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Radical reactions with nano-particles suspended in aqueous solutions

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Radicals are formed near surfaces in a variety of processes, e.g. in catalytic processes, in electrochemistry, in photo-catalytic processes, in environmental processes etc. It was therefore decided to measure the mechanisms and kinetics of reaction of M°-NPs, M=Ag; Au; Cu; Pt; Pd, Pt/Au-alloy-NPs and TiO_2-NPs with methyl radicals. (All the M°-NPs were prepared by reduction of the corresponding salts with $NaBH_4$). These reactions are very fast, approaching the diffusion-controlled limit, forming long-lived transients with (M°-NP)-$(CH_3)_n$ s bonds. These transients decompose to yield C_2H_6 for Ag°-, Au°- and TiO_2-NPs, CH_4 for Cu°-NPs, for Pt°- and Pd°-NPs most methyls remain bound to the NPs, and are released as methane when H_2 is added to the suspension, though some C_2H_6, C_2H_4 and oligomerization products are formed and for the Pt°/Au°-NPs, even for [Pt]/[Au] = 3 the main product is C_2H_6 though some methyls remain bound to the NPs.

M°-NPs, M= Au and Ag, catalyze the reduction of water by the $^{\cdot}C(CH_3)_2OH$ radicals. Surprisingly Pt°-NPs do not catalyze this reaction. The reaction of $^{\cdot}C(CH_3)_2OH$ radicals with M°-SiO_2-NCs is more complicated. At low [M°-SiO_2-NCs] catalyze the reduction of water by these radicals, for M=Pt the NCs are clearly a catalyst while the NPs are not, for M=Ag the NCs catalyze the reduction of water but considerably less than the MPs, for M=Au both the MPs and the NCs catalyze the reduction of water. At high [M°-SiO_2-NCs] the reduction of water is considerably decreased and at high doses of radicals the Pt°- and Ag°-NCs do not catalyze the reduction of water by the $^{\cdot}C(CH_3)_2OH$ radicals and induce their disproportionation, and their reduction by H_2, on the NCs surfaces. Thus the SiO_2 support affects considerably the properties of the M°-NPs and the nature of this effect depends on the nature of the M°-NPs.

Biography

Dan Meyerstein has completed his PhD at The Hebrew University of Jerusalem, Israel in the year 1965 and later he is a research fellow at Argonne National Laboratory, USA. Presently, he is a Professor of Chemistry, Biological Chemistry Department, Ariel University, Israel. He is known for the application of radiation-chemical techniques to the solution of problems in Inorganic and Bioinorganic Chemistry; especially reactions of radicals with transition-metal complexes and with metal surfaces, properties of transition-metal complexes with uncommon oxidation states and properties of transient complexes with s metal-carbon bonds in aqueous solutions. The systems chosen relate mainly to catalysis, radical processes in biological systems and to environmental problems. These studies are often involved also the use of electrochemical techniques; stopped-flow; EPR etc.

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