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A Mechanism for Selectivity in Heterogeneous Redox Catalysis

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Selective acceleration of metal cation oxidation by silver halide in the presence of silver nanoclusters is observed only when the diameters of the cations correspond to the spacing of the regular set of interatomic hollows of the catalyst surface; this is probably associated with their longer retention in the reaction zone due to the increase in the coordination number in the coincidentally occurring compact packing.

Atom-dimensional correspondence of the reacting molecules and catalyst surfaces has long been considered an important factor in the efficiency of heterogeneous catalysis.[1,2] It is shown below that its role is determining in redox reactions with electron transfer through the conducting particle, and the catalytic character is revealed only for substances with particle diameters almost the same as the spacing of the regular set of interatomic hollows on the heterogeneous catalyst surface.

Photographic developing substances are catalytically oxidized by silver halide in the presence of silver nanoclusters of latent image[3] (NLI) created by photolysis. Non-developing reducing agents react with the exposed and unexposed silver halide at the same rates and give no traces of a visible image under any conditions. It has been observed[4] that the newest values for the effective diameters[5] of monoatomic developing particles are close to the interhollow distances of the surface (111) of silver with the closest packing of atoms.

In a century and a half of photography, almost all of the elements of the periodic table have been checked with respect to their developing properties. The developing monoatomic ions and atoms[3,6–10] are listed in Table 1 and form two groups.[4] The first includes particles with radii 0.075–0.093 nm and with coordination number 6. The second group includes particles with radii 0.140–0.150 nm with coordination number 9 (not accounting for slight differences[11] for atoms of coordination number 12). They all cover intervals

Table 1 Correspondence between the sizes of the developing monoatomic particles and the spacing of the regular set of interatomic hollows on the silver surface (111).

Developing particle	Particle radius/nm	Average radius/nm	Half-distance between hollows/nm	Coordination number
Cu^{+}	0.091			
Co^{2+}	0.079 ls [a]			
Cr^{2+}	0.087 ls [a]			
Fe^{2+}	0.075 ls [a]			
Mn^{2+}	0.081 ls [a]			
Ru^{2+}	0.085			
V^{2+}	0.093	0.084	0.083	6
Mo^{3+}	0.083			
Ti^{3+}	0.081			
V^{3+}	0.078			
W^{4+}	0.080			
U^{5+}	0.090			
Eu^{2+}	0.144			
Au^{0}	0.144			
Cd^{0}	0.149			
Ge^{0}	0.140 [b]	0.145	0.144	9
Hg^{0}	0.150			
=O	0.140			
≡N	0.150			
Tl^{+}	0.164	0.164	0.166	6

[a] Low-spin state[5] (ls). [b] In alloys.[11]

one order of magnitude less than the whole range of ionic radii.[5]

Ions of non-selective reducing agents have other sizes,[5] for example, As^{3+} (0.072/6), Ce^{3+} (0.115/6 and 0.134/9) in carbonate solution,[12] and Sn^{2+} (0.110/6 and 0.125/9 from the properties of neighbours in the periodic table). Of the ions Mn^{2+} and Mn^{3+} (0.072/6)[13] with suitable potentials, only the first one develops; the second develops for ions Ti^{2+} (0.100/6) and Ti^{3+}, and the latter develops among U^{3+} (0.117/6), U^{4+} (0.103/6) and U^{5+}.[6a]

The developing cations are usually used in the presence of ligands, which provide the redox potential, *i.e.*, the ratio of the concentrations of free oxidizing and reducing ions of the given metals must not be higher than a certain level, if this is allowed by the instability constants of their complexes. The developing activity of a cation is provided by ligands of various sizes, for example, in the case of Fe^{2+} they vary from monoatomic fluoride, which binds only with Fe^{3+} and is known as a single halide never adsorbing on silver, to multiatomic formate, oxalate, citrate, ethylenediamine tetraacetate, and others,[3] in whose presence the ratio of the concentrations of the free ions Fe^{2+} and Fe^{3+} exceeds the required level.

The simplest non-ionic developers are deposited selectively on NLI without a chemical reaction. Mercury or cadmium[7] vapours themselves develop daguerreotypes or accelerate a routine development. The latter was also noticed in preliminary treatment with germanium hydrosol.[8] Gold(I) disproportionates and precipitates gold atoms on NLI which results in the acceleration of the routine development[9] or the formation of a gold image.[10] However, copper (0.128 nm) or tin (0.151–0.159 nm) with unsuitable atom sizes are not precipitated selectively by disproportionation of Cu^{+} and Sn^{2+} (for example, under the conditions in ref. 14).

Any multiatomic developing molecule[3] contains at least one oxygen or nitrogen atom with van der Waals radii[15] which are within the second group of dimensional correspondence (see Table 1). Covalently-bound atoms of other elements have unsuitable radii:[15,16] hydrogen, 0.120; fluorine, 0.135; chlorine and carbon, 0.180; sulfur, 0.185; phosphorus, 0.190 nm; *etc.* Their presence in the molecule does not provide developing ability. Borohydride ion BH_4^{+} with intrinsic radius about 0.210 nm[17] and external tetrahedron of hydrogen atoms reduces silver halides non-selectively.

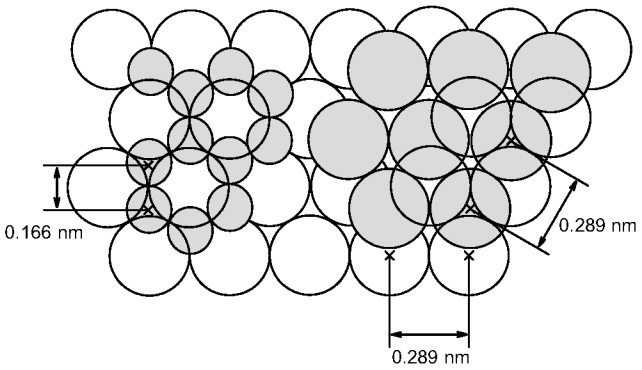

Fig. 1 Surface packing of particles with high coordination numbers. Atoms of the silver surface (111) (light circles); monoatomic particles of two sizes, for which catalytic acceleration of the condensation processes (for atoms) or electron loss (for ions) are observed (shaded circles).

The average radii in both groups of particles coincide with the half-distances between the interatomic hollows of the surface (111) of silver. When all of the hollows are filled, the particles with radii 0.083 nm are closely packed (see Fig. 1) but particles with radii 0.144 nm are closely packed only when each second hollow is filled (as if a new layer of silver atoms were packed). When each third hollow is filled, a particle radius of 0.166 nm with coordination number 6 corresponds to the closest packing. Although Tl^{+} (0.164 nm) does not develop independently due to the blocking of NLI with insoluble compounds of Tl^{3+}, it considerably accelerates the development by ions and neutral molecules,[18] which are capable of regenerating Tl^{+}. All vigorously developing multiatomic particles[3] contain pairs of O or N atoms at distances of 0.28–0.30 nm or multiples,[11,16] *i.e.*, they can be packed in the hollows simultaneously by two such atoms.

Balandin[1a] was the first to notice the special role of interatomic hollows on the catalyst surface. Atoms of reacting molecules in them "are attracted especially strongly for the same reason as that by which metal atoms tend to be arranged in the closest packing in the crystallization. The minimum of the potential energy exists here due to the possibility of interaction with several surrounding atoms... Here we have a monolayer surface alloy of sorts... The interaction of the catalyst with the substrate occurs under the action of valent-chemical forces, and the potential energy barrier of the reaction decreases because bonds inside the molecule weaken".[1b]

All this relates in full measure to metal atoms, which form metallic bonds with the substrate in the condensation development and, perhaps, to multiatomic developing molecules. However, atom-dimensional correspondence fitting the principle of formation of close-packed states are also found for developing metal cations. In this case, the possibilities of the formation of valent-chemical bonds and chemisorption on silver are far from evident, and the mutual coulombic repulsion must counteract a prolonged close packing of particles in the surface layer.

In this connection it seems helpful to account for the dynamic aspect of the electron transfer reaction through the conducting catalyst to the surface of the oxidizing salt. Since ions in contact with the surface for a short time may not succeed in transferring the electron, additional retention of the particle in the reaction zone must increase the probability of electron transfer. When the particle encountering the surface of silver nanoclusters turns out to be in the surroundings of the close-packing neighbours, its coordination number and at least van der Waals retention forces become two or three times greater than those at other interhollow distances on the surface of silver chelate, which does not provide sufficiently close proximity.

Several compensating electrostatic factors[3] may favour this. First of all, cations can be attracted to the surface due to the considerable negative charge of the silver halide microcrystals prepared in excess of halide anions. NLI in modern photographic layers most often appear on the crystalline faces {111} of silver halide, whose surface is completely formed from halide anions. In addition, the reaction considered occurs in the medium of a polar solvent with the highest dielectric constant. Oriented molecular dipoles of water create electrostatic fields sufficient even for the breaking of ionic bonds in the dissolving of salts. Impacts with the surface may rearrange the mobile (without a rigid structure) hydrate surrounding of cations into the ordered counterlayers of negative charges, whose electrostatic field weakens the mutual repulsion of the adjacent cations. The van der Waals radius of the bound oxygen and the average length of the hydrogen bond in water (*ca.* 0.280 nm) also favour efficient structural correspondence between the joining charged monolayers of oriented water dipoles.

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