

Oriented Adsorption of Amino Acids on (001) Nickel Surface

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The epitaxial growth of amino acids such as L-phenyl alanine, L-alanine and L-gultamic acid on nickel crystal was investigated by electron microscopy and diffraction. Amino acids were crystallized from dilute aqueous solutions on (001) nickel films prepared by vacuum-condensation with KCl cleavage as the substrate. The most preferable positions for the mutual orientation of both crystals, the substrate nickel and overgrown amino acids, were determined by statistical treatment of the angular distribution of appearance frequency.

L-phenyl alanine, which assumes three preferable interaxial positions, always shows the same habit plane, indicating a certain state of oriented adsorption at the interface. L-alanine is crystallized in a polymorphic form of unknown structure, suggesting the existence of strong interaction of adsorbed molecules and substrate nickel atoms, which even controls the epitaxial nucleation having a crystal structure different from that of free growth. L-gultamic acid shows different angular distributions of preferred orientation, depending upon the temperature at which the nickel film has been modified in advance with the same species of amino acid. The molecular position was inferred from the mutual orientation to form O-C-O bridge on two neighboring nickel atoms at the interface.

INTRODUCTION

The interaction of organic molecules with solid surface is an important factor to consider the fundamental process of the heterogeneous catalysis as well as the epitaxial nucleation of the molecular crystal. It is our contention that the state of oriented adsorption can be presumed by knowing the mutual orientation of solid surface and the molecular crystal overgrown on it, because very often the adsorbed molecules are found to behave as the epitaxial nuclei.

The extensive work performed by Izumi and his collaborators of Akabori's Group¹⁾ revealed that the Raney nickel catalyst, which is usually known to convert ketones ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$) through contact reduction into asymmetric alcohol ($\text{R}-\overset{\text{OH}}{\underset{|}{\text{C}}}-\text{R}'$) having racemic composition, produces optical active alcohol, when modified with various amino acids of either D- or L-type in advance of actual reaction. In general, when L-amino acids are used for modifying the Raney nickel catalyst, the produced alcohol becomes dextrorotatory, whereas, with D-amino acids as the modifiers, the product alcohol exhibits levorotatory behaviors, both as the result of asymmetric reduction. It is considered that the amino acid molecules adsorbed on nickel surface exert certain steric influence on this peculiar catalytic process. In order for the mechanism of such an interesting behavior to be interpreted, it seems to be the basic requirement to know

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the adsorption state and, if any, to know the most possible orientation of these modifier amino acids on nickel surface.

On the other hand, it has been found by some of the present authors²⁻¹⁰) that an organic crystallite grows on other single crystal face with a definite axial orientation and with a particular crystal habit, when the organic molecule is strongly adsorbed on the substrate surface. Conversely considering, one can find an approach to deduce the information about the most probable posture of the original molecule adsorbed on the substrate crystal face, if the axial orientation of the final crystal is determined by, for instance, electron diffraction and also if the molecular arrangement in the crystal has been well established by X-ray diffraction analysis.

In the present work, the application of the same principle to the nickel-amino acid system has been attempted in order to meet the above requirement concerning the adsorption state of various modifier molecules on Raney nickel catalyst.

ORIENTED ADSORPTION AND EPITAXIAL NUCLEATION

The leading principle for the approach followed in the present work is based on the well known phenomena which are usually referred to as the oriented overgrowth, or more simply as "epitaxy". When one species of crystal grows either from solutions or by vacuum-condensation on a clean active surface of other species of substrate crystal, it is often noticed that the major axes of both crystals assume a definite mutual orientation with respect to each other as the result of characteristic behavior of epitaxy. Most of the past investigations on the epitaxial growth were concerned with various pairs of metals or inorganic crystals.^{11,12)}

The theoretical approach was also tried by many investigators. Although a perfect treatment seems to be still far beyond the realization, the essential point concerning the interaction between the nuclei of overgrowing crystal and the surface atoms of substrate crystal has never been overlooked. One of the most reliable approaches is that proposed by Walton and Rhodin,^{13,14)} who deduced that the nuclei of overgrowing crystal must assume definite orientation even at the very beginning of growth process and the number of atoms which build up the individual nuclei can be as small as three to four. It was also pointed out that an important factor which must be taken into account is the correlation between the attractive force of atoms to form a cluster, or nucleus, and the interaction of individual atoms with the substrate surface, the latter enhancing the stability of atomic cluster to form a rigid nucleus.

This consideration is essentially based on the results of experiments extensively performed by Rhodin¹⁵⁾ to show that the binding energy between the overgrowing and the substrate crystals roughly have a linear relationship with the order of epitaxy, that is, the stronger the adhesive force, the better the resulted epitaxy.

As to organic crystals, one would easily notice the particular situation that every molecule is itself a very stable cluster of atoms with a definite configuration and has a certain distribution of residual bond forces. This means that an organic molecule is considered to act as a nucleus for the epitaxial growth whenever the functional group in the molecule can nicely fit to individual atoms of the substrate, which render suitable sites for the sitting molecules to promote local interaction due to co-ordination, ion-

dipole, charge-transfer and hydrogen-bonding forces in addition to the simple Van der Waals force.

It should be noted, however, that the order of epitaxy must be increased, if the binding force at the interface is comparative to or stronger than that of molecules to form the crystal. That is to say, better epitaxial state will be attained with an adhesive force stronger than the cohesive force of the molecules. This kind of situation can be realized if one chooses organic crystals as the overgrown species. In such a case, it is expected that the final orientation of the overgrowing crystal is strongly governed by the initial state of adsorbed molecules which act as the epitaxial nuclei. Thence, the original state of oriented adsorption can be presumed by knowing the final growth state of the molecular crystals on the same substrate surface.

This principle is based on some past experiences with respect to epitaxial growth of many π -electronic molecular crystals such as various metal-derivatives of phthalocyanine,²⁻⁷⁾ nitrogen containing polycyclic aromatic compounds,^{2,4,8)} electron acceptors including tetracyano-quinodimethane^{9,10,16)} and tetrahalogeno-*p*-benzoquinones,¹⁷⁾ all found to form very neat epitaxial films on cleaved faces of alkali-halides and muskovites.

On the basis of foregoing principle, the epitaxial growth of various amino-acids was investigated in the present work. Since the knowledge of definite orientation of epitaxial film is the essential requirement for the deduction of oriented adsorption, transmission electron diffraction was applied to the system where single crystalline nickel films were adopted for the substrate as an alternative of the actual Raney nickel catalyst. When the deposit crystals are small, the selected area diffraction is applicable in a conventional electron microscope, which also enable one to examine the epitaxial state from a morphological view point.

Although the experimental results showed that no preference for a singular position in the mutual orientation was exhibited by most of the systems, the statistical treatment of data processing furnished reliable basis for the deduction of the initial state of adsorption for the individual amino-acids investigated in the present work.

EXPERIMENTAL

1. Preparation of Thin Films of Nickel Single Crystal

It is widely accepted that Raney nickel consists of very fine particles, rather close to amorphous solid, showing no well-defined crystallite planes. In the present work, however, single crystalline nickel was used in a form of thin film, because it is a basic requirement that the orientation of the substrate crystal is known for the determination of epitaxial relationship. As the substrate surface for this purpose, the (001) plane was chosen, since it is easily prepared also by epitaxial growth technique. Metallic nickel was evaporated in a vacuum vessel of about 10^{-6} Torr onto a (001) surface of cleaved single crystal of potassium chloride which was heated at 400°C. The resulted nickel film, whose thickness had been controlled to be about 300 Å, was wet-stripped in pure water and mounted on specimen grids for electron microscopy. After the fixation of the film to the grid by drying, the film was washed with pure water several times to

remove inorganic ions which might be left adsorbed coming from substrate KCl. The examination by means of electron diffraction indicated that the thin nickel film thus prepared is single crystal developed on the (001) plane of face centered cubic lattice.

2. Preparation of Epitaxial Films of Amino Acids on Nickel Films

a. *L-Phenylalanine*

A drop of 1% aqueous solution of L-phenyl alanine was placed on nickel film and dried in air so that thin crystalline film was formed on the substrate.

b. *L-Alanine*

Two species of epitaxial films were prepared for L-alanine. One of them was produced in the same way as above. The other species was prepared after cleaning the surface of nickel film, which was washed with diluted HCl and subsequently rinsed with pure water. This procedure was adopted to remove possible oxides and to expose active surface of metallic nickel. The films thus activated were subjected to the modification with L-alanine solution in the same way as above.

c. *L-Gultamic acid*

As it is known that the temperature, at which the Raney-nickel catalyst is modified, exerts a certain effect on the catalytic action in the case of L-gultamic acid, two specimens were prepared by dipping free nickel films in 2% aqueous solution of L-gultamic acid (pH=5) at 0 and 100°C, respectively. After washing with pure water, a drop of L-gultamic acid solution of 0.8% was placed on each modified nickel film after mounting on the grid mesh. These specimens may be called low and high temperature types for those modified in advance at 0 and 100°C.

These five specimens as well as the original nickel films were examined by electron microscopy combined with selected area diffraction. For each specimen, about 100 electron diffraction patterns from the area of the specimen of 2-3 μ^2 were recorded for statistical analysis. Since the mutual orientation of both crystals, nickel and each amino acid on it, is the most direct concern in this work, both diffractions were always recorded on the same photographic plate. The most difficult part of the experiment was the control of the electron beam strength, which is apt to damage the amino acids. However, sufficient enough brightness was attained for 100 kV electrons to record the diffractions from both crystals at the same time. The diffraction pattern from the nickel film was always used as the standard to determine the camera-constant for the analysis of that from amino acid.

RESULTS AND DISCUSSION

The electron micrographs in Fig. 1 show the appearance of nickel film prepared on the cleavage face of potassium chloride. One of them (a) is an example of continuous film and the other (b) is that of discrete one built up of connecting islands. The characteristic features, common to both types, were revealed by combined interpretation of selected area diffraction patterns, (c) and (d), which were obtained from the films shown in (a) and (b), respectively. The nickel films were identified to assume (001) orientation, that is, they are single crystalline films as a whole whose habit surfaces are extended over the (001) plane. The electron diffraction also indicates

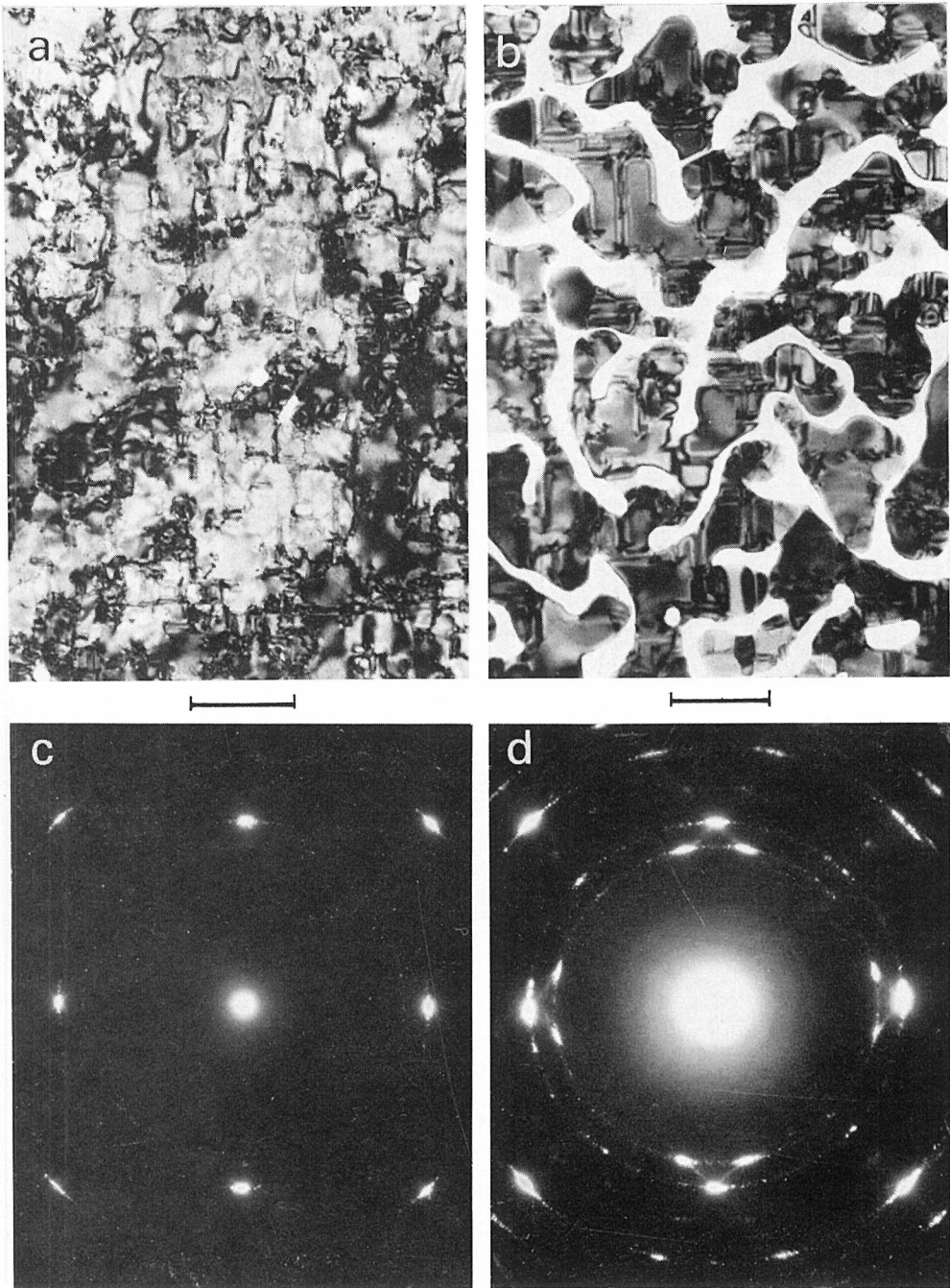


Fig. 1. Electron micrographs of nickel films prepared on KCl cleavage by vacuum-condensation. Scale shows $1\ \mu\text{m}$.

- (a) Continuous film with dislocations.
- (b) Discrete film of island-structure with twins.
- (c) and (d) Selected area electron diffraction patterns obtained from films in (a) and (b), respectively.

that these films contain small amount of twin structure which is abundant in the discrete type like (b). In the electron micrograph, they are apparent from the peculiar contrasts which show groups of parallel fringes meeting to each other at right angle. Inclusions of dislocations are also observed exhibiting small irregular fringes in both films.

1. L-Phenyl Alanine

Figure 2 is to show some example of electron micrograph (a) and diffraction pattern (b) obtained from epitaxial crystallites of L-phenyl alanine together with substrate nickel film on which the amino acid was over-grown. The strong reflections which appear in a square arrangement are due to the (001) nickel film, whereas the weaker spots arranged in the small rectangular lattice are due to amino acid crystal.

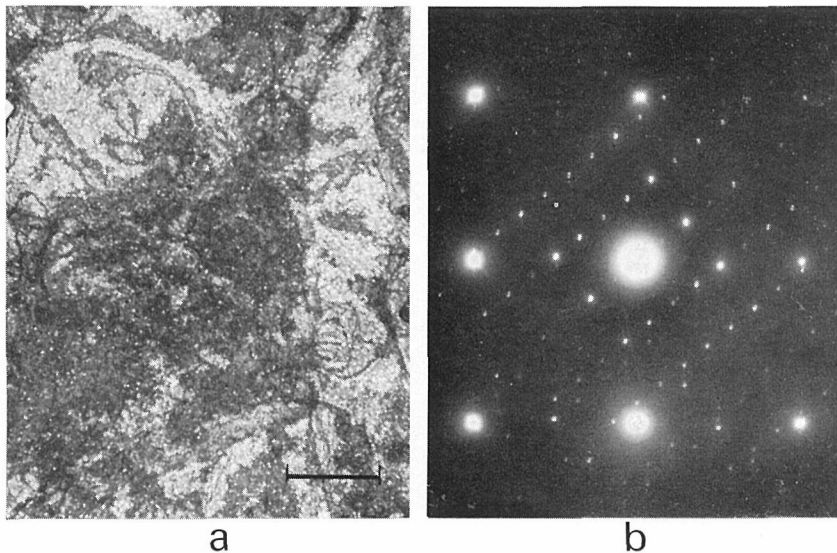


Fig. 2. Electron micrograph (a) and selected area electron diffraction pattern (b) of (001) nickel film with L-phenyl alanine overgrown on it. Scale shows 1 μm .

The mutual lattice orientation of two crystals is defined in terms of the angle between the major reciprocal axis of nickel and the equator of amino acid, which is the rectangular axis with shorter period, as schematically shown in Fig. 3a. Taking it into account that the substrate has four-fold symmetry and the other has two-fold one both around the normal of their interface, the interaxial range was defined between 0 to 45°. Since this angle did not converge to a single definite value, the most probable position was sought by taking the angular distribution of appearing frequency.

The result obtained with about 100 similar diffraction patterns is shown in Fig. 3(b) as a histogram. It is apparent that there are three peaks in the frequency distribution which are considered to be the most preferable positions for mutual lattice orientation. Figure 4 shows the fitting of two lattices at the interface, where the plain circles show the array of surface nickel atoms and the rectangles represent the

unit cells of amino acid. Unfortunately, the crystal structure of L-phenyl alanine has not been determined. However, it is obvious from the symmetry of the diffraction, one can expect a molecule sitting at every corner of the unit cell as shown by black disks. The lack of knowledge about the precise orientation of these molecules prevents the inference about the adsorption state of the individual molecules at the interface. However, it becomes clear at least that amino acid has a certain tendency to assuming preferred orientation on nickel crystal surface.

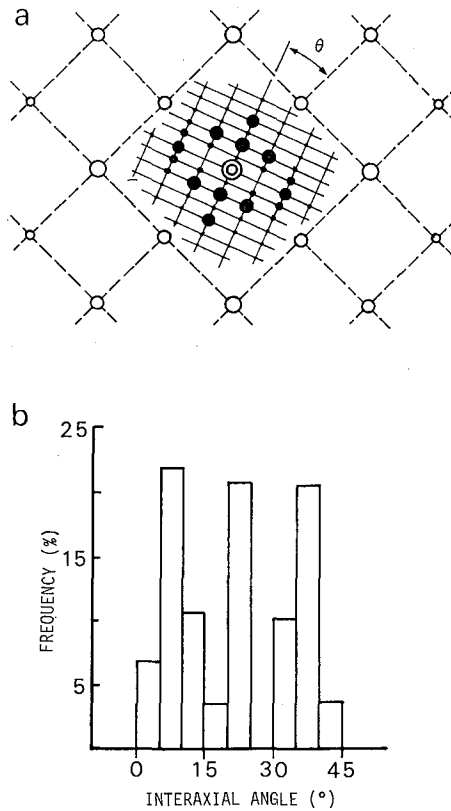


Fig. 3. Schematic diagram of electron diffraction pattern of (001) nickel and overgrown L-phenyl alanine (a) and distribution of angular position for preferred orientation between both crystals (b).

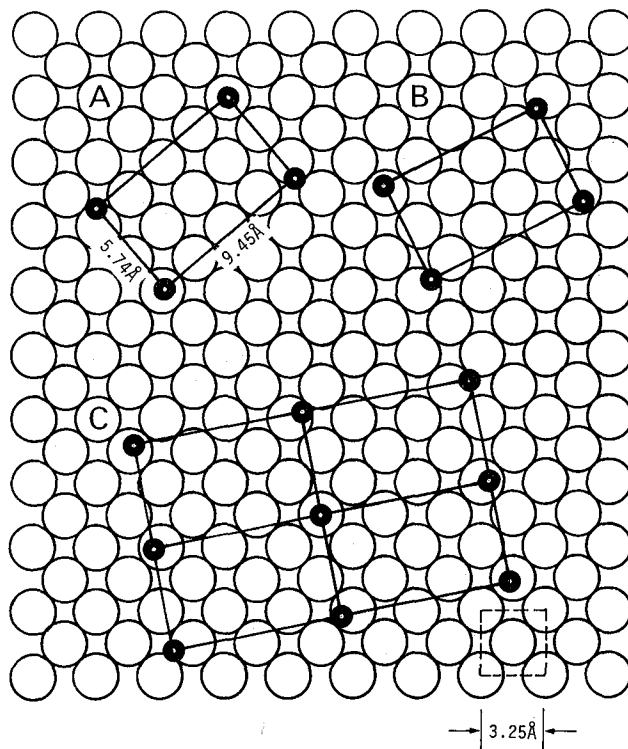


Fig. 4. Schematic drawing of lattice orientation of L-phenyl alanine on a (001) nickel film.

2. L-Alanine

As to L-alanine, different results were obtained according as whether or not the nickel film was treated with HCl in advance.

a. Nickel film without HCl treatment: Figure 5 (a) is an example of electron diffraction from L-alanine overgrown on nickel film which was not subjected to HCl treatment. The crystal structure of L-alanine, which is grown from aqueous solution, is determined by Simpson and Marsh,¹⁸⁾ who also reported the natural crystal habit to be illustrated in Fig. 5 (f), and also that the crystal is orthorhombic with the unit-cell dimensions of $a=6.032$, $b=12.343$, and $c=5.784$ Å. The analysis of the above electron diffraction shows that the thin film of L-alanine assumes different crystal habit, although the structure is interpreted to be the same as that reported by Simpson.

As illustrated in Fig. 5 (c), the lattice periods along the rectangular axes are 12.6 and 5.78 Å, corresponding to b - and c - axes, respectively. This result indicates that the predominant habit face lying on the nickel film is (010) plane instead of the natural (110) as shown in Fig. 5 (e). Taking into account the analytical data given by Simpson, it was deduced that the L-alanine molecule at the interface has a possibility to locate its oxygen atom of carboxylic group and nitrogen atom in amino group, as shown in Fig. 6 (a), which shows a presumed adsorption state viewed in the direction normal to the cross-section indicated in Fig. 6 (b).

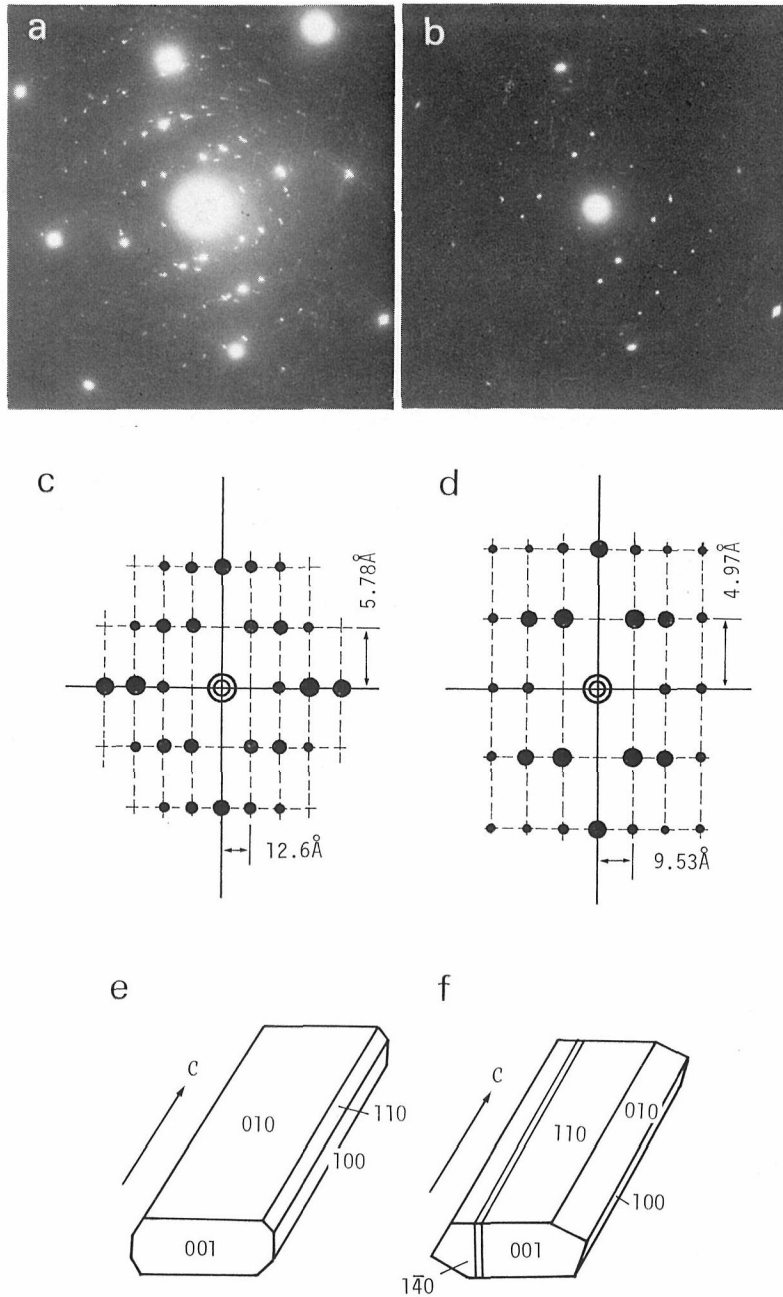


Fig. 5. Selected area electron diffraction patterns and schematic reproductions of L-alanine overgrown on (001) nickel films (a and c) and on those treated with HCl solution (b and d). Also, comparison of crystal habits of L-alanine between epitaxial growth (e) and natural growth (f).

Adsorption of Amino Acid on Nickel Surface

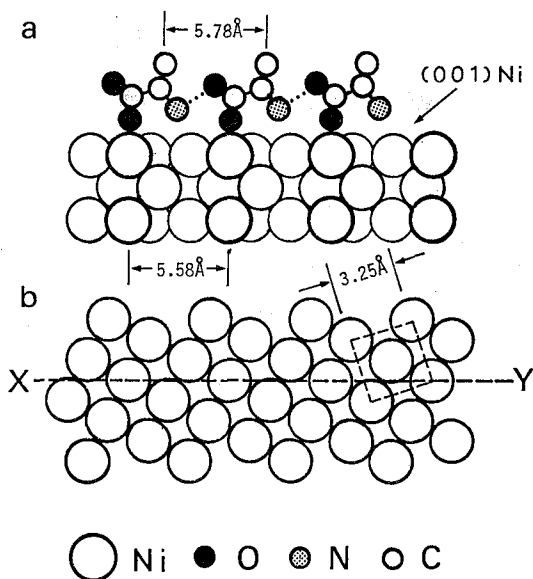


Fig. 6. Oriented adsorption of L-alanine molecules on (001) nickel film cleaned with HCl.
(Drawing is based on the position indicated by the electron diffraction in Fig. 4a.)

b. Nickel film with treatment in HCl: In order to make the surface of nickel as clean as possible, it was washed with dilute HCl solution and subsequently rinsed with pure water. When L-alanine crystallites were overgrown on such films, the electron diffraction pattern appeared in a quite different manner as shown in Fig. 5(b).

The schematic representation of the diffraction pattern (d) indicates that the lattice periods, 9.53 and 4.97 Å of rectangular axes, cannot be interpreted in terms of the above data given by Simpson *et al.*¹⁸⁾ Among various reasons considerable for the appearance of different diffraction pattern, the most plausible is the formation of a polymorph. The effect of this kind has been found in other organic crystals such as tetraiodo-*p*-benzoquinone¹⁷⁾ which is known as a strong electron acceptor and certain interaction with ions can be anticipated on the surface of alkali halides used as the substrate. It is reasonable to consider that the growth of polymorph which has a molecular arrangement different from that assumed in a naturally grown crystal is due to the original nucleation in a different form. It should be emphasized here that the effect of this kind is also a certain evidence for the strong adsorption of molecules at the interface, where the definite orientation of the adsorbed species even alters the molecular arrangement in the individual nuclei. Unfortunately, however, the adsorption state itself was not revealed again in this case since the molecular arrangement of the new polymorph is not known at all.

The frequency distribution of the preferred orientation was also calculated as shown in Fig. 7 for the nickel film treated with HCl. The probability is predominant in ranges of 45–50° and 85–90°. The peak around 70° which was observed in the case of L-phenyl-alanine on nickel films without HCl treatment does not exist in this case. It is said that catalytic activity of Raney nickel declines when it is treated with HCl.

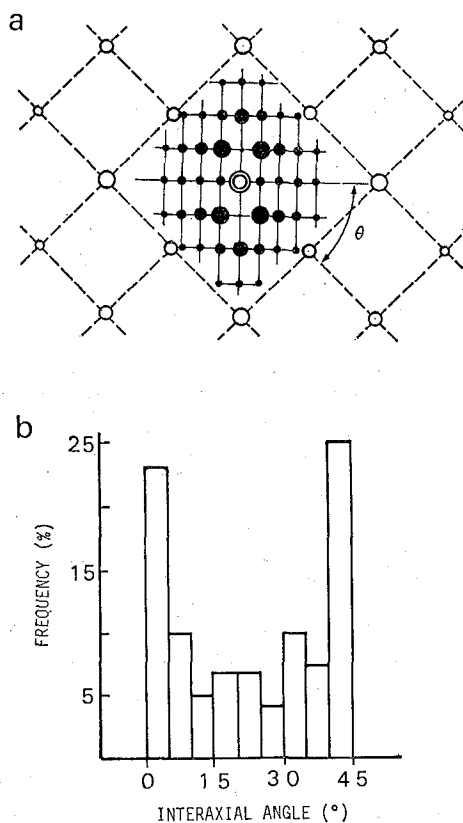


Fig. 7. Schematic drawing of electron diffraction pattern of nickel and L-alanine (a) and distribution of angular position for preferred mutual orientation between both crystals (b).

This deactivation effect seems to have some correlation with the disappearance of the peak at 70°.

3. L-Gultamic Acid

It was reported by Izumi *et al.*¹⁾ that the asymmetric yield of 3-hydroxybutylate produced by the catalytic reduction of methylacetoacetate is greatly decreased as the increase in the temperature of modifying Raney nickel catalyst with L-gultamic acid. When Raney nickel is modified at low temperature as 0°C (low temperature type), the optical rotation of the product becomes minus, whereas with a modifying temperature raised over 80°C (high temperature type), the optical rotation turns to plus. In view of elucidation of the correlation between this effect and the adsorption state of L-gultamic acid, two species of nickel films were investigated in this work by modifying one at 0°C and the other at 100°C both in 2% aqueous solution of L-gultamic acid (pH=5). Although the crystallite of L-gultamic acid was overgrown from 0.8% aqueous solution after rinsing the modified nickel film with pure water, the epitaxial growth was considered to take place with gultamic acid molecules as nuclei, which are strongly adsorbed on nickel. The possibility of existing residual molecules is

presumed from the experimental results reported by Izumi *et al.* that the temperature effect does not change even after washing modified nickel catalyst with water.

The electron diffraction patterns in Fig. 8, a and b, are obtained from nickel films of low and high temperature types, respectively, with L-gultamic acid overgrown on them. In both cases, crystallites of L-gultamic acid were found to assume the β -form

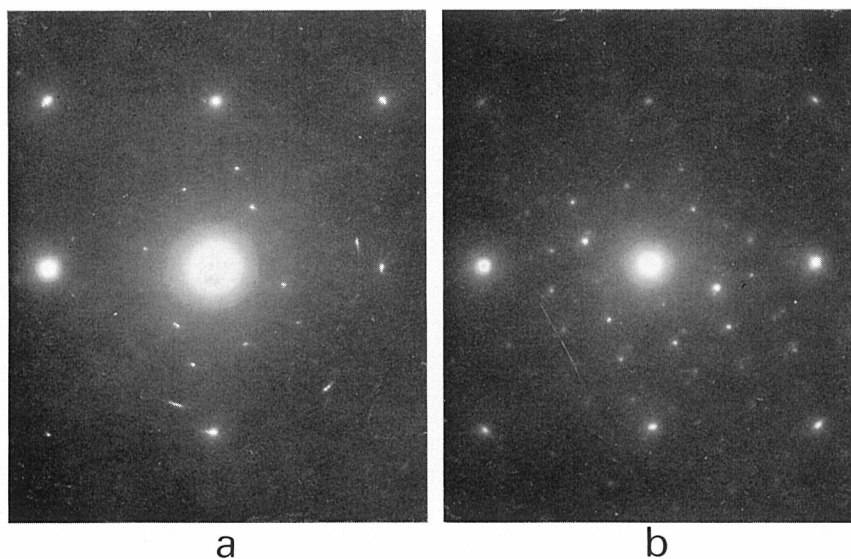


Fig. 8. Selected area electron diffraction patterns of L-gultamic acid overgrown on (001) nickel film modified at 0°C (a) and that modified at 100°C (b).

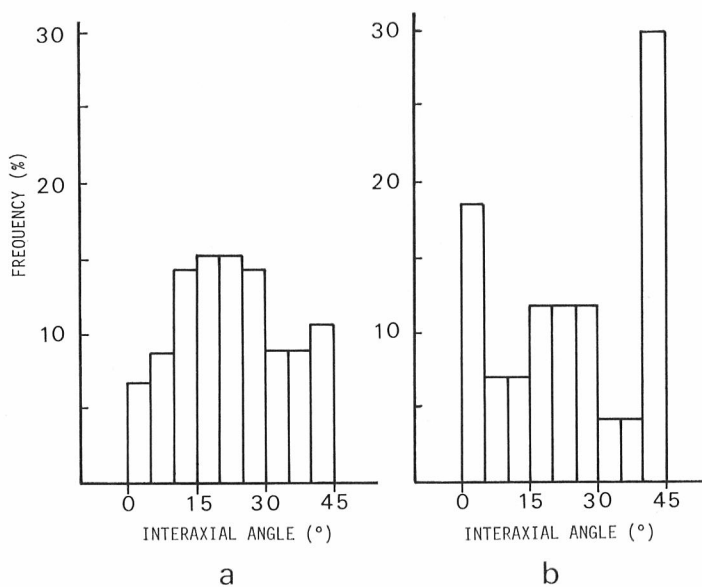


Fig. 9. Angular distribution of preferred mutual orientation between modified nickel film and overgrown L-gultamic acid.

(a) high temperature type; (b) low temperature type.

with the (010) parallel to the surface of nickel film. The statistical distribution of interaxial angle of mutual orientation is illustrated in Fig. 9 for both types. The angular positions of peak differ according as the modifying temperature. For the low temperature type, most preferable position appears in a rather broad range of 15–30°, whereas for the high temperature type, peaks appear at ranges of 0–10° and 40–45°. A small and broad peak exists at the 15–30° range, similar to the former, even for the high temperature type. The existence of this peak range means the predominant tendency to take this adsorption state common to both types.

The structure of overgrown L-glutamic acid in this case was analysed to accord with that determined by Hirokawa,¹⁹⁾ assuming crystal data as follows: $a=5.17$, $b=17.34$ and $c=6.95$ Å for an orthorhombic unit cell. Taking into account these data, the mutual orientation of the basal unit cell on nickel surface lattice was revealed to appear as shown in Fig. 10, where A, B, and C correspond respectively to the three dominant orientations with the axial angles around 0°, 45°, and 20°. In all cases, the corner atoms which are assigned as oxygen of carboxylic group of L-glutamic acid, can sit on nickel atoms with misfit value within 3% at the largest. Since the molecular arrangement in the crystal is known, the mutual relation of molecules at the interface will appear like that illustrated in Fig. 11 (a) for the Type A for an example which is a lateral view along a face-diagonal of the unit cell of substrate nickel. The one of the oxygen atoms of carboxylic group closely fits on nickel atom and the other is located very close to it. Figs. 11, b and c, also show interfacial molecules in the epitaxial crystallites of L-glutamic acid, corresponding to B and C in Fig. 10, respectively. The

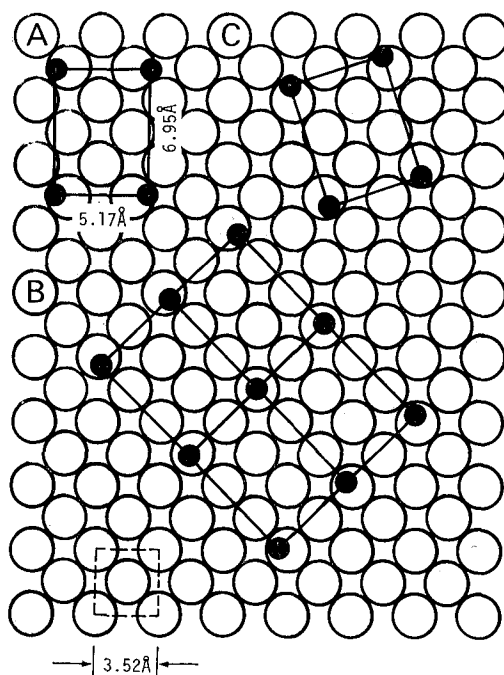


Fig. 10. Lattice fitting for (001) nickel surface and overgrown L-glutamic acid.
A and C: Specific for low temperature type and B: Common to both types.

Adsorption of Amino Acid on Nickel Surface

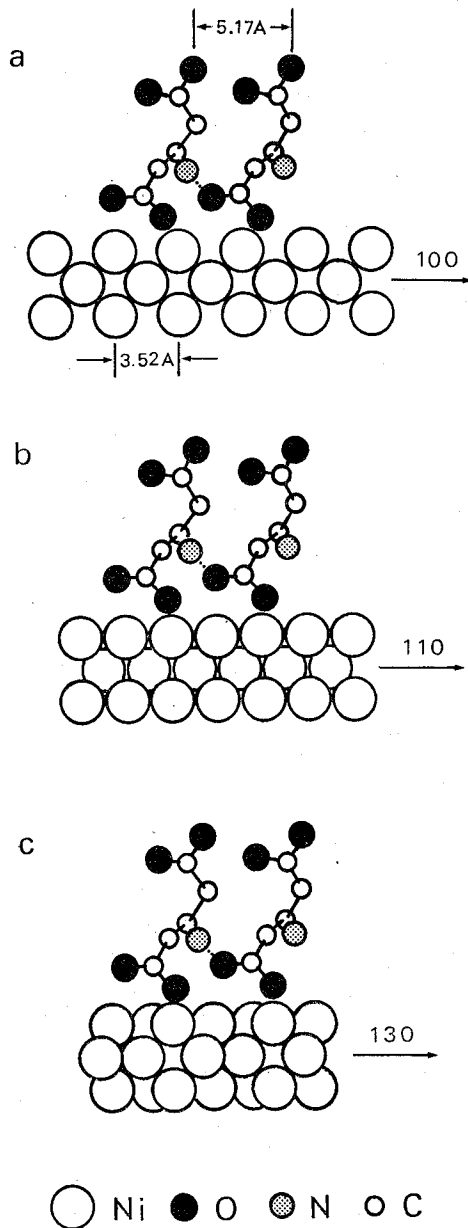


Fig. 11. Presumed position of L-gultamic acid molecule on (001) nickel surface.
 (a) molecular fitting at the interface of substrate nickel and overgrown crystal,
 and state of oriented adsorption for low temperature type (b) and common to
 both types (c).

molecular posture is viewed along the c-axis of amino acid, which is parallel to $[1\bar{1}0]$ and $[1\bar{3}0]$ axes of substrate nickel. In all cases, a molecule of glutamic acid can adequately stand on a nickel atom with one of carboxylic branches. Although these situations are found in epitaxial crystallites, a similar state of molecular orientation may be well realized for closely adsorbed surface, where a hydrogen bonding between

the amino-group and the free carboxylic branch of the adjacent molecule can be anticipated as shown by dotted lines in Fig. 11.

The presumed state of adsorption itself is not different between low and high temperature types, excepting the arrangement of nickel atoms on which the molecule is resting (Fig. 11). This causes different situation in the arrangement of nickel atoms on which no amino acid molecules are adsorbed. This gives rise to different space configuration for the reacting molecules to adsorb, which would assume different positions in relation to the amino acid molecules already sitting nearby. This is considered to be the plausible reason for the conversion of rotatory power or the asymmetric yield of the reduction product depending upon the temperature of the modification.

Obviously, the actual surface of Raney nickel catalyst is not so simple as the specified surface used in the present work. Even in the idealized system, one cannot exclude other important surfaces such as (111) and (110). It is considered, however, that the adsorption state may not be so considerably different from that deduced in the specified experiment in the present work.

SUMMARY

1. L-phenyl alanine crystallites overgrown from solution on the (001) surface of nickel film assume three preferable positions for the mutual orientation. The appearance of definite habit face indicates the possibility of oriented adsorption of molecules on nickel atoms for the nucleation of epitaxial growth.

2. As to similar crystallites of L-alanine, both amino and carboxylic groups are considered to contact to nickel atoms on the (001) face which is not treated with HCl solution. With nickel films treated in HCl in advance, two preferred orientations were observed to appear. In both cases, the overgrown L-alanine crystal assumes a polymorphic form other than that of free growth. This effect indicates that the strong adsorption of molecules even controls the nucleation to form different molecular arrangements.

3. As to L-gultamic acid, three different preferred orientations were assumed in the case of nickel films modified in advance with L-gultamic acid at 100°C (high temperature type). On the other hand, one angular range of interaxial position, though rather broad, appeared for nickel film modified at low temperature near 0°C (low temperature type). This range is common to both types. The initial state of oriented adsorption of L-gultamic acid molecules was presumed by taking into account the molecular arrangement in the crystal. The one of oxygen atoms of O-C-O group is considered to contact to a nickel atom,

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