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Observing the *in situ* chiral modification of Ni nanoparticles using scanning transmission X-ray microspectroscopy

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ABSTRACT

Enantioselective heterogeneous hydrogenation of C═O bonds is of great potential importance in the synthesis of chirally pure products for the pharmaceutical and fine chemical industries. One of the most widely studied examples of such a reaction is the hydrogenation of β-ketoesters and β-diketoesters over Ni-based catalysts in the presence of a chiral modifier. Here we use scanning transmission X-ray microscopy combined with near-edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) to investigate the adsorption of the chiral modifier, namely (R,R)-tartaric acid, onto individual nickel nanoparticles. The C K-edge spectra strongly suggest that tartaric acid deposited onto the nanoparticle surfaces from aqueous solutions undergoes a keto-enol tautomerisation. Furthermore, we are able to interrogate the Ni $L_{2,3}$-edge resonances of individual metal nanoparticles which, combined with X-ray diffraction (XRD) patterns showed them to consist of a pure nickel phase rather than the more thermodynamically stable bulk nickel oxide. Importantly, there appears to be no "particle size effect" on the adsorption mode of the tartaric acid in the particle size range ~90–~300 nm.

1. Introduction

Chemical routes to enantio-enriched, and ultimately enantio-pure, compounds have attracted great interest in the past decades, stimulating remarkable progress in homogeneous enantioselective catalysis. The culmination of this was the award of the Nobel Prize in Chemistry in 2001 to Noyori, Sharpless and Knowles for their inputs in advancing homogeneous asymmetric hydrogenations and oxidations [1,2]. In contrast to the numerous examples of enantioselective homogeneous catalysts reported in the literature the number of successful heterogeneous systems is small — despite the numerous advantages of heterogeneous systems over their homogeneous counterparts. Various strategies have been pursued to design heterogeneous enantioselective catalysts that combine high catalytic activity with suitable stereochemical control of the reaction, the most successful of which include the modification of the catalytic metal surface by a strongly adsorbing chiral compound, the modifier [3–5]. The progress in heterogeneous enantioselective catalysis is reflected by the rapidly growing number of scientific publications and a number of recent reviews of the subject [4,6–10]. The importance of chirally modified metals in asymmetric synthesis has also stimulated a number of surface science studies aimed at understanding the fundamental properties of the adsorption of chiral molecules at catalytically relevant surfaces. These studies usually combine model surfaces, *i.e.* single crystals, with 'ideal' adsorption conditions, *i.e.* ultra-high vacuum [11–13]. There are relatively few studies published, with the notable exception of the work of Jones and Baddeley [14] who studied the adsorption of tartaric acid from solution under a number of different conditions, that utilise 'real' catalytic materials and/or conditions — this is something we address in this paper.

To date the heterogeneous catalytic systems that have undergone the most interrogation include the enantioselective hydrogenation of α-ketoesters over Pt-based catalysts [3,15–17] and the enantioselective hydrogenation of β-ketoesters and β-diketoesters over Ni-based catalysts [4,18–20].

These enantioselective surface reactions are controlled by the presence of an adsorbed chiral molecule on the surface of the active metal. In the case of the Ni/β-ketoester system, (R,R)-tartaric acid (R,R-TA) or amino acids, such as alanine and aspartic acid [21,22], are used as the chiral modifier and an enantiomeric excess [23] of R-methyl-3-hydroxybutyrate (R-MHB) is observed following the hydrogenation of methylacetoacetate (MAA) (Fig. 1).

The precise pathway of the reaction and the mechanism of this enantioselective control have, however, not been yet verified; though several models of the modified surface have been proposed to explain the activity [3,24–26]. One possible explanation being a two-point hydrogen-bonding (H-bonding) model in which the protons of the hydroxyl groups of the tartaric acid H-bond to the β-ketoester or β-diketone oxygen atoms. This arrangement sterically favours the

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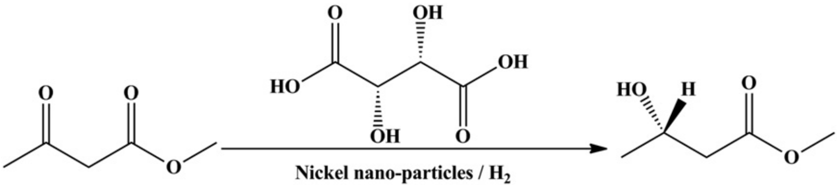

Fig. 1. Schematic diagram of the β-ketoester hydrogenation reaction showing a typical reactant, methylacetoacetate, the major product, (R)-methyl-3-hydroxybutyrate ((R)-MHB) and the chiral modifier, (R,R)-tartaric acid. When (S,S)-tartaric acid is substituted as the chiral modifier the major product is the S-enantiomer, (S)-MHB.

adsorption of one β-ketoester conformer over the other, thus resulting in enantioselective hydrogenation (Fig. 2) [24–26]. Satisfyingly, this model also explains both of the diastereoisomers formed in the chiral dehydrogenation of acetylacetonate [27]. Furthermore it accounts for the hydrogenation of prochiral ketones containing sterically hindered alkyl groups, which can form only one hydrogen bond, with the net result being a very striking reversal of enantioselectivity. In Fig. 2, it is clear that hydrogenation of MAA in this conformation would result in the R-form of MHB being formed. An alternative proposed model involves the formation of 2-dimensional chiral co-crystalline domains on the metal surface formed by the propensity of the chiral adsorbate molecules to self-assemble into ordered structures [4]. This template surface model is a reasonable one when used in relation to extended surfaces (for example single crystals or the larger nanoparticles used in this study) but may reach limitations on very small nanoparticles due to limited terrace widths. There have been many attempts to further understand the active site in TA-Ni catalysts for the hydrogenation of MAA but no clear explanation of the catalytic phenomena has been proposed which would bring this into light [4,25–27].

In this paper we aim to collect detailed *in situ* photoabsorption spectra of species involved in the topical enantioselective hydrogenation reaction of methylacetoacetate. We will use the excellent spatial resolution afforded by the PolLux scanning transmission X-ray microspectroscopy (STXM) beamline of the Swiss Light Source to locate individual nanoparticles and subsequently measure the Ni $L_{2,3}$-edge NEXAFS spectra as well as the C K-edge NEXAFS spectra of the adsorbed tartaric acid molecules.

There are numerous articles in the literature where STXM has been used to study polymer systems [29–31], carbon nanotubes [32,33] and clays [34,35] but, to our knowledge, none that examine the adsorption of chiral modifier molecules (or any other small organic molecule) onto catalytically relevant metal nanoparticles. Here we report, for the first time observed using STXM, the adsorption of tartaric acid onto Ni nanoparticles; an investigation that will contribute to the understanding of the mechanism of this important and topical enantioselective heterogeneous hydrogenation reaction.

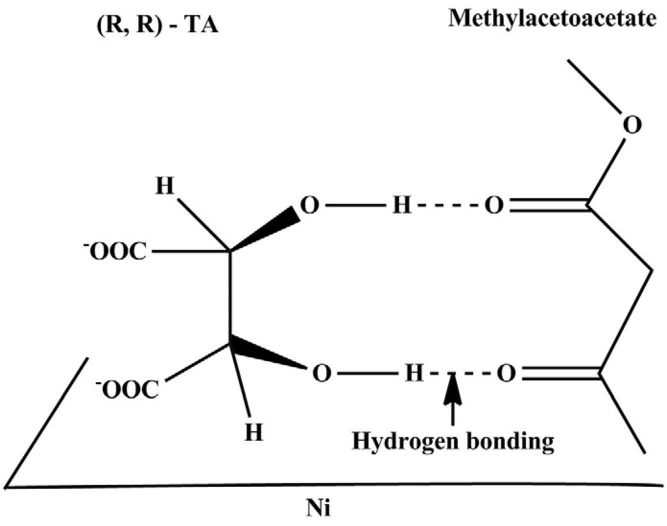

Fig. 2. Schematic representation of one of the models for the mechanism of the interaction between (R,R)-tartaric acid adsorbed at the catalyst surface and methylacetoacetate. Adapted from reference [28].

2. Materials and methodology

Nickel chloride (anhydrous) (98%), hydrazine ($N_2H_4.H_2O$) (98%), sodium-hydroxide (≥99%), methyl 2-hydroxyethyl cellulose (98%), (R,R)-tartaric acid (99%) and methyl acetoacetate (99%) were all purchased from Sigma-Aldrich (UK) and were used without further purification.

2.1. Nanoparticle synthesis

Ni nanoparticles were prepared by adding methyl 2-hydroxyethyl cellulose (0.2 wt.%) to 1.2 M aqueous $NiCl_2$ solution at 90 °C. NaOH solution (20 wt.%) was added drop-wise until a pH of 11 was achieved. From this point two different procedures were carried out depending on the intended use of the resulting nanoparticles. A) For Ni catalysts to be used for XRD analysis and high-pressure hydrogenation reactions: 6.2 M $N_2H_4.H_2O$ was added directly to the solution either with or without simultaneous addition of sufficient α-Al_2O_3 to result in a 10% metal loading. B) For Ni catalysts to be used for STXM analysis: Prior to the addition of the 6.2 M $N_2H_4.H_2O$ (the reduction step) silicon nitride windows were immersed into the reaction mixture until the reduction of the metal salt was complete. Two types of window were used: either 'clean' Si_3N_4 window (Silson Ltd, UK) or Si_3N_4 windows that had previously been modified with 10 nm of alumina applied from an aluminium evaporator source located in a vacuum system with an O_2 partial pressure of $\sim 1 \times 10^{-6}$ mbar. The alumina coated windows were further heated in air for 12 h to ensure that the aluminium was fully oxidised and also to relieve lattice strain that could damage the membrane, the 'clean' windows were used without further treatment. Finally, the product was washed with distilled water and ethanol several times to remove impurities, and then dried at room temperature.

2.2. Nanoparticle modification with tartaric acid

Tartaric acid was adsorbed onto the samples, when required, from aqueous solution. A single droplet of 0.5 M (R,R)-tartaric acid (pH = 1.8, T = 298 K) was placed onto the sample window. The solution was allowed to sit for 3 min and then the window was washed three times in clean Milli-Q water before drying prior to insertion into the vacuum chamber.

2.3. Powder X-ray diffraction

The phases present in the products were identified from their powder X-ray diffraction (PXRD) patterns, which were collected on a Bruker D8 diffractometer using Ni filtered Cu Kα radiation (λ = 1.540598 Å) operated at a voltage of 40 kV and a current of 30 mV. The measurements were carried out with a step scan mode: step size = 0.02 (degrees 2θ), time per step = 18.87 s, in the range of 50–140 degrees 2θ. The goniometer was calibrated with a cubic α-quartz standard (a_h = 5.4309 Å). Corrections for systematic deviation in 2θ were applied.

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