The Infrared Absorption Spectra of Nickel Metal Surfaces Modified with Optically Active α-Alanine from Its Aqueous Solution[1)]

Aritada Hatta, Yoshihiro Moriya, and Wataru Suëtaka
Laboratory of Interface Science of Metals, Faculty of Engineering, Tohoku University, Aramaki, Aoba, Sendai 980

(Received February 19, 1975)

The infrared absorption spectra of thin films of α-alanine formed on pure nickel and "Raney nickel" surfaces, modified with its aqueous solution, were measured by the high-sensitivity reflection method. From the infrared dichroism in the reflection spectra, the molecular orientations in the thin films were derived. In the thin film formed on pure nickel modified at 5 °C, the CO_2^- group of α-alanine is oriented nearly vertical to the metal surface and the O· · ·O axis is inclined to the surface. On the other hand, when the "Raney nickel" film is modified at 5 °C, the C_α–C_0(carboxylate) bond is oriented obliquely to the surface. When the "Raney nickel" film is modified at 100 °C, the Ni-alanine chelate is formed on the surface: the C_α–C_0 bond and the NH_2 group are nearly parallel to the substrate surface, while the O· · ·O axis is vertical to that surface.

It is well recognized that infrared spectroscopy is one of the most powerful tools for investigating the adsorptions of a reactant or an intermediate on a catalyst. Adsorptions on metal supported on such carriers as silica and alumina are most often investigated by employing the transmission method.[2)] In this case, however, the metal particles give rise to background scattering, and the interaction of the supported metal with the carrier is also inevitable[3)]; hence, straightforward explanations of the observed spectrum are, in general, difficult to give. In addition, the transmission method can not give any direct information about the orientations. On the other hand, the high-sensitivity reflection method,[4)] which is relatively new, has been employed by a few investigators[5)] in studying the adsorptions of simple gaseous molecules to evaporated metals. In this method, the infrared radiation in the vicinity of the reflecting surface is markedly polarized normal to the mirror surface and the observed spectrum is closely correlated to the orientation of molecules existing on the metals. This technique may also be used in the investigation of the structure of thin crystal films formed on a metal substrate. In fact, it has been found that the crystal structures in thin films are often different from those in bulk materials.[6)] This result can be interpreted by taking account of the interaction of the metal substrate, which may determine the structure of the crystal nuclei on the substrate.

The asymmetric hydrogenation of the C=O double bond using Raney nickel modified with optically active amino acids or hydroxy acids has been systematically investigated by Izumi and his co-workers.[7)] In such an asymmetric synthesis, what we are interested in is the relationship between the absolute configuration of the modifying reagent and the asymmetric direction of the catalyst. In connection with this mechanism, it seemed that it might be interesting to observe the infrared dichroism arising from the preferred orientation of modifying molecules on the nickel metal surface.

Recently we have obtained results for the cases in which L-β-phenyllactic acid and L-β-phenyl-α-alanine were used as modifying reagents.[8)] In the latter case, the spectrum was in accord with an orientational model where the COO^- ion is asymmetric in alignment to the nickel surface. Recently, Groenewegen and Sachtler[9)] reported the spectrum of L-α-alanine adsorbed on silica-supported nickel; the spectrum they obtained was the same as that of a nickel chelate, but no details about the orientation were given. The objective of this paper is to obtain information about the orientation of α-alanine molecules in thin films formed on the nickel substrate. Although the direct determination of the orientation of species strongly adsorbed on the metal surface is quite desirable, the signal from the species was too weak to provide any available information, so the spectra of the thin films formed on modified nickel were observed in the present paper.

The thin films treated in this paper are probably a few hundred angstroms thick. Therefore, the reflection spectra of films with such a thickness cannot directly reveal the orientation of the species chemisorbed on the substrate. However, the orientation of the molecule in a thin film is very often determined by the orientation of the species which are adsorbed strongly on the substrate and which, consequently, act as the nuclei of the epitaxial overgrowth.[10,11)] The molecular orientation determined by the posture of the molecule at the interface is also known in liquid and liquid-crystal thin films on solid substrates.[12,13)] The orientation of the species strongly adsorbed on the substrate surface may, therefore, be deduced from the molecular orientation in the thin films.

α-Alanine was used in the present work because α-alanine is one of the simplest compounds which are practically used as modifying reagents in the asymmetric synthesis.[14)] It is, therefore, considered to be well-suited for the fundamental study of the mechanism of modification. In addition, the vibrational assignment[15)] for this molecule is almost completely established and, based on the available data, the reflection spectra can easily be analyzed.

Experimental

The infrared spectrum was obtained by means of a JASCO IR-G grating spectrophotometer with an assembly designed for use in single-beam reflection operation. Signal averaging and background-subtraction procedures were performed on a JEOL model JEC-5 spectrum computer. By using this technique, the absorptions of atmospheric water vapor was removed satisfactorily and the signal-to-noise ratios were greatly improved. The guaranteed-grade reagents of L- and D-α-alanine were obtained from the Wako Pure Chemicals Co. and were used without further purification. In the present experiment, an electrolytical nickel (99.9% pure) plate and a thin "Raney nickel" film formed on a nickel plate were used as substrates and mirrors. The "Raney nickel" alloy was prepared, for convenience, by the vacuum deposition of aluminum onto nickel surfaces and by subsequent annealing at 550 °C for 3 hr under a nitrogen or hydrogen atmosphere.

Nickel metal plates with and without Al-Ni alloy layer were treated with a 20% aqueous sodium hydroxide solution at 80 °C and then rinsed in distilled water. The substrate, nickel or "Raney nickel," was modified with a 0.5% aqueous solution of L- or D-α-alanine at 5 °C and 100 °C. The pH-value of the solution was about 5.9 at room temperatures. The modified sample were then dried in air and subjected to the reflection measurement. Very fine crystals of the amino acids grew on the strongly adsorbed molecules, with the evaporation of water. The background spectra were obtained by using a pure nickel or thin "Raney nickel" plate just before modification.

Results and Discussion

Figure 1 shows the infrared absorption spectrum of L-α-alanine obtained as a KBr pellet in the frequency range from 1800 cm^{-1} to 900 cm^{-1}. The vibrational assignment of the infrared spectrum of DL-α-alanine was previously made on the basis of a normal coordinate treatment.[15] The high-sensitivity reflection spectra of bulk nickel plates, which were modified at 5 °C over periods between a few hours and two weeks with 0.5% aqueous solutions of L-α-alanine (labeled a) and D-α-alanine (labeled b) and then covered by thin film crystals of these compounds, are shown in Fig. 2. No remarkable differences were detected in the spectra of different modifying times.

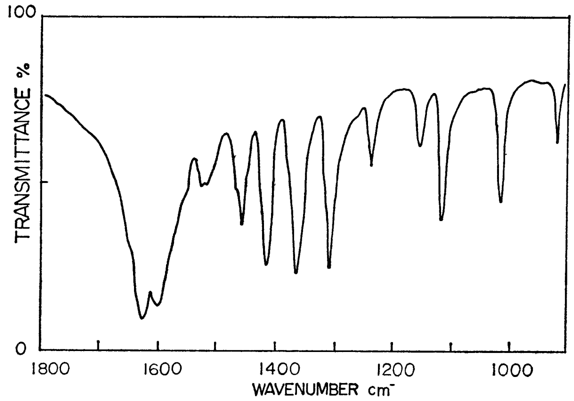

Fig. 1. Infrared transmission spectrum of L-α-alanine (KBr pellet).

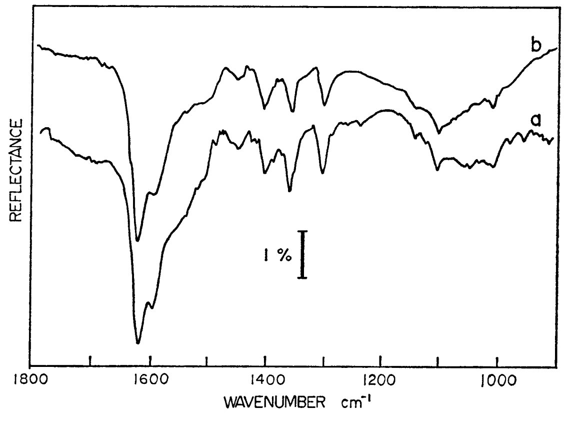

Fig. 2. High-sensitivity reflection spectra of bulk nickel plates modified at 5 °C with 0.5% aqueous solutions of L- and D-α-alanine. a: L-α-alanine; b: D-α-alanine.

The most remarkable difference in the thin film spectra from bulk crystals, which can be clearly seen in Fig. 2, is the broad absorption with the maximum falling near 1070 cm^{-1}, probably due to the surface hydroxyl groups formed on the nickel substrate in the course of modification in an aqueous solution. Except for this band, however, the spectra of modified nickel plates with L-α-alanine and also D-α-alanine are in agreement with that of bulk L-α-alanine or D-α-alanine, except for band shifts to a slightly lower frequency, indicating that the α-alanine molecule in the film over the nickel surface is intact. Therefore, this allows us to compare the relative intensities of the bands of modified nickel with those of bulk crystals in order to determine the orientation of the α-alanine in the film on the nickel surface. As can be seen in Fig. 2, the most striking feature of the spectra of thin films on nickel is the enhanced intensity of the 1620 and 1600 cm^{-1} bands, which are assigned to NH_3^+ degenerate deformation and COO^- antisymmetric stretching respectively.[15] However, the band intensity of the COO^- antisymmetric stretching relative to that of the NH_3^+ degenerate deformation vibration somewhat decreases in comparison with the spectrum of the non-oriented sample (KBr pellet). The broad band centered at 1515 cm^{-1} in the thin film spectra, which is very weak in the spectra of Fig. 2 and which corresponds to the 1520 cm^{-1} band of bulk crystals, may be attributed to the NH_3^+ symmetric deformation. The same spectral feature was also obtained for thicker crystal films of α-alanine grown on nickel-metal surfaces during the evaporation of solvent water.

As has been mentioned above, the spectrum obtained by means of the high-sensitivity reflection method may be regarded as a polarized spectrum because it results from the interaction of molecular vibration with infrared radiation polarized normal to the reflection plane or the metal surface. Therefore, the relative intensities of the observed band in each vibrational mode depend on the orientation of the vibrational transition moments. On this basis, our attention is focused on the orientations of the CO_2^- and NH_3^+ ions, for which an approximate quantitative treatment is possible.

The transition moment of the antisymmetric CO_2^- stretching mode at 1600 cm^{-1} is parallel to the O–O direction, while that of the symmetric CO_2^- stretching mode at 1400 cm^{-1} is normal to the O–O direction. These moments are shown schematically in Fig. 3, where μ_a and μ_s refer the vibrational transition moments of antisymmetric and symmetric CO_2^- stretching vibrations respectively. The model is placed in a coordinate system where the C_α–C_0 axis lies on the yz plane, but the CO_2^- plane does not coincide with it. The rotation of the O–O axis about the C_2 axis is designated by the angle θ. The projection of μ_a on the yz plane is, therefore, given by $\mu_a \cos\theta$. Then,

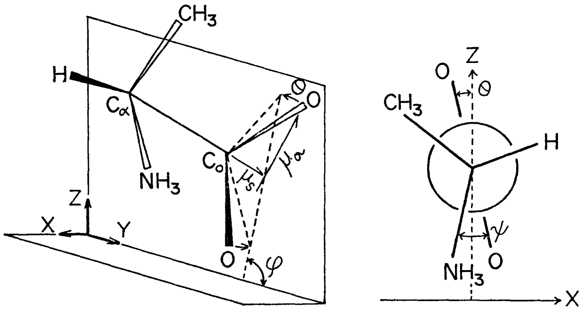

Fig. 3. Coordinates and angles for the oriented D-α-alanine. The conformation is shown as viewed along the C_α–C_o bond.

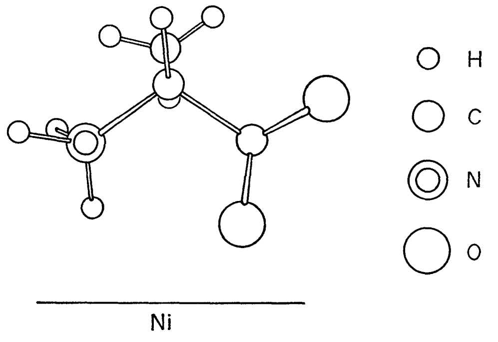

Fig. 4. Orientational model in thin D-α-alanine crystal formed on nickel metal surface at 5 °C.

the component of μ_a parallel to the radiation, polarized in the z direction, is equal to $\mu_a \cos\theta \sin\varphi$, where φ is the angle which the yz plane projection of μ_a makes with the xy plane (nickel surface). The transition moment of CO_2^- symmetric stretching, μ_s, lies along the C_α–C_o bond, regardless of the rotation of the CO_2^- group. The μ_s component parallel to the polarized radiation is, therefore, given by $\mu_s \cos\varphi$.

The electric vector of infrared radiation in the vicinity of the metal surface is practically vertical to that surface or parallel to the z axis. Accordingly, the band intensity to be observed in the high-sensitivity reflection spectra is proportional to the square of the transition moment in the z direction. Consequently, the band intensity of CO_2^- symmetric stretching relative to that of CO_2^- antisymmetric stretching can be expressed in the term: $R=(\mu_s^2/\mu_a^2)\sec^2\theta\cot^2\varphi$. The expression derived above is valid only when neither of the vibrational modes interacts with any other modes. In the present work, the coupling of the vibration is not important and so is neglected. Here, μ_s^2/μ_a^2 can be taken from the spectrum of randomly oriented α-alanine molecules. If the value is assumed to remain unchanged in the KBr matrix, the data from the spectrum shown in Fig. 1 can be used. The R value is, of course, obtained from the reflection spectrum exhibited in Fig. 2.

While the values of φ and θ can not be obtained separately, if θ is assumed, for simplicity, to be 0°, the values of φ may be calculated to be 57° and 60° for D- and L-α-alanine respectively. The difference obtained here is not significant in view of the uncertainties involved. When the θ value of 30° is used, $\varphi=61°$ is obtained from the spectrum of D-α-alanine.

The second point of special interest is the orientation of the C–NH_3^+ fragment. Information concerning the alignment of the C–N bond with respect to the CO_2^- group can be obtained from the NH_3^+ symmetric deformation band based on the assumption that the C–NH_3^+ group holds C_{3v} symmetry. The value of 110°, which is taken from the literature,[16] is used for the ∠C–C–N angle of L-α-alanine. Assuming $\theta=0°$ and $\varphi=57°$, the azimuthal angle, ψ, of the C–N bond measured from the CO_2^- plane is obtained to be 8°. If $\theta=7°$ and $\varphi=57°30'$ are chosen, the result of $\psi=16°$, which is near to the value 17° calculated by Hayashi *et al.*[17] from the X-ray data,[18] can be obtained. The orientational model of D-α-alanine is depicted in Fig. 4. The model agreed very closely with that previously obtained for L-β-phenyl-α-alanine.[8] Therefore, there seems to be no remarkable effect exerted on the molecular orientation in converting the methyl group of α-alanine to a phenyl group.

Recently Tanabe and Uyeda investigated the thin film of L-α-alanine, formed from an aqueous solution on nickel film, by electron microscopy and diffraction; they found that L-α-alanine overgrows epitaxially in a polymorphic form on the substrate surface. Different crystals were obtained according to whether or not the nickel film was treated with HCl, suggesting the occurrence of the original nucleation in a different form. However, it should be noted here that the orientation of the L-α-alanine molecule on the nickel film without HCl treatment agrees very well with that shown in Fig. 4.

The reflection spectrum of the nickel surface modified with D-α-alanine at 100 °C resembles that of the nickel surface modified at 5 °C, but several differences can be seen between them. The most noticeable are that the band intensity of the NH_3^+ degenerate deformation was much decreased on the 100 °C modified nickel surface, relative to that of the CO_2^- antisymmetric stretching band, and that the latter overcame the former, indicating a high orientation of the CO_2^- group normal to the nickel surface. In addition, the broad band centered at 1070 cm^{-1}, which was also observed with the 5 °C modified sample, was observed as a more intense band.

The reflection spectrum of the 100 °C modified nickel changed with time, showing that the thin film underwent a spontaneous change. The spectral change was complete after several hours, and the spectrum finally reached that of the 5 °C modified nickel. This fact shows that the crystal structure in the thin film, formed at 100 °C, is unstable, and that a rearrangement of the molecules to a more stable structure occurs. Although the reproducibility in band intensity was not very good, repeated experiments definitely showed that the bands due to the CO_2^- symmetric stretching as well as the NH_3^+ degenerate deformation increased in intensity with the change in the structure of thin films, whereas the CO_2^- antisymmetric stretching decreased. On the basis of the facts presented above, the orientation of the important part of the molecule in the unstable film on the surface modified at 100 °C can be determined; the C_α–C_0 bond lies approximately parallel to the nickel metal surface, with the remaining part randomly oriented. This results in an orientation which can be said to be near to that shown in Fig. 7 for the "Raney nickel" surfaces.

The reflection spectra of the unstable and the stable films can be elucidated without supposing the formation of a nickel–alanine chelate, which was found on the "Raney nickel" surface. This fact, however, does not exclude the presence of the chelate in a small amount at the interface, because the signal from the chelate must be very weak and may be masked by the bands of the molecules in the film.

The molecular orientation in the unstable film, which is similar to that in the film on the "Raney nickel" modified at 100 °C, may be determined by the orientation of chelates strongly adsorbed on nickel and acting as the nuclei of crystal growth. The chelate-nickel surface and/or chelate-alanine interaction may not be sufficiently strong, however, to maintain the unstable structure.

When a thin "Raney nickel" film was used as a substrate, the spectral behavior was different from that obtained using the bulk nickel plate mentioned above. It should be mentioned, however, that the "Raney nickel" used in this experiment contains aluminum oxide, undoubtedly developed while the vacuum-deposited aluminum film on a nickel plate was subjected to thermal treatment in order to prepare Ni–Al alloy layers on the nickel plate. The Al–O absorption band decreased upon treatment in an alkaline solution, the magnitude of the decrease depending upon the time-course of the treatment.

Figure 5 shows the high-sensitivity reflection spectrum of thin "Raney nickel" film modified with D-α-alanine at 5 °C. The most intense band, appearing at 940 cm^{-1}, is ascribed to the Al–O stretching; the intensity was unaltered despite prolonged modification at 100 °C. Except for the Al–O band, the spectrum is characterized by the strong absorption of the NH_3^+ degenerate deformation band at 1620 cm^{-1} and the weak absorption of the CO_2^- antisymmetric stretching band at 1595 cm^{-1}. Since the bands are essentially at the same frequencies as those of the bulk crystals shown in Fig. 1, the oxide layer at the substrate surface probably exerted an influence only upon the molecular orientation. The weak absorption of CO_2^- antisymmetric stretching can probably be ascribed to the molecular orientation in which the vibration has a small component of the transition moment normal to the substrate surface. The deduction regarding the orientation of the CO_2^- group can be supported by the fact that the band at 1400 cm^{-1} due to the CO_2^- symmetric stretching appears strong relative to the CO_2^- antisymmetric stretching, as is shown in Fig. 5. The orientation requires that the C_α–C_0 bond should be largely tilted from the parallel direction with respect to the substrate surface. This orientation differs from that of molecules on pure nickel plates, shown in Fig. 4.

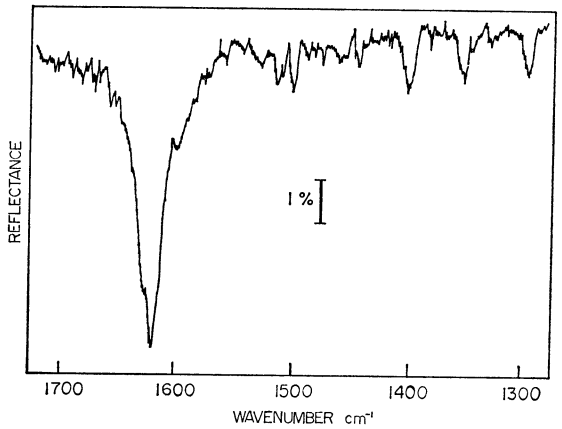

Fig. 5. High-sensitivity reflection spectrum of thin "Raney nickel" surface modified with D-α-alanine at 5 °C.

The modification of thin "Raney nickel" containing aluminum oxide with D-α-alanine at 100 °C resulted in the spectrum shown in Fig. 6. The spectrum obtained for L-β-phenyl-α-alanine is also shown in this figure for reference. The absorption at 1070 cm^{-1} is much stronger here than in the other cases mentioned above. The absorptions at 1070 and 3500 cm^{-1} (not shown in the figure) were intensified in a way parallel with each other by prolonged modification, implying that they belong to the same functional group, probably

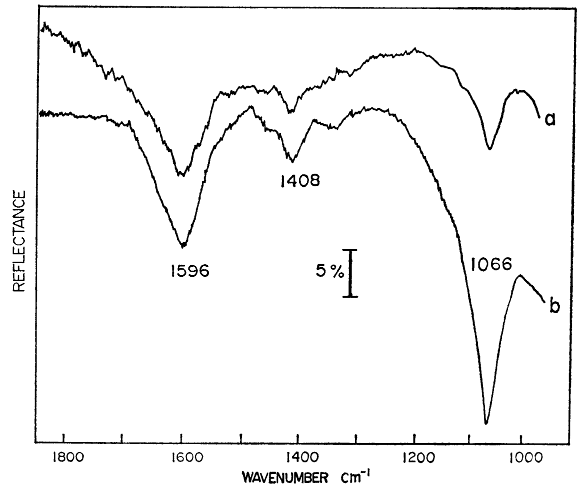

Fig. 6. High-sensitivity reflection spectra of thin "Raney nickel" surfaces modified with D-α-alanine and L-β-phenyl-α-alanine. a: D-α-alanine; b: L-β-phenyl-α-alanine.

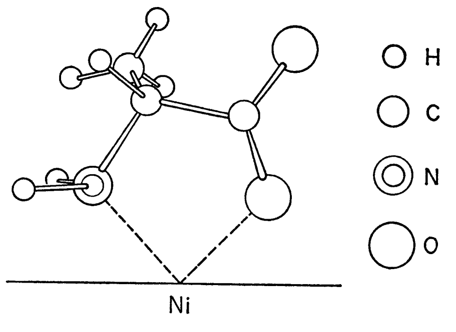

Fig. 7. Orientational model in thin D-α-alanine crystal formed on "Raney nickel" surface at 100 °C.

to the Ni–OH described above. Aside from the Ni–OH and Al–O bands, the spectrum consists of a strong CO_2^- antisymmetric stretching absorption and a weak CO_2^- symmetric stretching absorption. The absence of the NH_3^+ degenerate and symmetric deformation bands in Fig. 6 can be considered to be due to the formation of a nickel-alanine chelate on the substrate surface. It should be pointed out in this connection that this argument is valid also for the case of L-β-phenyl-α-alanine (see Fig. 6). The most probable model for molecular orientation in this case is shown in Fig. 7.

It is known that, on the chelate formation, the bands due to the NH_2 group appear instead of those of the NH_3^+ group.[19] The infrared spectrum of the nickel–alanine chelate, $Ni(L\text{-}\alpha\text{-}ala)_2\cdot 5/2H_2O$, exhibits two intense bands, at 1600 and 1570 cm^{-1}, and two medium bands, at 1085 and 1050 cm^{-1}. Based on the band assignment given for $Ni(DL\text{-}\alpha\text{-}ala)_2$, the former bands were assigned to the CO_2^- antisymmetric stretching and the NH_2 scissoring vibrations respectively, and one of the latter (1085 cm^{-1}), to the NH_2 wagging vibration.[19] Therefore, the orientational model shown in Fig. 7 is in accord with such a spectral feature that the NH_2 scissoring vibration is absent in Fig. 6, because its transition moment is parallel to the substrate surface and because the vibration is inactive in the reflection method employed in this experiment. On the other hand, the NH_2 wagging vibration should be observed, if the molecular orientation shown in Fig. 7 is the case, since the transition moment of the NH_2 wagging vibration lies along the direction normal to the substrate surface. However, no evidence of the NH_2 wagging band could be detected in the region where the band was expected to appear; it may be considered that the NH_2 wagging band was obscured by the overwhelming Ni–OH band, because these two bands are near in frequency. The nickel–alanine chelation observed with the "Raney nickel" modified at 100 °C is considered to be caused by its nature being more active than that of the bulk nickel plate.

Recently, Groenewegen and Sachtler[9] have examined the infrared spectra of L-α-alanine and a few amino butyric acids evaporated on Ni/SiO_2 and SiO_2. They reported that the chemisorption complex of L-α-alanine formed on Ni was very similar to the bulk complex $Ni(ala)_2$. Although it is difficult to compare the results of Groenewegen and Sachtler with ours because the experimental conditions are different, the suggestion can be made that the α-alanine reacts with the surface nickel to yield the α-alanine chelate complex at high temperatures and that this chelate formation would influence the catalytic properties of the Raney nickel.

A change in the modification temperature resulted in a change in the molecular orientation in the thin films on the bulk nickel surface as well as on the "Raney nickel" surface. This fact may correspond to the change in the optical activity of the compound obtained by the asymmetric synthesis with the modified catalyst.

References

1) Presented in part at the 29th Fall Meeting of the Chemical Society of Japan, Hiroshima, Oct., 1973.

2) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press Inc. Ltd., London (1966).

3) For example, R. P. Eischens and W. A. Pliskin, *Advan. Catal.*, **10**, 1 (1958).

4) W. Suëtaka, *Sci. Rept. Tohoku Univ., Ser. A*, **18**, Suppl., 129 (1966); R. G. Greenler, *J. Chem. Phys.*, **44**, 310 (1966).

5) J. Pritchard and M. L. Sims, *Trans. Faraday Soc.*, **66**, 427 (1970); H. G. Tompkins and R. G. Greenler, *Surface Sci.*, **28**, 194 (1971); M. L. Kottke, R. G. Greenler, and H. G. Tompkins, *ibid.*, **32**, 231 (1972); M. Ito and W. Suëtaka, *J. Phys. Chem.*, **79**, 1190 (1975).

6) W. Suëtaka, *J. Spectroscop. Soc. Japan*, **16**, 219 (1968); K. Suzuki, A. Hatta, and W. Suëtaka, *Chem. Lett.*, **1973**, 189.

7) For example, Y. Izumi, *Yuki Gosei Kagaku Kyokai Shi*, **25**, 1013 (1967).

8) A. Hatta and W. Suëtaka, This Bulletin, **48**, 2428 (1975).

9) J. A. Groenewegen and W. M. H. Sachtler, *J. Catal.*, **33**, 176 (1974).

10) K. Tanabe and N. Uyeda, *Bull. Inst. Chem. Res., Kyoto Univ.*, **52**, 616 (1974).

11) M. Ashida, A. Hamada, and T. Watanabe, This Bulletin, **45**, 2312 (1972); N. Uyeda, Y. Murata, T. Kobayashi, and E. Suito, *J. Cryst. Growth*, **26**, 267 (1974).

12) A. Mellier and M. Léard, *J. Chim. Phys.*, **70**, 1360 (1973).

13) T. Uchida, H. Watanabe, and M. Wada, *Jap. J. Appl. Phys.*, **11**, 1559 (1972).

14) Y. Izumi, M. Imaida, H. Fukawa, and S. Akabori, This Bulletin, **36**, 155 (1963); F. Higashi, T. Ninomiya, and Y. Izumi, *ibid.*, **44**, 1333 (1971).

15) K. Fukushima, T. Onishi, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **15**, 236 (1959); S. Suzuki, T. Ohshima, N. Tamiya, K. Fukushima, T. Shimanouchi, and S. Mizushima, *ibid.*, **15**, 969 (1959); R. Adamowicz and E. Fishman, *ibid.*, **28A**, 889 (1972).

16) H. J. Simpson, Jr., and R. E. Marsh, *Acta Cryst.*, **20**, 550 (1966).

17) M. Hayashi, T. Shimanouchi, and S. Mizushima, This Bulletin, **29**, 802 (1956).

18) H. A. Levy and R. B. Corey, *J. Amer. Chem. Soc.*, **63**, 2095 (1941); J. Donohue, *ibid.*, **72**, 949 (1950).

19) J. F. Jackovitz, J. A. Durkin, and J. L. Walter, *Spectrochim. Acta*, **23A**, 67 (1967).