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On the Influence of γ-Irradiation upon Catalytic Selectivity

I. Oxidation of Ethylene over Supported Silver

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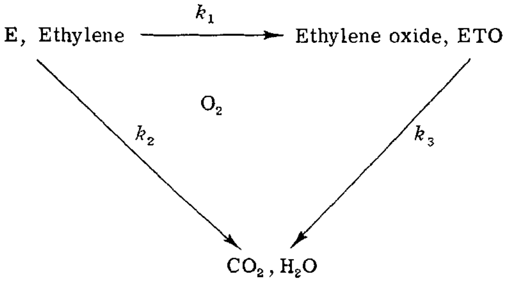
The yield of ethylene oxide in the oxidation of ethylene over a commercial (Engelhard) supported catalyst is significantly enhanced by preirradiation of said catalyst in a ^{60}Co γ-source. The effect is reversible in that reduction in H_2 and reoxidation restores normal behavior and reirradiation in air restores the enhancement. Electron spectroscopy chemical analysis studies reveal that irradiation prompts the appearance of Ca upon the surface which rediffuses into the bulk upon reduction and reappears upon reirradiation. The observed yield of ethylene oxide enhancement is attributed to chemisorbed superoxide (of Ca) formation upon the surface, a postulate in accord with the speculation that ethylene oxide is generated via surface O_2^- sites.

INTRODUCTION

The possibility of altering heterogeneous catalytic activity by high energy irradiation of the catalyst has engaged the attention of numerous investigators. Exhaustive review of the issue is found in the literature (*1*). While activity alteration has received prime attention, systems of a complex nature (multipathed reaction networks) would seem to be more attractive candidates for the assessment of high energy irradiation effects. For in such networks, yield (rate of desired species production relative to the rate of key reactant consumption) or selectivity (ratio of desired species production to that of an undesired species) might prove to be far more sensitive to catalyst modification by irradiation than simple conversion (activity). For this reason, it was deemed worthy that yield/selectivity of ethylene oxide in the catalytic oxidation of ethylene be studied over unirradiated (normal) supported silver and then over the same sample following exposure of that catalyst to γ-irradiation from a ^{60}Co source. Modifiers (e.g., ethylene dichloride) were *not* employed in these studies.

OXIDATION OF ETHYLENE OVER SUPPORTED SILVER

Consensus has it that gaseous ethylene oxidation in air or oxygen over certain solid catalysts is a triangular reaction network



We define for a totally backmixed reactor (*4, 6*)

$$S, \text{ selectivity} = \mathrm{ETO}/\mathrm{CO_2}$$
$$Y, \text{ yield} = \mathrm{ETO}/\mathrm{E_0}X$$
$$X, \text{ conversion} = (\mathrm{E_0} - \mathrm{E})/\mathrm{E_0}$$

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where E_0 is the initial (feed) concentration of ethylene.

The favored catalyst found to generate handsome yields of ethylene oxide is supported silver. Indeed, supported silver proves to be unique in that other metals which are obvious oxidation catalysts provide a very poor, often zero, yield of ethylene oxide.

Voge and Adams (*2*) and Margolis (*3*) have set forth extensive reviews of olefin and, in particular, ethylene oxidation and conclude that in the silver catalyzed oxidation of ethylene, two types of chemisorbed oxygen "sites" exist, such that in oxygen

$$\text{Ethylene}\left\{\begin{array}{l} + \text{ Metal}\cdot O_2 \xrightarrow{k_1} \cdots \text{ ETO} \\ + \text{ Metal}\cdot O \xrightarrow{k_2} \cdots \text{ } CO_2 \end{array}\right. \qquad (1)$$

Ignoring consecutive combustion of produced ethylene oxide, the above postulate would suggest that selectivity, as herein defined, is governed by the molecular to atomic chemisorbed oxygen ratio on the silver surface.

EXPERIMENTAL

Approach

To assess the influence of γ-irradiation upon a supported silver catalyst, the following plan was evolved:

(a) a sample of commercial supported silver catalyst was placed in a laboratory reactor and steady-state values of ethylene conversion, ethylene oxide and carbon dioxide yields were measured at a temperature of 280° in excess oxygen.

(b) The sample employed in (a) was removed from the reactor and exposed to γ-rays (Co-60) for a period of 10 hr. The dosage was 10^{18} eV/gm min.

(c) The irradiated catalyst sample was then returned to the reactor and measurements of conversion and yield were made as in step (a) above.

(d) The irradiated sample used in step (c) was then reduced *in situ* in H_2 for 3 hr at 300°, flushed with N_2 and exposed to air.

(e) The reduced and reoxidized sample was then tested for ethylene conversion and yield characterization.

(f) The catalyst sample was again removed from the reactor, reirradiated and tested as in steps (b) and (c) above.

Catalyst. An Engelhard commercial supported silver catalyst (Lot #E05-6-15) was employed in the initial phase of this investigation. This catalyst is deposited upon a low area (<1 m^2/g) support. Impurities present in the solutions employed in the preparation of this catalyst are, in parts per million (ppm): Pd: 0.05, Sn: 0.04, Fe: 0.19, Cu: 0.10, Si: 0.42, Mg: 0.09, Ca: 0.28, Al: 0.10, B: 0.10, Na: <1, Ba < 1.

Catalytic reactor. The Notre Dame Continuously Stirred Tank Catalytic Reactor (CSTCR), also termed the Spinning Basket Reactor was utilized in this study. As detailed earlier (*4–6*), this reactor is totally backmixed and so provides rate data free of spatial (interparticle) gradients which complicate integral reactor data analyses; yet finite, readily measurable conversions are realized. The reactor consists of a stainless steel cylindrical vessel (90 mm i.d. and 90 mm in height) equipped with four equally spaced 8 mm wide vertical baffles. The catalyst pellets are distributed equally in four baskets of one pellet thickness; said baskets are affixed to the main shaft which is rotated at 1600 rpm to assure perfect backmixing and therefore uniformity of temperature and concentrations throughout the gross confines of the reactor (*6*). While the interparticle gradients are suppressed, intraphase gradients within the pellet are, of course, determined by pellet size and the ratio of reaction velocity to that of diffusive transport within the porous pellet. Criteria phrased in terms of observables have been set forth by Wheeler (*7*), and Weisz and Prater (*8*) which permit ready assessment of intraphase diffusional intrusions. In this study, the low surface area catalyst and high value of reaction half-life (ca. 50–100 sec) assured an intraphase effectiveness of unity. Gradients external to the pellets (interphase) are easily computed since the rates of reaction and heat generation are uniform in the CSTCR and a computation of interphase mass and heat transfer coefficients then permits detection of a temperature and concentration gradients in the boundary layers surrounding the swirling pellets. Such an assessment was made in every run and interphase gradients were found to be zero.

Procedure

The CSTCR containing 9 g of catalyst was brought to reaction temperature in a flow of pure oxygen. Ethylene was then metered at the desired rate and gas chromatographic analyses were made of the effluent at frequent intervals until steady state was achieved. Feed and effluent compositions were then rechecked and temperature recorded. A simple material balance on key species then provides conversion X, and yield of ethylene oxide and carbon dioxide. Carbon balances checked within 2%. Only unreacted oxygen, ethylene and products ethylene oxide, CO_2 and water were found by chromatographic analyses.

The gas chromatograph was an F and M model 700 with a thermal conductivity detector. An 11 ft × ¼ in. column packed

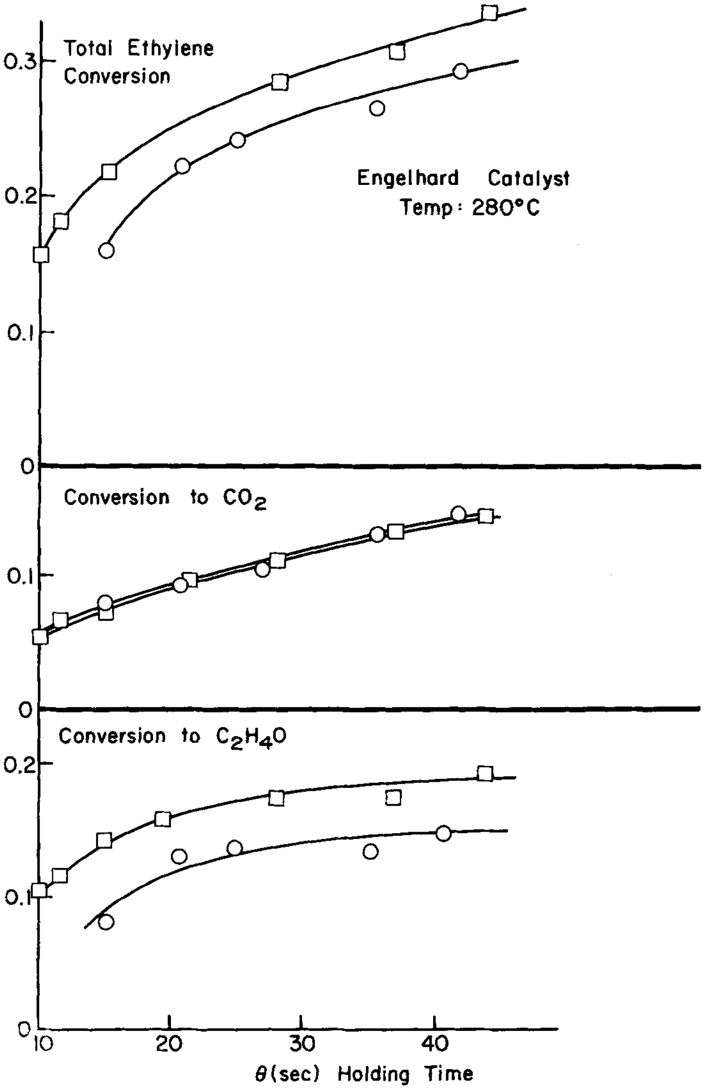

FIG. 1. Ethylene total conversion, and conversion to CO_2 and ethylene oxide vs reactor holding time for unirradiated (○) and irradiated (☐) catalyst.

with 100/120 Porapak Q was used for the separation and helium was the carrier gas flowing at 60 cc/min. A gas sampling valve with a 250 μl sample loop was used for continuous sampling of effluent gas. With the oven temperature at 100°, the relative retention times for the various gases are:

O_2	1.00	H_2O	2.76
CO_2	1.53	C_2H_4O	11.31
C_2H_4	1.86		

The reagents used were CP ethylene and extra dry oxygen and were pretreated, metered and mixed in the usual fashion.

Conditions

In all ethylene oxidation experiments, oxygen was in excess in the feed. The mole fraction of ethylene fed was varied between 0.038 and 0.025. Total pressure was about 1 atm. Studies were conducted at 280°. Residence time was varied between 9 and 44 sec.

RESULTS

In Fig. 1 are set forth the ethylene conversion, and conversions to ethylene oxide and carbon dioxide vs residence time for the

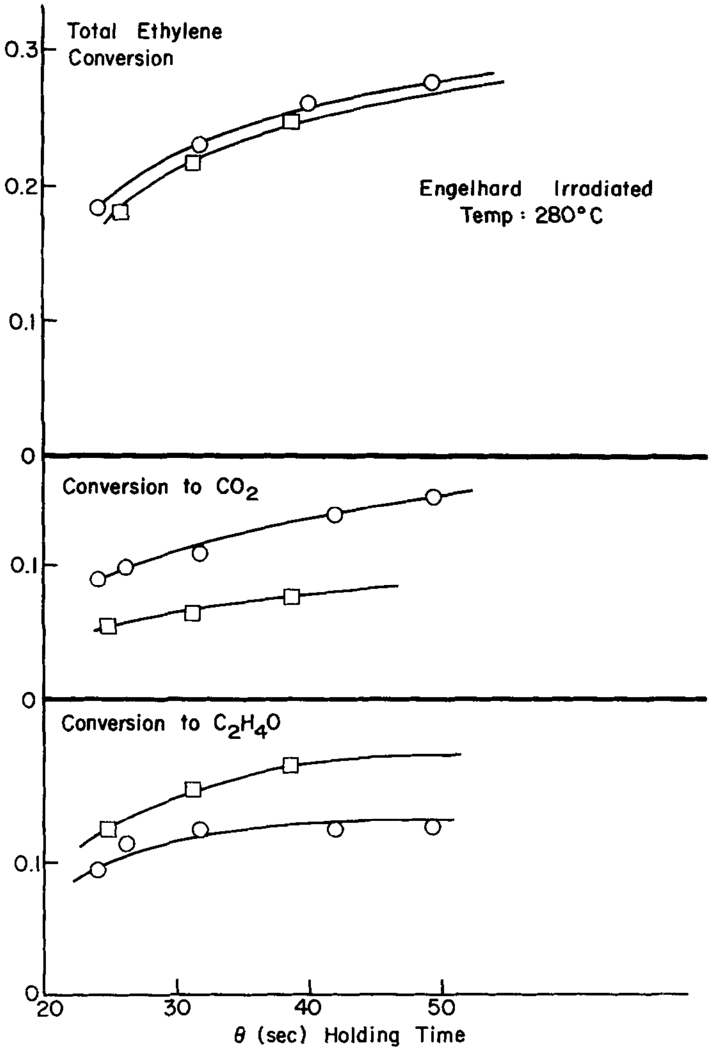

FIG. 2. Ethylene total conversion and conversion to CO_2 and ethylene oxide vs holding time for reduced-reoxidized-irradiated catalyst (○) and reirradiated catalyst (□).

normal and the irradiated catalyst sample at 280°. These data reveal that the irradiation of the catalyst sample gives rise to the following phenomenological effects:

(a) total conversion of ethylene is increased,
(b) yield of CO_2 remains unchanged,
(c) yield of ethylene oxide is increased.

Figure 2 displays the results for the reduced–reoxidized irradiated catalyst and that reirradiated following reduction–reoxidation.

The data of Fig. 2 indicate that reduction of the previously irradiated sample causes;

(a) restoration of normal activity,
(b) restoration of normal conversion to ethylene oxide and CO_2 while reirradiation of the previously irradiated–reduced–reoxidized catalyst causes;
(c) an increase in conversion to ethylene oxide,
(d) a reduction in conversion to CO_2.

In Fig. 3 is shown the yield of ethylene oxide vs conversion at 280° for the normal (A) and then irradiated (B) catalyst sample. Also shown is the reduced–reoxidized yield (C) and then that following reirradiated (D) (steps d–f as described under Experimental Approach).

These data suggest:

(a) The influence of preirradiation on conversion and yield is erased by reduction and reoxidation.
(b) The influence of irradiation is generally reversible since a cycle of reduction, oxidation and irradiation restores yield enhancement.

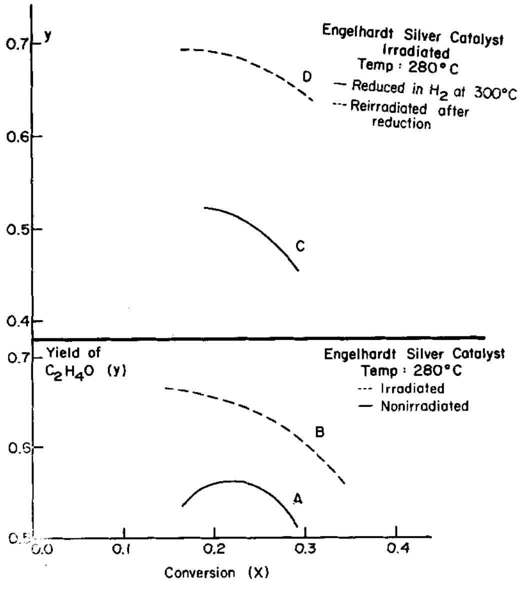

FIG. 3. Yield-conversion profile for catalyst treated as cited in Figs. 1 and 2.

Duration of Irradiation Influence

Tests conducted with a preirradiated catalyst sample over a period of three weeks revealed no decline in conversion-yield behavior.

ESCA Studies

The data secured in this initial phase of our study are provocative and as such, invite further, more detailed, microscopic studies in order that the fundamental causes of the observed phenomena be elucidated. Such detailed inquiries were undertaken by electron spectroscopy chemical analysis (ESCA). A Varian IEE-15 unit was used with a Mg source, $K\alpha$ energy line (*9*). The catalyst pellets were ground to a powder for ESCA.

In Figs. 4–7 are shown the ESCA scans of Ca for the catalyst, as received (Fig. 4); following irradiation (Fig. 5); following reduction and reoxidation (Fig. 6) and then

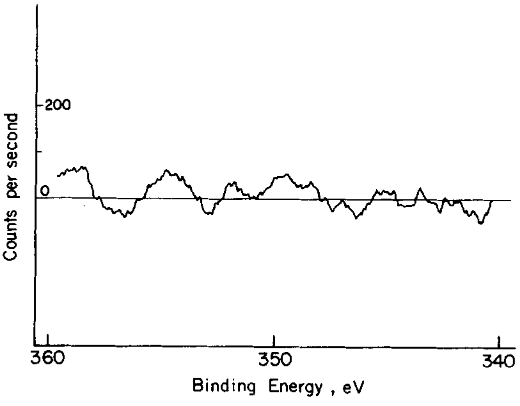

FIG. 4. ESCA scan for Ca for unirradiated catalyst.

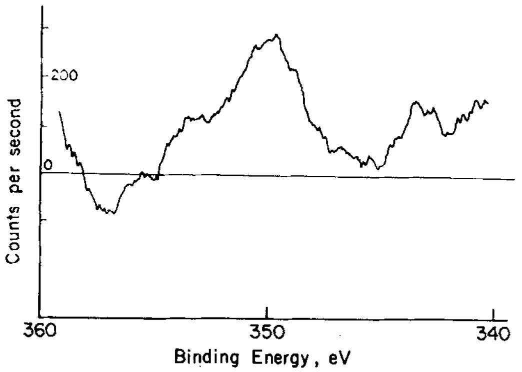

FIG. 5. ESCA scan for Ca for irradiated catalyst.

following reirradiation (Fig. 7). Scans of other species (e.g., Ag) are not shown as no change was noted following exposure to γ-rays.

DISCUSSION

Recent studies (*10*) confirm that the supported silver ethylene oxidation catalyst which generates fine yields of ethylene oxide, is indeed composed of a surface layer of two oxides which correspond to Ag_2O_3, equivalent, of course, to AgO (peroxide) and AgO_2 (superoxide). Forthcoming work points to two types of ethylene adsorption sites existing on oxygenated silver (*11*). Hence, the irradiation enhancement of yield noted by us may be traced to an increase in superoxide to peroxide ratio at the surface. This supposed population increase we ascribe to impurities, normally contained within the bulk crystal of supported silver, e.g., calcium. In accord with Gibbs adsorption theorem, little, if any, Ca would be found on the surface of the silver crystals under equilibrium circumstances (Fig. 4). For Ca surely would increase the surface tension of Ag were it to be upon the Ag surface. The appearance of Ca upon the surface following γ-irradiation (Fig. 5) may be rationalized with difficulty; however, given the evidence of its γ-ray sponsored appearance upon the surface, the corresponding enhancement in yield of ethylene oxide is readily rationalized. Pauling (*12*) noted the work of Ehrlich (*13*) who discovered the existence of the superoxide of calcium. Hence, the observed (via ESCA) appearance of surface Ca should increase the superoxide to peroxide ratio of chemisorbed oxygen to the benefit of yield. We note such a yield enhancement with the emergence of surface Ca.

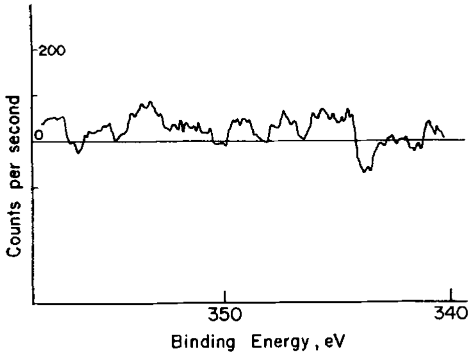

FIG. 6. ESCA scan for Ca following reduction-reoxidation of previously irradiated catalyst.

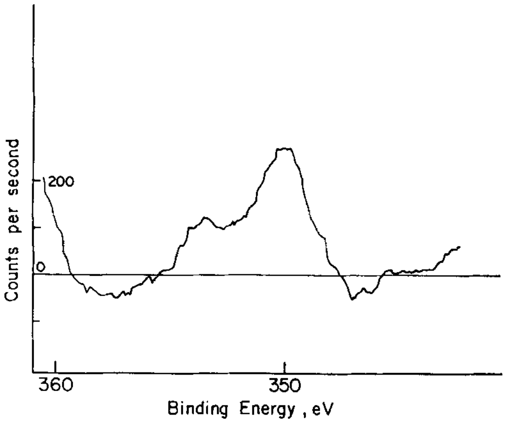

FIG. 7. ESCA scan for Ca following reirradiation of reduced-reoxidized irradiated catalyst.

Regarding the mechanism whereby Ca originally present in the bulk Ag is caused to appear upon the surface of Ag, naught but speculation can be tolerated. Measurable property changes in various materials, due to γ-irradiation, have been observed. At the energy level of our source (1.3 × 10^6 eV) the most important absorption process is the Compton effect. The resulting Compton electrons have sufficient energy to produce Frenkel pairs, but of a quantity insufficient to explain our observations. For while a process involving focusons may account for the ejection to the surface of Ca (at which point chemisorption of oxygen fixes these surface atoms), it is not clear as to how a relatively large number of focusons are created via the irradiation event.

In sum, our observations permit us to say that yield of ethylene oxide is increased with the appearance of surface Ca. With the emergence of Ca to the surface, the chemisorbed superoxide (O_2^-) to peroxide (O^-) ratio is increased to the benefit of ethylene oxide yield as noted. Reduction prompts rediffusion of the calcium hydride to the bulk (Fig. 6) and in accord with our thesis normal activity-yield behavior prevails which is then generally restored by reirradiation (Fig. 2) with reappearance of surface calcium (Fig. 7). The second irradiation seems to reduce CO_2 producing sites relative to that activity for the normal catalyst, but contrasting Figs. 1 and 2 it appears that reversibility with respect to ethylene oxide producing sites is manifest.

CONCLUSIONS

(a) Preirradiation by γ-rays of a supported silver catalyst causes activity (total ethylene conversion) enhancement at constant yield of CO_2; hence an enhanced yield of ethylene oxide (Fig. 1). Ca appears on the surface (Fig. 5) after irradiation.

(b) Reduction and reoxidation of the irradiated sample restores activity/yield generally characteristic of unirradiated catalyst (Fig. 3). Said treatment causes the disappearance of surface calcium (Fig. 6).

(c) Reirradiation of the irradiated–reduced–reoxidized catalyst restores yield enhancement (Fig. 3). Said treatment prompts the reappearance of surface calcium (Fig. 7).

(d) As calcium is capable of forming a superoxide (Pauling) the effect of γ-irradiation would seem to be that of increasing the population of ethylene oxide producing sites (O_2^-) relative to by-product CO_2 sites (O^-) as is suggested by the correlation of ethylene oxide yield with the evidence of surface calcium as revealed by ESCA.

Finally, insofar as yield alteration apparently linked to γ-irradiation induced alterations of the surface chemical composition of a supported metal catalyst is now demonstrated, one might expect that other catalytic systems may be affected in a like manner.

Note Added in Proof: Our recent studies suggest that calcium oxide is present in silver as a separate phase. Upon γ-irradiation ionization occurs (Varley mechanism); the consequent Coulombic repulsion causes Ca to be ejected into silver and thence to its surface.

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