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XPS studies of the effects of modification pH on the interaction of methylacetoacetate with (*S*)-aspartic acid-modified Ni surfaces

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ABSTRACT

The adsorption, from aqueous solution, of (S)-aspartic acid onto polycrystalline Ni was investigated as a function of pH via X-ray photoelectron spectroscopy in order to investigate why the hydrogenation of β-ketoesters over aspartic acid-modified Ni catalysts exhibits a very sharp maximum in enantioselectivity at modification pH 5. Following similar modification and washing procedures to those used in the real catalyst preparation, it was found that, under the optimum preparation conditions, the coverage of aspartic acid on the Ni surface drops below detectable levels. The implications for understanding the mechanism of the enantioselective hydrogenation reaction are discussed.

1. Introduction

The enantioselective hydrogenation of β-ketoesters over modified Ni catalysts is a heavily researched example of heterogeneous asymmetric catalysis [1–6]. Over one hundred modifiers, including amino acids, amino acid derivatives, peptides and hydroxyl acids, have been investigated for this system with the most successful modifiers being α-hydroxy acids (e.g. tartaric acid) and α-amino acids [1]. Over an unmodified Ni surface, hydrogenation of the simplest β-ketoester, methylacetoacetate (MAA), generates a racemic mixture of (*R*)- and (*S*)-methyl-3-hydroxybutyrate (MHB). In contrast, modification of the Ni catalyst from an aqueous solution of chiral modifier results in the reaction becoming enantioselective, as shown schematically in Fig. 1 [1].

There are many examples of ultrahigh vacuum (UHV)-based studies aimed at providing insight into the role of the surface and modifier [7–19]. In order to enhance the relevance of model studies, we have performed a number of investigations into chirally modified Ni surfaces prepared at the liquid–solid interface using surface vibrational spectroscopy in the form of reflection absorption infrared spectroscopy (RAIRS) [20–22]. In particular, we have shown that the tautomeric form of methylacetoacetate (Fig. 1) is very sensitive to the nature of the chirally modified surface. In particular, for the Ni/(*R,R*)-tartaric acid [22], Ni/(*S*)-glutamic acid [21] and Ni/(*S*)-aspartic acid [20] systems, it was determined that, following modification under conditions where enantioselectivity is optimised, MAA preferentially adopts the diketo tautomeric form. The preparation of chirally modified Ni catalysts involves treatment in an aqueous solution of modifier at a well-defined pH followed by washing and filtering. In the case of tartaric acid – the most successful modifier for this reaction – this preparation procedure results in approximately 20% of a saturated monolayer of tartaric acid [22,23] or ~0.05–0.06 ML of tartaric acid where 1 ML is defined as 1 tartaric acid molecule per surface Ni atom. In the case of (*S*)-aspartic acid, under modification conditions where the catalyst performs most enantioselectively [24] (Fig. 2a), we found that the washing procedure removes aspartate to levels below the detection levels of the RAIRS technique [20] (Fig. 2b). This paper uses X-ray photoelectron spectroscopy (XPS) in order to quantify the coverage of aspartate as a function of modification conditions. We wish to establish whether the enantioselectivity arises from a completely aspartate-free surface – i.e. the role of the aspartate is to create chiral active sites by corrosive leaching of Ni from the catalyst surface. Adsorbate-induced faceting is a well-established phenomenon following the adsorption of carboxylic acids at high molecular coverages in the submonolayer regime [25–28]. Zhao and co-workers demonstrated with STM that the adsorption of (*S*)-lysine led to the formation of chiral Cu facets on a Cu{0 0 1} surface, indicating that the adsorbate itself caused the surface Cu atoms to adopt an intrinsically chiral arrangement

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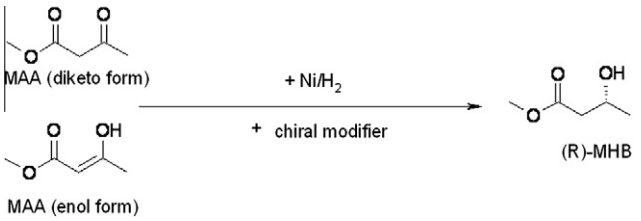

Fig. 1. Schematic reaction scheme of the enantioselective hydrogenation of MAA over modified Raney Ni catalyst showing both tautomeric forms.

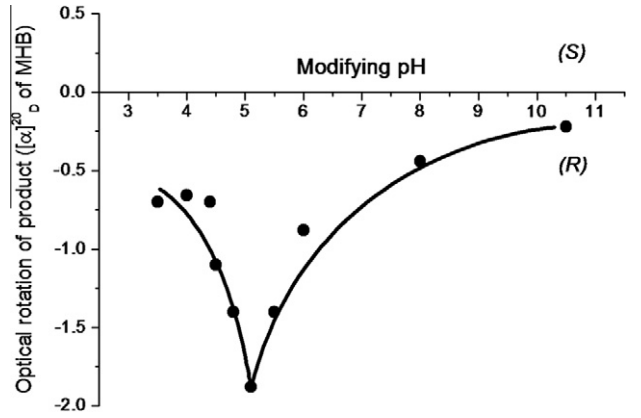

Fig. 2a. Effect of modifying pH of (*S*)-Aspartic acid on enantioselectivity of Raney Ni (RNi). Modifying conditions: 0 °C. Reaction conditions: MAA (neat), 60 °C, 80–100 kg/cm^2. Adapted from Ref. [24].

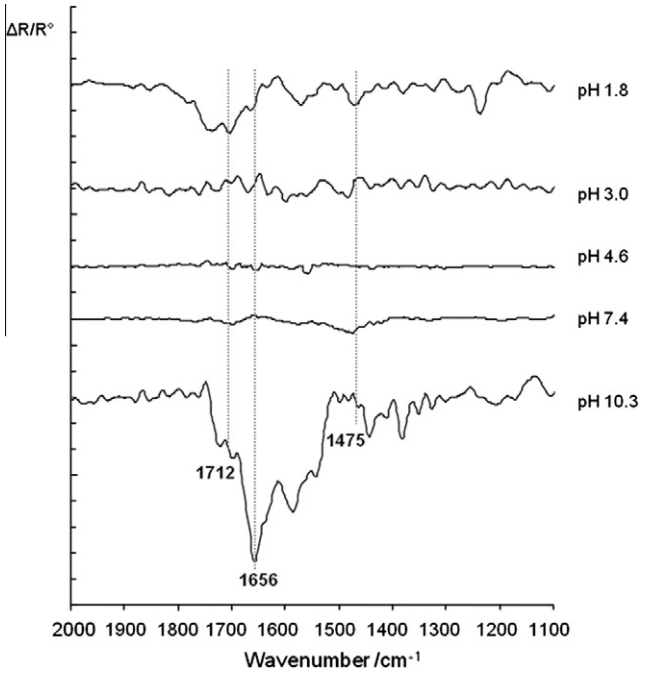

Fig. 2b. RAIR spectra following post-modification water wash of (*S*)-aspartic acid-modified Ni foil at 300 K as a function of pH. [20].

[29]. Gellman and co-workers pioneered studies on high Miller index step-kink surfaces which can exist in non-superimposable mirror forms [30]. Gellman's group subsequently demonstrated that the interaction of the two enantiomers of propylene oxide with the two mirror equivalent surfaces was measurably different [31]. In addition, Attard and co-workers demonstrated that two enantiomers of glucose undergo very different electro-oxidation behaviour at a chiral Pt surface [32], while Sholl and co-workers carried out several theoretical studies of hydrocarbons on chiral pure Pt surfaces and found differences in binding energies of chiral kink sites [33]. Chiral step-kink sites have also been shown, in work by Attard and co-workers, to contribute to the enantioselectivity of Pt catalysts for ethyl pyruvate hydrogenation. The use of Bi adsorption was used to selectively block step sites on the Pt surface leaving terrace sites available for adsorption. An increase in rate and a decrease in enantiomeric excess were observed leading to the conclusion that sites at, or near to, steps were more enantioselective than sites on terraces [34]. It is clear that, in principle, surfaces with chiral arrangements of metal atoms could operate as enantioselective catalysts. In this paper, we seek to establish whether the enantioselectivity of aspartic acid-modified Ni catalysts can be ascribed to a metal surface which is essentially free of amino acid adsorbates.

A second proposal is that, in the presence of a low but finite coverage of aspartate, perhaps bound to the kink sites, docking interactions may favour one pro-chiral molecule geometry, and this chiral recognition interaction may be amplified to influence the geometry of molecules further out into terrace regions. Gellman and co-workers studied the enantiospecific desorption of propylene oxide from chiral Cu{6 4 3} surfaces and showed that enantiospecificity was detected from terrace sites as well as from the kinked steps. It was suggested the effects of the adsorbate on the chiral kinked steps could transmit the chiral environment to nearby molecules on the terraces [35]. Similar such chiral amplification effects have also been suggested following co-adsorption of (chiral) tartaric acid and (achiral) succinic acid on Cu{1 1 0} [36,37].

2. Experimental procedure

Ten polycrystalline Ni foil samples (BDH Chemicals Ltd. $\geqslant$99.0%) of dimensions $10 \times 10 \times 0.15$ mm were sonicated for 900 s in $H_2SO_{4(aq)}$, rinsed in Millipore water (18.2 MΩ), dried under $N_{2(g)}$ and annealed at 973 K for 6 h in a 5% H_2/Argon stream and allowed to cool, in the same atmosphere, to room temperature. Aspartic acid samples used in the present investigation were deposited onto the Ni polycrystalline foil substrates by immersing in a 10 mM (*S*)-aspartic acid (Fluka Biochemika 97%) aqueous solution for 900 s at 300 K as a function of pH, in ambient conditions. The pH of the aspartic acid solutions was appropriately altered by the addition of 1 M NaOH or concentrated HCl. Six of the samples were then rinsed for several seconds in a flow of Millipore water, and three of these were subsequently immersed at 300 K in a 50:50 mixture of MAA (Fluka $\geqslant$99%) in tetrahydrofuran (THF) for 900 s. A tenth clean Ni foil sample was used as a control experiment. Prior to loading into UHV chamber, the samples were dried under a light $N_{2(g)}$ flow.

XPS measurements were carried out using a VG Sigma Probe spectrometer. Al Kα radiation with a 400 μm diameter spot (100 W) was incident on the samples. A concentric hemispherical energy analyser (CHA) with 80 eV pass energy (for full scan; 20 eV pass energy for component scans) was used, and a step size of 0.5 eV was used for the survey scan, while 0.1 eV was used for individual component scans, each with a dwell time of 40 ms. The angle between the surface normal and analyser direction was 53°. The operating pressure of the system was 1×10^{-9} mbar, which increased to approximately 1×10^{-8} mbar during the course of XPS experiments due to small amounts of residual solvent still present. All the measurements reported were carried out at room temperature.

XP spectra were processed using the program CasaXPS Version 2.3.14. To correct the shifts in binding energies of core levels due to

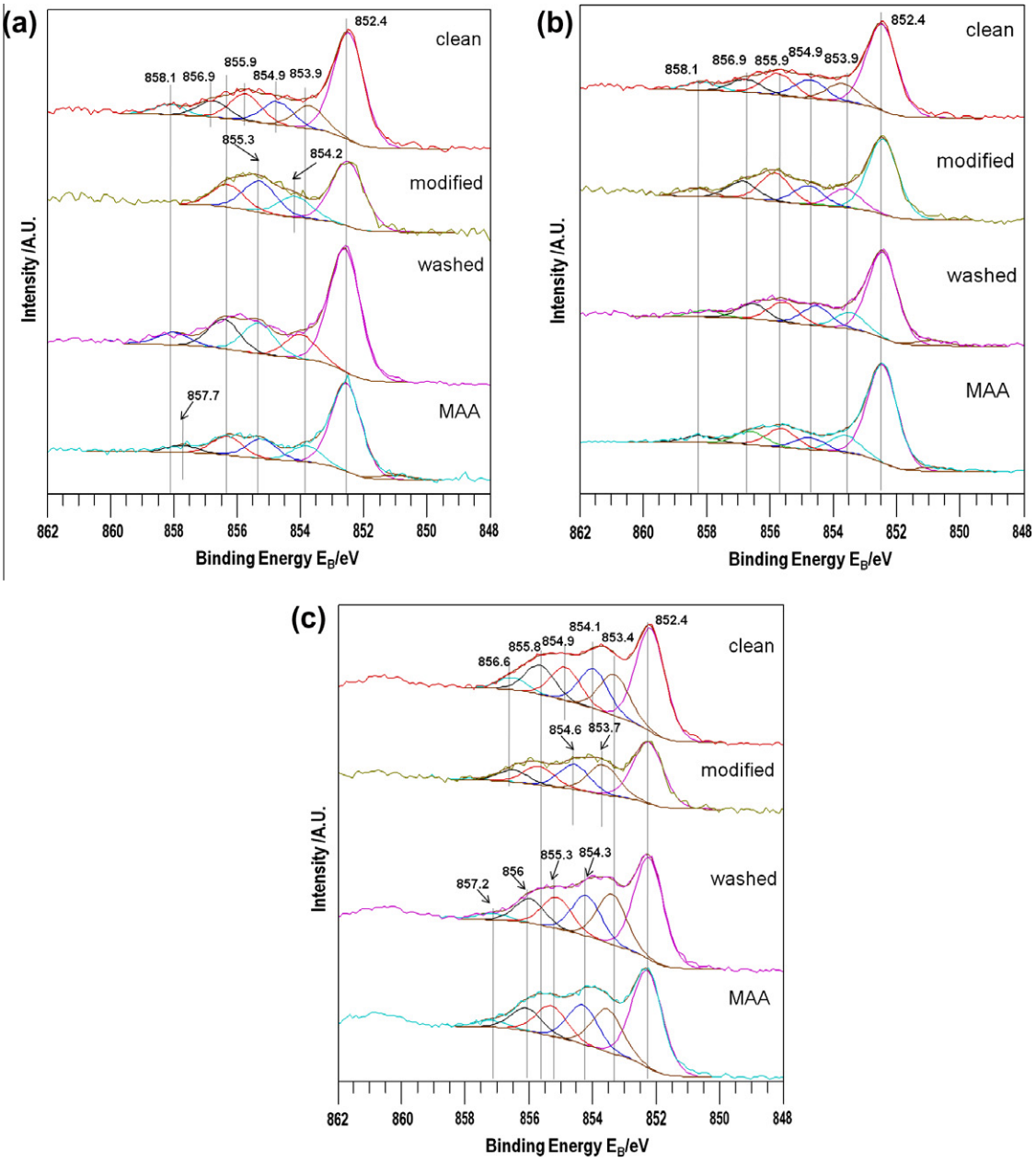

Fig. 3. Ni 2p XP region, for modification of Ni with (*S*)-Asp at (a) pH 2.4, (b) 5.3 and (c) 11.8. Herein, in each figure, the spectra should be read, from top, as clean polycrystalline Ni foil, modified Ni foil, post-modification water wash and interaction of MAA with modified Ni. Spectra are shown with reference to "clean" Ni foil treated in $H_2SO_{4(aq)}$ and annealed in 5% H_2/Ar as previously. Spectra are offset for clarity.

the charging effect caused by the insulating properties of amino acids, the graphitic C 1s peak at 284.5 eV has been used as an internal reference and all spectra calibrated relative to this peak (i.e. each spectra is offset by a fixed amount according to the difference between the experimental C 1s graphitic peak in each experiment and the literature value of 284.5 eV). Peaks assigned to each chemical species are fixed by their binding energy, peak shape and full width at half maximum height, with differences of up to ±0.1 eV in binding energy being allowed between spectra in order to optimise fits.

3. Results

To investigate the coverage and chemical nature of the modifier layers on the Ni foil, XPS measurements were performed on clean Ni, three samples of Ni modified with (*S*)-aspartic acid at pH 2.4, 5.3 and 11.8, respectively, three additional modified samples which had been washed with distilled water and three samples following MAA adsorption onto the (*S*)-aspartic acid-modified Ni foil surface which had been subjected to the washing procedure.

The XP spectrum of the clean Ni foil (not shown) reveals the presence of the native oxide on the Ni foil. Since the sample was exposed to air while transferring from the furnace to the UHV apparatus, there are large quantities of adsorbed C and O. Small quantities of Cl and N can be attributed to air-borne contaminants from the transferral process, and the presence of sodium can be attributed to the lubricants used in the rolling process of the foil [38]. It should be noted that no special effort is made to exclude air before and during the modification of Ni catalysts for this reaction [1].

Table 1
overlayer thicknesses (d) and volumes (V) for (*S*)-Aspartic acid-modified Ni foil.

	pH 2.4	Water wash	MAA	pH 5.3	Water wash	MAA	pH 11.8	Water wash	MAA
d (nm)	1.44	0.44	0.87	0.93	0.18	0.19	1.56	0.22	0.31
V (10^{-8} cm^3)	14	4.4	8.7	9.3	1.8	1.9	16	2.2	3.1

To obtain more detailed information concerning the energy positions and line shapes of the major components, individual scans were separately recorded of the N 1s, O 1s, C 1s and Ni 2p regions. The compositions were calculated by fitting theoretical peaks using the iterative Shirley technique.

3.1. Estimation of the surface coverage of aspartate on Ni

Fig. 3a–c shows the influence of modification pH on the Ni 2p XP spectra before and after modification, after washing with water and after exposure to methylacetoacetate solution. In each case, the peak at 852.4 eV is attributed to the Ni^0 peak, while peaks at 854.0 ± 0.1 eV represent the native NiO. The peak at 854.9 eV represents $Ni(OH)_2$, while the peaks at 853.4 eV, 855.8 ± 0.1 eV, 856.9 eV and 858.1 eV, although unassigned, are characteristic of the native nickel oxide [38]. The attenuation of the Ni^0 peak at 852.4 eV due to adsorption of aspartic acid can be used to estimate the thickness of the overlayer assuming that the overlayer has a uniform thickness [39]. Table 1 shows the calculated thicknesses of the aspartic acid layer using the formula $I = I_0\exp(-d/\lambda\cos\theta)$ [40] with a value of 2.01 nm for the inelastic mean free path of Ni $2p_{3/2}$ photoelectrons through an organic film of density 1.66 g cm^{-3} (the density of aspartic acid) [41]. The volume of the overlayer was calculated for each sample assuming the approximate area of each Ni foil to be 1 cm^2. It should be noted that in the calculations for the overlayer thickness of MAA adsorbed onto the modified and washed Ni surfaces, the Ni 2p signal is attenuated by both MAA and aspartate present and so the quoted overlayer thickness refers to the thickness of the film containing both aspartate and MAA. The main source of error in these calculations will originate from the assumption that the aspartate thin film is of a uniform thickness.

3.2. Quantitative analysis

3.2.1. Nitrogen 1s XPS spectra

The surface coverage of nitrogen on the Ni foil, both modified and unmodified, is a good indicator of the level of impurities on the bare Ni foil and enables a reliable estimation of the absolute concentration of aspartic acid on the surface. This transpires as the N 1s signal at 399.6 eV on the unmodified surface can be assigned to a nitrogen-containing impurity, possibly from traces of ammonia in the atmosphere, which is characteristic of the foils being prepared outwith the UHV chamber [38]. Despite the treatment in acid treatment and the hydrogen pre-treatment employed to reduce the amount of oxide formed on the Ni surface, the fact that the transportation of the foils and the modification are carried out under ambient conditions leads to a nitrogen-based impurity being present on all foils. We are able to subtract this background impurity level from the N(1s) signal to allow a reliable estimate of the number of N atoms on both the modified and washed surfaces, which can then be related to the number of aspartate species present (i.e. one N atom in each aspartate molecule). It is to be noted that, although spectra were collected, the N 1s XP spectra for the adsorption of MAA onto the modified and washed surfaces are not shown as any fluctuations in the N 1s signal no longer gives information exclusively on the aspartate surface coverage, but rather may also be attenuated by the co-adsorption of MAA.

Fig. 4a shows the N 1s spectra of the Ni foil modified at pH 2.4. The 399.6 eV peak becomes sharper and more intense after modification by (*S*)-Asp which suggests that this peak corresponds to the coordination of the aspartic acid to the Ni surface [42]. The binding energy of this peak is lower by 1.3 eV than the binding energy of aspartic acid in its zwitterionic form (400.9 eV) and much closer to that of a nickel amine complex (approximately 399.4 ± 0.1 eV [43]) and so confirms that the amino acid is coordinated to the Ni surface through the amino group [42]. Indeed, previous IR work found that, on chelate formation, bands due to the NH_2 group appear instead of the NH_3^+ group [44]. After the water wash, the peak at 399.6 eV shifts to a lower binding energy of 398.8 eV, suggesting a more nitride-like species [42].

Following modification at pH 5.3 (Fig. 4b), an intense contribution is observed from a peak at 401.1 eV. This peak has previously been assigned to the presence of a protonated amine group, or surface oxidised N [43]. The 399.4 eV peak indicates, as previously, the NH_2 group bound to the Ni surface. After the water wash, the N 1s spectrum is similar in peak position and overall intensity to the clean Ni foil.

Following modification at pH 11.8 (Fig. 4c), a peak is observed at 399.4 eV after deposition of Asp at pH 11.8 which corresponds to the —NH_2 group of aspartic acid [43], as well as a peak at 401.3 eV. After the water wash, the N 1s spectrum shows a decrease in intensity with the overall N 1s spectrum resembling that of the modified surface.

While the analysis of the N 1s peak in a qualitative manner is useful in that it allows assignment of different nitrogen-containing species present, the crux of this study is to identify whether the quantity of aspartate on the surface changes in relation to the form of aspartate present, as well as due to the post-modification washing procedure. Table 2 shows the number of N atoms present (and thus the number of aspartic acid molecules) on Ni foil with area dimensions 1 cm^2 and the aspartate film thickness as calculated in Table 1. Taking into account the density of Ni in the thermodynamically most favourable {1 1 1} plane is 1.86×10^{15} atoms cm^{-2}, the surface coverage of each species in monolayers (ML) is shown in the final row of Table 2. It is to be noted that XPS data for (*S*)-Asp at pH 11.8 were recorded on a separate occasion and so N 1s intensity values for a second "clean" Ni foil are used in necessary calculations and noted in Table 2. We estimate that the errors in the coverage measurement are approximately ±10% of the absolute coverage.

It is found that the level of N-based impurity on the Ni foil before modification (0.07 ML) is of the same magnitude of nitrogen present on sample which had been washed after modification at pH 5.3, whereas identical water washes following modification with aspartic acid at higher and lower pH values show residual modifier on the surface. This verifies in absolute terms that, at intermediate pH values of (*S*)-Asp (such as pH 5.3 as used in the XPS experiments), a water wash is effective in removing all measurable traces of aspartic acid from the Ni surface. By taking the coverage of aspartate molecules on the surface (i.e. subtracting the N-based impurity coverage from the modified surface and water-washed surface ML values), we conclude that the coverage of aspartate ranges from 0.3 to 0.6 ML, with 0.3 ML present under conditions of maximum enantioselectivity (at pH 5.3). After the post-modification water wash, the residual modifier coverage ranges from 0 to 0.1 ML, again with the lowest levels measured under conditions of maximum enantioselectivity.

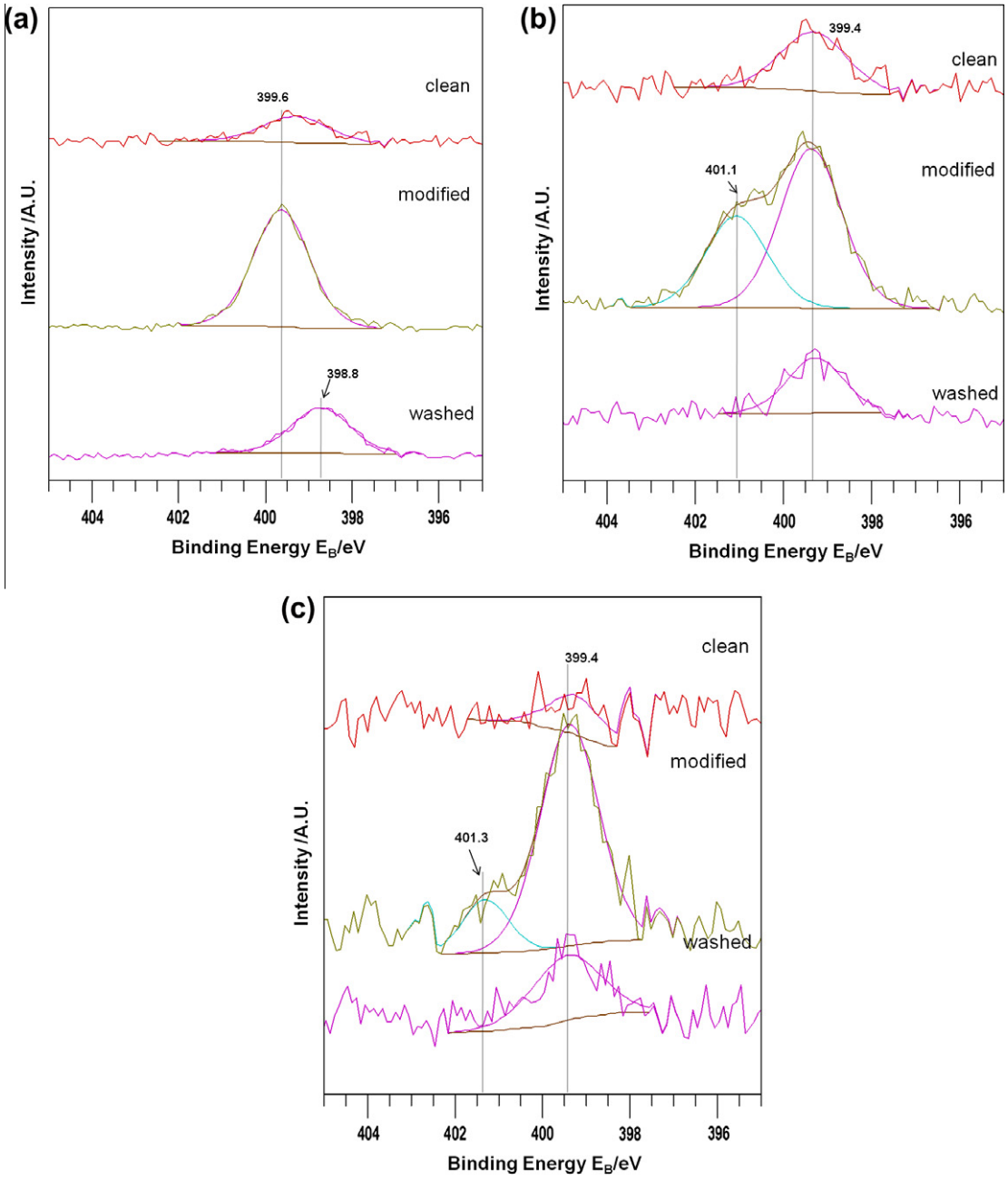

Fig. 4. N 1s XP region, following modification of Ni with (*S*)-Asp at (a) pH 2.4, (b) 5.3 and (c) 11.8. The spectra should be read, from top, as clean polycrystalline Ni foil, modified Ni foil and post-modification water wash. Spectra are shown with reference to "clean" Ni foil treated in $H_2SO_{4(aq)}$ and annealed in 5% H_2/Ar as previously. Spectra are offset for clarity.

Table 2
Absolute number of N atoms for Ni foil surfaces modified by aspartic acid at different pH values and after post-modification wash and MAA adsorption.

	Ni foil (for pH 2.4 & 5.3)	pH 2.4	Water wash	pH 5.3	Water wash	Ni foil (for pH 11.8)	pH 11.8	Water wash
d (nm)	–	1.44	0.44	0.93	0.18	–	1.56	0.22
V (10^{-8} cm^3)	–	14	4.4	9.3	1.8	–	16	2.2
$I_{N\ 1s}$	1727	10,380	6316	8074	1770	332	2766	951
N (10^{15} atoms)	0.132	1.1	0.33	0.7	0.135	0.05	1.2	0.15
N coverage (ML)	0.07	0.59	0.18	0.38	0.07	0.02	0.65	0.08

3.2.2. Carbon 1s XPS Spectra

In Fig. 5a–c, the C 1s XP spectra show that the majority of the carbon-containing species can be assigned to carbonaceous contamination (284.5 eV peak). From the remaining carbon surface peaks, much can be deduced about the chemical environment of the molecules on the surface.

In the first instance, the C 1s XP spectrum of the unmodified Ni foil matches that observed on the native nickel oxide [38]. The

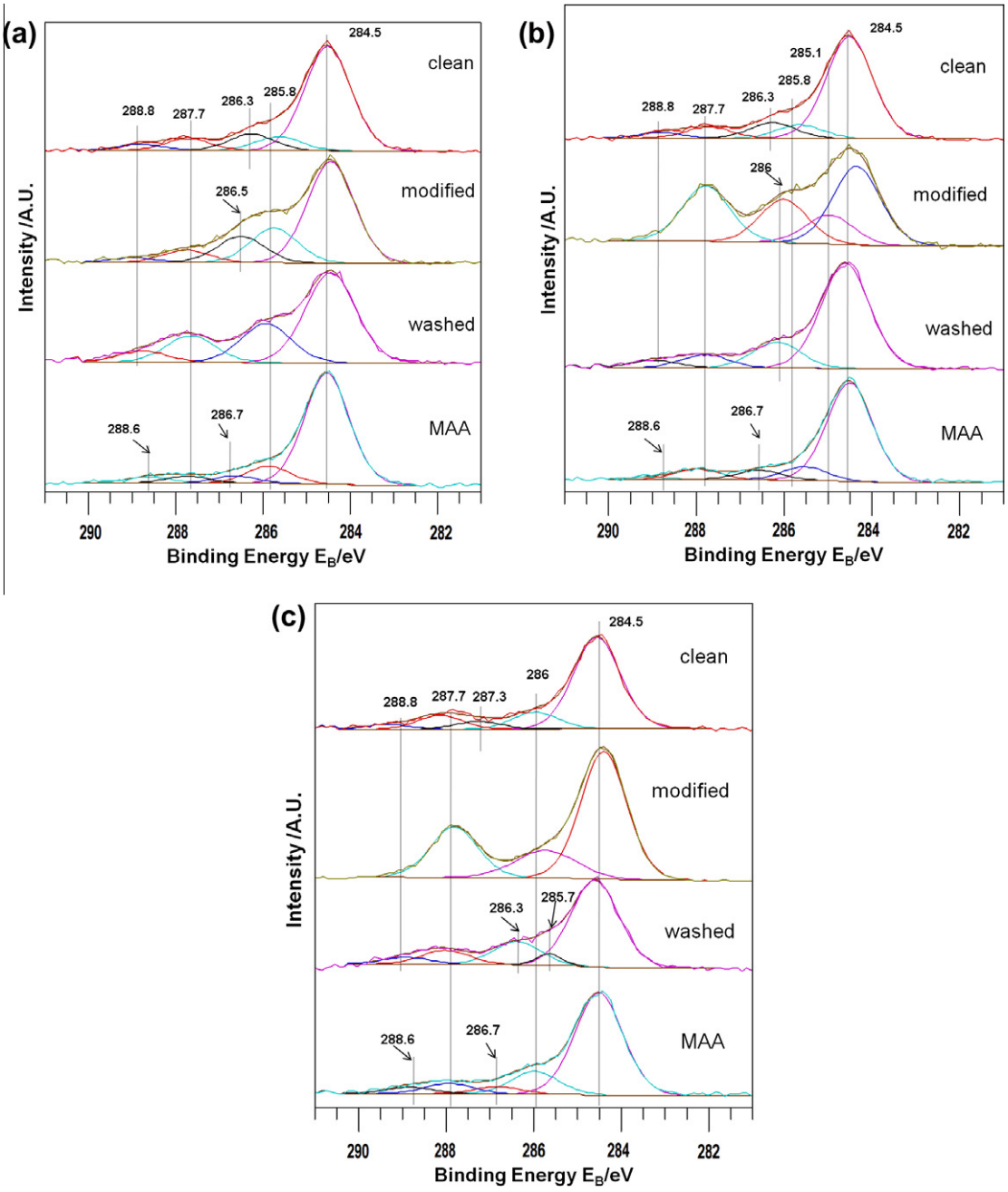

Fig. 5. C 1s XP region, following modification of Ni with (*S*)-Asp at (a) pH 2.4, (b) 5.3 and (c) 11.8. Spectra are shown with reference to "clean" Ni foil treated in $H_2SO_{4(aq)}$ and annealed in 5% H_2/Ar as previously. Spectra are offset for clarity.

peak at 285.8 eV represents C—OH or C—OR environments, while the peaks at 287.7 eV and 287.3 eV correspond to COOH or COOR. The highest binding energy peak at 288.8 eV is assigned to a CO_3 species.

Fig. 5a shows the XP spectrum of Ni modified with (*S*)-Asp at pH 2.4. An increase is observed in the intensities of the peaks at 285.8 eV and 287.7 eV which are assigned to C—OH and C=O groups, respectively. As the C—OH and C=O peaks change in intensity between the unmodified surface, modified surface and washed surface, the peaks can be used to judge the amount of modifier remaining on the surface after the water wash at each pH value (Table 3).

At modification pH 2.4, the modifier XP spectrum shows an increase in the peak at 285.8 eV which is assigned to a C—OH group [45]. After a post-modification wash, the same peak appears at a similar intensity to the modified surface. For the C 1s signal for the C=O group (287.7–288 eV) [45], a similar pattern occurs, with an increase in peak intensity after modification. If, as hypothesised, the two signals are from the aspartic acid modifier, they suggest that the amino acid is in its zwitterionic form at pH 2.4. When MAA is adsorbed onto the washed and modified surface at pH 2.4, the C—OH peak at 285.8 eV is at a lower intensity compared to the modified and unmodified surface and so suggests that the MAA adsorbate does not contain a hydroxyl group (and so is not in its enol form). Evidence of the MAA molecules being present in their diketo form transpires from an intensity ratio of the O—CH_3 and C=O signals (at 286.7 and 288.6 eV, respectively) of approximately 1:2 (Table 3) [42].

Table 3
Intensity of C 1s signal for Ni foil surfaces modified by aspartic acid at different pH values and after post-modification wash.

	Ni foil	pH 2.4	Water wash	MAA	pH 5.3	Water wash	MAA	Ni foil	pH 11.8	Water wash	MAA
I_{C-OH} (285.8 eV)	2630	3263	4082	1646	2403	2744	1528	1494	1771	1554	2247
I_{O-CH3} (286.7 eV)	–	–	–	420	–	–	699	–	–	–	1249
$I_{C=O}$ (287.7–288 eV)	1017	3000	2341	–	3463	1089	–	1903	1950	1490	–
$I_{C=O\ ester}$ (288.6 eV)	–	–	–	809	–	–	1350	–	–	–	1340
Ratio O–CH_3: C=O ester				1:1.93			1:1.93				1:1.07

In Fig. 5b, there are several noticeable changes which confirm that aspartic acid adsorbs in the anionic form. The peak at 285.8 eV is present only at levels comparable to the unmodified Ni surface and so it is suggested that no hydroxyl groups within the aspartic acid molecules are present on the surface. An increase in the peak intensity at 287.7 eV for the modified surface indicates a C=O functionality present in aspartic acid. Both of these observations, alongside the N 1s results, give confirmation that aspartic acid is in its anionic form, in agreement with our earlier RAIRS investigation [20]. After the water rinse, the C 1s XP spectrum appears very similar to that of clean Ni, with similar proportions of C present (Table 3). With MAA adsorbed onto the surface, the peak at 286.7 eV represents the carbon atom in the methoxy group, and emergence of the 288.6 eV peak represents the O=C–O ester group. These peaks are in an approximately 1:2 ratio and are consistent with MAA existing predominantly in its diketo tautomeric form on the surface.

In Fig. 5c, with modification occurring at (*S*)-Asp pH 11.8, the carbon atoms are in the same environment as at pH 5.3 with the only structural change being the deprotonation of the NH_3^+ group. This is apparent in the XP spectra for the modified surface, which shows no large increase in the C–OH C 1s peak (suggesting that there is no carboxylic acid group present), and an increase in the peak intensity for the C=O group. There is a substantial decrease in the intensity after the water wash, suggesting only small, but measurable, amounts of aspartate remaining on the surface. Adsorbing MAA onto the modified Ni surface results in an increase in the C–OH signal at 286.0 eV, suggesting the molecule contains this functional group. Furthermore, the ratio of the methoxy and ester group signals is now approximately 1:1 (see Table 3). Both of these features indicate the presence of the enol form of MAA on the substrate surface after modification and wash, which agrees with our previous RAIRS findings [20].

The O 1s XP spectra (not shown) verify that the Ni foil surface is dominated by the oxide, and the small increases or decreases to the component peak intensities can be linked to the different environments of aspartic acid on the surface, as shown in the C 1s spectra.

4. Discussion

In agreement with our earlier RAIRS study [20], the nature of the aspartic acid species as a function of modification pH follows a similar speciation pathway as observed in solution (Fig. 6) [46]. At a low pH (above the first pK_a value of the molecule), aspartic acid adopts a zwitterionic state on the metal surface. With an increase in pH, the amino acid deprotonates through its anionic form to a dianionic species. The N 1s spectra are useful in determining that the NH_2 or NH_3 group of the aspartate molecules bind to the Ni surface, due to positions of the N 1s deconvoluted peaks.

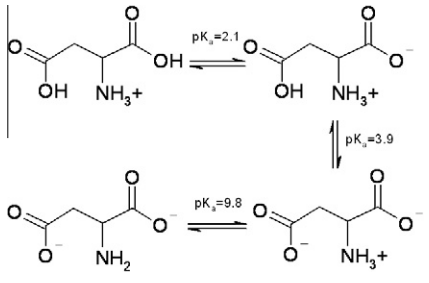

Fig. 6. Speciation of aspartic acid. Adapted from Ref. [46].

Washing the modified surface of the three samples gave different outcomes dependent on the modification pH employed. Under the conditions in which the catalyst operates most enantioselectively (at intermediate pH values as shown in Fig. 2a), XPS data verified that essentially no adsorbed aspartate species remain on the surface, certainly within detection levels of the XPS equipment.

In terms of MAA adsorption onto the modified surface with varying pH values, the XPS data substantiate our previous findings [20]. The XP spectra show that, with increasing pH of the aspartic acid modifier, the enol contribution of MAA on the Ni foil surface grows, illustrated by the change in the intensity ratios of the different C 1s environments of the C=O and OCH_3 groups. This change in the majority form of MAA present on the modified surface is explained by the fact that the diketo form of MAA, with two carbonyl groups, can act as a proton acceptor by forming hydrogen bonds with the protonated aspartic acid molecules, whereas, at higher pH, the enol form is preferable as it allows hydrogen bonding between itself and the deprotonated aspartic acid by acting as a hydrogen bond donor.

The most commonly proposed mechanism for the Ni-catalysed hydrogenation of β-ketoesters involves the docking of methylacetoacetate with a chiral modifier leading to a preference for adsorption via one enantiotopic face [1]. In contrast to the Pt-catalysed enantioselective hydrogenation of α-ketoesters [3], there is believed to be no rate enhancement for hydrogenation of methylacetoacetate species docked at chirally modified sites. If one assumes for the purposes of argument that the interaction with the chiral modifier leads exclusively to the (*R*) product, the rate of formation of (*R*) species could be expressed as the sum of the rates at modified sites and the racemic rate at unmodified sites. Similarly, the rate of formation of (*S*) product would be defined by the rate at unmodified sites. However, as the modifier coverage increases towards saturation coverage, the accessibility of methylacetoacetate to the metal surface becomes diminished. One would predict therefore that an optimum coverage exists whereby all methylacetoacetate molecules adsorb at modified sites and there is insufficient space for methylacetoacetate to adsorb at racemic sites. The RAIRS investigations by Jones and Baddeley of (*R*,*R*)-tartaric acid-modified Ni{1 1 1} [22] suggest that the surface coverage of modifier after washing is also strongly dependent on modification pH. In the case of tartaric acid, which is a much more effective modifier than aspartic acid [1], there is still a significant coverage of modifier after washing under optimised conditions (pH 5.0, 350 K). It appears that two pH-dependent effects operate simultaneously to optimise performance in the case of tartaric acid. First, the modification pH determines the extent of protonation of the modified surface. In the case of both tartaric acid- [22] and glutamic acid-modified Ni{1 1 1} [21], the pK_a of the various acidic protons on the molecule strongly influences the nature of the adsorbed

species. The extent of protonation of the modified surface strongly influences the interaction with methylacetoacetate such that the diketone tautomeric form is favoured. Secondly, the surface coverage needs to be optimised to provide space for methylacetoacetate adsorption [22,23]. In the tartaric acid-modified nickel system, the optimum modifier coverage is in the 0.05–0.07 ML range [23]. Jones and Baddeley showed that in this coverage regime, tartaric acid does not form ordered domains on a Ni{1 1 1} surface but is able to form extended 2D supramolecular structures with methylacetoacetate [9]. Intermolecular H-bonding with several modifiers is proposed to lead to stabilisation of one enantiotopic face on the Ni surface [9]. In the case of aspartic acid, it seems that modification pH also influences the ultimate tautomeric form of methylacetoacetate [20], but that increasing the coverage of aspartate is not helpful in enhancing enantioselectivity.

In the case of aspartic acid-modified Ni, the optimum enantioselectivity is known to occur following modification at pH 5 [24]. Under these conditions, the current XPS study, in agreement with our earlier RAIRS investigation [20], shows that the coverage of aspartate is essentially zero. Furthermore, modification at pH values either side of this optimum lead to a higher aspartate coverage on the surface, yet a poorer enantioselective catalyst. Glutamic acid is very similar in structure to aspartic acid, having one additional methylene unit in the aliphatic chain leading from the chiral centre to the terminal carboxylic acid. It is known that, at very low coverage, glutamic acid prefers to adsorb at step sites on Ni{1 1 1} [8]. A possible explanation for the observed behaviour with aspartic acid is that aspartate species adsorbed in the terrace regions of a Ni catalyst are non-selective and essentially block access to enantioselective sites at step defects. Glutamic acid is a more successful modifier for this reaction [1] and so it is possible that the slightly greater flexibility of the larger molecule allows an optimisation of the docking interaction with methylacetoacetate. Indeed, glutamic acid has recently been shown to form 2D assemblies with methylacetoacetate on Ni{1 1 1} [47]. An alternative mechanism requires consideration of the washing of aspartate-covered Ni surfaces, which is an important step in catalyst preparation. Washing will remove excess aspartic acid and is also likely to result in the displacement of nickel aspartate into aqueous solution. The corrosion of nickel from metal particles by a chiral adsorbate is likely to result in the formation of chiral defects on the metal surface. It has been shown that the growth of chiral copper oxides by electrodeposition occurs in the presence of chiral molecules (tartrates) [48]. It is reasonable to believe that the leaching of metal from a particle would leave behind a chiral surface arrangement of metal atoms. Reaction of methylacetoacetate at these defects could proceed enantioselectively and could account for the enantiomeric excess observed following modification at pH 5. The question is, therefore, can the RAIRS and XPS measurements distinguish between these two possible mechanisms in the Ni/aspartate system? If one assumes that aspartate decorates the steps of a Ni surface with a separation of 0.6 nm (typical for an intermolecular spacing of this type of molecule) and that the surface is covered by parallel steps separated by 3 nm, the area of the "unit cell" of aspartate molecules would be $\sim$1.8 nm^2 giving a surface density of aspartate (and also nitrogen) of 5.6×10^{13} molecules cm^{-2} (Fig. 7). The surface coverage of Ni atoms would be 1.85×10^{15} atoms cm^{-2}. Hence, the surface coverage of aspartate would be in the 0.03 ML range. It is unlikely that the step density is lower than this estimated value either on a polycrystalline Ni foil or on the facets of a nickel particle, so one would anticipate the coverage of step bound aspartate species to be at least 0.03 ML. Our XPS measurements imply that the coverage of aspartate after washing the catalyst surface prepared by modification at pH 5 is considerably lower than this value. We cannot rule out some contribution from modifiers adsorbed at step sites, but our results point to the greater likelihood of chiral defects contributing to enantioselectivity in the Ni/aspartate system. Attard and co-workers have shown, via electrochemical studies, that selective blocking of step and step-kink sites by Bi leads to a decrease in enantioselectivity in the Pt/cinchona/pyruvate system [34] implying that at least a contribution to enantioselectivity comes from such defects. In the present study, it seems highly plausible that a substantial contribution to the enantioselectivity of aspartate-modified nickel catalysts is derived either from chiral defects produced by adsorbate-induced corrosion or by the adsorption of chiral modifiers at defects.

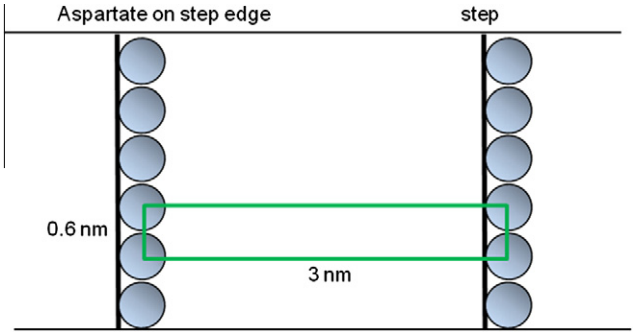

Fig. 7. Schematic diagram of estimated aspartate molecule "unit cell" on a stepped Ni surface at low aspartate coverage.

It is interesting to also note that, since methylacetoacetate is similar in dimensions to aspartic acid and tartaric acid, the saturation coverage of methylacetoacetate on Ni{1 1 1} would likely be in the range of 0.25 ML [23]. Assuming that 0.03 ML of methylacetoacetate could decorate step defects at any particular time, and the step defects catalysed the reaction enantioselectively while the remainder of methylacetoacetate is hydrogenated racemically at the same rate, at any instant, 0.22 ML of methylacetoacetate would be hydrogenated racemically (giving 0.11 ML of (R)-MHB to add to the 0.03 ML formed at enantioselective sites and 0.11 ML of (S)-MHB)), the enantiomeric excess would be predicted to be $100 \times [0.14 - 0.11]/[0.14 + 0.11] = 12\%$. This is actually very similar to the optimum enantioselectivity in the Ni/aspartate system [1]. If the influence of the chiral defects was amplified into the terraces, a much higher enantiomeric excess would be observed. This implies that chiral amplification does not play a significant role in the Ni/aspartate system.

5. Conclusions

The adsorption, from aqueous solution, of (*S*)-aspartic acid as a function of modification pH onto a polycrystalline Ni foil has been characterised by XPS. Under the modification conditions in which the enantioselectivity of the aspartate-modified Ni catalyst is optimised, the levels of aspartic acid remaining on the surface are essentially undetectable by XPS.

It is likely that highly enantioselective sites exist at step and/or step-kink defects on the Ni surface. These sites most likely consist of chiral defects created by the corrosive leaching of Ni from steps by aspartic acid. It is not possible to completely rule out the presence of a finite amount of residual aspartate species adsorbed at such step sites.

Lowering or increasing the pH from the optimum modification pH results in an increase in the surface concentration of aspartate. Catalytically, this results in a decrease in enantioselectivity. This implies that aspartate species adsorbed at terrace sites are not enantiodifferentiating and indeed that they may block access to the enantioselective sites at step defects.

In agreement with our earlier RAIRS study [20], the nature of the adsorbed aspartic acid species depends strongly on pH. With increasing pH, aspartic acid becomes progressively deprotonated.

The extent of protonation of aspartic acid influences the subsequent adsorption of methylacetoacetate with the diketone form favoured at low pH and the enol tautomeric form favoured at high pH.

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