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Influence of γ Irradiation Upon Catalytic Selectivity. II.

The Role of Ca in the Ag Catalyzed Oxidation of Ethylene

P. FORZATTI,* E. MARTINEZ, G. C. KUCZYNSKI† AND J. J. CARBERRY

Department of Chemical Engineering, and the Radiation Laboratory,‡ University of Notre Dame, Notre Dame, Indiana 46556

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In the partial oxidation of ethylene, calcium, present within supported Ag apparently as distinct oxide phase inclusions, is shown to be a necessary ingredient to cause yield of ethylene oxide enhancement due to pre-irradiation of said catalyst with γ rays in the presence of air.

INTRODUCTION

In the initial phase of our studies of the influence of pre-irradiation of a supported Ag catalyst upon yield of ethylene oxide in the oxidation of ethylene, we employed a commercial catalyst (Engelhard) and reported in this journal (*1*) the following:

(a) Yield of ethylene oxide was increased from about 50% to nearly 70% (moles ethylene oxide per mole of ethylene reacted) after the catalyst was irradiated (Co-60; dose 10^{18} eV/g min) for a period of 10 hr.

(b) Reduction and re-oxidation of the irradiated catalyst restored normal yield-conversion behavior. Re-irradiation then restored the enhanced yield-conversion character.

(c) ESCA revealed the absence of surface Ca prior to irradiation; its appearance following irradiation; its absence following reduction and its reappearance following re-irradiation (2).

The source of Ca in the catalyst remained unknown to us for proprietary reasons. Hence, we deemed it appropriate to fashion our own catalyst with and without Ca addition, and to test each in terms of ethylene oxide yield prior to and after irradiation. In spite of ESCA evidence (*2*) the necessity of the presence of Ca was not demonstrated. For while the changes in yield corresponded with the appearance of surface Ca, such could be fortuitous and so further experiments were fashioned to ascertain the role of Ca in the process.

If indeed Ca proved to be essential in the γ-ray enhancement of yield, it was thought that its distribution within Ag should be determined by ESCA following various degrees of etching of a Ag catalyst. We, therefore, made ESCA studies as a function of etching severity for a normal catalyst containing Ca in Ag.

Catalyst Preparation

The catalyst was prepared as follows:

Twenty grams of $AgNO_3$ are dissolved in 100 cc of distilled water, which solution is slowly mixed with a solution of 10 g of KOH in 100 cc of distilled water. The resulting precipitate is then dissolved with

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[*] Politecnico, Milan, Italy.

[†] Department of Metallurgical Engineering.

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85 cc of a 50% aqueous solution of NH_4OH. At this point, if Ca is to be added, 0.5398 g of $Ca(NO_3)_2$ together with 1.1255 g of Na_2SO_4 (which serves as a precipitation aid) are dissolved. This is solution (a).

The reducing solution (b) consists of 4.5 parts by weight of sucrose, 2 parts HNO_3, and 50 parts distilled water. This solution is boiled and then cooled. Then 100 cc of solution (b) are added to solution (a) in the presence of 80 g of the α-alumina support. Metallic silver is immediately deposited. This mixture is allowed to stand for 30 min after which the pellets are filtered, washed thoroughly with water, and then dried for 90 min at 200°C.

The catalyst when situated in the reactor is pretreated in pure O_2 at 300°C for about 3 hr.

Experimental Procedure

The Notre Dame CSTCR (*3*, *4*) was employed and analysis of feed and effluent was identical to that reported earlier (*1*). Reaction temperature was 245°C at atmospheric pressure. Feed composition was 2% ethylene, the balance being pure O_2. Gas phase moderators, e.g., ethylene dichloride were not used. Conversion variation was achieved by varying contact time at constant temperature.

Etching experiments were carried out with one sample of normal, unirradiated Engelhard catalyst. A solution of 2% HNO_3 was used and the etched catalyst was subjected to ESCA following etching times of 0, 2, 7, and 12 min. The estimates of the amount of silver removed (in atomic layers) are based upon average Ag particle size as determined by scanning electron microscopy. Specifically, an average value of the silver particle size is determined from the scanning electron micrograph. Then, based upon the density of silver and the measured amounts of silver etched, an estimate of the number of atomic layers of silver removed is established. Since, of course, there exists a distribution of particle sizes, the resulting estimate is indeed crude. However, the results of ESCA following each period of etching prove very revealing as will be noted below.

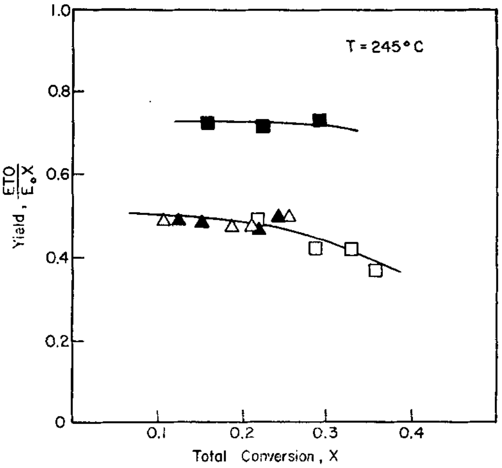

FIG. 1. Influence of pre-γ-irradiation upon yield of ethylene oxide—the effect of presence (□, ■) and absence (△, ▲) of Ca in the supported Ag catalyst. Before Irradiation △, □. After Irradiation ▲, ■.

Results

Yield of ethylene oxide Y vs total conversion of ethylene X is displayed in Fig. 1 for the normal Ag-Ca catalyst and for that same sample following 3 hr of exposure to γ-irradiation. The enhancement of yield is comparable to that reported earlier (*1*) for a commercial Engelhard catalyst.

Also shown in Fig. 1 is the Y vs X data for the supported silver prepared without calcium. Yields prior to and following γ irradiation are identical. In Table 1 are shown the results of the etching experiments with estimates of the average num-

TABLE 1
Results of Etching–ESCA Experiments Engelhard Ag Catalyst

Time of etching in 2% HNO_3	ESCA results	Estimated Ag removed, # of atomic layers
0	No Ca	0
2	Ca present	13
7	No Ca	24
12	Ca present	30

ber of silver atomic layers removed for each period of etching.

DISCUSSION

The unique role of Ca in sponsoring yield of ethylene oxide enhancement is now beyond question. We are thus free to contend that the irradiation sponsored yield enhancement can be attributed to the presence of surface Ca, fixed thereupon, following irradiation, by chemisorbed oxygen. A sample of Engelhard catalyst irradiated in N_2 and tested one month after irradiation revealed no yield enhancement. In contrast, samples irradiated in air and tested one year later exhibit yield enhancement identical to that reported earlier (*1*) and in Fig. 1.

As for the nature of Ca found in Ag, the etching experiments and results set forth in Table 1 suggest that Ca does not exist in solution within Ag but as separate-phase inclusions. This finding is consistent with the thermodynamic improbability of reducing Ca salt to the metal at the conditions of catalyst preparation. Crude though the etching experiments may be, the ESCA scans certainly suggest a lack of uniformity of Ca within the silver particles.

Further, since the prime effect of γ rays is that of ionization, only a distinct Ca oxide or hydroxide insulator phase could be ionized. If Ca existed in solution with electron-rich Ag, γ irradiation could exert no influence upon the Ca atom to cause its movement to the surface. That Ca is ejected to the surface is, as judged by ESCA (*1*, *2*), beyond doubt. The mechanism of ejection remains obscure; however, some tentative speculations are warranted. Two possible modes of Ca ejection exist:

1. The inclusions of Ca oxide or hydroxide are reduced by γ rays, the resulting Ca then diffuses along grain boundaries to the Ag surface where it is then fixed by chemisorbed oxygen.
2. Multiple ionization of Ca and O occurs in the inclusions; the resulting Coulombic repulsive force is more than sufficient to prompt ejection of the Ca to the surface, where, as above, it is fixed by chemisorbed oxygen.

The first mechanism requires diffusion against the thermodynamic potential gradient while the second involves new physics. Experiments are now underway which give promise of further clarification of this issue.

As for the observed disappearance of Ca from the surface upon H_2 reduction and its reappearance upon re-irradiation, we surmise that upon reduction of the surface Ca oxide (chemisorbed oxide of Ca), the hydride of Ca is formed which, at the reduction temperature of 300°C for three hours, diffuses into the bulk silver; therein the Ca oxide inclusions are formed from the oxygen residing within the silver particle. Re-irradiation then prompts reappearance of surface Ca as in the first instance.

CONCLUSIONS

Significant enhancement in the yield of ethylene oxide in the supported Ag catalyzed oxidation of ethylene by pre-γ-irradiation of the catalyst requires the presence of Ca within the Ag. Crude etching experiments complemented by ESCA suggest that the Ca is initially present as distinct, separate phase inclusions within Ag.

The likely mechanism of the γ-ray provoked transport of Ca from within the Ag particles to upon its surface is Ca ejection by Coulombic repulsive forces created via multiple ionization of the included Ca oxide by γ rays.

Insofar as it is generally acknowledged that ethylene oxide is created via O^-_2 sites on Ag, the yield enhancement correlation with the appearance of surface Ca may be attributed to the ability of Ca for form the superoxide (O^-_2) (*5*, *6*).

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