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γ-Irradiation Enhanced Yield in the Ag Catalyzed Oxidation of Ethylene

The Kinetics of the Irradiation Process

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Previous work revealed (via x ray spectroscopy chemical analyses) the pre-γ-irradiation of supported silver catalysts causes the appearance of surface calcium, with an associated enhancement in the yield of ethylene oxide in the oxidation of ethylene. Yield enhancement is now reported as a function of time of γ-irradiation. Analysis of these data suggests a tentative model of Ca ejection from inclusions within the Ag crystallites. The experimental rate coefficient for this heretofore unobserved Ca ejection event is extracted to yield the cross-sectional area of the process.

INTRODUCTION

The partial oxidation of ethylene, generating as it does over supported silver, valued ethylene oxide and, via simultaneous and consecutive reaction paths, CO_2 and H_2O, is a catalytic reaction rich in challenge, since apparently only Ag sponsors significant yields of ethylene oxide in contrast with other notable oxidation catalysts which prompt virtually total combustion of ethylene.

In response to this challenge, we inaugurated an extensive program involving, initially, a commercial (Engelhard) supported Ag (*1–3*) and later a formulation of our own (*4*); each being employed in the study of ethylene oxidation before and after exposure of the catalyst to γ-irradiation from a ^{60}Co source. With these conversion and yield studies in the 240–280°C temperature range, we also employed x ray spectroscopy chemical analyses (ESCA) and scanning electron microscopy (SEM) in our explorations of surface chemical and morphological changes as might be induced by irradiation. These results published earlier (*1–3*) are briefly summarized insofar as they are relevant to the present inquiry:

(a) Preirradiation of the supported Ag catalyst causes a significant enhancement in the yield of ethylene oxide relative to said yield of the normal (unirradiated) catalyst at a given conversion (*2*). This enhancement is only found when Ca is present in the original catalyst (*4*).

(b) Associated ESCA studies revealed that preirradiation sponsored the appearance of Ca upon the surface of the Ag crystallites (*1*). Ca disappeared upon reduction and reappeared following reirradiation. Ethylene oxide yield correlated with the presence of surface Ca (*2*).

(c) Spherodization of the Ag particles cor-

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related with the presence of surface Ca (*3*).

(d) Irradiation in an oxygen-free atmosphere did not result in yield enhancement (*4*).

(e) Etching experiments followed by ESCA for various degrees of etching severity suggest the presence of Ca (oxide or hydroxide) as an included distinct phase within the Ag particles (*4*). These inclusions seem to exist at approximately 10 atom layers below the Ag particle surface of the normal catalyst.

While the necessity of Ca and its presence as inclusions is established (*4*), and, further, its γ-irradiation sponsored surface presence is beyond doubt, the precise mechanism whereby the included Ca is caused to migrate from within the Ag to its surface remained obscure.

Endeavoring to shed light upon this heretofore unobserved phenomenon, we fashioned an experimental program designed to establish the kinetics of the irradiation-induced Ca migration process.

EXPERIMENTAL PROGRAM

A supported silver catalyst, the preparation of which was detailed earlier (*4*), was employed in the oxidation of ethylene at 245°C and a total pressure of one atmosphere, after the catalyst sample had been exposed to γ-irradiation (dose = 10^{18} eV min^{-1} gm^{-1}) for cumulative periods of 0, 10, 20, 50, and 110 minutes at room temperature in air. Yield of ethylene oxide (moles ethylene oxide/mole ethylene reacted) was determined for various levels of total ethylene conversion. The reactor and processing network have been described earlier (*2*).

RESULTS

In Fig. 1 there are displayed the yield-conversion data for the same catalyst sample after the above-noted cumulative periods of irradiation. Maximum yield appears to be achieved after a total of fifty minutes of preirradiation. In our earlier studies, one total period of ten hours of irradiation was used (*2*).

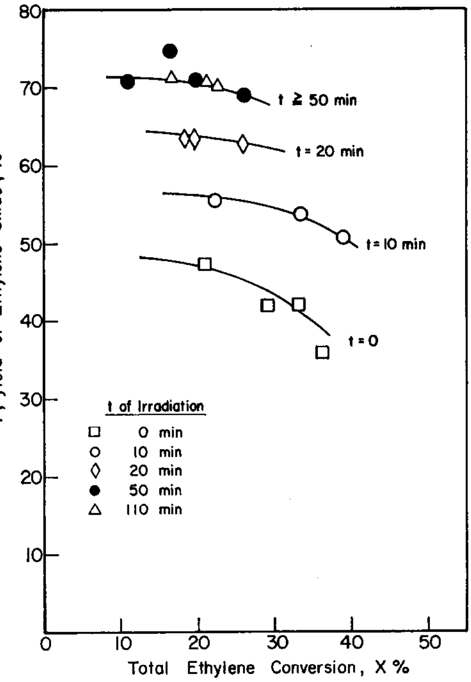

FIG. 1. Yield of ethylene oxide vs total ethylene conversion following various period of preirradiation of a supported Ag catalyst by γ-rays (Dose 10^{18} eV min^{-1} gm^{-1}).

INTERPRETATION AND DISCUSSION

Based upon our earlier findings which indicate (a) preirradiation prompts migration of included Ca from within the Ag to its surface and (b) ethylene oxide yield enhancement correlates nicely with the presence of surface Ca, then as a basis for interpretation of the data of Fig. 1, it is assumed that the removal of included Ca is directly proportional to yield improvement. So, defining Y_∞ as the ultimate yield; Y_t the yield following a cumulative period of preirradiation, t; and Y_0 the normal (unirradiated) yield, the data of Fig. 1 can be expressed in the form

$$1 - (Ca_s/Ca_0) \equiv (Y_\infty - Y_t)/(Y_\infty - Y_0) = f(\text{time}) \quad (1)$$

where Ca_s is the number of surface Ca atoms and Ca_0 that number originally present as bulk inclusions. Analysis of the data recast in the general form of Eq. 1 indicates a first order process, i.e., (Fig. 2),

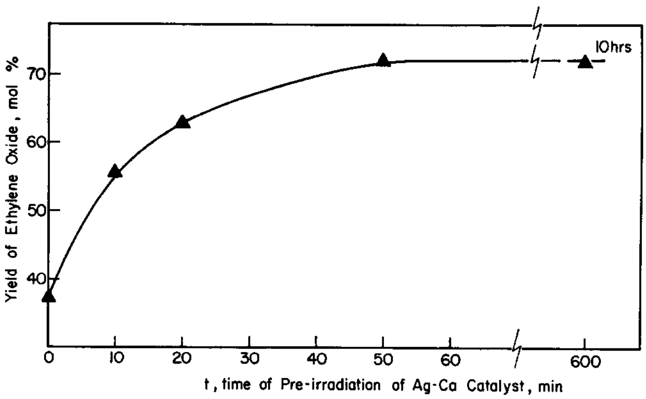

FIG. 2. Yield of ethylene oxide at 20% total conversion vs time of preirradiation of the catalyst.

$$(Y_\infty - Y_t)/(Y_\infty - Y_0) = \exp[-\lambda t], \quad \text{at a total conversion, } x = 0.2. \quad (2)$$

Hence the kinetics of irradiation follow the linear rate law

$$-d(Ca_0 - Ca_s)/dt = \lambda(Ca_0 - Ca_s). \quad (3)$$

(The proportionality constant relating yield to the population of surface Ca cancels by reason of the observed linearity.)

The model is rooted in Fig. 1 values, at $x = 0.2$, of $Y_\infty = 0.73$, $Y_0 = 0.48$, and $Y_t = 0.48$, 0.56, and 0.63 at $t = 0$, 10, and 20 min respectively. The rate coefficient λ is found to be

$$\lambda = 8 \times 10^{-4} \text{ sec}^{-1}.$$

Now Eq. 3 simply states that irradiation-sponsored Ca migration through about a dozen atomic layers of Ag to the surface (with commensurate yield alteration) is proportional to the number of Ca atom inclusions remaining in the bulk of Ag. Thus the process whereby the migrating species is *created* appears to be rate controlling, rather than the transport step, *per se*. Surely if diffusional migration from the bulk inclusion to the Ag surface is rate-controlling, a square root rather than exponential dependency of yield upon time would be manifest.

If it be supposed that as previously suggested (*2*, *3*), γ-rays create secondary particles (Compton electrons, x rays, Brehmsstrahlung) which cause multiple ionization of CaO, with consequent Coulombic ejection of the positive Ca and O ions, then

$$\lambda = I_0\sigma,$$

where

I_0 = radiation flux (quanta $\text{cm}^{-2}\ \text{sec}^{-1}$)

and

σ = cross-section of the process (cm^2).

Given the dosage of our ^{60}Co source (10^{18} eV $\text{gm}^{-1}\ \text{min}^{-1}$) and the geometry of the source-target network, I_0, is computed to be

$$I_0 = 1 \times 10^{12} \text{ quanta cm}^{-2} \text{ sec}^{-1}.$$

From this value of I_0 and the experimental value of λ, we compute

$$\sigma = 8 \times 10^{-16} \text{ cm}^2$$

or

$$\sigma = 8 \text{ Å}^2,$$

As the mechanism of this complex ionization–transport process remains obscure, a precise interpretation of σ is not possible at this time.

To be sure, insofar as the transport step (between bulk inclusion and the Ag surface) is obviously quite rapid relative to the species generation step, we are unable to characterize that mode of transport. Two possibilities exist: (a) diffusive transport of the Ca along grain boundaries in the Ag crystallite, or (b) Coulombic field ejection of the Ca and O through the surrounding Ag crystallite.

Transport mechanism (a) requires diffusion against the chemical potential and is therefore suspect, while transport mechanism (b) knows no precedent. Rather large repulsive energies would be required to prompt transport of energized Ca through, perhaps, several or more atom layers of surrounding Ag. However, if the role of γ-irradiation is that of multiple ionization of the included Ca oxide or hydroxide phase, the resulting Coulumbic forces would be more than sufficient to sponsor rapid ejection of the Ca from within the Ag to its surface.

An alternative mechanism can be suggested involving creation of photoelectrons or Compton electrons via γ-rays. The creation of photoelectrons is unlikely at the energy level of our photons and the mass of the atoms involved. While Compton electrons are surely produced, their number is far too small to produce the noted displacement of Ca atoms.

Future research includes study of the influence of temperature of irradiation upon λ since the temperature dependency of the generation process should be zero, while that of Ca transport must be finite. While we are unable to vary I_0, it is apparent that the effects of irradiation on the catalytic property responsible for yield enhancement can be realized in very short times indeed by the simple expedient of increasing λ by merely increasing I_0.

CONCLUSIONS

The kinetic law governing γ-ray sponsored migration of Ca from inclusions within supported Ag crystallites to the surface, has been established as a first order process, thus suggesting that the creation of the transported Ca species is the rate-controlling step, while the transport process *per se* is comparatively rapid.

The experimental rate coefficient for this irradiation process has been analyzed and a value of the cross-sectional area of the process involved is secured.

Since the Ca species generation step is rate-controlling, the time required for Ca ejection to the Ag surface, with consequent benefit to ethylene oxide yield in the oxidation of ethylene can be drastically reduced by increasing the γ-irradiation flux, said flux being a simple function of source dose and geometry of the sample irradiation network.

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