaching during the modification and reaction steps: $t_{mod} = 2$ h; $T_{mod} = 373$ K; [TA] = 0.02 mol dm^{-3}; $t_{reaction} = 32$ h; $T_{reaction} = 343$ K

pH	ΔpH[a]	Ni (ppm)	
		modifying solution	reaction mixture
–[b]	–	–	<1
1.5	1.7	430	4
2.5	1.7	418	3
3.2	1.6	400	5
4.0	1.3	381	5
5.1	1.3	360	8
6.0	0.8	318	9
7.0	0.5	273	19
8.2	0.3	227	45
9.0	0.1	188	58
10.0	0.0	175	69
11.2	0.1	164	75
11.8	0.0	158	77

[a] Reproducible to ±5%.
[b] No modification.

NiTA species. The product samples resulting from catalysis over the samples modified in basic media exhibited a green coloration, suggesting the presence of dissolved nickel. The concentrations of nickel in the modifying solution and associated reaction product mixture for a representative temperature/TA concentration regime and a range of modifier pH are given in table 3. The data suggest that while TA modification in the pH range 8.2–11.8 is less corrosive, a proportion of the surface NiNaTA generated is weakly held on the carrier and goes into solution during the prolonged reaction step. The product mixtures generated by catalysts modified with acidic TA solutions contain negligible concentrations of nickel. The more severe acidic TA treatment must remove all weakly bound enantioselective sites during modification. Preliminary studies have also shown that the nickel containing product mixtures are also catalytic. Upon adding fresh ketone to these mixtures, and bubbling hydrogen through the solutions, up to 70% of the added MAA was converted to MHB.

4. Conclusions

From the data reported in this paper it can be concluded that (a) tartaric acid adsorption on Ni/SiO_2 takes place on the available surface nickel metal and, under the stated experimental conditions, the amount of TA adsorbed increases with the duration of modification (up to 1.5 h) and with increasing modifier concentration and temperature; (b) treatment with TA is corrosive and the amount of nickel leached from the catalyst surface, which depends on t_{mod}, T_{mod}, $[\mathrm{TA}]_{\mathrm{initial}}$, is lower when the modification is carried out in basic media; (c) some of the surface nickel is also lost (particularly in the case of the basic TA treatments) during the hydrogenation step; (d) the metallic phase supported on the P/D surface is less susceptible to leaching; (e) the fractional surface coverage by TA is governed by the extent of TA uptake from the liquid phase and the number of adsorption sites which survive the corrosive leaching by TA; (f) under identical modification conditions, the impregnated surface exhibits a higher coverage of the more poorly dispersed metal adsorption sites; (g) while enantioselectivity is induced on treating the reduced catalysts with TA the apparent reaction rate is also increased and the highest reaction rates were recorded for catalysts modified in basic media; (h) the optimum enantioselectivity, regardless of the modification pH, corresponds to a TA coverage of 0.2: (i) at coverages >0.2, modification in basic media, where the enantioselective site can be considered to be a surface nickel sodium tartrate complex, yielded higher levels of enantiomeric excess than was observed for the acidic TA treatment.

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