

Physicochemical Characteristics of Cobalt Selenides & Their Catalytic Activities

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The decomposition of H_2O_2 on cobalt selenides ($CoSe$, $CoSe_{1.5}$ and $CoSe_2$) surfaces has been studied. Electrical conductivity, magnetic susceptibility, surface areas of cobalt selenides have also been determined. The effect of pH of the medium and concentration of hydrogen peroxide on its decomposition has also been investigated. It is inferred that cobalt atoms rather than anions are responsible for the decomposition of H_2O_2 .

IN earlier papers, we have reported the decomposition of hydrogen peroxide on cobalt oxides¹, cobalt sulphides² and cobalt tellurides³. The activity of cobalt oxides has been related with electrical properties, chemical composition and other physical properties. Hart *et al.*⁴ investigated the decomposition of hydrogen peroxide on oxides of first transition metal series and reported a definite pattern of activity. In general *p*-type oxides were more active than *n*-type. Presently we have studied the decomposition of H_2O_2 on cobalt selenides which are metallic conductors. It will be of interest to correlate catalytic activity with conductivity. Perusal of literature shows that no such work has been done on cobalt sulphides, selenides and tellurides. We have also compared the catalytic activity selenides with those of oxides, sulphides and tellurides, studied earlier.

Materials and Methods

Catalysts — Cobalt powder (Alfa Inorganic Ventron, USA, -50 BSS, 99.9%) and selenium (99.9%, BARC, India) were taken in a silica tube of 6 mm diameter. The silica tube was evacuated to $>10^{-5}$ mm Hg and sealed. The ratio of the cobalt to selenium was varied to prepare compounds of different compositions, i.e. $CoSe$, $CoSe_{1.5}$ and $CoSe_2$. The mixture was gradually heated to 900° and maintained there for 48 hr. The rate of heating was 4°/min. After heating the samples were quenched in cold water. Every time, a fresh silica tube was used for preparing the sample.

Hydrogen peroxide decomposition — Decomposition of H_2O_2 was studied according to the procedure described by earlier workers⁵. The reaction was studied at three temperatures, viz. 30°, 40° and 50°. The concentration of H_2O_2 taken was 0.5% and 50 mg of the catalyst were taken for each run. Kinetic parameters such as apparent energy of activation, pre-exponential factors were determined making use of the Arrhenius equation. Measurements of electrical conductivity, surface area and magnetic susceptibility were made as given in an earlier publication¹.

Results and Discussion

Whereas $CoSe$ is active for the decomposition of hydrogen peroxide, $CoSe_{1.5}$ and $CoSe_2$ are inactive. The rate of decomposition is first order with respect to H_2O_2 . The energy of activation for the decomposition of H_2O_2 is of the order of 8.6 kcal mol⁻¹, 15.5 kcal mol⁻¹ for cobalt oxides¹ and for cobalt sulphide² it varies from 8 to 19 kcal mol⁻¹. The values of rate constants, energy of activations and frequency factors, for cobalt oxides, sulphides, tellurides and selenides are given in Table 1. The activity pattern of cobalt chalcogenides follows the order: cobalt oxides > cobalt sulphide > cobalt selenide ($CoSe$) > cobalt telluride ($CoTe$).

In cobalt oxides and sulphides both Co^{2+} and Co^{3+} species are present. Co^{3+} plays the dominant role in the decomposition of H_2O_2 . But in $CoSe$, $CoSe_{1.5}$, $CoSe_2$ only Co^{2+} exists. This is why the activity of cobalt selenide is much less as compared to the activity of cobalt oxides or cobalt sulphides.

Electrical conductivity, magnetic susceptibility and catalytic activity — Whereas cobalt oxides are *p*-type semiconductors, cobalt sulphides are partly semiconductors and partly metallic^{6,7}. Though a definite relationship between catalytic activity and electrical conductivity was found in the case of oxides, no such relationship was found to exist in the case of cobalt sulphides, selenides and tellurides.

TABLE 1 — KINETIC DATA FOR DECOMPOSITION OF H_2O_2 (0.5%, WT/VOL)

Catalyst	Rate constant (<i>k</i>) × 10 ² (min ⁻¹) at 40°	<i>E_a</i> (kcal/mole)	Log ₁₀ A	Ref.
$CoO_{1.16}$	45.90	7.7 ± 0.1	5.0	1
$CoS_{1.69}$	20.72	8.4 ± 0.1	5.2	2
$CoTe$	1.34	1.7 ± 0.1	1.4	3
$CoSe$	2.49	8.6 ± 0.1	3.5	—
$CoSe_{1.5}$	Inactive	—	—	—
$CoSe_2$	do	—	—	—

The amount of catalyst taken: oxide and sulphide, 10 mg; and $CoSe$, $CoTe$, 50 mg.

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In the case of oxides, rate constants for decomposition of H_2O_2 decreases as the χ_g value decreases except for $CoO_{0.92}$ where cobalt is in excess¹. The cobalt sulphides are highly paramagnetic. They are also active for the H_2O_2 decomposition, but no definite relationship could be established between the rate constants and χ_g values. Whereas $CoSe$, $CoSe_{1.5}$ are ferromagnetic ($\chi_g = 4.2 \times 10^{-6}$ c.g.s.g) $CoSe_2$ is paramagnetic. In general, catalytic activity seems to be linked to the paramagnetic behaviour.

Relationship between surface area and catalytic activity—A definite relation between the catalytic activity and the surface area has been found for the oxides and sulphides; the surface area decreases as the temperature of the preparation increases. This is true irrespective of the starting material for the preparation of oxides and sulphides^{1,2}. Cobalt selenides were prepared at comparatively higher temperature. The values of the surface areas are $CoSe = 2.8$, $CoSe_{1.5} = 2.7$ and for $CoSe_2 = 2.6$ m^2/g . The surface area of selenides are low, so are their catalytic activities. Since all of them possess almost equivalent surface area, the difference in their activity cannot be attributed to the surface area alone.

Effect of varying pH on decomposition of H_2O_2 —During the course of the autodecomposition of 0.5% (w/v) H_2O_2 , the pH of the solution changes from 3.2 to 6.4. The rate of decomposition does not change on adding standard buffer up to pH 4 to 7, beyond that, the rate of decomposition of hydrogen peroxide becomes very fast. The rate is not affected to any appreciable extent either in the acidic or alkaline medium in the presence of selenides. The values of the rate constant for oxides, sulphides, selenides and tellurides at pH values are given in Table 2.

Effect of concentration on the decomposition of H_2O_2 —In order to find the optimum concentration of H_2O_2 for the decomposition on cobalt chalcogenides, the rates of decomposition of H_2O_2 at different concentrations were determined. It is observed that the rate of evolution of oxygen increased up to 1.5% H_2O_2 , beyond which it started decreasing. The decrease occurred beyond the concentration of 0.96% (w/v) in the case of sulphides. There is no decrease of evolution of oxygen up to 1.8% (w/v) H_2O_2 on cobalt selenide (Fig. 1). In spite of low surface areas of cobalt selenides, no saturation of the

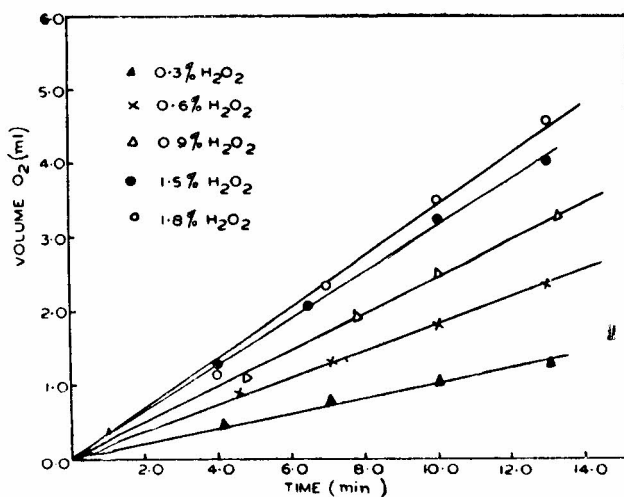


Fig. 1 — Decomposition of H_2O_2 on cobalt selenides at different concentrations of H_2O_2 (% wt/vol)

surface seems to occur even at a concentration of 1.8% (w/v) H_2O_2 . Unlike oxides and sulphides, the species adsorbed on selenide surfaces are not HO_2^- .

Crystal structure of cobalt selenides—The X-ray photographs of cobalt selenides $CoSe$, $CoSe_{1.5}$ and $CoSe_2$ were taken. $CoSe$ was found to possess hexagonal NiAs type structure with unit cell parameters $a = 3.621$ Å, $c = 5.289$ Å, $c/a = 1.462$. $CoSe_{1.5}$ was found to be a mixture of $CoSe$ and $CoSe_2$. These observations are in conformity with those given in the literature. $CoSe_2$ has a pyrite type (FeS_2) structure with unit cell ($a = 5.285$ Å). $CoSe_2$ is formed continuously from $CoSe$ by a partial loss of the metal atom. This loss of Co per unit area may be responsible for the loss of activity. The difference in the catalytic activity of different cobalt selenides may be due to a difference in their crystal structure. In NiAs type the coordination number for cobalt atom is 6:6 while in pyrite type structure, it is 4:6.

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TABLE 2 — EFFECT OF pH ON THE DECOMPOSITION OF H_2O_2 (0.5%, WT/VOL) AT 40°

Catalyst	$k \times 10^2$ (min ⁻¹) at pH			
	3.4	4.0	7.0	8.4
$CoO_{1.46}$	44.90	1.88	3.13	12.66
$CoS_{1.96}$	22.46	3.05	5.98	89.12
CoTe	1.34	1.28	1.15	2.69
CoSe	4.92	4.58	2.77	5.18