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Enantioselectivity of Nickel Catalysts Modified with Tartaric Acid or Nickel Tartrate Complexes

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The enantioselective hydrogenation of methylacetoacetate to optically active methyl hydroxybutyrate has been studied in a static reactor at initial hydrogen pressures of 100 bar with nickel catalysts modified with *S,S*-(−)-tartaric acid or with complexes derived from it. Enantioselectivity was found to be comparable for SiO_2-supported, unsupported, and Raney Ni catalysts, but significantly lower for γ-Al_2O_3-supported Ni. Separate tests showed that no racemization takes place on γ-Al_2O_3. Upon modifying catalysts with tartaric acid in a defined atmosphere, it was found that enantioselectivity increases with the modification temperature and that it is much higher after modification under air than under hydrogen. These results suggest that formation of the enantioselective site is an activated process, viz. a corrosive chemisorption where an Ni atom is pulled out of the metal surface and an Ni–tartrate complex is formed. This hypothesis was, indeed, confirmed by modifying Ni-metal with discrete Ni–tartrate or Na–Ni–tartrate complexes. Under our conditions none of these complexes displayed hydrogenation activity in the absence of metallic Ni and hydrogenation was nonselective for Ni modified with the corresponding Cu–tartrate complexes. Having established that both the Ni-tartrate complex *and* the Ni-metal are essential we propose a mechanism in which the Ni atom in the Ni–tartrate complex is the enantioselective site, while H atoms generated at the Ni-metal surface by dissociative chemisorption of H_2 reach this site by migrating over the oxygen atoms of the tartrate ligands. These ligands thus serve both as transport routes for H atoms and as templates favoring the formation of one enantiomer.

INTRODUCTION

Since 1960 much information has been gathered on the enantioselective hydrogenation of methylacetoacetate (MAA) to methylhydroxybutyrate (MHB) over modified Ni catalysts (*1–3*). Two groups of compounds were used as modifiers: α-aminocarboxylic acids and α-hydroxycarboxylic acids. In particular, the effect of changing the modifying compound and the conditions of modification have been studied. One of the most interesting observations is that with S-amino acid as a modifier *R*-(−)-MHB is obtained in excess whereas with *S*-hydroxy acid the *S*-(+)-MHB enantiomer is predominantly formed.

On the basis of ir data a mechanistic model (*4*) was proposed which explains most of the experimental results. In this model MAA, amino acid, and hydroxy acid are assumed to be adsorbed on metallic Ni as enolate, chelate, and carboxylate, respectively. Steric and chemical interactions between adsorbed MAA and amino or hydroxy acid on the surface of the Ni catalyst are thought to be responsible for the observed enantioselectivity. However, some doubts have arisen about this model.

(i) It has been reported that MAA and 2,2′-dimethyl MAA (*3, 5*) are hydrogenated with comparable enantioselectivity over a Ni catalyst modified with tartaric

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acid, although enolate formation is impossible in the case of 2,2′-dimethyl MAA.

(ii) The ir spectrum of α-amino acids adsorbed on Ni metal is indistinguishable from the spectrum of the corresponding Ni–amino acid coordination compounds (*6*, *7*), and one therefore wonders whether chemisorption of the amino acid is corrosive resulting in an Ni–amino acid complex above the surface. In other words, are Ni atoms pulled out of the surface and complexed by amino acid molecules? Support for this idea is provided by Tanabe, Kazuo, and Izumi (*8*) who found comparable enantioselectivities for Ni catalysts modified with an amino acid and an Ni–amino acid complex, respectively.

(iii) In the case of the tartaric acid modifier the question of the structure of the effective surface complex is even more complicated: Many chelate complexes of α-hydroxy acids with transition metals are known (*9*) and this suggests that a chelate might also be formed upon chemisorption of tartaric acid on Ni. The stability constants of transition metal chelates are often lower for hydroxy acids as compared to amino acids (*10*, *11*), but in the case of tartaric acid the chelates with transition metals are reported to be even more stable than for many amino acids (*11*, *12*). Both for the carboxylate and the chelate one can further ask whether chemisorption of the α-hydroxy acid is corrosive as is suggested for α-amino acids (*8*). Yasumori *et al.* (*13*) mention a low enantioselectivity for an Ni catalyst modified with an Ni–tartrate complex although they do not specify the conditions of this experiment. The same authors report that the X-ray photoelectron spectroscopy (XPS) signals of tartaric acid-modified Ni show a chemical shift typical of metallic Ni. Unfortunately, this argument is not conclusive as the escape depth of XPS signals is much larger than a monolayer (*14*). These data do not therefore exclude that upon corrosive adsorption of tartaric acid a monolayer of a chelate-type Ni–tartrate is formed.

In order to elucidate the mechanism of the enantioselective hydrogenation of MAA over modified Ni catalysts a better knowledge is required of the nature of the Ni modifier adsorption complex and its role in the catalytic reaction. A possible method is to compare the enantioselectivity of an Ni catalyst modified with hydroxy or amino acid and the same catalyst modified with Ni–hydroxy acid or Ni–amino acid complexes. These catalytic measurements are likely to provide more reliable results concerning the mechanism of enantioselective catalysis than spectroscopic measurements, since in the latter case the experimental conditions are usually very different from reaction conditions. In the present study we selected tartaric acid and Ni–tartaric acid complexes as modifiers because in previous work most experiments with hydroxy acids have been carried out with tartaric acid.

We have measured the enantioselectivity of the catalytic hydrogenation of MAA over the modified Ni catalysts. Particular attention was given to the modification conditions, which might have an effect on the resulting adsorption complexes. Second, we have studied effects of the materials other than Ni in the catalysts, e.g., the aluminum oxide which is thought to be present in Raney Ni catalysts and the carrier in supported catalysts. Therefore, we have used Ni on silica and alumina as representatives of supported catalysts as well as Raney Ni and compared these samples with unsupported Ni powder.

EXPERIMENTAL

A. Catalyst Preparation

For each experiment a fresh catalyst was prepared using one of the following methods.

Raney Ni. NiAl 50/50 alloy (4.5 g) (Brocades) was leached by adding the powder during 15 min in small portions to 60 ml 20% aqueous sodium hydroxide solution, keeping the temperature at 20 ± 2°C. Then, the suspension was kept at 85°C for 45 min. After cooling to room temperature the NaOH solution was decanted and the catalyst was washed with portions of 100 ml of degassed distilled water (each washing during 15 min) until the pH of the washing water was below 8.0. After each washing the catalyst was precipitated with a strong magnet and the washing water was decanted without the catalyst becoming dry. The estimated surface of this catalyst is of the order of 100 m^2/g alloy.

Ni powder. $Ni(NO_3)_2 \cdot 6H_2O$ (10 g) (Merck 6721) was dissolved in 85 ml 25% wt aqueous ammonia. On heating nickel hydroxide and precipitated complexes dissolved and the blue color of the nickel–ammonia complex appeared. The solution was refluxed for 4 hr to evaporate NH_3 slowly and a green suspension of nickel hydroxide in water was obtained. The solid was filtered off and dried for 3 hr at 110°C. Thereafter, the catalyst was reduced in purified hydrogen at 400°C and 200 ml min^{-1} for 15 hr. The surface of this catalyst measured with the BET method was 4 m^2/g cat.

Supported Ni 5% wt. $Ni(NO_3)_2 \cdot 6H_2O$ (1 g) and the corresponding quantity of silica (Merck 7754) or γ-alumina (Merck 1095) were mixed in 25 ml of distilled water. The water was slowly evaporated on a steambath with stirring. Thereafter, the catalyst was dried for 3 hr at 110°C. The catalysts were reduced under the same conditions as the Ni powder catalyst. The estimated Ni surface of this catalyst was of the order of 200 m^2/g Ni.

B. *Tartrate Complexes*

The following nomenclature will be used. TA is used for a tartrate ion with both carboxyl hydrogen atoms dissociated; thus tartaric acid is H_2TA. When one or both hydroxyl hydrogens are dissociated the notation for the ion becomes TA′ or TA″, respectively. Na–tartrate and Ni–tartrate are therefore written as Na_2TA and NiTA, but Na–Ni–tartrate as Na_2NiTA''.

NiTA. To 100 ml of well-stirred 0.5 *M* aqueous *S,S*-(−)-H_2TA solution (Merck 799) kept at 90°C, $NiCO_3$ was slowly added in small portions, causing CO_2 evolution. A light green precipitate was formed. After adding an equimolar amount of $NiCO_3$, the pH was about 5.0. The precipitate was filtered off and dried for 3 hr at 110°C. On dissolving it in water, a 0.02 *M* aqueous NiTA solution with a light green color was obtained. This solution was used for the catalyst modifications.

Na_2NiTA''. To 1 liter of a stirred 0.04 *M* NaOH aqueous solution 1 liter of 0.02 *M* NiTA aqueous solution was slowly added during 1 hr. The pH of the solution was then below 9.0. This 0.01 *M* solution was used for modification.

CuTA and Na_2CuTA''. CuTA and Na_2CuTA'' were prepared in analogous ways.

C. *Modification*

Modification of an Ni catalyst in air at various temperatures was performed in an Erlenmeyer flask over 1 hr with occasional shaking (preventing, however, the formation of air bubbles). When modifying with tartaric acid 100 ml of 0.5% wt aqueous *S,S*-(−)-H_2TA solution was used, brought to pH = 5.0 with 1 *N* NaOH aq. For modification with a complex 0.5 liter of 0.02 *M* NiTA aq at pH 4.5–5.5 or 1 liter of 0.01 *M* Na_2NiTA'' was used.

Modification in hydrogen or nitrogen atmosphere was performed in a simple apparatus (see Fig. 1). Supported Ni and Ni powder catalysts were modified *in situ* directly after reduction in the same apparatus. The catalyst was placed on a glass

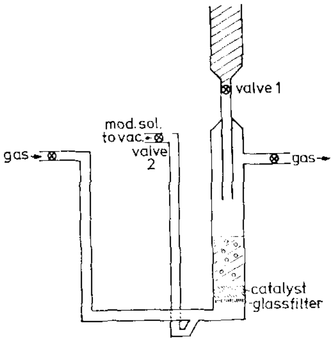

FIG. 1. Glass apparatus for catalyst modification under controlled atmosphere.

filter and portions of 50 ml of modifying solution were introduced via valve 1. The apparatus was placed in a thermostated bath and hydrogen or nitrogen was bubbled through the solution for 15 min suspending the catalyst. After that the modifying solution was sucked off via valve 2 and a new portion of solution was introduced. The total amount of modification solution was equal to that used for modification under air.

After the modification the catalyst was transferred to four centrifuge tubes, centrifuged for 1 min at 3000 rpm and decanted. Distilled water (10 ml) was added to each tube. After stirring with care the catalyst was centrifuged and decanted again. This procedure was repeated twice with water and twice with methanol. Then, the catalyst was immersed in MAA and transferred to the autoclave.

D. *Hydrogenations*

Hydrogenations were carried out in a 0.5-liter Deutsch & Neuman autoclave with a shaking mechanism and a 100-ml homemade autoclave with a Vibromix system. In the 0.5-liter autoclave 50 ml MAA was used with the described amount of catalyst while in the 100-ml autoclave 12.5 ml of MAA was used with one-quarter of the described amount of catalyst. The starting pressure of purified hydrogen was 90 to 100 bar and the reaction was followed manometrically. The reaction temperature varied from 65 to 100°C and the conversion after 15 hr was 40 to 100%. Although the reaction rates were not reproducible some trends were detected which will be discussed elsewhere.

E. *Analysis*

Reaction products were filtered off and distilled under reduced pressure. The conversion was measured with glc (Packard Becker 427, with 10% Carbowax on chromosorb column). Optical rotations were determined with a Bendix NPL 143 D automatic polarimeter.

For the average enantioselectivity (ES) the definition

$$\mathrm{ES} = \frac{\%(+) - \%(-)}{\%(+) + \%(-)} \times 100\%$$

was used, where %(+) is the percentage of dextrorotary MHB and %(−) the percentage of levorotary MHB in the total amount of MHB formed. ES was calculated by dividing the observed value of α_D^{20} of the product by 18.9°, the α_D^{20} of optically pure (+)-MHB, correcting for the conversion and multiplying by 100%.

RESULTS

A. *Influence of SiO_2 and Al_2O_3*

The enantioselectivity of several Ni catalysts modified with tartaric acid at 293°K is shown in Table 1. Raney Ni

TABLE 1

Influence of Carrier on Enantioselectivity of Ni Catalysts, Modified with Tartaric Acid at 293 K, in the Hydrogenation of MAA at ~343 K

Catalyst	ES (%)[a]
Raney Ni	+13 to +14
Ni/Al_2O_3	0
Ni/SiO_2	+8 to +10
Ni powder	+9 to +15

[a] Numbers give the range of data of different experiments.

modified with *S,S*-(−)-tartaric acid shows an enantioselectivity of +13 to 14% under these conditions which is of the same sign but lower than the best values reported by other workers (*1–3, 15*) for Raney Ni. There is good evidence that the enantioselectivity of modified Raney Ni depends very critically on the details of the preparation (*3*) and on the Al content (*16, 17*).

The Ni/SiO_2 catalyst modified with *S,S*-(−)-tartaric acid displays under the same conditions an enantioselectivity of the same sign and nearly the same magnitude as Raney Ni. It thus appears from the present work that a silica support has only a minor effect on the enantioselectivity of a modified catalyst.

For Ni powder modified with *S,S*-(−)-tartaric acid and with the same experimental conditions we find again an enantioselectivity comparable to that of Raney Ni. As already pointed out by Harada *et al.* (*18*) the hydrated Al_2O_3 present in Raney Ni samples might influence the enantioselectivity and hence limit the reproducibility of the results.

Ni supported on γ-Al_2O_3 shows very low enantioselectivity in all experiments. In order to establish whether this poor enantioselectivity is caused by a secondary racemization of optically active MHB over γ-Al_2O_3 we studied this reaction separately. It was found that the optical activity of a sample of (+)-MHB did not change upon shaking for 16 hr with γ-Al_2O_3 or SiO_2 samples of the types used as supports for the above-mentioned Ni catalysts.

We decided to use Ni/SiO_2 and Ni powder as catalysts in the further work of this study.

B. Influence of Temperature and Ambient Atmosphere during Modification

In Table 2 the enantioselectivity of an Ni/SiO_2 catalyst is given upon modification with tartaric acid at 273 and 373 K, both under air and hydrogen. Upon increasing the modification temperature from 273 to 293 K the enantioselectivity is found to increase. This phenomenon has been reported in the literature for Raney Ni (*15*) and Ni–Pd-supported catalysts (*16*). Two explanations seem possible: (i) at elevated temperatures an Ni–tartaric acid surface complex is formed which differs in structure from the complex formed at lower temperatures or (ii) the same complex is formed but to a higher degree at elevated temperatures.

TABLE 2

Influence of Ambient Atmosphere and Temperature during Modification with Tartaric Acid on Enantioselectivity of Ni Catalysts in the Hydrogenation of MAA at ~343 K

Catalyst	T_{mod} (K)	ES (%)	
		Hydrogen	Air
Ni/SiO_2	293	+3 to +4	+9 to +10
Ni/SiO_2	373	+5 to +7	+17 to +18

The effect of the ambient atmosphere during the modification of Ni/SiO_2 catalysts with tartaric acid is very striking. From the results compiled in Table 2 it appears that the enantioselectivity of catalysts modified in air is approximately three times larger than that of catalysts modified under hydrogen. Observations of this type have, to our knowledge, not been reported in the literature. Modification under nitrogen gave approximately the same result as under hydrogen. It follows that the oxygen in air is responsible for the more effective modification in process. Oxygen can dissolve in water, reach the catalyst, and take part in the modification. Two additional observations illustrate the effect of oxygen. First, the tartaric acid solution turns light green during modification; clearly this color is caused by a dissolved Ni complex. The intensity of the color was much larger in the case of modifying under air as compared to

TABLE 3

Enantioselectivity of Ni Catalysts in the Hydrogenation of MAA at ~343 K

Catalyst	T_{mod} (K)	Modifier			
		H_2TA (air)	NiTA (air)	Na_2NiTA'' (air)	Na_2NiTA'' (H_2)
Ni powder	293	+9 to +15	+40 to +45	0[a]	—
Ni powder	373	+15 to +25	+2 to +4[b]	+30 to +35	—
Ni/SiO_2	373	+17 to +18	+3 to +4[b]	+18 to +19	+18
Ni/Al_2O_3	373	0	0 to +1[b]	+1 to +2	—

[a] Complex not adsorbed.

[b] Complex precipitates.

modifying under nitrogen. Second, if a quantity of Ni powder catalyst is immersed in 50 ml 0.5% wt aqueous H_2TA solution at pH 5.0 in the apparatus described in Fig. 1 and air is bubbled through this suspension at 373 K the color turns green and a considerable quantity of complex precipitates.

C. Enantioselectivity of Ni Catalysts modified with Ni–Tartrate or Cu–Tartrate Complexes

The results of the previous section strongly suggested to us that formation of an Ni–tartrate complex might be essential for effective modification. This hypothesis was therefore tested by a number of experiments. In Table 3 the results of modifying Ni with tartaric acid, Ni–tartrate, and Na–Ni–tartrate are shown. Modification of an Ni powder catalyst under air at 293 K with the complex with stoichiometric formula NiTA results in an enantioselectivity three to four times larger than modification with tartaric acid under identical conditions. However, catalysts which were brought into contact with the same complex at 373 K showed an enantioselectivity much lower than that of the same catalyst modified with tartaric acid. This is not surprising as we observed precipitation to occur at this temperature. It is obvious that under such conditions the pores in the catalyst were not modified, perhaps due to the pore mouths being plugged.

No precipitation occurred with the complex of stoichiometric formula Na_2NiTA'' during the modification at 373 K of Ni/SiO_2 on Ni powder catalysts. Ni catalysts modified with this complex gave an enantioselectivity of the same value or somewhat larger than the corresponding catalysts modified with tartaric acid. At room temperature no adsorption of Na_2NiTA'' took place. This was concluded from the absence of a color decrease of the modifying solution and further confirmed by the absence of any decrease of its optical rotation after contact with the catalyst. Ni/Al_2O_3 catalyst modified with either complex showed a small enantioselectivity.

These results support the view that the structure of the surface complex which is formed upon adsorption of tartaric acid on Ni and which is thought to be the center of enantioselectivity is not much different from the structure of a complex with stoichiometric formula Na_2NiTA'' in hydrogen. As expected no effect of the gas on the enantioselectivity was found in this case, in sharp contrast to the results with tartaric acid.

These results would still be consistent with a mechanism where enantioselective hydrogenation takes place on sites of the metal surface proper, but in the immediate vicinity of adsorbed tartrate complexes. To check for this possibility, we have modified Ni catalysts with complexes of stoichiometric formula CuTA and Na_2CuTA''. The following observations were made. CuTA was not adsorbed at 293 K and enantioselectivity was, consequently, zero. For modifying temperatures of 355 and 373 K, enantioselectivity was very low (always $<5\%$), but under these conditions the formation of NiTA from CuTA + Ni could not be ruled out. These complicating phenomena were absent in the case of Na_2CuTA''. With this complex the enantioselectivity was zero notwithstanding whether modification had been carried out at 293, 353, or 373 K. The results are strong evidence that an Ni–tartrate complex is required for enantioselectivity of Ni catalysts.

D. Hydrogenation in the Absence of Ni Metal

The possibility was considered that enantioselective hydrogenation is a process on an immobilized metal–organic complex without any active participation by Ni metal. The complexes Na_2TA, NiTA, CuTA, and Na_2CuTA'' in solid form and as impregnates of silica were autoclaved under hydrogenation and more severe conditions ($T = 512$ K). No hydrogenation occurred from which it was concluded that metallic Ni is essential in the hydrogenation.

DISCUSSION

A. Influence of the Support

Our observation that alumina lowers the enantioselectivity of modified Ni catalysts is in accordance with results by other workers. Gross and Rys (*17*) compared Raney Ni catalysts and found the lowest optical yields for samples with highest concentrations of aluminum. Likewise, Harada *et al.* (*18*) showed that the presence of aluminum or related metal compounds lowers the enantioselectivity of Raney Ni. As aluminum in Raney Ni is present mainly in the form of hydrated alumina, these observations show the detrimental effect of alumina. For other transition metal catalysts Orito *et al.* (*16*) found that NiPd exhibited a lower enantioselectivity when supported on alumina as compared to kieselguhr. Vedenyapin *et al.* (*19*) report a zero enantioselectivity for alumina-supported modified ruthenium catalysts. None of these authors gives an explanation of the negative effect of Al_2O_3 on the enantioselectivity or provides relevant experimental data for the cause of this effect. From the results in the present paper it is clear that Al_2O_3 does not catalyze a secondary racemization reaction. As will be shown below, it is more realistic to assume that the complex formed by chemical interaction of the modifier will be strongly adsorbed on the alumina leaving the Ni surface insufficiently modified. Another possibility would be a nonselective hydrogenation taking place on the alumina surface with hydrogen migrating from the Ni to the Al_2O_3 by means of the spill-over effect. For silica supports we did not observe a significant effect on the enantioselectivity. This is in accordance with the findings reported by Klabunovskii *et al.* (*20*) who reported no lowering of the enantioselectivity of Ru by supporting this metal on silica, in striking contrast to the effect of alumina mentioned above.

It is interesting that Orito *et al.* (*16*) report strong differences for different silica-supported Pd–Ni catalysts, the enantioselectivity being much lower on synthetic silica gel than on natural kieselguhr. No explanation was given and the nature of the silicas was not specified.

B. The Enantioselective Center

The strong effect of oxygen during modification and the high enantioselec-

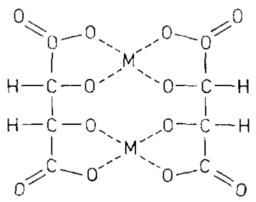

FIG. 2. Schematic projection of binuclear metal tartrate anions according to Tapscott (*22*).

tivity obtained by modifying Ni catalysts either with tartaric acid in air or with Ni–tartrate or with Na–Ni–tartrate is very good evidence that the formation of an Ni– or Na–Ni–tartrate complex is essential for enantioselectivity. Previous authors who used tartaric acid as the modifier usually adjusted the pH with NaOH to a value of 5. It is known that under these conditions well over 80% of the tartaric acid in the solution has exchanged two protons for sodium ions. We therefore assume that the complex formed on the surface is actually an Na–Ni–tartrate. This proposal is supported by the observation (*15*) that high enantioselectivity is found for catalysts modified at pH 9, i.e., above the equivalence point of the tartaric acid–sodium hydroxide system, whereas the enantioselectivity is low for catalysts modified at pH 2, i.e., pure H_2TA. Further support is found in the observations of Tanabe *et al.* (*8*) who compared catalysts modified in the presence of either KOH, NaOH, LiOH, or NH_4OH and found a large effect of the alkali metal on the enantioselectivity. Evidently this must be expected for an active site consisting of an alkali–Ni–tartrate complex. For a precise definition of the stereochemistry of enantioselective hydrogenation on these catalysts it is necessary to know the exact structure of the Na–Ni–tartrate surface complex. Unfortunately, X-ray diffraction determination of the structures of such complexes appears not to have been reported in the literature. Structural data are available, however, for the analogous complexes $Cu_2TA \cdot 6H_2O$ (*21*), $(NH_4)_4(VO)_2TA'' \cdot 2H_2O$ (*22*), and $Fe_2L_6(SbTA'')_2$ (*23*) where L stands for a ligand. For the Ni complexes Hoffmann and Ulbricht (*24*) concluded from kinetic studies that they are binuclear, i.e., two Ni atoms and two tartrate groups form one complex ion as do indeed all the metal tartrates for which reliable structural data are known. For the class of transition metal tartrate complexes Tapscott (*25*) has recently proposed a general structure, a planar projection of which is shown in Fig. 2. It is likely that the surface complex will have a structure using a similar pattern so that each Ni atom is coordinated with four oxygen atoms from two different tartrate molecules. This does not preclude that some of the hydroxyl groups will remain undissociated and that a dynamic equilibrium exists between dissociated and undissociated hydroxyl groups. We assume that one of the Ni atoms in the surface adsorption complex is the site on which the enantioselective hydrogenation of MAA takes place. The tartrate ligands act as the template. Stereochemical interaction of the adsorbed MAA and/or the transition state to MHB is the reason that the formation of one of the two enantiomers is favored over the other.

The thus defined site consisting of an Ni atom (or ion) in the alkali–Ni–tartrate surface complex and its tartrate ligand we shall call the "enantioselective site," because here the transition states leading to the R and S forms of MHB have different free energies, $\Delta G^{\neq}_{R}$ and $\Delta G^{\neq}_{S}$, respectively. Other Ni atoms not disrupted from the Ni lattice and able to act as active sites for nonselective hydrogenation of MAA to MHB we shall refer to as racemic sites, for there $\Delta G^{\neq}_{R} = \Delta G^{\neq}_{S}$. The overall efficiency of the catalyst is then defined by the number of enantioselective and racemic sites, their specific turnover numbers and the degree of selectivity on the enantioselective sites being given by $\exp[(\Delta G^{\neq}_S - \Delta G^{\neq}_R)/RT]$.

C. Influence of Modification Conditions

In the case of modification with tartaric acid generation of the enantioselective site requires the pulling of Ni atoms out of the Ni lattice (corrosive chemisorption), a process which is known to have a finite activation energy and which depends on the crystal face. It is easy to understand that enantioselectivity is higher if the modification is carried out at higher temperatures, as we have found in agreement with previous authors (*14*). Also the increase in enantioselectivity upon increasing the modification time at high modification temperature as observed by Orito *et al.* (*26*) can be understood in terms of a low rate of complex formation for Ni atoms in smooth crystal planes.

The concept of two types of hydrogenation sites, enantioselective (in adsorbed complexes) and racemic (on bare Ni surface) also provides a simple rationalization of the finding, reported by Orito *et al.* (*16*), that organic acids added to the reaction mixture increase enantioselectivity. These acids may be preferentially chemisorbed on Ni metal thus blocking the racemic sites (maintained after modification or created during hydrogenation).

The positive effect of oxygen upon complex formation is understood by considering the relevant thermodynamic data. If H_2TA stands for the modifying acid and NiTA for the complex formed we have to compare

$$\mathrm{Ni} + \mathrm{H_2TA} \rightarrow \mathrm{NiTA} + Q_1$$

$$\mathrm{NiO} + \mathrm{H_2TA} \rightarrow \mathrm{NiTA} + \mathrm{H_2O} + Q_2$$

$$\mathrm{Ni} + \mathrm{H_2TA} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NiTA} + \mathrm{H_2O} + Q_3$$

Using known data it is seen that Q_1 and Q_2 have similar values, but $Q_3 - Q_1 = 250$ kJ mol^{-1}. These data therefore suggest that the large positive effect of oxygen on the enantioselectivity is due to the enhanced formation of the desired complex because of the higher exothermicity of the process in which the Ni atom is disrupted from the surface. This positive role of oxygen is in particular understandable if we consider that the species to be chemisorbed is a tartrate ion and that the hydrogen atoms which must be exchanged for an Ni atom in the modification process include hydroxyl hydrogen atoms which have, of course, a low acidity. If these hydrogen atoms can react with oxygen, this may accelerate the formation of the surface complex.

D. Mechanism

Three facts are, in our view, crucial for the mechanism described hereafter.

(i) For enantioselectivity an Na–Ni–tartrate complex on the surface of the catalyst is essential (see previous section).

(ii) In the absence of metallic Ni, Na–Ni–tartrate complexes have no measurable catalytic activity for the hydrogenation of MAA under our conditions.

(iii) Ni modified with a Cu–tartrate or Na–Cu–tartrate complex is able to hydrogenate MAA, but the enantioselectivity is zero (except under conditions where the Cu ions in the complex can exchange with the Ni atoms in the surface).

For the hydrogenation of MAA on an enantioselective site as defined in the previous section, the Ni metal has three functions: (i) it is the carrier for the surface complex, (ii) it enables the hydrogen molecules to dissociate into two chemisorbed atoms, and (iii) if the modification is done with tartaric acid or Na–tartrate then Ni serves as a chemical reagent for the *in situ* formation of the Na–Ni–tartrate complex.

As for the mechanism of hydrogenation proper, it is also significant that in all metal–tartrate complexes for which the structure is known, the transition metal

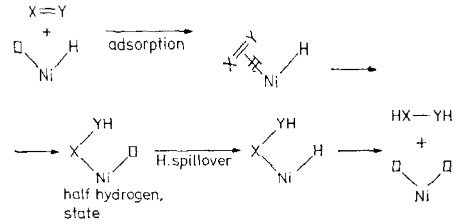

FIG. 3. Scheme for hydrogenation at an Ni atom with two available coordination sites. $X = Y$ stands for $R_2C = CR_2$ or $R_2C = 0$, etc.

atom is tetra-coordinated. Since Ni has six stable ligand sites, this means that two vacant sites are available for the hydrogenation reaction. Assuming a classical Horiuti–Polanyi (*27*) mechanism, the species with the double bond is first transformed into a half-hydrogenated state by adding one hydrogen atom. Addition of a second adsorbed H atom completes the hydrogenation. Each of the two H atoms reaches the vacant site from the surface of metallic Ni by a spillover transport via the tartrate ligands. The mechanism is shown schematically in Fig. 3.

The concept that chemisorbed H atoms are not directly added to an unsaturated molecule, but that hydrogenation takes place via a strongly chemisorbed complex, was introduced by Thomson and Webb (*28*). We refer to their paper for the arguments that hydrogenation is a special case of self-hydrogenation.

In the case of enantioselective hydrogenation this concept implies that a vacant ligand position on an enantioselective site is occupied by an H atom from the tartrate complex, and in the next step the stoichiometry of the tartrate complex is reestablished by transfer of a chemisorbed H atom from the metal surface to the complex. Finally, the vacant sites on the metal surface are filled by hydrogen chemisorption.

This concept explains why both the Ni atom in the tartrate complex and the Ni metal surface are required for enantioselective hydrogenation. Previously, Takeuchi *et al.* (*29*) had shown that an isolated Ni atom with two vacant ligand sites is able to catalyze the protium–deuterium exchange between C_2D_4 and C_2H_4, but *not* the hydrogenation of ethylene. Application of their ideas leads to the conclusion that hydrogenation does become possible if a mechanism exists which permits migration of hydrogen atoms from a metal adsorption site to one of the vacant ligand sites of the Ni atom, while the other available site is used first to adsorb the unsaturated species and then to hold the half-hydrogenated group.

We have formulated the mechanism in rather general terms, making use of the data obtained in this work and of the concepts described by Thomson and Webb and by Takeuchi, Tanaka, and Miyahara, besides the general and well-established principles of hydrogen migration (spillover) and the classical mechanism of hydrogenation. Our model also takes into consideration that the results on metal alloy catalysts have provided evidence that hydrogenation of olefins and dehydrogenation of paraffins requires one metal atom with two vacant sites (*30*). It is, of course, also possible to become more specific but a variety of mechanisms is consistent with the general principles given here. In the case of MAA one can visualize hydrogenation of either the keto or the enol form of the molecule. In previous work in this laboratory (*4*) a mechanism has been formulated describing the adsorbed MAA in its form identified by infrared spectroscopy, i.e., as an adsorbed enolate. It is also possible, however, that the active form is different from the stable form identified spectroscopically. For instance, one can imagine that the keto form of the molecule is hydrogenated. We now have some preference for this latter possibility, because it was shown by Tai (*5*) and Smith (*3*) that enantioselective hydrogenation is very similar for MAA and for dimethyl-MAA, although the latter molecule, of course, cannot form an enol.

The general principles are not confined to hydrogenation with catalysts modified by tartaric complexes and should also be applicable to catalysts modified with asymmetric amino acids.

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