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Study of the promoting effects in ethylene epoxidation

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The promoting effects in the ethylene epoxidation reaction on an electrolytic silver surface by chemical modification with Ba and Cs compounds were studied. Ba increases the conversion of ethylene and decreases a little of the selectivity to ethylene oxide. In contrast, Cs increases the selectivity to EO at the expense of conversion of ethylene. Changes in the work function and the TPD of oxygen adsorption on modified Ag surfaces were measured. Promoting effects are explained by the idea that atomic oxygen is the crucial species for epoxidation.

Keywords: Ethylene oxide; epoxidation; silver; promoted ethylene

1. Introduction

Supported silver is the unique catalyst used for commercial production of ethylene oxide by oxidation of ethylene with molecular oxygen. For almost half a century it has been an important topic both for development work and basic research.

Many promoters have been tried to improve the performance of the silver catalyst, such as compounds of alkali and alkaline earth metals. The function of these promoters has been studied by many authors. McBee [1] found that Ba modified Ag catalyst becomes "more active and a longer live". Spath et al. [2] concluded that the newly formed $BaCO_3$ in the reaction, as a semiconductor, improves the activity. Recently Lambert et al. [3–9] and Campbell et al. [10] studied the promoting effects of alkali and alkaline earth metal compounds by surface science techniques. However most of these experiments were carried out on single Ag crystals with lower indices than model catalysts.

The present work was done on an electrolytic silver surface. From the data of Deng et al. [11], the adsorbed oxygen species on this kind of Ag surface are

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mainly adsorbed atomic oxygen and subsurface oxygen. According to the assumption that atomic oxygen is the crucial species for ethylene epoxidation, the electrolytic Ag would have catalytic function for this reaction. Based on this idea the electrolytic Ag was chosen as the active component which was modified by compounds of Ba and Cs for studying their promoting effects.

2. Experimental

PREPARATION OF CATALYST SAMPLES:

A required quantity of $Ba(NO_3)_2$ or Cs_2CO_3 was dissolved in water which was limited just enough to immerse the electrolytic silver granules. The silver granules were obtained from Fudan University. It is a polycrystallite silver prepared by electrolytic refining for three times. It has a specific area of 0.016 m^2/g (measured on Digisorb 2600 with Kr) and a size of 30 to 40 meshes.

The Ag granules were added to the water solution in one portion and stirred with a glass rod. It was then transfered onto the watch glass and dried in a muffle furnace under forced air flow. The temperature was raised up to 100°C within an hour and maintained for another hour. It was then heated further up to 250°C, maintained for 3 hrs., and cooled down to room temperature.

Catalytic performance of the samples was obtained in a microflow reactor of diameter 6×1 mm stainless turbine with 1 ml sample. The feed gas was composed of 20.3% C_2H_4, O_2 7%, and N_2 72.7%. It was operated with the conditions of S.V. 7000 hr^{-1}, pressure 2.10 ± 0.05 MPa. At the begining of the reaction the sample had to be aged by raising the temperature gradually up to about 200°C within 30 hrs. At this temperature the EO could be detected in case of a practical catalyst sample. It was then that the temperature was raised further according to the required conversion of ethylene. The gas compositions were analyzed by on line GC. Conversion was calculated as the ratio of moles of ethylene reacted in the outlet gas to moles of ethylene in the feed gas. Selectivity to EO was calculated as the ratio of moles of EO formed to moles of ethylene reacted. Assumed was that the volume change between feed gas and outlet gas was negligible.

3. Results and discussions

1. PRELIMINARY TEST

The electrolytic silver has been used as catalyst for the manufacture of formaldehyde from methanol but has never been reported as a catalyst for ethylene epoxidation before. To prove the idea suggested for the present work as mentioned above three preliminary tests were carried out as follows.

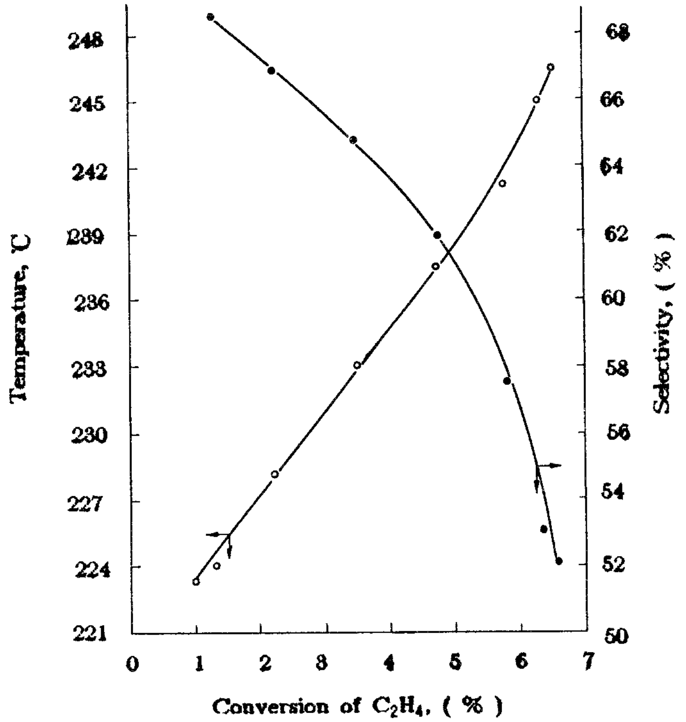

Fig. 1. Activities of ethylene epoxidation on polycrystallite Ag catalyst.

a. It was evaluated in a microflow reactor with ethylene-oxygen-nitrogen mixture under operating conditions as described above. The results are shown in fig. 1.

b. It was tested with an ethylene-oxygen-nitrogen mixture containing 6.3% of CO_2 and 0.22 ppm of ethylene dichloride. This feed gas mixture was used for the evaluation of practical Ag catalyst samples. Little conversion occurred even at 267°C. It may be due to the poison effect of ethylene dichloride in feed gas.

c. Ag surface was modified with a certain amount of $Ba(NO_3)_2$ and then tested as above. The results are shown in fig. 2.

From the results of the above preliminary tests the following conclusions can be drawn:

a. The electrolytic Ag does catalyze the epoxidations reaction of ethylene with molecular oxygen.

b. Ba does enhance the activity of the silver surface.

c. Although the specific surface area of the electrolytic silver is far lower than that of the high surface area practical Ag catalyst, it had almost the same performance for ethylene epoxidation under the same reaction conditions, i.e. the same space time velocity with the same concentration of ethylene and oxygen in feed gas excluding ethyldichloride and CO_2.

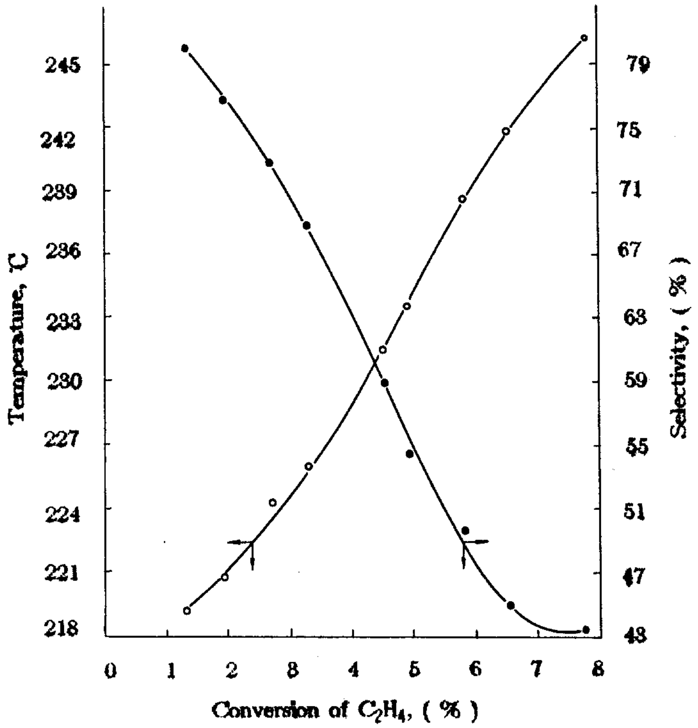

Fig. 2. Activities of ethylene epoxidation on Ag-Ba catalyst.

2. PROMOTING EFFECT OF Ba

a. The samples were prepared as described above. The amounts of Ba on the electrolytic Ag surface were as follows:

Sample	Ag	Ag-B1	Ag-B3	Ag-B4	Ag-B5
Ba (wt%)	0	0.11	0.32	0.58	0.96

The results of the evaluation of these samples are shown in fig. 3a and 3b. The conversion of ethylene becomes higher and the selectivity to EO lower as compared with the unmodified Ag surface at the same temperature.

b. Structure of Ba compound on the Ag surface.

It was detected by FT-IR (Bruker Ifs 88). The $Ba(NO_3)_2$ was the only form on the Ag surface before and after the reaction. However no N was detected by AES. It might be due to the decomposition of NO_3^- radical during the treatment of the surface of the Ba modified Ag sample before AES testing.

c. Change in specific area.

It was measured on Digisorb 2600 with Kr as adsorbate. The data were shown as follows (m^2/g):

Sample	Ag	Ag-B3	Ag-B5
Fresh	0.016	0.019	0.023
After reaction	–	0.021	0.039

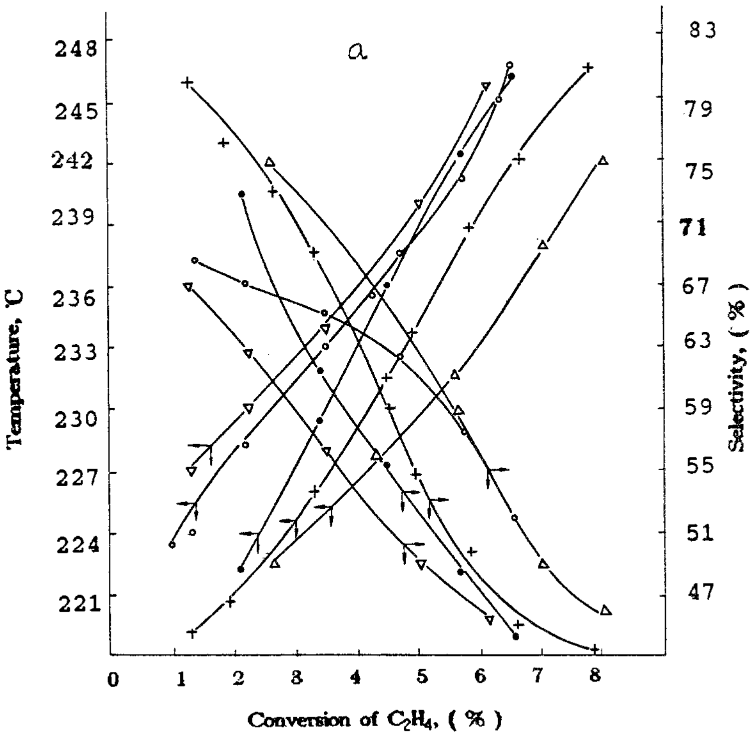

Fig. 3a. Activities of ethylene epoxidation on Ag and Ag-Ba catalysts, o——o: Ag, +——+: Ag-B_1, △——△: Ag-B_3, •——•: Ag-B_4, ▽——▽: Ag-B_5.

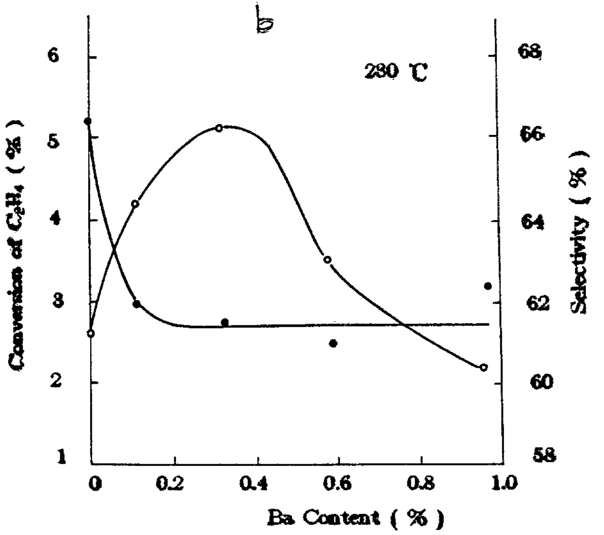

Fig. 3b. The change of conversion of C_2H_4 and selectivity with Ba content o——o: conversion of C_2H_4, •——•: selectivity for EO, reaction temperature 230°C.

There was almost no change in specific area. A little increase of the specific surface area of the after reaction samples may be due to the carbon deposition formed during the oxidation reaction.

d. Temperature programmed desorption of adsorbed oxygen on Ag surface.

It was conducted in a high vacuum adsorption-desorption apparatus with a quadrupole mass spectrometer. The surface of the samples was cleaned by repeatedly Ar etching and high temperature annealing. It was then evacuated to 10^{-9} Torr. Resulted TDS are shown in fig. 4a and three desorption peaks α, β and γ can be observed. For characterization of the oxygen species adsorbed on Ag surface, it was treated with CO five times that of exposure of oxygen [11].

Then the residual CO was pumped out and the desorption spectra of oxygen were recorded as shown in fig. 4b. The α- and β-peaks disappeared as shown by curve 2. So α- and β-peaks correspond to adsorbed atomic oxygen.

According to the desorption temperature of the γ peak it would be the desorption curve of subsurface oxygen according to the literature [11–13]. In comparasion with the oxygen TDS of the unmodified electrolytic silver surface there is no difference except the maximum peak temperature of Oa (β peak) shifted to the lower end by 60 K. The small α peak may be due to the desorption of an atomic oxygen from the Ba oxide which formed from $Ba(NO_3)_2$ during the cleaning of the Ba modified Ag surface. Meanwhile the desorption energy of the adsorbed atomic oxygen from the β peaks was also calculated. It is 99.6 kJ/mol, i.e. 24 kJ/mol lower than that of the unmodified electrolytic Ag surface [12].

e. Work function change ($\Delta\phi$) measurement.

Work function change ($\Delta\phi$) is an important property of an adorption system to describe directly the electronic charge transfer between adsorbate and

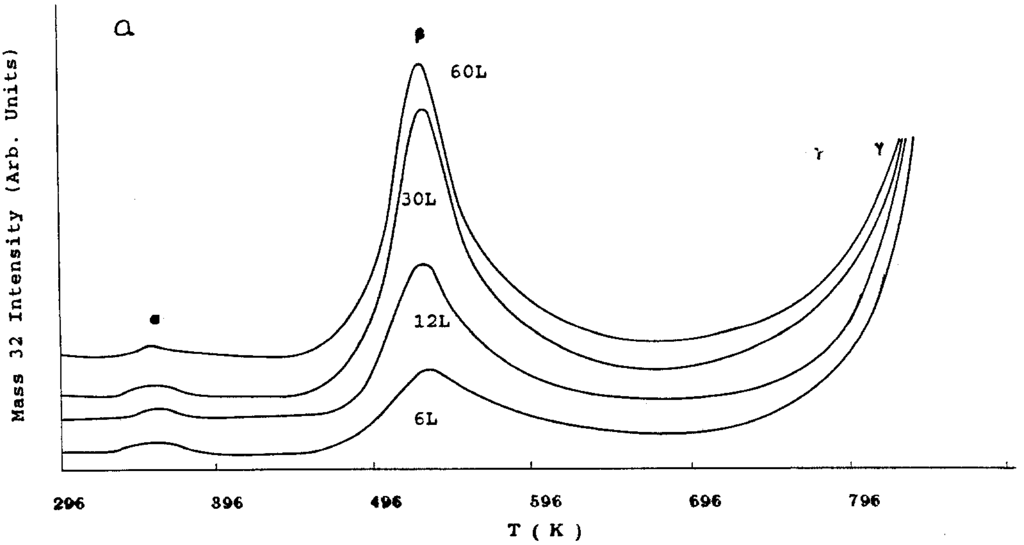

Fig. 4a. TDS of oxygen on Ag-Ba surface. Adsorption temperature is room temperature.

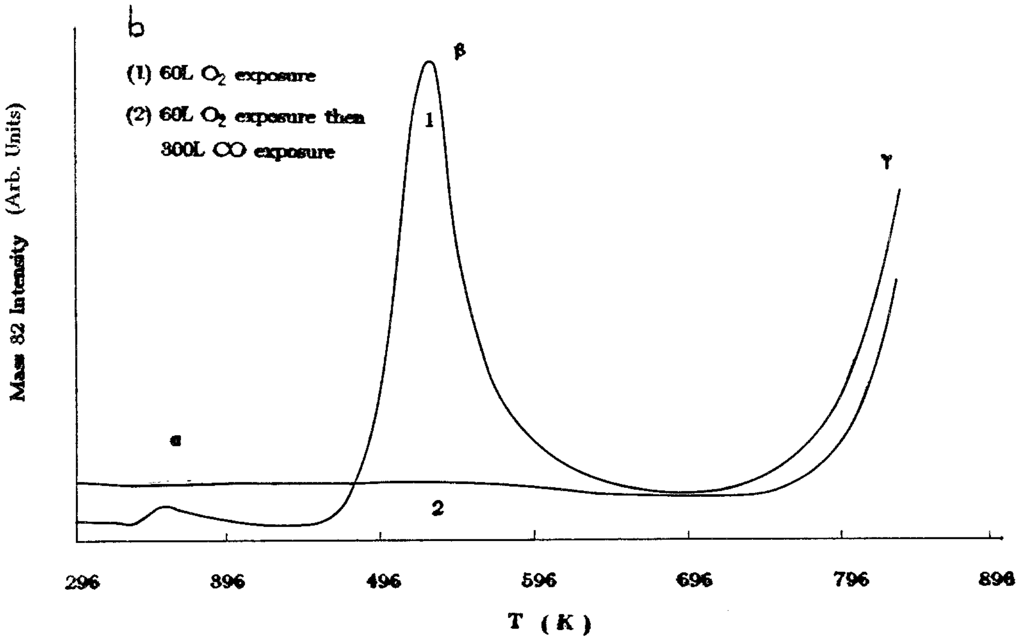

Fig. 4b. TDS of oxygen with and without adsorbing CO on Ag-Ba surface.

metallic surface. So the work function change ($\Delta\phi$) of the Ag-Ba-O_2 adsorption system was measured. It is 0.42 eV, i.e. 0.08 eV lower than that of the unmodified Ag-O_2 system [14]. The effect of Ba used as promotor in ethylene epoxidation can be explained readily (in relation to the idea atomic oxygen is the crucial species in the ethylene epoxidation reaction [15]) as follows.

In comparison with the unmodified electrolytic Ag surface the work function change ($\Delta\phi$) of oxygen adsorbed on the Ba modified Ag surface became lower. This means the adsorption bond energy of the adsorbed atomic oxygen is weaker. So the Ba modified Ag is more active for the epoxidation reaction, i.e. higher than the ethylene conversion. The lower desorption activation energy E_d of adsorbed atomic oxygen on Ba modified Ag surface also favors the activity for epoxidation.

3. PROMOTING EFFECT OF Cs ON SILVER SURFACE

a. The samples were prepared as above and the quantities of Cs in the samples are shown as follows:

Sample	Ag	Ag-C1	Ag-C2	Ag-C3
Cs (ppm)	0	2.2	3.6	7.2

The catalytic performance of three Cs modified Ag samples were evaluated with the method mentioned above. The results of each sample are shown in figs.

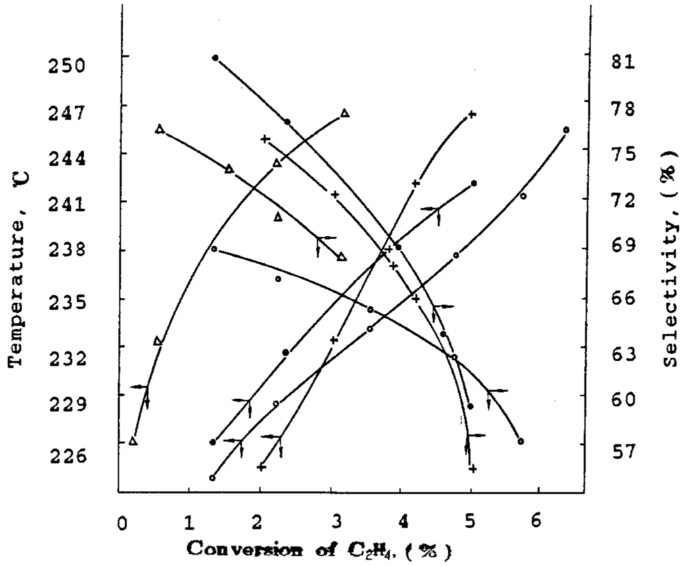

Fig. 5a. Activities of ethylene epoxidation on Ag and Ag-Cs catalysts, o——o: Ag, •——•: Ag-C_1, +——+: Ag-C_2, △——△: Ag-C_3.

5a and 5b. The conversion of ethylene for all the samples is lower than that for unmodified Ag while the selectivity to EO is higher. The conversion is decreased further as the quantity of Cs increased but the selectivity to EO did not change.

It is very interesting to see in fig. 5a that the selectivity to EO of all the Cs modified Ag samples dwindled down as the conversion of ethylene approached 5%. The corresponding reaction temperature is above 242°C which nearly

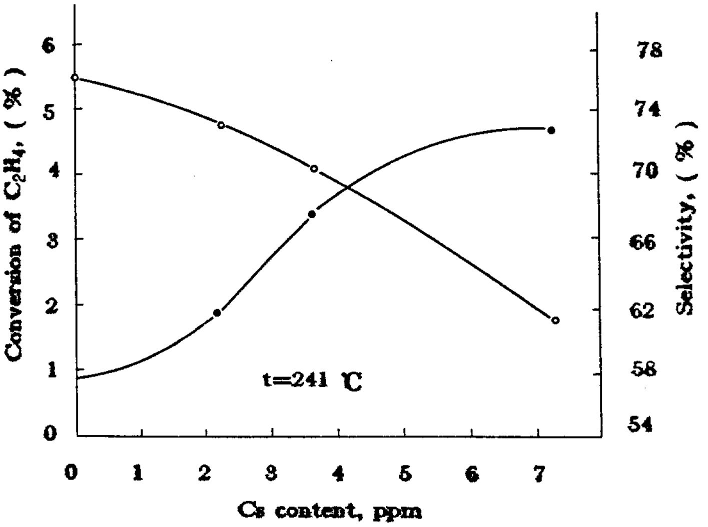

Fig. 5b. Variation of conversion of C_2H_4 and selectivity with Cs content, o——o: conversion of C_2H_4, •——•: selectivity for EO, reaction temperature 241°C.

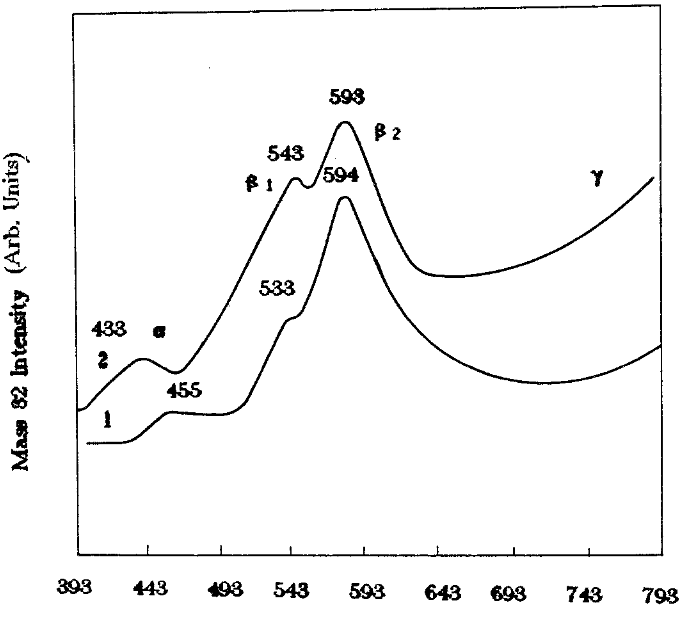

Fig. 6. TDS of O_2 and Ag-Cs surface treated by oxygen at high temperature. 1: $\beta = 50$ K/min, 2: $\beta = 70$ K/min.

corresponds to the temperature of discomposition of the Cs compound on the Ag surface (see fig. 6).

b. TDS of oxygen adsorption.

Two kinds of oxygen adsorption TDS were obtained in the same adsorption-desorption apparatus. The Ag surface was first treated only by 5×10^{-6} Torr vacuum before adsorption of oxygen, but oxygen was difficult to be adsorbed. It was then heated up to 500°C and treated with a 5×10^{-6} Torr oxygen flow, then cooled down to room temperature and evacuated to 3×10^{-6} Torr. It was then treated with 3×10^{-4} Torr oxygen for 10 minutes at room temperature. The TDS of oxygen adsorption are shown in fig. 6.

There are four desorption peaks: α, $\beta 1$, $\beta 2$ and γ. The maximum desorption temperatures of the α, $\beta 1$, and $\beta 2$ curves are 433 K, 543 K and 593 K respectively. According to previous work on unmodified electrolytic silver surface [11], the $\beta 1$ peak corresponds to adsorbed molecular oxygen, the $\beta 2$ peak to the absorbed atomic oxygen and the γ peak to the subsurface oxygen. Referring to the results obtained by Lambert et al. [9], the $\beta 1$ peak is the oxygen from the decomposition of Cs oxide or carbonate.

Another TDS (fig. 7b) was obtained under different conditions for surface cleaning. It was cleaned before adsorption of oxygen by repeatedly Ar etching and high temperature annealing as above. Obtained oxygen adsorption TDS are shown in fig. 7a.

The oxygen adsorbed Cs modified sample was treated with CO as in the case of the Ba modified sample. Peak β on the TDS of the CO treated sample (see fig. 7b) had disappeared. So the β peak corresponds to adsorbed atomic oxygen while the α and γ peaks correspond to adsorbed molecular oxygen and subsurface atomic oxygen respectively. The disappearance of the $\beta 1$ peak of fig. 6 in fig. 7b is due to Cs_2CO_3 or CsO_x already decomposed to a lower state oxide during the surface cleaning. The desorption activation energy E_d of adsorbed atomic oxygen was also calculated. It is 148 kJ/mol, i.e. 14 kJ/mol higher than that of unmodified Ag surface.

The work function $\Delta\phi$ of the Ag-Cs-O_2 adsorption system was also measured. It is 0.60 eV, i.e. 0.10 eV higher than that of the unmodified Ag-O_2 adsorption system. From the results obtained above it was shown that Cs does enhance the selectivity to EO at the expense of conversion (activity) of ethylene. These promoting effects of Cs can be explained as follows.

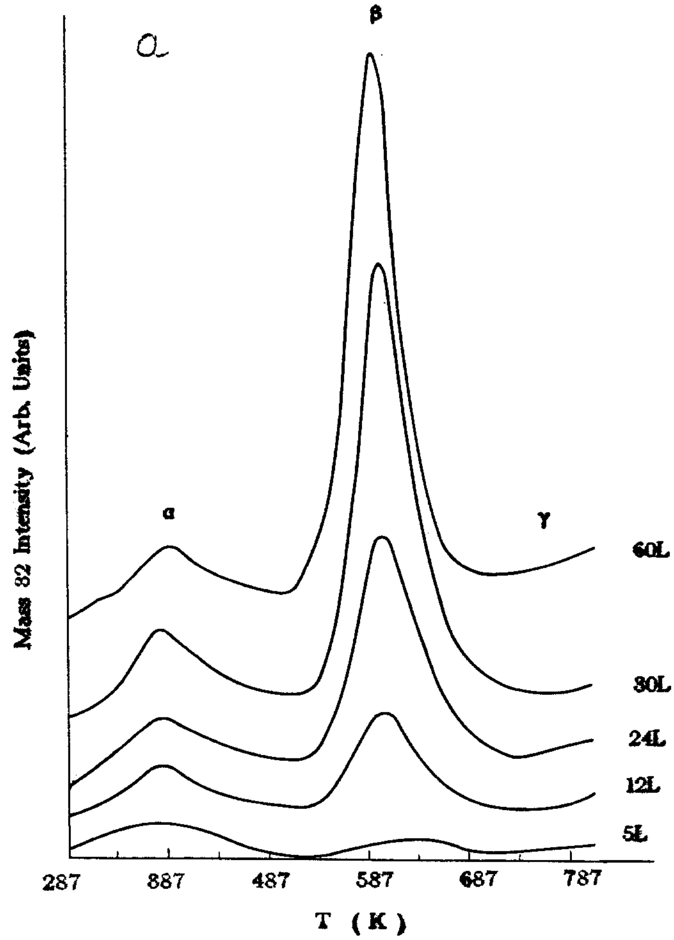

Fig. 7a. TDS of oxygen on Ag-Cs surface. Adsorption temperature is room temperature.

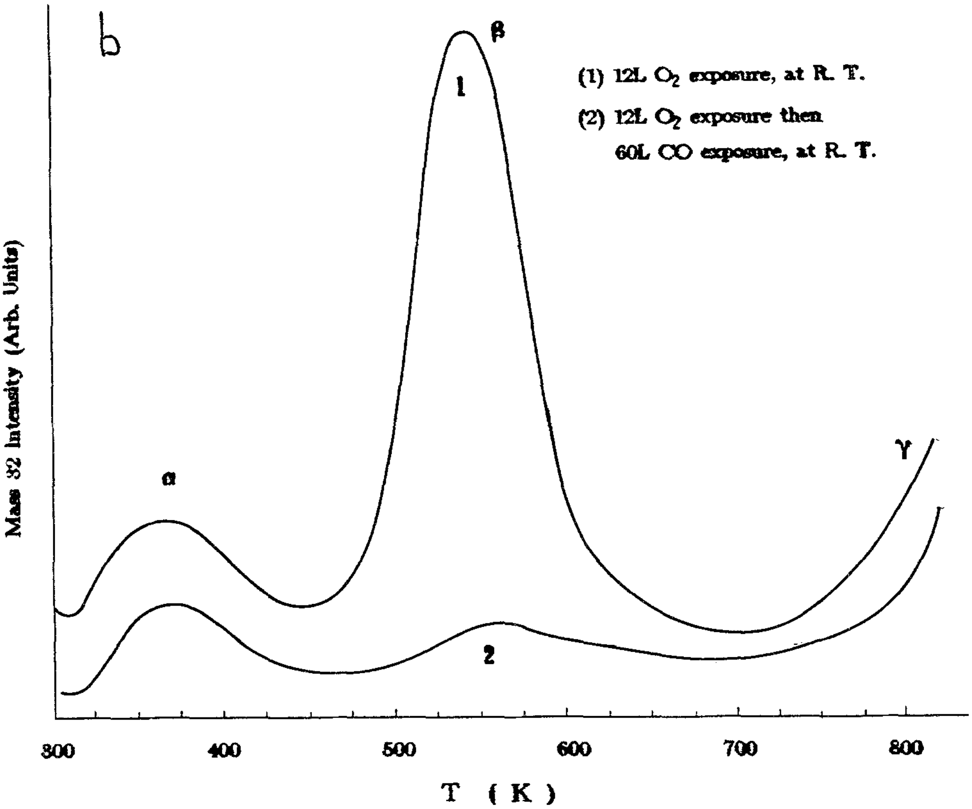

Fig. 7b. TDS of oxygen with and without adsorbing CO on Ag-Cs surface.

The work function change ($\Delta\phi$) of oxygen adsorption on Cs modified Ag surface is higher than that of the unmodified Ag-O_2 system. It means the adsorption bond energy of adsorbed atomic oxygen becomes higher. So it is less active for epoxidation reaction, i.e. lower conversion of ethylene. Less activity of the Cs modified Ag surface can also be explained by higher adsorption activation energy E_d of adsorbed atomic oxygen. However the enhancement of selectivity to EO by Cs modified Ag would be explained by the retardation effect of Cs for isomerization of EO to aldehyde as has been studied by many authors.

4. Conclusion

Ba enhances the activity but lowers a little the selectivity to EO in Ag catalyzed epoxidation reaction of ethylene while Cs gives higher selectivity but less activity. The effects of both promoters can be explained by the idea that adsorbed atomic oxygen is the crucial species for this kind of reaction and by the work function change ($\Delta\phi$) with Ba or Cs during the adsorption of molecular oxygen on modified silver surface.

Acknowledgments

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References

[1] E.T. McBee, H.B. Hass and P.A. Wiseman, Ind. Eng. Chem. 37 (1957) 432.
[2] H.T. Spath, G.S. Tomazic, H. Wurm and K. Turkur, J. Catal. 26 (1972) 18.
[3] R.A. Marbrow and R.M. Lambert, Surf. Sci. 61 (1976) 923.
[4] R.A. Marbrow, D. Briggs and R.M. Lambert, Surf. Sci. 65 (1977) 314.
[5] P.J. Goddard and R.M. Lambert, Surf. Sci. 79 (1979) 33.
[6] P.J. Goddard and R.M. Lambert, Surf. Sci. 107 (1981) 513.
[7] M. Kitson and R.M. Lambert, Surf. Sci. 109 (1981) 60.
[8] M. Kitson and R.M. Lambert, Surf. Sci. 110 (1981) 205.
[9] R.B. Grant and R.M. Lambert, Langmuir 1 (1985) 29.
[10] C.T. Campbell, J. Phys. Chem. 99 (1985) 5789.
[11] Bao Xinhe and Deng Jingfa, Surf. Sci. 163 (1985) 444.
[12] Dong Shuhong, Xiao Fanhau and Deng Jingfa, J. Catal. 109 (1988) 170.
[13] C. Backx, J. Catal. 72 (1981) 364.
[14] Bao Xinhe, Doctoral dissertation, Fudan University, 1989.
[15] R.B. Grant and R.M. Lambert, J. Catal. 92 (1985) 364.
[16] R.P. Nielson, USP.3, 702, 259 (Shell Oil Co.) 1972.
[17] R.B. Grant and A.M. Lambert, J. Catal. 93 (1985) 92.