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Gamma-Irradiation Effect on the Catalytic Behavior of Binary Oxide Catalysts

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Decomposition of hydrogen peroxide in aqueous solution was used for testing the effect of gamma radiation on the catalytic activity of $Co_xFe_{3-x}O_4$, with $0 \leqslant x \leqslant 3.0$. The activity variation was interpreted in terms of the catalysts electronic structure. The presence of Co^{2+} on octahedral sites is superior to Fe^{2+} in the catalytic process. However, γ-irradiation can produce a considerable effect on the catalytic activity due to its influence on the active site concentration and cation distribution.

Results of most studies[1-3] on H_2O_2 decomposition indicate that among the decisive factors governing the catalytic activity is the presence of ions in various valency state as a catalytically active component. Cobalt-iron spinel oxides which can be represented as $Co_xFe_{3-x}O_4$ with $0 \leqslant x \leqslant 3.0$ were reported[4] to possess an activity towards H_2O_2 decomposition. As the activity can be explained in terms of intrinsic factors such as the electronic structure of the catalysts, the sensitivity of catalysts to ionizing radiation can be account.

Effect of γ-irradiation on the activity of various catalysts has been studied by several workers.[5-7] Caffrey and Allen[5] have found that the catalytic activity of silica gel in the decomposition of pentane was increased by γ-irradiation. Kohn and Taylor[7] have reported that these changes in the catalytic activities of silica gel and alumina in deuterium-hydrogen exchange were related to changes in the internal pore structures of the irradiated catalysts.

The present study is devoted to the effects of γ-irradiation on the catalytic behavior of cobalt iron oxides, in which intrinsic factors are taken into account.

Experimental

Cobalt-iron oxides over the complete composition range of the system ($0 \leqslant x \leqslant 3.0$) were prepared using analar basic cobalt(II) carbonate, iron(III) carbonate, and freshly prepared iron(II) carbonate. Iron(II) carbonate in molar ratio $(1-x)$ was added in the composition range $0 \leqslant x \leqslant 1.0$. The appropriate amounts of the carbonates were suspended in distilled water, stirred well, evaporated to dryness and then dried at 110 °C. The preparations were calcined in air at 300 °C for 4 h. The x values were 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0.

All samples calcined at 300 °C for 4 h, were γ-irradiated at ambient temperature with gamma rays using ^{60}Co cell with a dose rate of 27 rad s^{-1} for 70 h.

X-Ray diffraction patterns (XRD) for unirradiated and γ-irradiated samples were obtained with the aid of philips unit, type PW 2103100 using a Cu target and Ni filter.

Infrared spectra for specimens were recorded using the KBr technique in the range of 1000—200 cm^{-1} with the aid of infrared spectrophotometer Model 599B, Perkin Elmer.

The activity of the catalysts towards H_2O_2 decomposition was evaluated in the liquid phase using the gasometric technique of Cota et al.[8] Catalyst samples (100 mg) were introduced into a thermostated reaction vessel containing standardized 25 ml of 0.4 M H_2O_2 (1 M=1 mol dm^{-3}).

Results

The XRD patterns (Fig. 1) show that cobalt-iron spinel oxides have indeed been formed at 300 °C. The existence of XRD lines corresponding to d-values of 2.53, 1.48, and 1.61 Å as the more intensive lines in the spinels after γ-irradiation reveals that, at our experimental conditions, γ-irradiation preserves the spinel structure of all samples.

The recorded IR spectra for unirradiated and γ-irradiated cobalt-iron oxides are shown in Fig. 2. The expected absorption bands for the ferrites have two intense broad frequency bands sited in the region of 550—600 cm^{-1} (ν_1) and 370—390 cm^{-1} (ν_2) depending

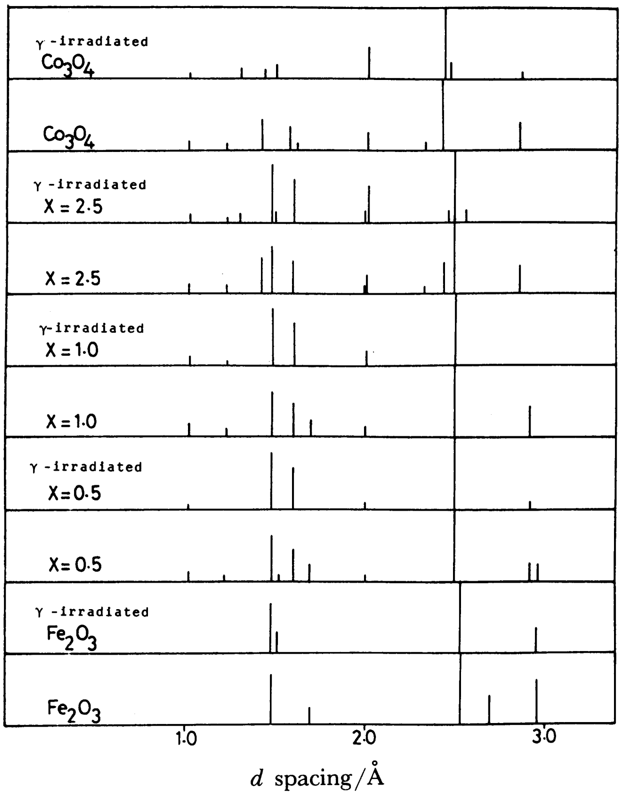

Fig. 1. XRD for unirradiated and γ-irradiated samples.

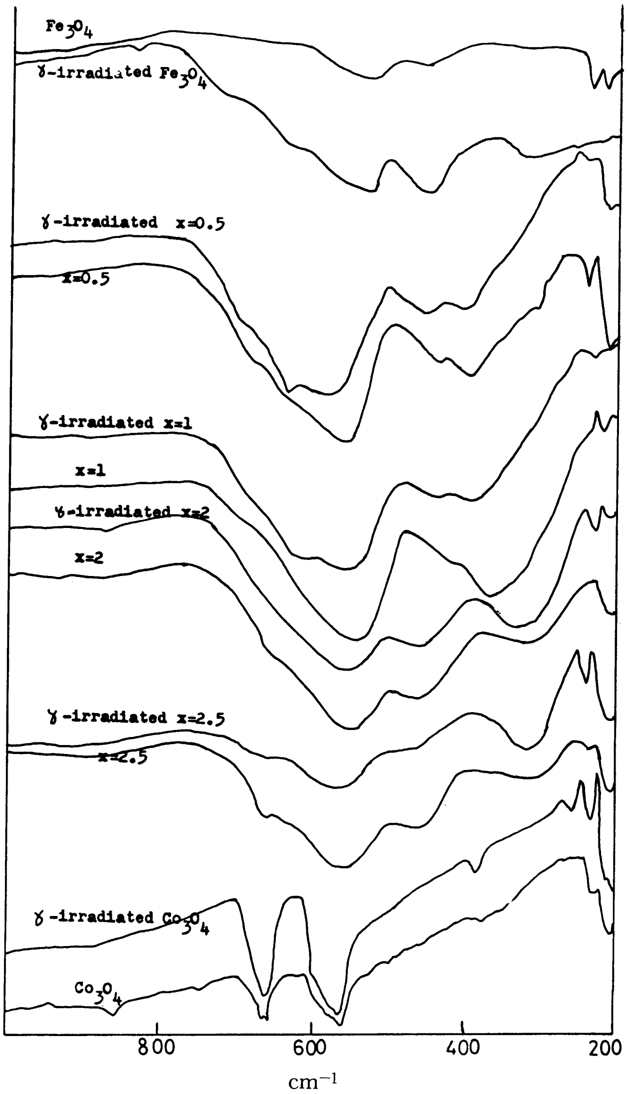

Fig. 2. IR spectra for unirradiated and γ-irradiated cobalt-iron oxides.

on the composition. At 330—350 cm^{-1} there is other band (ν_3) appeared with high concentration of cobalt (x=2.0, 2.5). At 260 cm^{-1} a small band (ν_4) was assigned. Waldron[9] attributed the ν_1-band to the intrinsic vibration of the tetrahedral groups and ν_4 to the octahedral groups. The ν_3-band was reported[9] to be assigned to the vibrations of the bivalent metal ion-oxygen complex. Preudhomme and Tarte[10] reported that ν_4 depends on the mass of bivalent tetrahedral cations. The presence of two-side band around 400 cm^{-1} in rich-iron specimens, in the present study, reveals the presence of Fe^{2+} ions in octahedral sites as confirmed in $Ni_{1-x-y}Fe^{2+}_{x}Zn_{y}Fe^{3+}_{2}O_4$.[11]

When cobalt-iron spinels were treated with gamma rays, a displacement of the frequency bands was observed. This displacement can be attributed to gamma-induced different metal valencies and/or cation redistribution. The appearance of ν_3 in both Co_3O_4 and Fe_3O_4 informed an increase in the crystallinity of Co_3O_4 and Fe_3O_4 after γ-irradiation.

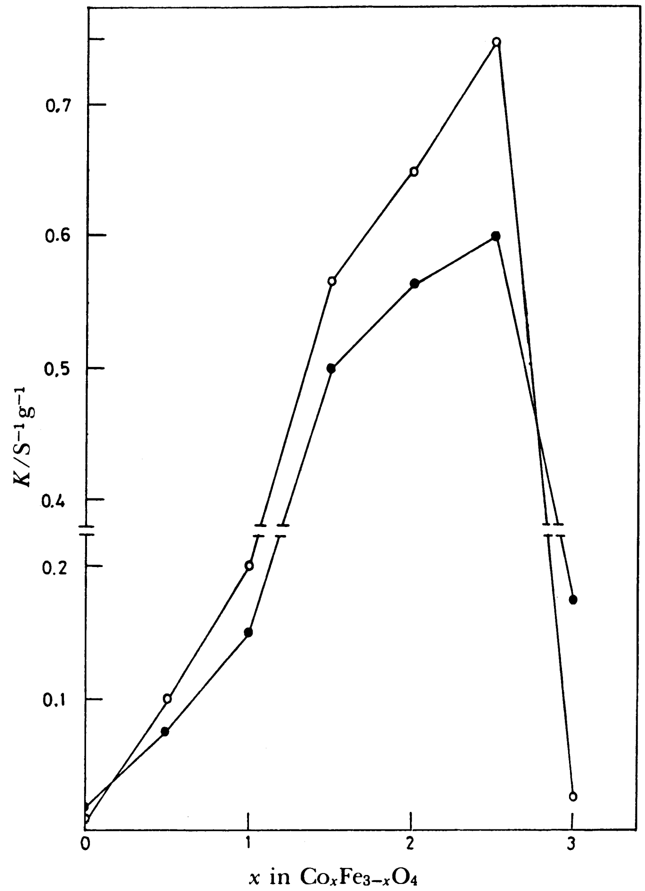

Fig. 3. Initial rate for H_2O_2 decomposition over unirradiated and γ-irradiated $Co_xFe_{3-x}O_4$, at 30 °C. ●: Unirradiated, ○: γ-irradiated.

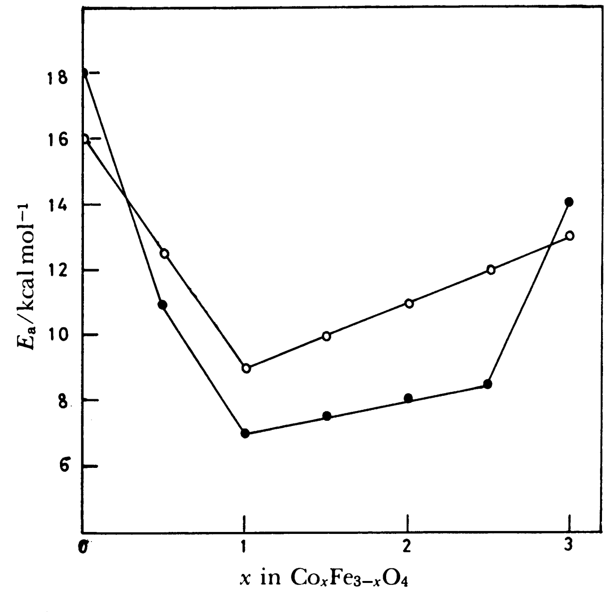

Fig. 4. Activation energy for H_2O_2 decomposition versus composition for unirradiated and γ-irradiated $Co_xFe_{3-x}O_4$. ●: Unirradiated, ○: γ-irradiated.

The reactivity of the unirradiated and γ-irradiated spinels is illustrated in Figs. 3 and 4. The H_2O_2 decomposition kinetics were found to follow a first order rate equation with respect to H_2O_2, with induced correction for self decomposition at the experimental conditions. Gamma-irradiation increased the specific rate constants for $0 \leqslant x \leqslant 3.0$ and decreased that of $x=3.0$ sample.

Since the initial rates are dependent on the catalyst microstructure, surface morphology[12] and activation energy was selected independently. As shown in Fig. 4, γ-irradiation induces a marked change in E_a for the catalytic decomposition of H_2O_2 over $Co_xFe_{3-x}O_4$.

Discussion

In cobalt iron oxides, there are two types of bivalent ions readily promoted to the trivalent state, i.e., Fe^{2+} and Co^{2+}. The electronic structures of Co_3O_4 and Fe_3O_4 were reported as $(Co^{2+})_t[Co_2{}^{3+}]_oO_4$[13] and $(Fe_1^{3+})_t$-$[Fe_1^{2+}Fe_1^{3+}]_oO_4$[14] respectively. Although Co^{2+} in Co_3O_4 is positioned on isolated tetrahedral sites, it has greater activity in H_2O_2 decomposition than octahedral Fe^{2+} ion in the inverse spinel Fe_3O_4, as seen in Fig. 4. Moreover Hart et al.[15] reported that p-type semiconducting oxides are more active catalysts for H_2O_2 decomposition than n-type which is confirmed in the present study. Jonker reported an n-type behavior for $x \leqslant 1.0$ in the $Co_xFe_{3-x}O_4$ system, while those with composition of $x \geqslant 1.0$ were p-type semiconductors. The fact that there is a contradiction between the trend of rate variation in Fig. 3 and activation energy values, reveals that the microstructure parameter controls the rate values. Cota et al.,[8] when normalized H_2O_2 decomposition rates to unit BET surface area yields intrinsic catalytic activities, which follow the trend of activation energy. Thus, the intrinsic factor in the present study is the activation energy.

Considering the spinel electronic structure as Co_x-$Fe_{3-x}O_4$, when cobalt ions are substituted into the Fe_3O_4 lattice, they first replace Fe^{2+} ions on the octahedral sites (B sites), while the Fe^{3+} ions still occupy the tetrahedral sites (A sites). In cobalt-rich region with $x \geqslant 2.0$, Co^{2+} ions occupy only the A sites as represents in Table 1.

The effect of γ-irradiation on the catalytic activity is shown in Fig. 4 can be interpreted according to the induced ionization of the ions (Co^{2+} and Fe^{2+}) with formation of free change carriers (electrons). The negative effect of γ-irradiation on the activity of p-type Co_3O_4 can be attributed to the creation of anionic vacancies, while the same effect for n-type Fe_3O_4 is attributed to the cation random distribution such as $(Fe_{1-\alpha}^{3+}Fe_\alpha^{2+})_t[Fe_{1-\alpha}^{2+}Fe_{1+\alpha}^{3+}]_oO_4$ as detected by ν_2-band lowering.

The catalytic behavior for γ-irradiated mixed oxides can be ascribed to the electron diffusion from the bulk to the surface, and recombining with the higher-valency states (Fe^{3+} and Co^{3+}). Hence the concentration of the active centers (Fe^{2+} and Co^{2+}) increased. For cobalt-rich spinels, ν_1- and ν_2-band intensities and increasing in ν_3-band intensity induced by X-irradiation suggest partially inverse structure, i.e., some Co^{3+} ions on B sites invert with Co^{2+}, giving a distribution of the form $(Co_{1-\alpha}^{2+}Co_\alpha^{3+})_t[Co_\alpha^{2+}Co_{2-x\cdot\alpha}^{3+}Fe^{3+}]_oO_4$ instead of the simple distribution $(Co_1^{2+})_t$-$[Co_{2-x}^{3+}Fe_x^{3+}]_oO_4$. In iron-rich region, highering of ν_1- and ν_2-bands by γ-irradiation reveals formation of lower-valency states as the active sites on both A and B sites, with larger ionic radius leading to an activity increase as predicted.

References

1) I. Mochida and K. Takeshita, *J. Phys. Chem.*, **78**, 1653 (1974).

2) V. A. Sadykov and P. G. Grulnikov, *Kinet. Katal.*, **18**, 137 (1977).

3) V. Múcka, *Collect. Czech. Chem. Commun.*, **46**, 1876 (1981).

4) J. R. Goldstein and C. C. Tseung, *J. Catal.*, **32**, 452 (1974).

5) J. M. Caffrey and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).

6) Y. Saito and Y. Makishima, *Nature (London)*, **183**, 388 (1959).

7) H. W. Kohn and E. H. Taylor, *J. Phys. Chem.*, **63**, 966 (1959).

8) H. M. Cota, J. Katan, M. Chin, and J. F. Schoenweis, *Nature* (*London*), **203**, 1281 (1964).

9) R. D. Waldron, *Phys. Rev.*, **99**, 1727 (1955).

10) J. Preudhomme and P. Tarte, *Spectrochim. Acta, Part A*, **27**, 1817 (1971).

11) V. A. Potakova, N. D. Zverv, and V. P. Romanov, *Phys. Status. Solidi A*, **12**, 623 (1972).

12) W. C. Schumb, C. N. Salterfield, and R. L. Wentworth,

Table 1. Properties of Cobalt Iron Oxides

Composition	Cation distribution[a]	E_a for unirrad. kcal mol⁻¹	E_a for γ-irradiated kcal mol⁻¹
$Co_0Fe_3O_4$	$(Fe_1^{3+})_t[Fe_1^{2+}Fe_1^{3+}]_oO_4^{2-}$	16.0	18.0
$Co_{0.5}Fe_{2.5}O_4$	$(Fe_1^{3+})_t[Co_{0.5}^{2+}Fe_{0.5}^{2+}Fe_1^{3+}]_oO_4^{2-}$	12.5	11.0
$Co_1Fe_2O_4$	$(Fe_1^{3+})_t[Co_1^{2+}Fe_1^{3+}]_oO_4^{2-}$	9.0	7.0
$Co_{1.5}Fe_{1.5}O_4$	$(Co_{0.5}^{2+}Fe_{0.5}^{3+})_t[Co_{0.5}^{2+}Co_{0.5}^{3+}Fe_{1.0}^{3+}]_oO_4^{2-}$	10.0	7.5
$Co_2Fe_1O_4$	$(Co_1^{2+})_t[Co_1^{3+}Fe_1^{3+}]_oO_4^{2-}$	11.0	8.0
$Co_{2.5}Fe_{0.5}O_4$	$(Co_1^{2+})_t[Co_{1.5}^{3+}Fe_{0.5}^{3+}]_oO_4^{2-}$	12.0	8.5
$Co_3Fe_0O_4$	$(Co_1^{2+})_t[Co_1^{3+}Co_1^{3+}]_oO_4^{2-}$	13.0	14.0

a) Cation distribution from Ref. 4.

"Hydrogen Peroxide," Reinhold, New York (1955), Chap. 8, pp. 472, 476.

13) J. P. Suchet, "Chemical Physics of Semiconductors," Van Nostrand, Amsterdam (1965), p. 77.

14) E. Verwey, *Philips Res. Rep.*, **5**, 173 (1950).

15) A. B. Hart, J. McFadyen, and R. A. Ross, *Trans. Faraday Soc.*, **59**, 1458 (1963).