Tartaric Acid Modified Nickel–Silica Catalysts; the Generation of Enantioselective Catalytic Species

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The treatment of Ni/SiO_2 with tartaric acid induces enantioselectivity and corrosively leaches nickel tartrate, which is also optically selective, into solution; in contrast to reports in the literature nickel metal is not essential for asymmetric activity.

Tartaric acid (TA) modified Ni/SiO_2 catalysts have been successfully used in the enantioselective hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB).[1–4] Modification of the activated catalyst is generally achieved in an aqueous solution of the optically active modifying reagent. The modified catalyst is then recovered, washed and immersed in an organic liquid phase containing the reactant. Although Hoek and Sachtler recognised that the modification procedure is corrosive[3] and provided limited data on the extent of nickel leaching,[2] the nature of the 'post' modification solution has largely been ignored. We report here that treatment of Ni/SiO_2 with TA results in the generation of two catalytic species, *i.e.* the previously observed silica supported optically active species and the nickel species leached out during modification. This latter species, when extracted into the reaction solvent, proves to be both catalytically active and enantiodifferentiating.

A silica (Cabo-O-Sil 5M, BET surface area 194 m^2 g^{-1}) supported nickel (15.2% w/w Ni) catalyst was prepared by homogeneous precipitation/deposition.[5] In addition, a sample of EURONi-1, also prepared by the same technique and characterised by the EUROCAT group,[6] was used. For each reaction, a 0.7 g sample of the catalyst precursor was reduced in a 150 cm^3 min^{-1} stream of hydrogen at 723 K for 18 h. The reduced catalyst was then immersed in aqueous TA solutions (100 cm^3) of varying concentration, adjusting the pH to 5.1 with 1 mol dm^{-3} NaOH, and stirred vigorously for 1 h at 343 K. After modification the catalyst was decanted and washed with distilled water, methanol and butanol before being stored in the latter prior to use. The modifier solution was analysed by atomic absorption spectrophotometry to determine the amount of nickel leached from the catalyst. The residual nickel was extracted from the aqueous TA solution by adding 200 cm^3 of a 70:30 butanol:methanol mixture and stirring vigorously for 1 h at room temperature. The green nickel precipitate was then isolated by filtration and dried at 373 K for 3 h. Nickel tartrate, which has been tentatively identified as the stereoselective site,[2,3] was prepared according to the method of Hoek and Sachtler.[3] The hydrogenation of MAA (10 cm^3) in butanol (40 cm^3) was carried out at 343 K by bubbling hydrogen through the suspension at a flow rate of 60 cm^3 min^{-1} under constant agitation. The reactions generally reached equilibrium after 28–46 h, at which point the catalyst was separated by filtration and the reaction products analysed by HPLC, to determine overall conversion, and by polarimetry, to determine the optical yields.

Data on the effects of varying the initial TA concentration on nickel leaching, hydrogenation activity and enantioselectivity are presented in Table 1. Under identical experimental conditions, values for enantiomeric excess (e.e.) were reproducible to within ±4%. It can be clearly observed that, while the modified catalysts exhibit a higher activity than the corresponding unmodified samples, the overall levels of conversion to MHB decrease with increasing TA concentration. Enantioselectivity, on the other hand, passes through a maximum at 0.01 mol dm^{-3} TA, then gradually decreases and remains constant at modifier concentrations in excess of *ca.* 0.1 mol dm^{-3}. As the initial concentration of TA is increased (up to *ca.* 0.07 mol dm^{-3}), the loss in activity is also accompanied by a progressive leaching of nickel from the catalyst surface. At TA concentrations in the range 0.07–0.2 mol dm^{-3}, the amount of nickel appearing in solution remained virtually constant. Indeed, at these TA concentrations, *ca.* 60% of the original nickel content has been lost from the support. Such a substantial leaching of the catalytically active material must represent a dramatic change in the nature of the active surface and the possible inclusion of an enantioselective species in the post-modifier solution.

Table 1 Effect of initial TA concentration on the extent of nickel leaching, catalytic activity and enantioselectivity of a 15.2% w/w Ni/SiO_2 catalyst: $T_{mod} = T_{reaction} = 343$ K; $t_{mod} = 1$ h; $t_{reaction} = 30$ h

[TA] $/10^{-2}$ mol dm^{-3}	Leached Ni /ppm	Mol% MHB	e.e. (%)
—	4	74.6	1.4
0.33	34	80.7	23.0
0.67	134	80.1	24.9
3.33	421	77.4	20.7
6.67	451	76.0	19.0
10.00	458	75.8	17.8
13.32	460	75.3	17.1
16.70	464	75.2	17.1
19.99	461	75.0	16.9

The latter possibility has been considered and the results of a series of asymmetric hydrogenation reactions over the leached nickel species resulting from a number of modification procedures are presented in Table 2. It should be noted that equilibrium conversions over these secondary catalysts were only attained after *ca.* 46 h and the resultant enantiomeric excesses were reproducible to within ±10%. These reactions were also heterogeneous and the catalytic agent could be recovered from the product and reused. Regardless, the ultimate conversion levels and enantioselectivities are comparable, albeit lower, than those observed for the more conventional silica supported catalysts. From the data presented in Table 2, it can be seen that enantiomeric excess is enhanced at higher catalyst to substrate ratios. The species isolated from the more concentrated TA solutions also proved to be the more active.

Hoek and Sachtler[3] have proposed a dual site mechanism in which hydrogen is dissociated on the surface of the nickel metal particles, followed by a migration of hydrogen atoms to the tartrate complex where they become attached to the adsorbed substrate molecule in two separate steps. This model presupposes the formation of surface Ni–TA complexes where the nickel atoms in the complex have two vacant ligand positions available for adsorbed hydrogen and substrate, respectively. They concluded that metallic nickel is essential for the hydrogenation process and ruled out any possibility of catalysis by an immobilized organometallic complex without any active participation by the nickel metal. In complete contrast, we have found that under identical reaction conditions, nickel tartrate (in which nickel is present as a divalent ion) without any pretreatment acts as an enantioselective catalyst. Catalytic activity and selectivity data for a series of reactions over nickel tartrate are presented in Table 3 and compared with corresponding data for a representative sample of the leached nickel. Reactions over nickel tartrate were also heterogeneous and the catalyst, upon recovery, was reusable for up to eight reaction cycles. It can be observed from Table 3 that the overall levels of activity and selectivity were very similar for both the synthesised nickel tartrate and

Table 2 Activity and enantioselectivity of the leached nickel species resulting from a range of modifications: $T_{reaction} = 343$ K; $t_{reaction} = 46$ h

[TA] $/10^{-2}$ mol dm^{-3}	Leached Ni $/10^{-2}$ g	Mol% MHB	e.e. (%)
0.67	1.0	60.2	10
3.33	2.1	63.3	11
6.67	3.1	66.1	13
13.32	3.3	70.7	14
	5.2	76.7	15
19.99	3.2	75.6	16
	5.3	78.8	16
	7.6	81.4	18

Table 3 The effect of $T_{reaction}$ on the activity and enantioselectivity of nickel tartrate and a sample of the leached nickel species: catalyst weight = 8×10^{-2} g; $t_{reaction} = 46$ h

	Nickel tartrate		Leached nickel	
T/K	Mol% MHB	e.e. (%)	Mol% MHB	e.e. (%)
308	20.1	10	12.1	13
323	48.8	14	44.3	19
333	60.2	15	61.5	20
343	79.1	15	81.4	18
353	85.1	12	88.6	14
368	93.4	8	97.3	8

the recovered leached nickel. Furthermore, both catalysts exhibited an increase in hydrogenation activity with reaction temperature and an accompanying maximum in enantioselectivity in the temperature range 323–343 K. We can therefore conclude that metallic nickel is not an essential component of the enantioselective catalyst. It is interesting to note, however, that the supported catalysts exhibit higher and more reproducible values of enantiomeric excess, even though the experimental evidence suggests that bare nickel catalyses the formation of the racemic product.

In the corrosive adsorption of TA on the supported nickel crystallite some of the resultant stereospecific complex will remain on the SiO_2 carrier to form a supported selective site and some will diffuse into solution, the concentration of the latter depending on a range of experimental parameters such as nickel loading, modifier concentration, the duration and temperature of modification. There must therefore exist a dynamic equilibrium between the adsorbed and dissolved NiTA. Indeed, the product samples resulting from catalysis over the modified, higher nickel loaded silicas exhibited a green colouration, suggesting that some of the weakly held NiTA which remained in contact with the support throughout modification went into solution during the prolonged reaction. Taking a EURONi-1 sample treated with *ca.* 0.01 mol dm^{-3} TA at 373 K as a representative case, the product resulting from the catalytic step was found to contain *ca.* 40 ppm Ni. Upon adding fresh ketone to a sample of the butanol–MAA–MHB solution and again repeating the catalytic step, in the absence of any supported catalyst, mol% conversion to MHB was raised from *ca.* 46 to *ca.* 78%, thus providing further evidence that the leached nickel species is catalytically active. Similar results have been obtained from a number of product samples. The overall levels of activity and selectivity therefore appear to arise from the combined action of NiTA which remains on the support and NiTA which is in the product mixture.

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