

Mössbauer spectroscopy and nuclear inelastic scattering studies on novel Gif-type polynuclear oxo-bridged iron catalysts

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Selective oxidations of alkenes using molecular O₂ are highly promising steps for synthesizing complex natural products and pharmaceutically active agents. For such oxidations Gif-type iron catalysts have proven to be efficient. These iron catalysts have to be characterized. It is the aim to replace high cost and hazardous heavy metal catalysts by efficient, non toxic and economic iron catalysts. In this poster we present first results obtained from Mössbauer spectroscopy (MS) on a tetranuclear oxo-bridged iron catalyst. The reaction kinetics were also measured using a freeze-quench technique. The vibrational density of states (VDOS) of ⁵⁷Fe atoms of the precursor as obtained from nuclear inelastic scattering (NIS) was compared to the VDOS obtained from density functional theory (DFT) calculations.

1. Aim

We study the kinetics of the alkene oxidation and the vibrational properties of the precursor as shown in Fig. 1.

A first X-ray crystallographic study on a water adduct indicates that the precursor is a tetranuclear iron complex as shown below. The metal geometry of the metal cluster may be described as a ‚butterfly‘ of type II, based on two edge sharing Fe₃(μ₃-O) triangular units [1].

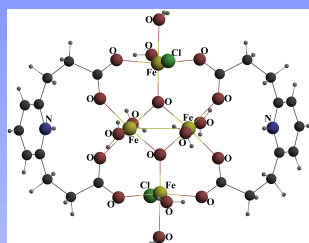
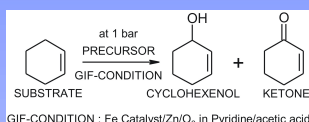


Fig. 1 Left: Oxidation reaction of cyclohexene, Right: Structure of the precursor; Empirical formula: Fe₄C₂₂H₄₄Cl₂N₆O₃₂ (for clarity four NO₃ ions and two H₂O molecules are not shown)

2. Mössbauer spectra

Mössbauer spectra (Fig. 2a) of the precursor reveal that the iron atoms are in a high spin (HS) Fe(III) state.

Spectra of the active catalyst (i.e., precursor in Zn + pyridine+ acetic acid) under inert gas (N₂) and O₂ (Figs. 2b and c) show the presence of a HS Fe(II) species. In addition, a second Fe(III) species is formed when the active catalyst is exposed to O₂. This Fe(III) species has a larger quadrupole splitting than the precursor. It is formed during the reaction.

The kinetics of the oxidation reaction was studied after three different reaction times as shown in Fig. 2d, e and f, which tells that the catalyst is oxidized slowly, but still the Fe(II) species is present as seen by the larger quadrupole doublet in Fig. 2f.

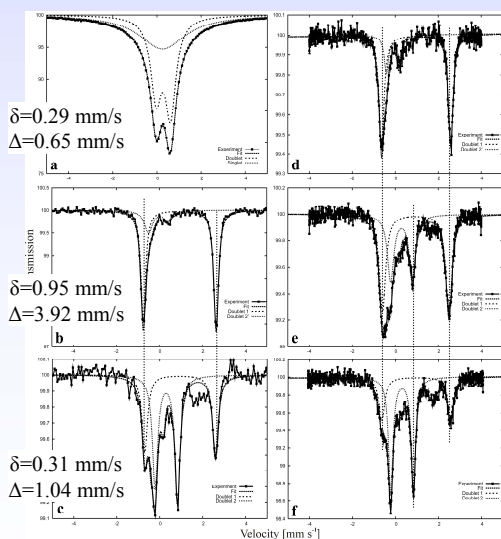


Fig. 2 Mössbauer spectra at 4.2 K of a) catalyst precursor, b) active catalyst under N₂ gas, c) active catalyst under O₂ gas, d) reaction after 1 minute, e) after 5 minutes and f) after 30 minutes

3. NIS

The Fe VDOS of the solid precursor obtained from the NIS experiment is shown in Fig. 3 [2]. For the NIS experiments, Fe(NO₃)₉H₂O, which is the starting material for the precursor, was prepared from 95.4% enriched ⁵⁷Fe. The arrows indicate the upper limit of the acoustic modes as predicted by the Debye approximation [3] and mode composition factor [4]. For comparison the VDOS predicted on the basis of DFT calculations using B3LYP hybrid density functional as implemented in Gaussion03 is also shown.

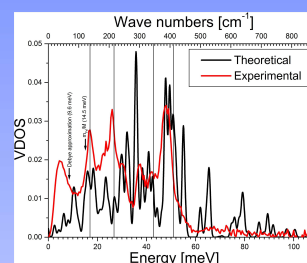


Fig. 3 VDOS of ⁵⁷Fe in precursor at ~70 K; arrows indicates the upper energy limit of the acoustic modes

Double zeta basis sets were used for C, H, Cl, N and O atoms. For the Fe atoms, the Stuttgart relativistic ECP pseudopotential was combined with the corresponding basis set for the Fe valence shells [5]. On the basis of a normal coordinate analysis, the VDOS is calculated [6].

For an initial analysis, the 24 hydrogen atoms at the carbon and nitrogen atoms were not included in the calculation.

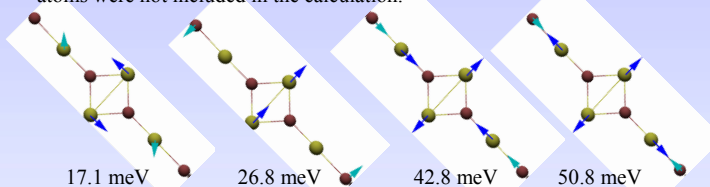


Fig. 4 Vibrations predicted by theoretical calculations and the corresponding peaks are indicated by vertical lines in Fig. 3

Vibrations in the high-energy region are mainly associated with displacements of all Fe atoms. Especially the peak at ~48 meV contains several modes as predicted by calculations.

Conclusion

First studies of a polynuclear iron complex using MS and NIS are presented. From the Mössbauer spectra we conclude that the Fe is in Fe(III) state. During the oxidation reaction, a second Fe(III) species is formed. From NIS, the VDOS is obtained and some of the peaks are assigned.

References

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