

Evidence for the anchoring of 2-amino-3-methyl-1-butanol at the surface of NiB₂ agglomerate by inelastic neutron spectroscopy

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Abstract

We have obtained by inelastic neutron spectroscopy physico-chemical evidence of the anchoring of 2-amino-3-methyl-1-butanol (AMB) on a metallic aggregate (NiB₂).

In the reduction of *p*-fluoroacetophenone with borane complex, this heterogeneous catalyst and the homogeneous catalyst prepared from AMB and borane behave similarly. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heterogenization of a homogeneous catalyst is an approach which attempts to combine high enantioselectivity (homogeneous catalysis) and the ease of separation (heterogeneous catalysis). Usually the strategy involves tethering of the homogeneous catalyst to an organic or inorganic surface. Our approach is to synthesize the chiral molecule simultaneously with its anchoring to the surface of the solid. 1,3,2-oxazaborolidines which are highly effective homogeneous catalysts for the enantioselective reduction of ketones to chiral secondary alcohol by borane [1], are prepared and bonded to the solid by reacting nickel boride (NiB₂) with an amino alcohol [2]. The solids NiB_{2-x}(Oxaza)_x catalyse the borane reduction of acetophenone with good yields and high

enantiomeric excesses in stoichiometric conditions [3] and in catalytic conditions [4].

The catalysts can be recycled two times with little or no loss of performance, and the reaction of an amino-alcohol with nickel boride produces one equivalent of hydrogen gas as expected. Thus we have chemical evidences for the formation of the oxazaborolidine ring, but since anchoring an organic molecule at the surface of a metallic aggregate is unusual, we looked for physico-chemical evidences of functional groups or adsorbed species. Laser Raman spectroscopy did not give information since the light absorption reinforced by the black colour of the sample, raised the temperature of the sample up to the thermal decomposition of the organic compound (graphite formation was observed). Diffuse reflectance did not demonstrate the presence of an organic compound at the solid surface.

The usefulness of inelastic neutron spectroscopy (INS) in observing vibrational modes involving hydrogen motion is well established. Thus we selected this spectroscopy to physically substantiate the formation

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of the oxazaborolidine ring, i.e. we looked for the disappearance of the OH deformation absorption in the spectrum of 2-amino-3-methyl-1-butanol after reaction with NiB_2 .

Among the borane reductants for homogeneous oxazaborolidine catalyzed reduction of ketones, *N,N*-diethylaniline borane complex is the borane source which affords the best enantiomeric excesses for aromatic and aliphatic ketones [5]. In order to test the applicability of *N,N*-diethylaniline borane in heterogeneous conditions, we reduced *p*-fluoroacetophenone with this reagent.

2. Experimental

2.1. Sample preparation

2-Amino-3-methyl-1-butanol (AMB, 1.98 g, 1.92×10^{-2} mol in 15 ml THF) was added to the stirred suspension of NiB_2 (9.6×10^{-2} mol in 200 ml THF), this compound was prepared by reducing nickel iodide with lithium borohydride according to our previous report [2].

After 2 h at room temperature and 7 h at reflux, the THF was decanted, it did not contain any amino-alcohol as shown by TLC analysis. The catalyst was washed three times with THF, transferred to a break-seal ampoule, heated up to 343 K under a flow of nitrogen, then maintained at this temperature for 3 h under vacuum, in such conditions unreacted AMB was removed since its bp is 348–350 K/8 mm. After cooling to room temperature, the ampoule was sealed under nitrogen. The ampoule contents were transferred, inside a glovebox purged with Ar, into a cylindrical vacuum-tight aluminium container. For comparison, the spectrum of AMB in the solid phase was also recorded.

The neutron experiments were performed on the IN1BeF spectrometer, at the Institut Laue-Langevin, Grenoble. The INS spectra were measured from 240 to 1800 cm^{-1} . A beryllium filter was placed between the sample and the detector. This setting gives a moderate energy resolution, the instrumental resolution varying from 25 cm^{-1} , at small energy transfers, to 50 cm^{-1} at large energy transfers. The frequency values given in the figures and in the text have been corrected from a systematic shift due to the beryllium filter. The

estimated absolute accuracy is $\approx 20 \text{ cm}^{-1}$. The spectra were recorded at 5 K, such a low temperature is required to decrease the mean-square amplitude of the atoms, and thus to sharpen the vibrational features [6].

The heterogeneous reduction was carried out according to the procedure II [4] but at room temperature. After removal of the catalyst, 20 ml of methanol were added to the liquid phase which was stirred for 20 min diluted with HCl (N, 5 ml) and extracted with ether after being stirred for 10 min. The ethereal extract was washed with HCl, brine, dried and evaporated.

The homogeneous reduction was carried out exactly in the same conditions but initially 9 mmol of $\text{BH}_3 \cdot \text{THF}$ were added to 9 mmol of AMB in 100 ml THF.

3. Results and discussion

The INS spectrum of AMB in the solid phase is shown in Fig. 1(a). Though AMB does not give a very efficient oxazaborolidine it was preferred to norephedrine and to 2-amino-1,2-diphenylethanol since in infrared the phenyl group shows bands in the region $1075\text{--}1060 \text{ cm}^{-1}$ assigned to the C–H in plane deformation modes [7] which might interfere with the OH deformation absorption. It should be remembered that there are no selection rules in INS so that all the vibrational modes are measured. However, the intensity of each mode is proportional to the hydrogen atoms amplitudes. This explains why the largest peaks in Fig. 1 can be assigned to methyl or methylene groups vibrations. For example, the peaks at 275, 968, and $1398\text{--}1485 \text{ cm}^{-1}$ correspond to methyl group torsion, rocking, symmetric and asymmetric bendings, respectively. Similar features were observed in the INS spectrum of neopentane [8]. To the best of our knowledge, a complete assignment of the vibrational modes of this molecule has not been performed, so that the weaker bands are more difficult to assign. However, the shoulder at 1065 cm^{-1} seems to correspond to the OH bending (this mode is observed at 1053 cm^{-1} in infrared).

After the reaction of AMB with NiB_2 , the solid was maintained at a temperature higher than the boiling point of AMB, thus, it cannot be significantly physisorbed. By comparing Fig. 1(a) with (b), it is clear that the molecule which is chemisorbed on NiB_2

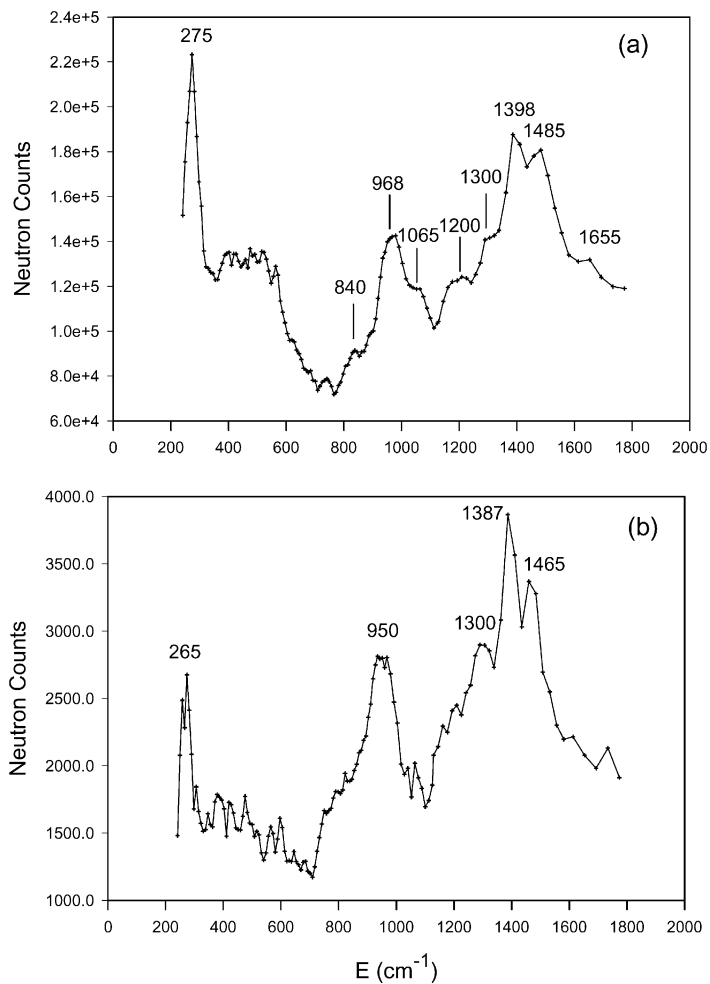


Fig. 1. INS spectra of AMB (a) in the solid phase and (b) after reaction on NiB_2 .

Table 1

Enantioselectivity in the reduction of *p*-fluoroacetophenone, in THF, at room temperature ratio AMB/ketone = 0.1, ratio BH_3 /ketone = 1.1

Catalyst ^a	Reducing agent	Enantioselectivity		
		ee 1st reduction	ee 2nd reduction	ee 3rd reduction
A	$\text{BH}_3 \cdot \text{DEA}$	65	43	44
A	$\text{BH}_3 \cdot \text{THF}$	29	14	8
B	$\text{BH}_3 \cdot \text{THF}$	29	Unnecessary	Unnecessary
B	$\text{BH}_3 \cdot \text{DEA}$	76	Unnecessary	Unnecessary

^a Catalyst A: NiB_2 + 2-amino-3-methyl-1-butanol; catalyst B: 2-amino-3-methyl-1-butanol + BH_3 .

has retained its main vibrational features, although shifted in frequency. The band intensities are also modified and some bands have disappeared, such as the OH bending. Indeed, this group disappears during the anchoring reaction. A normal coordinate analysis, as was done for benzene on Raney nickel [9], would be necessary to find out the origin of the weaker bands. However, we assume that an AMB molecule strongly chemisorbed on NiB₂, without OH bonding, which enantioselectively catalyses the reduction of *p*-fluoroacetophenone by borane is no longer an amino alcohol but an oxazaborolidine.

The ee's observed in the reduction of *p*-fluoroacetophenone with homogeneous or heterogeneous catalyst prepared from AMB (Table 1) demonstrate that the borane DEA complex is obviously a more enantioselective agent than the borane THF complex. Both the homogeneous and heterogeneous catalyst behave in a similar manner, thus, the explanations of the properties of the DEA complex through an oxazaborolidine mechanism which are given in homogeneous conditions apply to the heterogeneous catalyst and afford another indirect evidence of the oxazaborolidine formation.

4. Conclusion

Although the spectroscopic data do not by themselves demonstrate the formation of an oxazaboroli-

dine ring, inelastic neutron scattering shows that an organic molecule is present on the surface after heating over the boiling point of AMB.

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