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Spectroscopic Detection of New Surface Species on Activated Nickel Particles

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Many chemical transformations that occur at metal surfaces require "activation" in order to produce a chemically reactive surface. Synthetic chemists have developed many methods of activating metal powders including mechanical agitation,[1] chemical cleaning of the surface,[2] the use of alloys (e.g., Raney nickel, amalgams), reduction of metal halides,[3] ultrasonic irradiation of metal powders,[4,5] ultrasonic irradiation of metal powders during chemical reduction,[6,7] and metal atom techniques.[8] The premise is that the special preparation cleans the surface of contaminants, increases dispersion, or perhaps favors production of some more reactive plane in the metal surface.[9] Raman spectroscopy of the metal suspension formed by lithium reduction of NiI_2 in ethereal solvents suggests another mechanism of activation: production of new species by reaction of the metal surface with the solvent.

Activated Ni powders were formed by reduction of nickel(II) iodide with lithium in an ethereal solvent. Nickel powders produced in this fashion have shown exceptional reactivity in stoichiometric reactions[3] and in the catalysis of hydrosilylation[10] and dehydrogenative coupling of hydrosilanes.[11] Sonicating the reaction mixture during reduction significantly increases the reactivity of the nickel powder.[6] Generally, powders produced in this fashion[12] form smaller particles than those produced under refluxing conditions.[13]

The Raman spectrum of nickel powder prepared by lithium reduction of NiI_2 in THF in a bath sonicator is presented in Figure 1 along with a reference spectrum of THF. The most striking differences in the spectra are the presence of two sharp peaks at 1956 and 2051 cm^{-1}, diagnostic of metal carbonyls.[14] The spectrum also contains all the THF peaks with a new peak occurring at 1063 cm^{-1}. An open question is the nature of the metal carbonyl. Does it represent free $Ni(CO)_4$ or a surface species?

To address this question, the spectrum of the activated Ni after evaporation of solvent was obtained and is presented in Figure 2. Figure 2A shows the spectrum after evaporation of solvent in air, and Figure 2B shows the spectrum after evacuation to 10-μm pressure for 2 h. Both spectra show the persistence of the peaks attributed to metal carbonyl. We conclude that the metal carbonyl species is formed at the metal surface and probably is caused by the formation of both bridged (1956 cm^{-1}) and terminally bound (2051 cm^{-1}) carbonyl species.[15] Figure 2 also contains new bands, which may correspond to coordinated THF, although bands in the region 1100–1700 cm^{-1} have been attributed to the presence of graphitic carbon.[16]

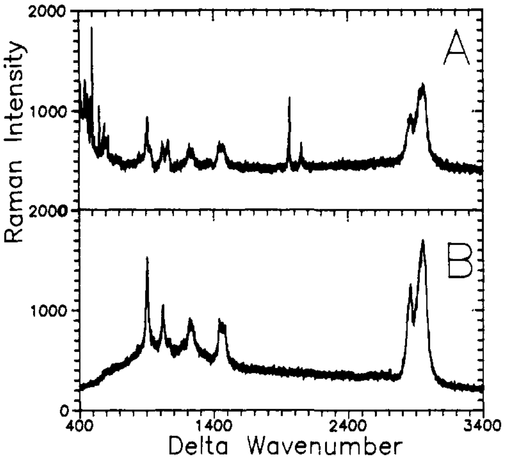

Figure 1. (A) The Raman spectrum of activated nickel formed by ultrasound-promoted reduction of NiI_2 in THF and (B) the Raman spectrum of freshly distilled THF. Both spectra are referenced to the 488-nm line of the Ar$^+$ laser. Spectrum A represents a collection time of 10 s/data point and spectrum B a collection time of 1 s/data point.

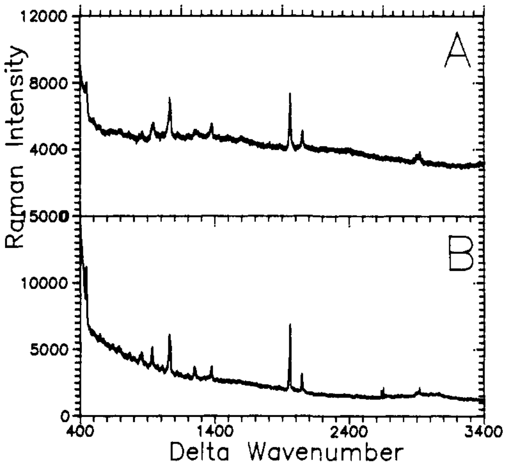

Figure 2. (A) The Raman spectrum of the activated nickel powder formed after evaporation of the THF solvent, in air. (B) The spectrum of the same nickel powder after evacuation to 10-μm pressure for 2 h. Both spectra are measured relative to the 488-line of the Ar$^+$ laser, and the data collection time was 10 s/data point. The same carbonyl species are seen from ether as from THF.

Formation of surface carbonyl species is not restricted to reaction in THF, nor does it require ultrasound. Surface carbonyl formation was observed in the Raman spectra of activated Ni formed in diethyl ether and of activated nickel produced by simply refluxing THF, lithium, and NiI_2. We also observed that nickel dispersions produced by sodium reduction of NiI_2 in toluene formed surface carbonyls when exposed to THF following removal from toluene. The carbonyl peaks were significantly less intense in these cases compared to ultrasonically aided reactions. No carbonyl peaks were observed on the nickel produced in toluene prior to exposure to THF.

The formation of surface carbonyl species affects the reactivity of the nickel. We recently observed that nickel powders with

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surface carbonyls are several orders of magnitude more reactive in oxidative addition reactions with silanes than non-carbonyl-containing nickel samples.[17]

Destruction of solvent by the metal particles has been inferred from analysis of reaction products[18] in several of the methods used in producing active metal powders. Auger spectroscopy of nickel powders subjected to ultrasonic irradiation has indicated the presence of both surface carbon and significant quantities of surface oxygen (Ni:O rations of 1:2).[4]

The magnitude of the surface Raman signal tempts one to infer some surface enhancement of the Raman signal, and evidence for surface enhancement of the Raman spectrum for molecules adsorbed on nickel has precedent in the literature.[19,20] In the absence of an excitation profile, this conclusion is unwarranted, and the magnitude of the signal is attributed to the large surface area seen in the morphological experiments[13] and the large quantity of surface oxygen observed in the Auger experiment.[4]

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Inversion of Enantioselectivity in the Kinetic Resolution Mode of the Katsuki-Sharpless Asymmetric Epoxidation Reaction†

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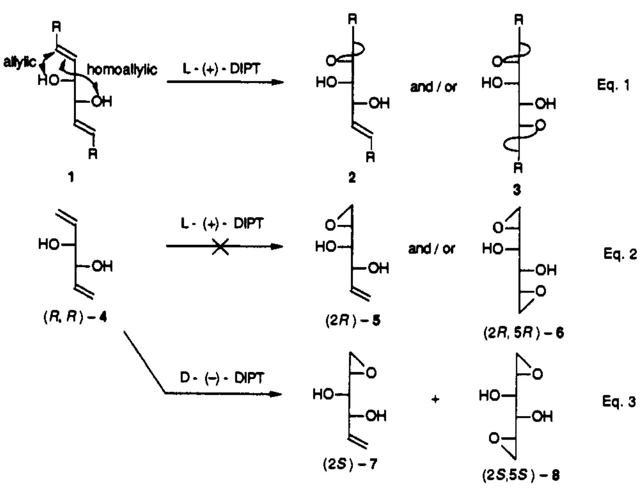
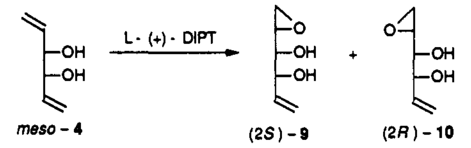
It is reported that the enantiofacial selection in the Katsuki-Sharpless asymmetric epoxidation[1,2] is opposite for allylic and homoallylic alcohols.[3,4] Since C_2-symmetric DL-1,2-dialkenylethylene glycols (**1**) may be regarded as either allylic or homoallylic substrates, we were intrigued by the possibility that an opposite stereogenic effect between the allylic and homoallylic relationships might synergistically amplify the enantiofacial selectivity in the chiral epoxidation of these symmetric substrates[5] (Scheme I, eq 1). We therefore examined the reaction of optically active C_2-symmetric (1*R*,2*R*)-1,2-divinylethylene glycol[6] [(*R*,*R*)-**4**], which led us to make a new and unexpected discovery relative to the Katsuki-Sharpless kinetic resolution process.

Since the empirical rule[1-4] embodied in asymmetric epoxidation predicts that 1*R*,2*R* glycol [(*R*,*R*)-**4**] would react at a much faster rate in the presence of diisopropyl L-(+)-tartrate [(+)-DIPT] to furnish *R* epoxide [(2*R*)-**5**] and/or *R*,*R* diepoxide [(2*R*,5*R*)-**6**], we first carried out the reaction of (*R*,*R*)-**4** with *tert*-butyl hydroperoxide (TBHP) in the presence of a stoichiometric amount of (+)-DIPT and Ti(O-*i*-Pr)$_4$ and 4-Å molecular sieves[7] (Scheme I, eq 2). However, the reaction did not occur and the starting material was recovered unchanged. Surprisingly, when (−)-DIPT in place of (+)-DIPT was used (Scheme I, eq 3), the reaction took place facilely to afford *S* monoepoxide [(2*S*)-**7**] accompanied by a minor amount of *S*,*S* diepoxide [(2*S*,5*S*)-**8**] with 1.2 equiv of TBHP (Table I, entry 1) and the diepoxide [(2*S*,5*S*)-**8**] accompanied by a minor amount of the monoepoxide [(2*S*)-**7**] with 3 equiv of TBHP (Table I, entry 2). Correlation of the products with diethyl L-(+)-tartrate[8] and D-mannitol[9] established their stereochemistry unambiguously. This inversion of enantioselectivity and diastereofacial selectivity was also observed in the kinetic resolution of racemic DL substrate[10] [(±)-**4**] in the presence of (+)-DIPT, which furnished a mixture of *R* monoepoxide [(2*R*)-**7**], *R*,*R* diepoxide [(2*R*,5*R*)-**8**], and unreacted glycol [(*R*,*R*)-**4**] (Table I, entries 3 and 4).

Scheme I



Scheme II



Interestingly, the monobenzyl ether[11] of optically active DL substrate [(*R*,*R*)-**4**] was epoxidized only in the presence of (+)-DIPT to afford the monoepoxide with the *R* configuration, matching the prediction of the empirical rule (Table I, entry 5). When *meso*-1,2-divinylethylene glycol[10] [(*meso*)-**4**] was epoxidized for comparison in the presence of (+)-DIPT, the reaction occurred again in an unexpected mode to afford a 7:1 mixture of diastereomeric monoepoxides (2*S*)-**9** and (2*R*)-**10** (Scheme II) (Table I, entries 6-8), which could be separated after conversion into acetonides and correlated with (*S*)-*O*-benzylglycidol[12,13] to establish

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† Dedicated to Professor George Büchi on the occasion of his 70th birthday.

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