Radical Mechanism of a Place Exchange Reaction of Au Nanoparticles

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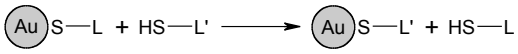
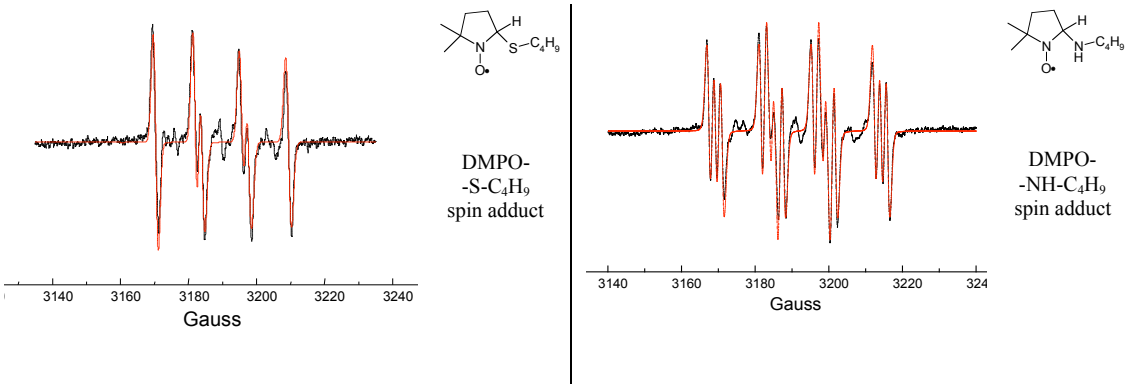
Ligand exchange reaction (1) is a convenient method to prepare functionalised metal nanoparticles, but its mechanism is not fully understood. The reaction is facilitated under oxidising conditions, for example in the presence of air.



(1)

The aim of this project was to investigate if free radicals are formed during place exchange reaction using spin-trapping technique.

Experimental results showed that thiol radicals are formed in an amount of 3-12% when triphenylphosphine protected gold nanoparticles were mixed with thiols in the presence of a spin-trap, DMPO. The formation of thiol spin-adduct by Forrester-Hepburn or Eberson mechanism was ruled out by several control experiments. Moreover, gold nanoparticles were found to act as oxidation catalysts for other substrates, for example amines can be oxidised to the corresponding radicals.



A mechanism for radical formation is proposed, in which oxygen is absorbed on gold surface to form an active species, which abstract a hydrogen atom from the substrate, leading to the formation of a short-lived radical. This mechanism is consistent with other experimental and literature data.

References

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