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Heterogeneous Enantioselective Hydrogenation: pH Dependence and Interplay between Catalytic Efficacy and Surface Composition

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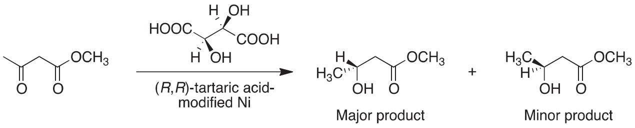
The performance of a catalytic system consisting of metallic Ni powder, tartaric acid (TA), and NaBr in the enantioselective hydrogenation of methyl acetoacetate was strongly influenced by the pH of TA solution upon chiral modification, which is attributable to the pH-induced change in the surface composition of Ni catalyst as unambiguously confirmed by X-ray photoelectron spectroscopy for the first time.

Optically active compounds are one of the most fundamental elements of all living organisms, also playing a key role as in the traditional fields of pharmaceuticals, agrochemicals, perfumery, bioadditives, and in the newly emerging technologies related to nanoscience, supramolecular chemistry, biomimetics, chirality, and enantioseparation. Amongst various methods for manufacturing enantiopure molecules, the heterogeneous catalytic approach is of particular importance owing to facile handling, simple separation, easy recovery, effective reuse, time- and cost-saving, and environmentally benign procedures.[1–5] In the case of hydrogenation reactions, catalytic systems based on tartaric acid (TA)-modified metallic nickel are known to be highly efficient in reducing activated prochiral ketones, such as β-ketoesters and 2-alkanones, to yield the corresponding chiral alcohols. There are several influencing factors controlling the efficacy of this process including the pH of TA solution used for the modification of the Ni surface.[4,6–10] Previously, it was experimentally shown that pH 3.2 is optimal for the catalytic performance of different types of metallic Ni in terms of enantiomeric excess (ee).[4,8,10] Apparently, this is due to the structure and composition of catalytic surface optimized at this specific pH for the enantioselective hydrogenation. However, the detailed investigation of surface properties related to the overall catalytic outcomes (i.e., ee and conversion) has yet to be done. In the present study, we revealed the structural and compositional origins of the strong pH dependences of the ee and conversion values by using X-ray photoelectron spectroscopy (XPS).



Scheme 1. Enantiodifferentiating hydrogenation of MAA with the TA-modified Ni catalyst.

Table 1. The pH effects on the enantiodifferentiating hydrogenation of MAA with the TA-modified Ni catalyst

Modification pH	Conversion/%	ee/%
2	50	89
3	92	91
3.2	99	90
4	100	88
5	100	80
6.5	100	82

As a base of metallic nickel, commercially available 5 µm Ni powder was chosen because this kind of catalyst is especially promising for industrial applications as shown recently.[11,12] After standard treatment with (R,R)-TA[13]/NaBr solution at different pH values, the chirally modified Ni powder was used for the hydrogenation of methyl acetoacetate (MAA), a benchmark substrate, to yield a pair of enantiomeric alcohol (Scheme 1 and Supporting Information for experimental details).[12,14] The resulting ee and conversion values are shown in Table 1. As one can see, the conversion value was rather low for the modification at pH 2 but was gradually enhanced with increasing the modification pH and reached the quantitative value at pH >3.2. However, the ee was consistently high (88–91%) at the modification pH ranging from 2 to 4 follow by considerable deterioration down to 80–82% at the modification pH >4, thus exhibiting the contrasting behavior to the conversion. Considering the combination of these two factors, the ee and conversion, pH 3.2 was established to be the best value for this particular catalytic system as well. Apparently, this optimization was achieved as a result of the trade-off of two oppositely working effects of pH: the removal of nickel oxide and other oxidation products from the surface of catalyst, which accelerates the hydrogenation process, is more effective at low pHs, while the formation of sodium tartrate, which is essential for obtaining high ee, is favorable at high pHs, as reported earlier.[4]

These results corroborate the previous data obtained with different types of metallic nickel,[4,8,10,12] and hence, unequivocally indicating that the catalyst surface composition is a more important factor for controlling the catalytic performance than the Ni source itself. In order to prove this hypothesis and also to elucidate the surface composition, the Ni powders modified with TA at three representative pHs of 2, 3.2, and 6.5 were subjected to the corresponding XPS analysis (see, Supporting Information for experimental details).[14] Figure 1 shows the deconvoluted areas of nickel species of different valencies, relative abundance of which is of particular significance in discussing the catalytic performance since the distribution of metallic versus cationic form of Ni can be quantitatively evaluated. Hence, the ratios of Ni^0 to $Ni^{2+} + Ni^{3+}$ were found to be 17/83 at pH 2.0, 43/57 at pH 3.2, and 35/65 at pH 6.5. These results are in good agreement with the obtained hydrogenation data. In particular,

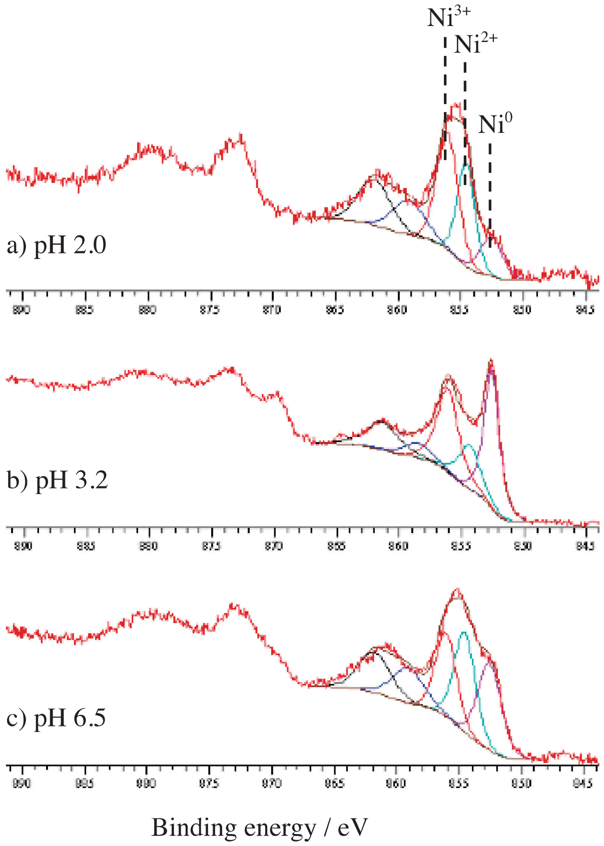


Figure 1. Ni $2p_{3/2}$ and Ni $2p_{1/2}$ areas of XP spectra of Ni powder modified with the TA–NaBr system at different pHs.

the calculated population of each TA form (free acid, monosodium tartrate, and disodium tartrate) at different pHs reveals that at pH 2.0 the corresponding free acid as the dominant species of TA (see, Supporting Information).[14] Therefore, on the one hand the free acid form effectively removes the oxidized nickel products from the surface, while on the other hand it corrodes the metallic nickel to yield the corresponding tartrates. Subsequently, this tendency of reducing Ni^0 area nicely accounts for the lower hydrogenation ability and hence the conversion reduced to 50%. Nevertheless, the enantiodifferentiating ability is rather high owing to the adsorption of free acid and a modest amount of monosodium tartrate on the Ni surface. While the substantial amount of nickel tartrate is obviously formed under these conditions as evidenced by the saturated green color of modification solution and the corresponding XPS analysis, the major contributors to the enhanced ee value are apparently the free acid form and monosodium salt of TA as was previously established in the case of Raney Ni[10] and also observed in the hydrogenation experiments at the concentrated (1 M) TA conditions.[15] At pH 3.2 the less corrosive monosodium tartrate becomes the main form of TA (see, Supporting Information),[14] which in combination with a portion of free acid can effectively remove the oxidized nickel species from the surface. This leads to the considerable increase of the Ni^0 contribution and consequently the conversion value up to 99%. The superior enantiodifferentiating ability of monosodium tartrate adsorbed on the surface also enhances the ee value up to 90–91% at pH 3.0–3.2. Further increasing the pH up to 6.5 produces disodium tartrate as the main form of TA (see, Supporting Information),[14] which possesses poor abilities to remove the oxidized Ni, resulting in the reduced Ni^0 peak in comparison to that at pH 3.2. However, this amount of Ni^0 is fairly sufficient to maintain the quantitative conversion, but the ee value is considerably decreased to 80–82% apparently as a result of the inferior enatiodifferentiating ability of disodium tartrate.

Other energy regions of XP spectra were also in agreement with the above-mentioned explanation of the surface composition of modified Ni. Thus, the corresponding signals associated with TA, the O–C=O and H–C–O peaks of C 1s region and the O–C and O=C peaks of O 1s region, are almost of the same relative intensity. This indicates that the amount of TA adsorbed on the Ni surface is essentially comparable in the whole pH range studied, while the relative composition of free acid, nickel tartrate, mono-, and disodium tartrate differs at each pH (see, Supporting Information).[14] However, the reliable quantitative analysis is not feasible for these peaks due to possible carbonaceous and oxygen contamination of the surface. It is also to note that the Na 1s peak of sodium tartrate was detected in the catalysts modified at pH 3.2 and 6.5, but was absent in that modified at pH 2 (see, Supporting Information).[14]

In conclusion, we have revealed unambiguously that the optimal surface composition can be obtained by the TA modification at pH 3.2 for the efficient hydrogenation of MAA as a representative β-ketoester substrate. Hence, the quantitative conversion and high ee value of up to 91% are simultaneously achieved by removing the oxidized Ni species and having TA adsorbed as monosodium salt, yet preventing the formation of nickel tartrate.

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13 Although the opposite enantiomer of TA has not been tested for this particular catalytic system, previously it was shown by using Raney Ni as a base for metallic Ni that (*S*,*S*)-TA yields the antipodal alcohol as the major product, see: M. Nakahata, M. Imaida, H. Ozaki, T. Harada, A. Tai, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2186.
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
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