OXIDATION OF ETHYLENE TO ETHYLENE OXIDE BY SELENIUM MODIFIED SILVER CATALYST

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ABSTRACT: *Oxidation of ethylene to ethylene oxide over silver catalyst and selenium modified catalyst has been studied by continuous flow and pulse techniques over the temperature range of 230-280°C. The results are discussed in terms of reaction mechanisms proposed by others, rejecting mechanisms which involve peroxide formation. It has been shown that not only selectivity towards ethylene oxide production increases considerably by introduction of 0.01 atom percent of selenium into silver, but the reactivity increases also. Above 270°C selectivity drops almost to the level of unmodified catalyst because selenium atoms diffuse into the grooves between silver crystals on the surface of catalyst. It has also been shown that intermolecular conversion of ethylene oxide to acetaldehyde decreases.*

KEY WORDS: *Ethylene, Ethylene oxide, Silver catalyst, Modified silver catalyst, Oxidation, Selenium.*

INTRODUCTION

It has been well established that silver is one of the best catalysts for oxidation of ethylene to ethylene oxide and addition of small amounts of electronegative elements to the gas phase during the course of reaction or during the course of catalyst preparation enhances the selectivity of catalyst towards ethylene oxide production [1-13].

Mechanistically oxidation of ethylene to ethylene oxide over modified silver catalyst have

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been studied by many investigators. Based on the IR spectra, *Force* and *Bell* [7,8] have proposed that positively charged silver ions formed on the oxygenated silver are the proper sites for ethylene adsorption. It has been suggested by these authors that the formation of ethylene oxide and complete oxidation occur via $Ag\text{-}O\text{-}CH_2\text{-}\dot{C}H_2$ and $Ag\text{-}O\text{-}\dot{C}H\text{-}CH_3$ intermediates respectively. They have also suggested that selectivity towards ethylene oxide production, which depends on relative rate of formation of these two intermediates; can be enhanced by increasing the surface concentration of adsorbed ethylene and O^- ions.

Cante and *Hall* [8] have indicated that the probable involvement of peroxide intermediates in the formation of ethylene oxide and its complete oxidation. *Echigoya* et al [10] have suggested that positively charged adsorbed ethylene reacts with the negatively charged adsorbed diatomic oxygen to form an intermediate which produces either ethylene oxide and atomic oxygen or carbon dioxide and water. They have also suggested that the $Ag\text{-}O\text{-}CH_2\text{-}\dot{C}H_2$ and $Ag\text{-}O\text{-}\dot{C}H\text{-}CH_3$ intermediates proposed in Force and Bell mechanism are also produced via a pathway through peroxide intermediates.

Temkin et al [12,13] have shown that addition of 10^{-4}-10^{-2} atom percent of selenium to the silver catalyst during it's preparation enhances reactivity three to four times while selectivity increases at selenium concentration more than 10^{-2} atom percent. Selenium has been considered by these authors as a noble modifier among other additives because it's not washed away during operation.

In this work we have re-investigated the oxidation of ethylene to ethylene oxide over silver and modified catalyst by continuous and pulse techniques in order to study the role of selenium on ethylene oxide production.

EXPERIMENTAL

Apparatus

A stainless steel U tube of 4 mm diameter was used as a reactor (Fig. 1). This reactor consisted of two parts. Part A, 75 cm long, packed with 19.5 g of catalyst 16-24 (mesh). Both ends of this portion were packed with chromosorb-P as solid support and then with glass wool. Part A was connected by a joint to part B, an empty tube 60 cm long, designed to hold the thermocouple tube. By a six way valve the system could readily be changed from continuous flow to pulsed operation and vice versa. In the pulse mode a given amount of gas sample could be injected into the reactor head by a tight syringe. The reactor was placed in a salt bath (51% KNO_3 and 49% $NaNO_2$) with melting point of 143°C. The electronic thermoregulator controlled the bath temperature within ±1°C.

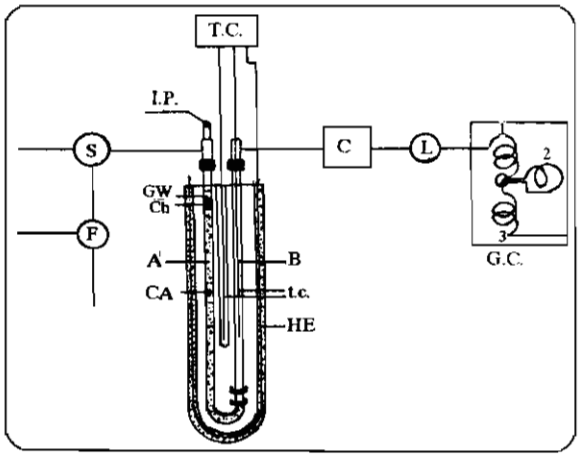

Fig. 1: Schematic diagram of the apparatus used: T.C.: Temperature controller; I.P.: Injection port; S: Six way valve; F: Flow meter; GW: Glass wool; Ch: Chromosorb-p; CA: Catalyst; t.c.: Thermocouple; HE: Heating element; C: Condenser; L: Sample loop; A: Reactor, part A; B: Reactor, part B; G.C.: Gas chromatograph.

Chromatographic Column

Quantitative analysis of oxygen and nitrogen as well as other components in the gas effluent from the reactor, was carried out via a special three column gas chromatograph. The first and third columns were 230 cm long (0.3 cm diameter) packed with chromosorb 102, 60-80 mesh. These columns were capable of separating all gases present in the reaction mixture with the exception of oxygen and nitrogen. The second

column, with the same diameter, was 215 cm long packed with molecular sieve 5A, 40-60 mesh. This column was capable of separating oxygen and nitrogen, and very sensitive to carbon dioxide. A known volume from the reactor effluent was trapped in a loop and injected into the carrier gas (helium). Two minutes after injection*, the effluent gas from first column was guided to the third column. When the recorder showed that all compounds had passed through the third column, carrier gas was passed through the second and third columns in order to separate oxygen from nitrogen.

The main role of the third column in this special setup was to equalize the flow of effluent gas into the detector.

*Catalyst***

In order to evaluate the effect of addition of selenium on the catalyst two types of catalyst were prepared and treated under the same conditions. Type 1 contained only silver on α-alumina support (unmodified catalyst), type 2 is the selenium modified silver catalyst (one selenium atom per 10^4 silver atom) also deposited on $\alpha-$alumina support. To evaluate the stability of selenium -silver catalyst over the silver, another catalyst was prepared and treated with more selenium (one selenium atom per 10 atom of silver) and treated exactly as catalyst type 2. This catalyst was placed in the reactor and after 360 hours of operation at 300°C the catalyst was removed and analyzed for its selenium according to the method suggested in references 14 and 15. The analysis showed that within experimental limits of analysis, selenium had not been removed from the catalyst. This result agrees very well with the result of *Temkin* et al [12] in which radiochemical measurements of radioactive selenium have shown the lack of selenium loss after 88 hr of operation at 303°C. Scanning Electron Microscopy (SEM) and Energy Dispersion Spectrometry (EDS) of unmodified catalyst shows that surface of $\alpha-$alumina completely is covered by silver and surface of modified catalyst is completely covered by silver along with on uneven distribution of selenium.

Continuous Operation

The operation a continuous stream of feed, mixtures of air and ethylene, with the ratio of 10 to 1, with flow rate of 60 mL/min was passed over catalyst at 250°C. The effluent gas from the reactor was fed to the chromatograph at the rate of 60 mL/min. In the early stages of the operation the recorded chromatogram showed that the effluent gas from the reactor contained only ethylene, oxygen and nitrogen. After 8 hr of operations two peaks due to ethylene oxide and carbon dioxide appeared and after 50 hr of operations the catalyst reached a constant activity at constant temperature.

Pulsed Operation

In this mode of operation the catalyst was first stabilized by a continuous operation. Then by mean of a six way valve operation was switched to pulsed mode. The carrier gas (helium) was passed over catalyst until all adsorbed gases were removed from the reactor. The surface of both catalysts were deoxygenated by injection of 5 mL of ethylene to the helium stream. The injections were repeated until the chromatogram of the effluent gas from the reactor indicated that none of oxidation products were present. At this stage catalyst was considered deoxygenated.

To study of effect of a given gas, a pulse of the gas with a known volume was injected to the stream of carrier gas via the injection port on portion A of the reactor.

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* By trail and error it was found that under operation condition (injection port temperature of 300°C, column temperature of 100°C and carrier gas flow rate of 20 mL/min.) it takes 2 min for air to exit from column 1 and reach column 2, where it was trapped for later analysis.

** The preparation methods for both catalysts are propriotory of the NIORC and may not be revealed at this point.

RESULTS AND DISCUSSION

Continuous Operation

Conversion of ethylene to products at different temperatures for unmodified silver catalyst are summarized in Table 1 and for modified catalyst in Table 2. Comparison of these result shows that modified catalyst is stable in 230-260°C region. At temperatures higher than 270°C conversion of ethylene to ethylene oxide over selenium modified catalyst decreases.

When the experiments in 230-270°C range were repeated for this catalyst it was found that selectivity had been reduced to that of unmodified catalyst, indicating that at temperatures higher than 270°C the catalyst somehow becomes deformed.

Conversion of ethylene to product over unmodified catalyst and selenium modified catalyst before and after deformation are compared in Figs. 2 and 3. The selectivities are compared in Fig. 4. As it is apparent from Figs. 3 and 4 conversion to ethylene oxide (including inter-conversion to acetaldehyde and selectivity

Table 1. Effect of temperature on conversion and selectivity(s) of silver catalyst[a]

T (°C)	CO_2 (%)	Et_2O (%)	MeCHO (%)	Total conversion (%)	S (%)
200	0.9	0.0 (0.0)[b]	0.0	0.9	0.0
210	3.9	3.6 (3.6)	0.0	6.5	55.3
230	21.0	15.9 (11.8)	4.1	36.9	43.1
245	24.3	27.8 (22.3)	5.8	52.4	53.6
260	31.0	24.7 (17.8)	6.8	55.6	44.2
270	42.0	23.3 (13.6)	9.7	65.3	35.7
280	51.0	24.7 (13.6)	11.1	75.7	32.6

a) To change conversion to the rate of production (mol/hr g cat.) multiply each entry by 5.7×10^{-5}.

b) Conversion to ethylene oxide excluding inter-conversion to acetaldehyde.

Table 2: Effect of temperature on conversion and selectivity(s) of selenium modified silver catalyst[a]

T (°C)	CO_2 (%)	Et_2O (%)	MeCHO (%)	Total conversion (%)	S (%)
230	3.2	46.5 (42.7)[b]	3.8	49.7	93.5
245	2.8	50.0 (36.7)	13.3	52.8	94.7
260	6.6	51.1 (35.9)	15.2	57.7	88.6
270	30.1	35.9 (32.5)	3.4	66.0	54.4
280	59.1	35.1 (28.6)	6.5	94.2	7.3
230[b]	22.9	24.7 (24.7)	0.0	47.6	51.9
260[b]	27.9	36.5 (34.2)	2.3	64.4	56.7
260[c]	1.4	51.3 (51.3)	0.0	52.7	97.4

a) To change conversion to rate of production (mol/hr g cat.) multiply each entry by 5×10^{-5}.

b) Selenium modified silver catalyst deforms above 270°C.

c) Flow rate has increased from 60 mL/min to 150 mL/min.

defined as ratio of ethylene oxide to total conversion for unmodified catalysts) passes through a maximum at 245°C. For unmodified catalyst conversion to ethylene oxide is slightly higher than conversion at 245°C but selectivity is maximum at 245°C. Conversion to ethylene oxide and selectivity for modified catalyst considerably is higher than that of unmodified catalyst, for example, at 245°C conversion of ethylene to ethylene oxide, including acetaldehyde over the unmodified catalyst is 28.1% and over selenium modified catalyst is 50% and at 260°C it is 24.6% and 51.2% respectively. Since for both catalysts maximum selectivity has been obtained at 245°C for flow rate of 60 mL/min, we conclude that 245°C is the optimum temperature for both catalysts.

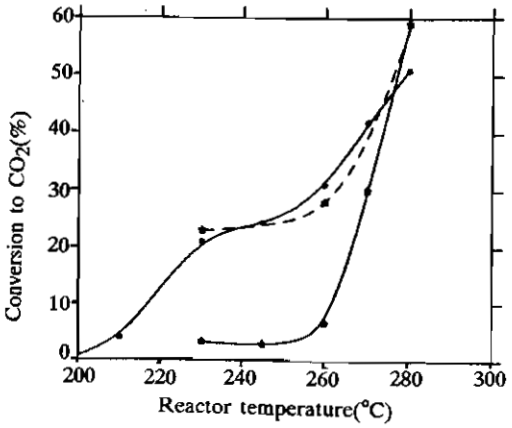

Fig. 2: Conversion of ethylene to carbon dioxide over modified and unmodified catalysts.

■ ——— *Unmodified catalyst.*

★ ——— *Selenium modified catalyst.*

★ ------ *Deformed selenium modified catalyst.*

As mentioned above at temperatures higher than 270°C the activity of selenium modified catalyst almost reduces to the level of unmodified catalyst. As it has been shown by *Temkin* et al and our experiment with catalyst type 3, loss of activity can not be attributed to the loss of sclenium from the catalyst surface. Energy Dispersion Spectrometry of the deformed catalyst reveals that selenium atoms have been accumulated in the grooves between silver crystals on the surface of the catalyst. Therefore, in contrast to *Temkin* et al who contend that by increasing the temperature a uniform distribution of selenium over silver will be obtained, we believe at temperatures higher than 270°C due to selenium migrations, the catalyst loses it's particle uniformity.

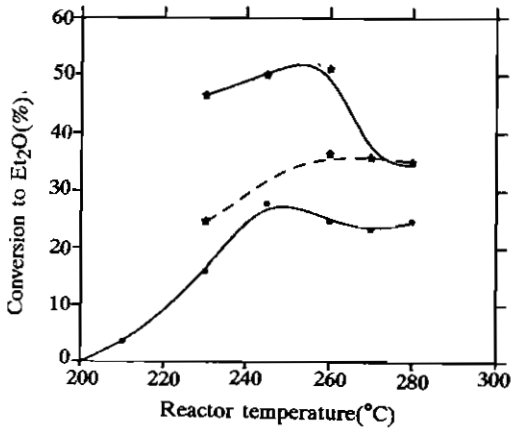

Fig. 3: Conversion of ethylene to ethylene oxide over modified and unmodified catalysts.

■ ——— *Unmodified catalyst*

★ ——— *Selenium modified catalyst.*

★ ------ *Deformed selenium modified catalyst.*

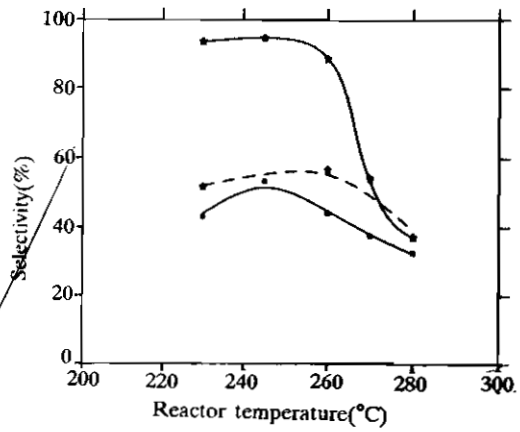

Fig. 4: Selectivity towards ethylene oxide production over silver and modified silver catalysts.

■ ——— *Silver catalyst.*

★ ——— *Selenium modified silver catalyst.*

★ ------ *Deformed selenium modified catalyst.*

Twigg et al [15] have reported that less than 0.1% of ethylene oxide internally is converted to

acetaldehyde. Our results for both catalysts show that internal conversion of ethylene oxide to acetaldehyde which is a temperature dependent process is much higher than this value (see Tables 1 and 2). By increasing the flow rate from 60 mL/min to 150 mL/min or reducing the contact time by factor of 2.5 at 260°C, the acetaldehyde peak for modified catalyst disappears (see Fig. 3). In addition selectivity increase and conversion to ethylene oxide remains constant (see Table 2). This suggests that subsequent oxidation of ethylene oxide to carbon dioxide has decreases by decreasing the contact time. This conclusion is in agreement with that of *Eliyas* et al [5] who show that oxidation of ethylene oxide decreases with a decrease in contact time. Yet our results is in disagreement with those of *Echigoya* et al [10] for unmodified catalyst and *Petrov* et al [4] for the catalyst moderated with dichloroethane, who report that conversion decreases and selectivity remains constant with decreasing contact time.

94% selectivity could not be explained by those mechanisms which place a limiting selectivity on the reaction. That is, by peroxide intermediates, since in this kind of mechanism as *Sachlter* points out [11] the oxygen atoms freed from epoxide formation must be consumed in complete oxidation to carbon dioxide and water. Therefore, we prefer the mechanism suggested by *Force* and *Bell*, [7], that is, the formation of two Ag-O-$\dot{C}H_2$-CH_2 and Ag-O-$\dot{C}H$-CH_3 intermediates. Since as it is suggested by these authors the first intermediate leads to epoxide formation by a first order reaction and the second intermediate which leads to complete oxidation via a second order reaction is produced from the first intermediate by an inter-conversion reaction. It seems that incorporation of selenium inhibits the formation of Ag-O-$\dot{C}H$-CH_3 intermediate.

It is interesting to compare the moderation of silver catalyst by selenium and dichloroethane with each other. Moderation with dichloroethane leads to a reduction in reactivity and ability of the catalyst for ethylene adsorption and increased selectivity, whereas for selenium modified catalyst the ability for ethylene adsorption remains unchanged, reactivity increases to some extent and selectivity increases considerably.

Pulsed Operation

Adsorption of oxygen on the surface of catalyst

To study catalyst capacity for oxygen absorption 1 mL of air was injected into the carrier gas stream and passed over the catalyst. With the three column in series pulsed chromatogram was recorded and from the areas under nitrogen and oxygen peaks the mol numbers of oxygen adsorbed on the surface of both catalysts were calculated. The pulse injection and calculation were repeated until the mole ratio of nitrogen to oxygen became equal to that of air. Total moles of oxygen adsorbed on the surface ot the catalyst calculated to be 3.06×10^{-5} and 2.13×10^{-7} mol for the unmodified and selenium modified catalyst respectively. Considering that 19.5 g catalyst with surface area of $2m^2g^{-1}$ were used in these experiments, the unmodified catalyst is saturated with 7.8×10^{-7} and selenium modified catalyst with 5.46×10^{-7} mol per square meter of the catalyst. Therefore, addition of one atom selenium per 10^4 atom silver reduces the active sites of catalyst for oxygen adsorption by 30%. Nevertheless the activity of the selenium modified catalyst not only does not decrease but slightly increases presumably, because the number of $Ag^{\delta+}$ sites increases considerably.

Stability of the Reaction Oxygen

Flank and *Beachell* [18] have suggested that the adsorbed oxygen can readily migrate into the subsurface layers and this oxygen can not readily participate in the reaction. *Mikami* et al [17] have shown that in their experiment no appreciable amounts of adsorbed oxygen could have migrated into subsurface layers presumably because of low temperature (200°C) used in their experiment.

In order to examine the stability of the

reactive oxygen 5 mL of air was injected to the carrier gas and passed over the deoxygenated catalyst. After 10 min 400 μL of ethylene were injected and pulse chromatograms were recorded. The pulse injections of 400 μL were repeated after 20, 40, 60, 80, 100 and 120 min intervals and pulse chromatograms of the effluent gas from the reactor were recorded. The results show that for helium flow rate of 60 mL/min at 245°C production of carbon dioxide and ethylene oxide remains constant. Since our experiment were conducted at higher temperatures (245°C), and at longer time intervals (10 to 120 min), we conclude that migrated oxygen into sublayer could participate in the oxidation reaction as easily as the surface oxygen.

Finally pulse injections of ethylene reveals that addition of selenium to silver catalyst does not change the tendency of deoxygenated surface towards ethylene adsorption, and pulse injection of carbon dioxide shows that the behavior of both catalysts, modified and unmodified, towards carbon dioxide are the same.

CONCLUSIONS

The results of this work show that selectivity toward ethylene oxide production (ethylene oxide + acetaldehyde) is more than 94% for selenium modified catalyst at 245°C. Reactivity not only has not decreased even at this high contamination which has reduced the active site for absorption of oxygen by 30%, but on average it has increased by 25 to 1% in the range of 230-270°C. This is attributed to increased $Ag^{\delta+}$ sites.

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