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Retardative Effect of Amine on Ethylene Oxidation over Silver

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Ethylene oxidation was studied on a silver catalyst by adding small amounts of amines in a stepwise manner in its steady state. Dynamic retardations of the oxidation were followed by gas-chromatographic analysis of the reaction products and by temperature-profile measurements of the catalyst bed. The inlet amine concentration dependence on the retardation of the ethylene oxidation followed an inverse sigmoid shape. The boundary concentration of the amine (C_b) which can maintain the steady state of the retarded oxidation was found to differ from amine to amine. A logarithmic linear relationship was observed between the vapor pressure of the amine and C_b. The relationship indicates the existence of a correlation between the gas–liquid equilibrium constants of the amines and both adsorption constants of the amines on the catalyst surface during ethylene oxidation and combustion rates of the amines themselves. On the other hand, regardless of the nature of the amines, the boundary space–time conversion of oxygen which can maintain the steady-state retardation of the oxidation showed an intrinsic value for each catalyst. The added amine showed a selective retardation of the formation of carbon dioxide for a catalyst which has relatively high combustion activity even at low temperatures and a nonselective retardation of the formation process of both ethylene oxide and carbon dioxide for a catalyst which has desirable epoxidation activities at higher temperatures.

INTRODUCTION

It is well known that carbon dioxide (CO_2) shows a strong inhibiting effect on the gaseous oxidation of ethylene over silver (*1*, *2*). Such moderation is recognized as steady-state retardation of the oxidation which is linearly proportional to the concentration of the surface CO_2 adsorbed onto the silver following Langmuir's adsorption isotherm (*3*, *4*). It is considered that this kind of retardation is brought about by a strong adsorption of the acidic CO_2 on the basic surface of the oxygen-covered active silver under the reaction conditions. There are, in general, no significant differences in the modes of the CO_2-caused retardation of both the reactions of epoxidation and combustion.

In the present study, ammonia and amines of a basic nature were added to the oxidation system in anticipation that another type of moderation would take place. The occurrence of different retardations on the two different courses of the oxidation to both ethylene oxide (EO) and CO_2 can give a clue to the elucidation of different mechanisms of the two different routes. From this viewpoint, amines were added in different concentrations to the ethylene oxidation over two silver catalysts of considerably different oxygen-adsorbing properties. Thus, steady-state moderations of oxidation were observed, and a comparison was made between the reaction rates and the amine types associated with

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the different catalysts. The results were surveyed in view of the surface characters of the catalysts.

EXPERIMENTAL METHODS

Apparatus

A continuous-flow fixed-bed reactor was used in the present study. The reactor consisted of a Pyrex glass U-tube of 12-mm i.d. Five milliliters of a catalyst were placed in the lower half of one side of the U-tube, making the length of the catalyst bed 5 cm. The other side of the U-tube was filled with small Pyrex distillation rings serving as an inert packing for the preheater section. Temperature control was provided by immersing the reactor in a thermostated molten salt bath. A thermocouple was used to measure the axial temperature profile within the reactor. The probe was inserted into a 4-mm-o.d. Thermowell concentric with the reactor.

Catalyst Preparation

Catalyst I. Porous silica–alumina particles of 20- to 30-mesh size, which had been heat treated at a higher temperature, were immersed in an impregnating ammoniac complex silver carbonate solution. After impregnation, the catalyst was dried thoroughly at a temperature below 70°C, followed by heat treatment at 180°C in air to decompose the silver carbonate into oxide. The oxide was then reduced to metallic silver at 120°C in a stream containing 15% hydrogen in nitrogen, followed by heat treatment for 1 hr at 400°C in pure hydrogen. The product was white in color, and its silver content was analyzed as 16.9% by weight. The BET surface area of the supported silver itself measured by using oxygen as an adsorbate (*5*) was 1.5 m^2/g of Ag.

Catalyst II. An ammoniac complex silver carbonate solution was sprinkled over nonporous alumina porcelain particles of 30- to 60-mesh size. The catalyst was dried, followed by heat treatment at 180°C in air to decompose the silver carbonate into oxide. This operation, from the sprinkling to the heat treatment, was repeated once. The catalyst was hydrogen treated in the same manner as used for catalyst I. The product was white in color and its silver content was analyzed as 22% by weight. The BET surface area of the supported silver itself was 0.5 m^2/g of Ag.

The temperature ranges at which the process of ethylene oxidation are steadily maintained are from 190 to 230°C and from 220 to 270°C for catalysts I and II, respectively. For both catalysts, stable activities were obtained within several minutes following the introduction of reaction gas at the reaction temperature.

Reaction Operation

The reaction was carried out under atmospheric pressure. The reaction gas was introduced from the top of the ring-packed side of the U-tube. The gas first passed downflow through the ring to be thoroughly preheated to the reaction temperature and then passed upflow over the catalyst bed.

The standard reaction conditions were: a feed reaction gas containing 15% oxygen and 85% ethylene by volume; a feed-gas space velocity (SV) of 950–1000 hr^{-1}; and the temperature of the molten-salt bath in the range of 210 to 215°C for catalyst I and 260°C for catalyst II, respectively. The amines were added into the feed reaction mixture by passing at least a part of the feed oxygen through a saturator containing liquid amine which was maintained at a desired temperature in a dry ice-ethanol bath. These were added stepwise in small concentrations to the oxidation reaction over the catalysts performing stable activities. An axial temperature profile was measured by moving the thermocouple up and down in the Thermowell. While the amine addition was continued and stopped repeatedly, transitional and steady-state retardations of the ethylene oxidation were observed by the temperature-profile measurement and prompt analysis of the reaction products by gas chromatography.

Estimation of Axial and Radial Heat-Transfer Coefficients

In order to confirm the reliability of our observation method for the oxidation of ethylene, heat-transfer coefficients were determined by Kunii's method (*6–8*). A sample calculation was carried out for the oxidation reaction at heating-bath temperature (θ_b) of 215°C over catalyst I which has the largest reaction rate (cf. Table 1).

The results with intermediate values at different stages of calculation are as follows: radial effective heat conductivity of the catalyst bed, $k_e = 0.345$ kcal/m·hr·°C; axial effective heat conductivity of the catalyst bed, $k_{ez} = 0.359$ kcal/m·hr·°C; film heat-transfer coefficient at the reactor wall, $h_w = 650$ kcal/m^2·hr·°C.

These values were used to obtain the following values for a variety of heat-transfer resistances (R) expressed in units of reciprocal kilocalories per hour per degree centigrade: radial heat-transfer resistance: $R_e = 5.08$; apparent heat-transfer resistance at the reactor wall, $R_w = 0.818$; heat-transfer resistance of the reactor glass, $R_g = 0.634$.

Further, by using these values, the following heat fluxes were calculated as follows: radial heat transfer, $q_2 = \Delta\theta_{av}/(R_e + R_w + R_g) = 2.22$ kcal/hr; heat carried out from the reaction zone by the reaction gas stream, $q_1 = C_p \cdot G' \cdot \Delta\theta_e = 0.014$ kcal/hr.

In the above equations, $\Delta\theta_{av}$ is the average value of the difference between the catalyst bed temperature (θ) and θ_b, $\Delta\theta_e$ is the difference between θ at the exit of the catalyst bed and θ_b, C_p is the constant-pressure heat capacity of the reaction gas, and G' is the mass velocity of the reaction gas.

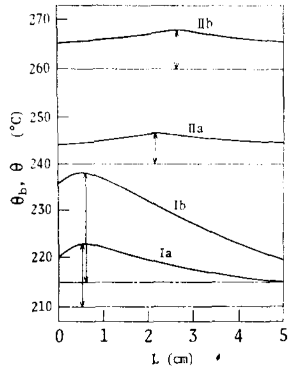

FIG. 1. Catalyst-bed temperature profiles of the standard reactions. L, catalyst-bed length; θ_b; bath temperature (dot-dashed line); θ, catalyst-bed temperature (solid line); Ia, Ib: for catalyst I; IIa, IIb: for catalyst II.

The reliability of the result of the above calculations is confirmed by the comparison of $q_1 + q_2$ (2.24 kcal/hr) and the reaction heat (2.28 kcal/hr) calculated from the composition of the reaction products, which are in good agreement.

Thus it is clear that the ratio of axial heat transfer to reaction heat in the catalyst bed is not greater than 0.6%.

Furthermore, it is also confirmed that there is a substantial linear correlation between oxygen space–time conversion (O_2 STC) and the $\Delta\theta_{av}$ in the range from 0.5 to 6 mol/liter·hr as follows: $O_2 \text{ STC} = 0.375 \cdot \Delta\theta_{av}$.

Consequently, in the reaction system of the present study, the axial temperature profile of the catalyst bed may be regarded as an axial reaction-heat profile.

RESULTS AND DISCUSSION

Characteristics of the Standard Steady-State Reaction

For a standard steady-state oxidation, the reaction conditions and results are shown in Table 1, and the axial temperature profiles are shown in Fig. 1.

Catalyst I has high activity and performs an equal EO space time yield (STY) of 1.2 mol/liter·hr to catalyst II even at a temperature lower by 45°C. However, the selectivity of EO by catalyst I is relatively low.

Catalyst II has a higher EO selectivity compared with catalyst I. A comparison of the temperature profiles of the two catalysts at 215 and 260°C, which give the same EO formation, indicates that catalyst II has a smaller $\Delta\theta$ with a comparatively uniform profile corresponding to the smaller O_2 STC than catalyst I by a factor of 0.5. This implies that the product's inhibition on catalyst II is smaller than on catalyst I.

In order to minutely observe the effect of the amine retardation, it is preferable to adopt a standard reaction condition which gives a smooth catalyst-bed temperature profile with a greater $\Delta\theta$. Hence, the θ_b value for catalysts I and II were chosen as 210 and 260°C, respectively.

TABLE 1

Data of Standard Reaction

Catalyst	I		II	
Bath temperature (°C)	210	215	240	260
Temperature profile curve shown in Fig. 1	Ia	Ib	IIa	IIb
Conversion (%)				
C_2H_4	5.34	6.60	3.26	4.77
O_2	51.5	68.6	26.8	34.6
O_2 STC (mol/liter·hr)	3.49	4.16	1.80	2.32
EO STY (mol/liter·hr)	0.89	1.17	1.03	1.20
EO selectivity (%)	46.6	46.8	70.6	67.6
Product concentration (%)				
EO	2.1	2.6	2.3	2.7
CO_2	4.8	6.0	2.0	2.6
Activation energy for O_2 STC (kcal/mol)	17.3		6.6	

Dynamic Processes in the Amine Retardation Cycles

The dynamic responses of the oxidation reaction were observed by repeatedly adding amines in the small amounts stated below to catalyst I performing stable activity under the above-mentioned standard reaction condition. The amount of ammonia was less than 1.7% by volume in the inlet gas, and the amounts of monomethylamine, dimethylamine, monoethylamine, diethylamine, triethylamine, ethanolamine, and diethanolamine were less than 1.0% by volume in the gas.

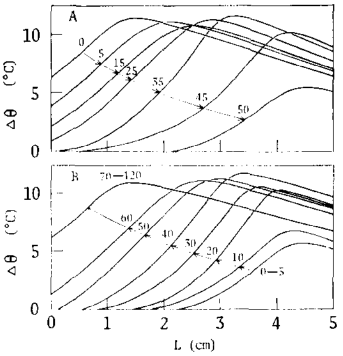

FIG. 2. Changing catalyst-bed temperature profile of catalyst I by the retardation–reaction cycle with 0.83% monomethyl amine at 210°C. A, Progress of retardation with amine addition; B, recovery from the retarded state by the termination of the addition. Numerals indicate the times (in minutes) after the beginning of the addition or its termination.

Figure 2 shows the dynamic response of the temperature profile observed by adding 0.83% monoethylamine and by stopping the addition. Figure 2A shows that lowering of the temperature profile started at the inlet of the catalyst bed, followed by accelerated lowering of the profile toward the center and the exit of the bed 30 min after the beginning of the addition. Figure 2B shows that the termination of the amine addition 50 min after the beginning gave rise to a temperature-profile recovery in the reverse direction of the retardation. Recovery to restore the temperature profile took a little longer than the retardation did to lower it. The recovered profile was stable and coincident with the standard state

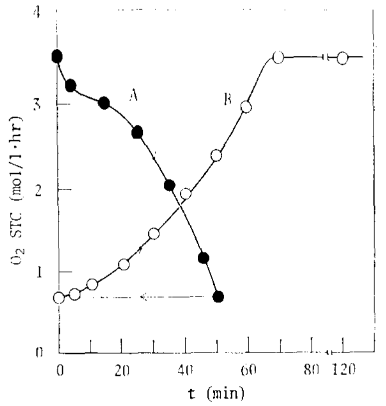

FIG. 3. Changing O_2 STC with the time corresponding to the retarded reaction cycle shown in Fig. 2.

that had been established before the addition.

Plots of the O_2 STC corresponding to the temperature profiles in Fig. 2 follow a reverse sigmoid shape as shown in Fig. 3. Throughout the course of the run, neither amine nor nitrogen oxides were detected, and nitrogen corresponding to be amount of the added amine was observed in the effluent gas. Therefore, the added amine was considered to be completely converted to carbon dioxide, water, and nitrogen by combustion and probably by the subsequent reactions in the catalyst bed. Even if nitrous oxide formed as an oxidation intermediate of amine, it might be easily decomposed to nitrogen gas and adsorbed oxygen on the surface of the silver catalyst (*9*).

Additions of different amines resulted in a similar retardation–regeneration cycles of the oxidation reaction with the above example, except that ammonia caused a weaker retardation effect. In the case of ammonia, even as large a concentration as 1.7% in the feed resulted in only a 30% decrease of the stable temperature profile over one-third of the catalyst bed from the inlet.

In both cases, the standard activity of the catalyst was recovered almost completely by the stoppage of the amine addition. Even when a small retardation remained, the regeneration treatment of the catalyst at 300°C in a stream of ethylene for 1 hr completely restored the initial standard temperature profile, reaction rate, and selectivity.

Relationship between the Added Amine Concentrations and the Steady-State Retardation of the Ethylene Oxidation

An example of retardation by triethylamine is shown in Fig. 4. The addition of amines, less than 0.025% in the feed gas, was sufficient to maintain the steady-state retardations of the oxidation for at least 1.5 to 2.0 hr corresponding to the amounts of the added amine as shown by profiles b, c, and d of Fig. 4. The addition of the 0.034% amine, however, pushed the retardation slowly but continuously toward complete deactivation of the catalyst within 55 min after the beginning of the addition. This is shown by the temperature profiles e_1 to e_3 in Fig. 4.

The maximum concentration of the added amine in the feed gas which is able to keep the retarded oxidation reaction in a steady state, as for example the above-

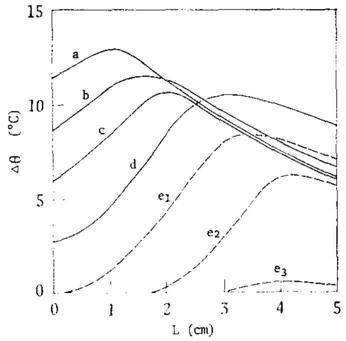

FIG. 4. The steady-state catalyst-bed temperature profiles of catalyst I under the triethyl amine additions with various concentrations at 210°C. Solid line, steady-state retardation; broken line, nonsteady retardation. Amine concentration (as a percentage) for each profile is: a, 0; b, 0.0086; c, 0.017; d, 0.025; e, 0.034. The time elapsed in the case of e (in minutes) is: e_1, 15; e_2, 35; e_3, 52.

mentioned 0.025% for triethylamine, is called the boundary concentration of the amine. The amount of concentration of the added amine which must be fed to completely inhibit the oxidation, as for example 0.013 mol/liter of catalyst for triethylamine calculated from the 0.035% amine in the feed gas, is called the boundary amount of the amine. A plot of the reaction values against the concentration of the added amine, both derived from Fig. 4, gives a retarded-oxidation curve of an inverse sigmoid shape as shown in Fig. 5. The same type of retardation reaction is observed in the acetaldehyde-retarded oxidation of ethylene or propylene over silver (*10*).

As shown by curve b in Fig. 5, EO STY is increased by 10% over the standard level by adding 0.025% triethylamine. This indicates that an addition of the amine not greater than the boundary amount results in a selective moderation of ethylene combustion. The different effects of the amine on the formation activities of both EO and CO_2 like this are discussed later with a variety of amines.

The boundary amounts of the amines and the boundary O_2 STC associated with the addition of such amounts are given in Table 2. Their steady-state temperature profiles are shown in Fig. 6.

It is apparent from this figure that the amines with comparatively larger value of the boundary concentration, and therefore with comparatively weaker retardation ability, lead to temperature profiles with

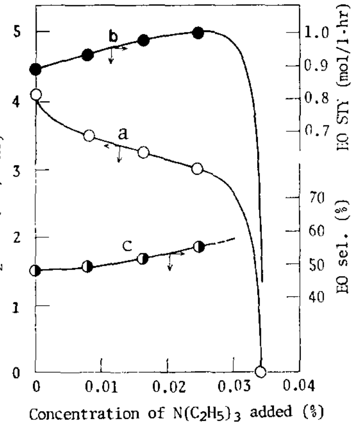

FIG. 5. The amine concentration dependence of the oxidation rate and the EO selectivity of the steady state. The temperature profiles of each reaction are shown in Fig. 4. a, O_2 STC; b, EO STY; c, EO selectivity.

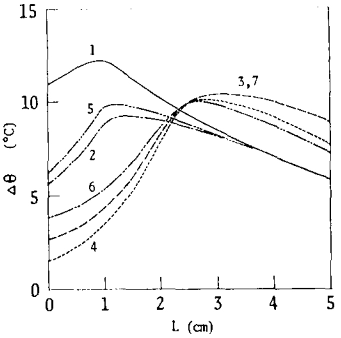

FIG. 6. The steady-state catalyst-bed temperature profiles of catalyst I under the addition of various amines, each with its boundary concentration at 210°C. The boundary concentration of the amines (as a percentage): 1, non-addition; 2, NH_2CH_3, 0.40; 3, $NH(CH_3)_2$, 0.19; 4, $N(CH_3)_3$, 0.06; 5, $NH_2C_2H_5$, 0.25; 6, $NH(C_2H_5)_2$, 0.053; 7, $N(C_2H_5)_3$, 0.025.

TABLE 2

The Boundary Concentration of Various Amines and the Boundary O_2 STC for Catalyst I

Amine	Bath temperature (°C)	Boundary concentration (%)	Boundary O_2 STC (mol/liter·hr)	O_2 STC ratio[a]
Non-addition	210	0	3.54	1.00
NH_2CH_3	210	0.40	2.93	0.83
$NH(CH_3)_2$	210	0.19	2.98	0.84
$N(CH_3)_3$	210	0.060	2.62	0.74
$NH_2C_2H_5$	210	0.25	3.02	0.85
$NH(C_2H_5)_2$	210	0.053	2.88	0.81
$N(C_2H_5)_3$	210	0.025	2.98	0.84
Non-addition	213	0	3.86	1.00
$NH_2(C_2H_4OH)$	213	0.03	3.12	0.81
$NH(C_2H_4OH)_2$	213	0.02	3.12	0.81
Non-addition	215	0	4.61	1.00
NH_3	215	1.7	3.71	0.81

[a] The non-addition reaction in each series are selected as standard.

TABLE 3

The Boundary Amounts of Various Amines for Catalyst I

Amine	Concentration of amine (%)	The time required to stop the reaction (min)	Boundary amount of amine[a] (mol/liter of catalyst)
NH_2CH_3	0.45	110	0.324
$NH(CH_3)_2$	0.25	100	0.162
$N(CH_3)_3$	0.075	100	0.050
$NH_2C_2H_5$	0.28	67	0.120
$NH(C_2H_5)_2$	0.057	100	0.040
$N(C_2H_5)_3$	0.034	55	0.013
$NH_2(C_2H_4OH)$	0.050	80	0.028
$NH(C_2H_4OH)_2$	0.025	10	0.002

[a] The amount of amine which must be fed to completely inhibit the oxidation. θ_b = 210°C for alkyl amines, 213°C for ethanol amines.

only their front parts lowered. But in such cases, ethylene oxidation suddenly begins to show a tendency to stop with a very small supplement of amine concentration. Examples of these amines are monomethylamine and monoethylamine. In contrast to this, the amines with a comparatively smaller boundary concentration, and therefore with comparatively stronger retardation ability, lead to the temperature profiles with their front parts strongly lowered and their rear parts even more enhanced than the standard ones. This is apparently because the most active reaction zone is shifted backward due to lower oxygen consumption in the front zone. Examples of these amines are diethylamine, dimethylamine, trimethylamine, and triethylamine.

The above facts illustrate the following two points:

(a) Adsorption of amines takes place exclusively in the front part of the catalyst bed, the length of which is from one-fifth to two-fifths of the total catalyst bed. The extent of lowering of the temperature profile corresponds to the retardation strength of the amine. No adsorption occurs in the other part of the bed.

(b) In a steady state of retarded oxidation, all of the added amine is consumed by combustion. The combusion rate is coincident with the feed ratio of the amine.

As explained earlier, the steady-state oxidations were maintained at the time of addition of the boundary amounts of the amines. O_2 STC can be regarded as an average reaction rate of the catalyst bed in spite of the fact that the adsorption of the amine does not occur to an equal extent all over the catalyst. The value of the ratio of retardation is defined as the quotient of the moderated O_2 STC by the standard. As shown in Table 2, it is noteworthy that the values centered around 0.83 with an aberration of 0.02 regardless of the nature of the amines. This fact suggests the existence of intrinsic boundary activity of the catalyst which can maintain the steady-state oxidation against the retardation of the amines. The added amines are consumed by combustion and do not get discharged from the bed until the oxidation of ethylene completely stops. Therefore, the boundary

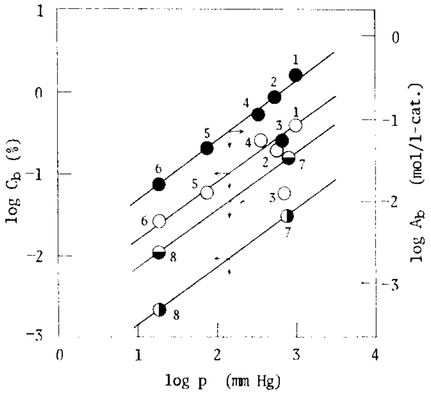

FIG. 7. Logarithmic linear relationship between the vapor pressure of the amine and the boundary values C_b and A_b. p, vapor pressure of amine at 0°C (○, ●), and at 170°C (◒, ◑); C_b, the boundary concentration of amine; A_b, the boundary amount of amine; 1, NH_2CH_3; 2, $NH(CH_3)_2$; 3, $N(CH_3)_3$; 4, $NH_2C_2H_5$; 5, $NH(C_2H_5)_2$; 6, $N(C_2H_5)_3$; 7, $NH_2(C_2H_4OH)$; 8, $NH(C_2H_4OH)_2$.

amount of the amine is the sum of the combustion-consumed amount through the course of the dynamic retardation and the retained amount on the catalyst. The values are shown in Table 3.

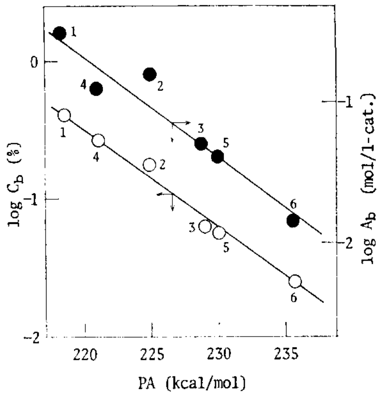

FIG. 8. Semilogarithmic linear relationship between the PA and the boundary values, C_b and A_b. PA, basicity of amine in vapor phase (*12*); 1, NH_2CH_3; 2, $NH(CH_3)_2$; 3, $N(CH_3)_3$, 4, $NH_2C_2H_5$, 5, $NH(C_2H_5)_2$; 6, $N(C_2H_5)_3$.

Relationship between the Boundary Quantities and the Properties of the Amines

It is found that there are logarithmic linear relationships between the vapor pressures of amines and both the boundary amounts and the boundary concentrations of the amines as shown in Fig. 7. It is also found that the relationships for each amine are parallel with one another. This fact indicates the existence of correlations of the gas–liquid equilibrium constants of the amines both with adsorption constants of the amines on the catalyst surface during ethylene oxidation and with the combustion rates of the amines themselves. This fact is explained by assuming that an amine with a higher boiling point occupies adsorption sites on silver more strongly without being oxidized and that such an amine has a higher efficiency in stopping the oxidation, the chain oxygen-consuming step of the combustion, of ethylene.

The order of retardation strength of the amines is as follows:

$$NH_3 \ll NH_2CH_3 < NH(CH_3)_2 < NH_2C_2H_5 < N(CH_3)_3 < NH(C_2H_5)_2 < NH_2(C_2H_5OH) < N(C_2H_5)_3 < NH(C_2H_4OH)_2.$$

It was also found that there is a semilogarithmic linear relationship between the basicities (PA) (*11*) of the amines in a gas phase and both their boundary concentrations and their quantities, as shown in Fig. 8. The basicity is expressed by a

TABLE 4

The Effect of Amines for Catalyst I

Amine	Concentration of amine (%)	Bath temperature (°C)	EO STY (mol/liter·hr)	EO selectivity (%)	$\frac{1}{2}CO_2$ STY (mol/liter·hr)	O_2 STC (mol/liter·hr)
Non-addition	0	210	0.885	46.6	1.01	3.49
NH_2CH_3	0.43	210	0.810	54.9	0.665	2.41
$NH(CH_3)_2$	0.19	210	0.860	50.0	0.860	3.01
$N(CH_3)_3$	0.075	210	1.01	60.2	0.660	2.48
$NH_2C_2H_5$	0.28	210	0.818	59.2	0.563	2.10
$NH(C_2H_5)_2$	0.060	210	0.840	61.8	0.526	2.00
$N(C_2H_5)_3$	0.024	210	1.01	54.1	0.860	3.08
Non-addition	0	213	1.03	47.9	1.12	3.86
$NH(C_2H_4OH)_2$	0.02	213	1.04	54.6	0.866	3.12
Non-addition	0	215	1.17	46.8	1.34	4.61
NH_3	1.7	215	1.05	53.0	0.936	3.71

TABLE 5

The Effect of Amines for Catalyst II[a]

Sequence of experiment	Operation	EO STY (mol/liter·hr)	EO selectivity (%)	$\frac{1}{2}CO_2$ STY (mol/liter·hr)	O_2 STC (mol/liter·hr)
1	Non-addition	1.20	67.6	0.572	2.32
2	$N(C_2H_5)_3$ (13 ppm): treatment with C_2H_4, flow for 1 hr at 350°C	0.972	60.0	0.623	2.34
3	Non-addition	0.991	58.9	0.692	2.57
4	NH_3 (30 ppm)	0.882	58.0	0.639	2.36
5	Non-addition: treatment with C_2H_4, flow for 1 hr at 340°C	0.752	58.6	0.523	1.95
6	Non-addition	0.838	51.5	0.790	2.79

[a] θ_b = 260°C; reaction time of each run = 1–2 hr.

value of enthalpy with a sign the inverse of that of the addition reaction of protone. An organic acid with a larger alkyl group shows a stronger acidity in a gas phase (*12*). Such an acid with a consequent larger molecule has a larger retardative effect on the catalytic reaction (*13*). It is realized, therefore, that the strength of the basicity or acidity of a retarder is not directly associated with the strength of retardation of catalytic surface reactions. It is also clear that the basicity of the amine has an apparent correlation with the strength of the retardation through a positive correlation between the basicities and the vapor pressures of the amines.

Points for trimethylamine of Fig. 7 fall off the lines drawn. Although it is difficult to elucidate the reason for this quantitatively, it is considered that the general nature of the tertiary amine, whose chemical reactivity is considerably lower than that of the primary or secondary amine, is reflected in this oxidation over a silver catalyst. That is, since trimethylamine itself may not oxidize very easily, its retardative effect should be comparable with the others differing by only smaller amounts from those expected from the effects of mono- and dimethylamine. Moreover, the fact that this exception is shown only in trimethylamine may be understood by analogy with the fact that the catalytic combustion of methane is more difficult than that of ethane or propane. In such a case, it is useful to refer to the relation between the chemical nature of the amine and C_b or A_b as illustrated in Fig. 8.

Mechanism of the Amine Retardation on the Oxidation of Ethylene

The reaction orders of the oxidation of ethylene with and without amine addition are listed in Tables 4 and 5, for catalysts I and II, respectively.

The results of Table 4 for catalyst I with higher activity at lower temperatures are understood as follows. While EO STYs are slightly influenced by the addition of amines in the range of 10% decrease to 14% increase compared with the standard reaction, CO_2 STYs show a remarkable decrease of 15% to 48% with consequent increase of EO selectivity by 3 to 15%. That is to say, the amine possibly competes for the same adsorption site as EO does resulting in an acceleration of the desorption of formed EO. As a result, the amine gives rise to the above-mentioned selective retardation of a chain oxygen-consuming step of combustion.

For the sake of argument, if a small amount of nitrous oxide, which is a possible oxidation intermediate of an amine, had reacted with ethylene, the extent of the reaction with ethylene should be very small compared with that of the reaction between oxygen and ethylene (*14*). Therefore, the effect of such an intermediate is negligible.

In the case of catalyst II, a very small concentration of the amine, even one-tenth of the value required for catalyst I, has an apparent influence. In this case, ammonia leads to a nonselective retardation of both EO and CO_2 formation activities; however, trimethylamine shows a selective retardation of EO formation activity. In addition to these features, the change in catalyst activity caused by the addition of the amine tends to remain. As a result, the amine-treated catalyst is found to have a tendency to regenerate its O_2 STC but not to completely regenerate EO STY with heat treatment in an ethylene stream at 350°C. The surface of a catalyst like catalyst II, which has desirable epoxidation activities at higher temperatures, has a small oxygen-adsorbing capacity and considerable reducing property with less active sites. Consequently, even a very small amount of the amine exerts an influence by poisoning the active sites which are few in number. The lessening of the number of the sites gives rise to a shortage of oxygen which takes part in the chain reaction, leading to nonselective retardation of both activities. Furthermore, since catalyst II originally has a greater activity for EO formation, the influence on the greater activity becomes dominant.

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