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Selectivity Characterization of Ethylene Oxidation Reactions: Oxygen Chemisorption

The ethylene oxidation reactions over silver catalyst have been the subject of many studies and there are several review articles on the subject (*1–4*). The unique selectivity exhibited by the silver catalyst, structure-sensitive nature of the reactions (*5*, *6*), and not so simple catalysis involving oxygen adsorption are perhaps the reasons why this reaction system has attracted so much attention. Well over 15 different reaction mechanisms reported in the literature are an indication how intriguing the reaction system is. While the kinetics depend on how the catalyst is prepared or what the reaction conditions are, there must be some underlying cause for the diverse kinetic behavior observed. This paper presents an attempt to describe the apparently diverse kinetic behavior in terms of some basic measurement relevant to the catalysis. In particular, an attempt is made to relate the selectivity to oxygen chemisorption behavior for the catalyst prepared, heat-treated, and sintered in a variety of ways. Such a characterization would enable us to isolate a set of conditions in terms of a basic measurement that could lead to better performance of the catalyst.

EXPERIMENT

A recycle reactor was used to generate kinetic data in the temperature range of 421 to 489 K and in the ethylene concentration range of 1 to 9 mole% at atmospheric pressure with excess oxygen and no moderator. We found through theoretical calculations and experiments that a pellet size of 3 mm or less and a recycle ratio of 20 for the feed rate of 100 ml/min yield intrinsic kinetics with less than 1% error in treating the recycle reactor as a continuously stirred tank reactor (CSTR). The maximum temperature gradient under typical reaction conditions along the axis of the reaction zone was measured to be less than 1 K. The line from the reactor to the gas chromatograph was at around room temperature such that no post-reactor reaction (*7*) occurred.

An extensive investigation revealed that the following procedures yield consistent and reproducible results: (1) As a standard pretreatment, the catalyst is oxygenated at 673 K for 45 min by feeding pure oxygen at 20 ml/min into the recycle reactor. (2) Immediately following the pretreatment, the reactor temperature was brought down to the required reaction temperature, which took less than 15 min. (3) A mixture of ethylene, oxygen, and helium (as the diluent) was then introduced into the reactor through a multiple channel electronic mass flow controller at the desired rates and composition. Usually, the system reached steady state within 45 min. (4) When the steady state was reached, the exit stream was analyzed for the composition and the analysis repeated after 15 min, concluding a kinetic run. The system including the gas chromatograph was purged completely between runs. A Tracor 550 gas chromatograph (dual column) with a thermal conductivity detector and Porapak-Q columns (3.2 mm o.d. and 3.65 m long) set at 323 K was used for the composition analysis. Research grade gases used in the experiments were further purified by passing them through molecular sieves.

The catalyst used for the determination of intrinsic kinetic data was prepared using silver oxide dissolved in a solution of lactic

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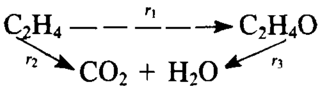
acid and distilled water (*8*) to form silver lactate. The solution was heated to around 368 K. Small fused alumina pellets (BET area of 1 m^2/g) were added to the solution. The impregnation of silver lactate onto the pellets was carried out at around 368 K for 1 hr. The excess solution was decanted and the dried pellets were decomposed at 643 K in helium for 16 hr for conversion to metallic silver. This catalyst will be referred to as lactate catalyst. For comparison purposes, another type of catalyst referred to as nitrate catalyst was also prepared using silver nitrate instead of silver oxide (*9*).

A dynamic pulse method similar to the one used by Wanke *et al.* (*10*) was used to determine the amount of oxygen chemisorbed as a function of adsorption temperature. We found that the following procedures yielded consistent, reproducible results: (1) Clean the silver surface off oxygen prior to chemisorption by maintaining the bed at 573 K and passing the purified hydrogen at 20 ml/min for 1 hr. (2) Bring the temperature down to the desired level and purge hydrogen by switching to the carrier gas (helium) at 60 ml/min. This purging is usually completed in 30 min. This can be checked by observing the thermal conductivity signal on the recorder. (3) Inject oxygen pulses at approximately 5-min intervals. Approximately 7–10 pulses were adequate for the completion of chemisorption. Research grade gases further purified through liquid nitrogen trap were used and the weight of catalyst used in the experiments was approximately 10 g. The thermal conductivity signal was calibrated in the entire range of the oxygen concentration of interest based on peak area (*11*). We did not observe any oxygen adsorption on fused alumina (*12*) that we used as the support.

EXPERIMENTAL RESULTS

For the ethylene oxidation reactions given by



$$\begin{tikzcd} C_2H_4 \arrow[rr, dashed, "r_1"] \arrow[dr, "r_2"'] & & C_2H_4O \arrow[dl, "r_3"] \\ & CO_2 + H_2O & \end{tikzcd}$$

we define the overall conversion of ethylene x as

$$x = \frac{\{(F_{C_2H_4})_{in} - (F_{C_2H_4})_{out}\}}{(F_{C_2H_4})_{in}} \tag{1}$$

the yield of ethylene oxide y as

$$y = \frac{(F_{C_2H_4O})_{out}}{(F_{C_2H_4})_{in}} \tag{2}$$

and the selectivity of ethylene oxide S as

$$S = \frac{y}{x} = \frac{(r_1 - r_3)}{(r_1 + r_2)} \tag{3}$$

where F_i is the molar flow rate of ith species. The selectivity data for various types of the catalysts described in Table 1 are summarized in Table 2 along with the corresponding conversions.

Experiments with both the lactate and nitrate catalysts showed a marked difference in activity. The lactate catalyst required much lower reaction temperatures (421–489 K) than the nitrate catalyst (463–533 K) for the same conversion range. These lower than usual reaction temperatures observed for the lactate catalyst are not unique. For instance, Hucknall (*13*) reported in a review that a special type of catalyst by Erdoelchemie GmbH, incorporating a blowing agent such as lactic acid hydrazide needed reaction temperatures as low as 433 K and the catalyst prepared by Morikana and Kiyoshi needed temperatures around 423 K. The reason for such a wide variation of reaction temperatures with various types of silver catalyst is not exactly known. Hucknall claims that the apparent advantage of using silver lactate is that it is less soluble than silver nitrate and therefore crystallizes faster during the drying period, which helps to give a more even silver deposit later, by reducing crystal growth. Our SEM micrographs did show that the lactate catalyst had smaller crystallite size than the nitrate catalyst (1500 vs 2500 Å) even though the average crystallite size of the supported silver catalysts could not be determined with confidence based on the micrographs.

TABLE 1

Chemisorption Data

Catalyst sample	Description	Adsorption temperature (°K)	Net oxygen adsorption (μl/g)	Metastable oxygen adsorption (μl/g)
A1	Batch A was prepared with 100 g fused alumina pellets. The silver loading on these pellets was not so uniform. The pellets with apparently heavier metal loading (~20 g) were hand-picked and stabilized by oxygenating at 573 K for 100 hr. This lot designated as Sample A1 was used for extensive kinetic study and its average metal loading was estimated to be ~12% by weight	375	20.9	0.0
		396	29.3	0.0
		423	50.5	0.0
		445	46.3	5.2
		481	11.2	12.1
A2	The remaining portion of Batch A was evenly divided into four parts. The average metal loading of each part was ~8.1% by weight. Part 1 was designated as Sample A2, which represented fresh and unsintered catalyst	373	21.4	0.0
		423	34.7	0.0
		430	25.4	7.0
		478	12.2	15.4
A3	Part 2 was sintered at 648 K for 500 hr in a stream of 5 mol % ethylene in air. This sintered catalyst was designated as Sample A3	372	19.3	0.0
		424	30.9	0.0
		477	7.7	9.8
A4	Part 3 was sintered at 773 K for 500 hr in a stream of 5 mol % ethylene in air. This sintered catalyst was designated as Sample A4	373	10.9	0.0
		424	20.4	0.0
		475	9.8	9.3
A5	Part 4 was sintered at 973 K for 500 hr in a stream of 5 mol % ethylene in air. This sintered catalyst was designated as Sample A5	374	9.2	0.0
		424	14.0	0.0
		485	2.8	10.6
B	A small batch was prepared a few months prior to Batch A, exactly the same way but with a different batch of chemicals. This batch of catalyst designated as Sample B was fresh and unsintered and had an average metal loading of ~8.0% by weight	374	14.5	0.0
		424	36.7	5.2
		477	4.6	15.3
C	Another small batch was prepared using the used chemicals of Batch A catalyst. This batch, designated as Sample C was also fresh and unsintered and had an average metal loading of 7.0% by weight	374	16.4	0.0
		421	32.6	8.1
		477	7.4	16.1
D	A fresh batch of catalyst was prepared using highly concentrated silver lactate solution to obtain a maximum silver loading of 8.5% by weight. This batch was designated as Sample D	373	13.0	0.0
		423	33.5	15.1
		473	4.0	20.6
E	Another fresh batch of catalyst was prepared using medium concentrated lactate solution to obtain a silver loading of 5% by weight. This batch was designated as Sample E	373	7.3	0.0
		423	17.0	2.9
		481	7.9	15.3
F	A last batch of catalyst was prepared using weakly concentrated lactate solution to obtain a silver loading of 2.9% by weight. This batch was designated as Sample F	378	10.8	0.0
		430	21.0	3.1
		480	12.0	10.8

Note. All the catalysts were prepared by lactate method as described by Klugherz and Harriott (*8*). The kinetic and adsorption studies were done using the same pellets from any sample. All the experiments were done with the same experimental setup using the same batch of gases.

TABLE 2

Selectivity Data

Catalyst sample	Reaction temperature (°K)	Reaction gas composition		Conversion (%)	Selectivity (%)
		% C_2H_4	% O_2		
A1	421	Range:	Range:	4.3	60.0
10.00 g catalyst	434	1.09–9.08 mol%	17.43–20.51 mol%	7.0	58.7
100 ml/min feed	448			11.4	57.3
	459			20.3	56.2
	473			36.5	48.0
	489			47.2	42.0
A2	431	4.58	19.83	8.0	58.0
10.07 g catalyst	448	4.26	19.28	14.6	55.0
100 ml/min feed	470	3.48	17.83	30.1	50.0
A3	431	4.94	20.27	1.9	58.0
9.88 g catalyst	450	4.76	20.02	5.5	52.0
100 ml/min feed	470	4.45	19.45	11.5	50.0
A4	428	4.92	20.06	3.2	57.0
10.06 g catalyst	450	4.74	19.77	6.7	55.0
100 ml/min feed	468	4.42	19.17	13.0	51.0
A5	433	4.89	20.22	5.0	52.0
10.98 g catalyst	449	4.68	19.87	9.1	54.0
100 ml/min feed	470	4.02	18.69	21.9	55.0
B	430	4.87	19.92	4.4	58.0
6.01 g catalyst	445	4.68	19.59	8.2	54.0
100 ml/min feed	466	4.39	19.03	13.9	50.0
C	429	4.76	20.01	3.0	59.0
5.77 g catalyst	449	4.55	19.65	7.2	55.0
100 ml/min feed	473	4.11	18.85	16.1	50.0
D	431	4.71	19.91	7.6	56.0
9.99 g catalyst	448	4.31	19.28	15.5	57.0
100 ml/min feed	468	3.58	18.25	29.8	60.0
E	432	5.00	20.86	2.5	55.0
9.99 g catalyst	450	4.66	20.27	9.1	52.0
100 ml/min feed	465	4.23	19.53	17.6	52.0
F	432	4.85	20.15	1.0	—
9.51 g catalyst	446	4.74	19.95	3.3	51.0
100 ml/min feed	466	4.40	19.38	10.2	52.0

This marked difference in activity between the lactate and nitrate catalysts, in fact, prompted us to examine the oxygen chemisorption behavior of the two catalysts which eventually led us to the correlation between selectivity and oxygen chemisorption behavior. As evident from Fig. 1. these two catalysts show markedly different behavior. We found that the activity of these catalysts was negligible for temperatures lower than the peak temperature, i.e., the temperature at which the amount of chemisorbed oxygen is at its maximum, which is approximately 423 K for the lactate catalyst and 473 K for the nitrate catalyst. This temperature dependence of the oxygen chemisorption was first reported by Czanderna (*14*) for the silver powder and in fact his

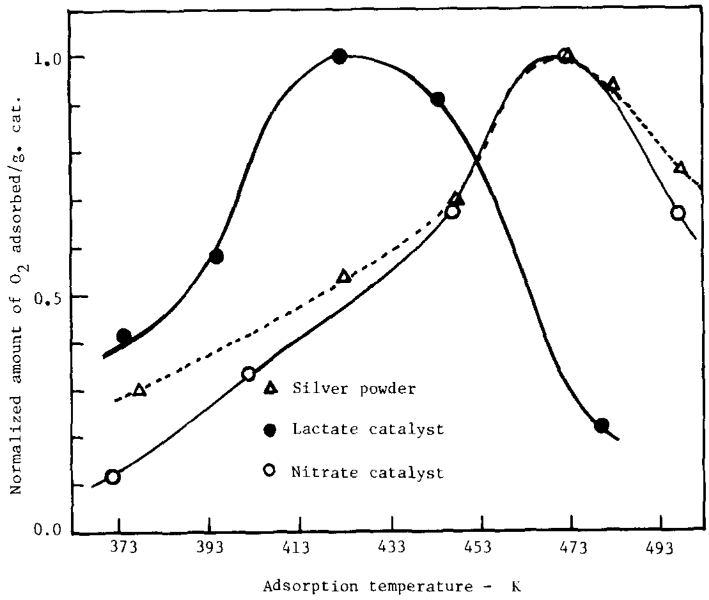


FIG. 1. Effect of temperature on oxygen chemisorption.

peak temperature was almost the same as that shown in Fig. 1 for the nitrate catalyst. Our own experiments with silver powder (2 to 3.5 μm) were in agreement with Czanderna's observations.

The chemisorption results obtained for the lactate catalysts prepared or sintered in a number of different ways are summarized in Table 1 as a function of temperature at which the chemisorption experiment was carried out. The eluted (unadsorbed) oxygen of each injected oxygen pulse appeared in two distinctly different shapes for temperatures below and above approximately 423 K. For temperatures below 423 K, the unadsorbed oxygen appeared as a single sharp peak. For temperatures above 423 K, however, this sharp peak is tailed by a relatively minor but distinct peak. This minor peak area reaches a steady state value, i.e., constant value. This steady state value is reported in the last column of Table 1 as the "metastable oxygen." The oxygen is metastable in the sense that it remains adsorbed in the presence of oxygen but desorbs in the absence of oxygen as evidenced by the appearance of the second peak when the injected oxygen is purged from the system by the carrier gas.

CHARACTERIZATION OF SELECTIVITY

The usual way of characterizing a reaction is to relate the specific rate (rate/catalyst surface area) to percentage exposed (dispersion). Our attempts to relate the specific rate to the percentage exposed based on the maximum amount of oxygen chemisorbed failed. The net rate of ethylene oxide formation, i.e. $(r_1 - r_3)$ divided by the maximum amount of chemisorbed oxygen, which is a measure of specific rate, goes through a minimum for sintered catalysts (catalysts A2 through A5 in Table 1) when plotted against the maximum amount of chemisorbed oxygen, which is a measure of (oxygen-active) dispersion. In contrast, the specific rate increases with increasing dispersion for fresh catalysts (catalysts D through F in Table 1). Similar trends were observed for the overall rate of ethylene consumption, i.e. $(r_1 + r_2)$. When all results were combined for all the catalysts in Table 1, the resulting plot of specific rate vs dispersion was so irregular that no pattern could be observed. This was also true when the selectivity was plotted against temperature.

In light of the above, the selectivity and oxygen chemisorption behavior in Tables 1 and 2 were compared and several observations were made. First, the selectivity is the highest in all cases at the temperature ("peak temperature") at which the amount of chemisorbed oxygen is the highest. This peak temperature is at around 423 K for all the catalysts in Table 1. Second, the maximum selectivity is relatively independent of the maximum amount of chemisorbed oxygen ("$(O_2)_{max}$") at the peak temperature (including the metastable oxygen) but appears to be somewhat higher for $(O_2)_{max} > 30$ μl/g-cat. than for $(O_2)_{max} > 24$ μl/g-cat. Third, the temperature dependence of the amount of chemisorbed oxygen such as the one shown in Fig. 1 is different for different types of catalysts in Table 1 but for a given catalyst, this dependence seems to be related to the selectivity although the selectivity at a given temperature is different for different types of catalysts. This observation suggests that the selectivity could be correlated to the oxygen chemisorption behavior. Further, the amount of chemisorbed oxygen at the reaction temperature could be an indication of the selectivity. In view of the fact that the maximum selectivity is relatively independent of the maximum amount of chemisorbed oxygen, the amount of chemisorbed oxygen normalized with respect to $(O_2)_{max}$ should be used instead of the absolute amount for the correlation. This normalized amount of chemisorbed oxygen is in fact the fraction of maximum amount of oxygen still remaining at the reaction temperature and therefore is the fractional coverage of oxygen-active sites ("oxygen coverage"). (Note that at the peak temperature, fractional coverage is equal to unity.) In calculating the oxygen coverage, the oxygen designated as the metastable oxygen (Table 1) was included. In view of the second observation, the data in Tables 1 and 2 were grouped into two, one for $(O_2)_{max} > 30$ μl/g-cat. and the other

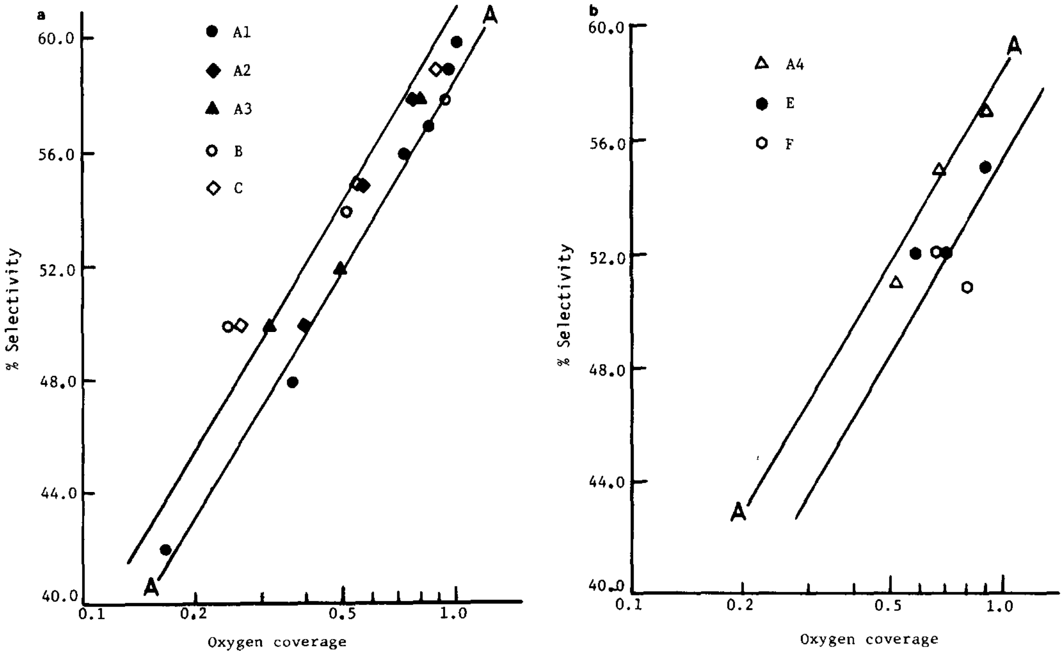


FIG. 2. Selectivity vs oxygen coverage for various catalysts.

TABLE 3

Selectivity Behavior of D and A5 Catalysts

Catalyst	Temperature (°K)	Selectivity (%)	Metastable O_2/ Net O_2 adsorption
	431	56	20.6/4.0 = 5.2
D	448	57	at 473 K
	468	60	
	433	52	10.6/2.8 = 3.8
A5	449	54	at 485 K
	470	55	

for $(O_2)_{max} < 24$ μl/g-cat., and the selectivity data were plotted for each group against the oxygen coverage. The results are shown in Fig. 2a for $(O_2)_{max} > 30$ μl/g-cat. and in Fig. 2b for $(O_2)_{max} < 24$ μl/g-cat. The upper line A–A in Fig. 2b coincides with the lower line A–A in Fig. 2a, consistent with the second observation. The correlation given in Fig. 2 is remarkable in view of the diversity of the catalysts not only in terms of preparation conditions but particularly in terms of the level of sintering. All points except for three are within approximately 2% selectivity in absolute value as bounded by the solid lines for a given oxygen coverage. The variation in the experimentally determined selectivity at a given temperature is of the order of 1% in absolute value for the A1 catalyst. All points in Fig. 2 except those for the A1 catalyst represent the selectivity determined only once and thus do not represent average values.

Some unusual selectivity behavior was observed for D and A5 catalysts, which are not included in Fig. 2. As shown in Table 2, the selectivity of these catalysts increased with increasing temperature, which is unusual. The oxygen chemisorption behavior of these catalysts was also unusual in terms of the relative amounts of stable and metastable oxygen chemisorbed as shown in Table 3, when compared with the other catalysts: the total amount of oxygen chemisorbed (stable + metastable) for these catalysts is made up almost by the metastable oxygen. In particular, the ratio of metastable to stable oxygen for these catalysts is much higher than that for the other catalysts at high temperatures; this ratio for A5 catalyst is larger than 5 whereas it is in the range of 0.9 to 2.2 for all the others except B catalyst which has a value of 3 at 473 K.

The correlation shown in Fig. 2 suggests that the oxygen loosely bound to the active sites is responsible for the ethylene oxide formation. This loosely bound oxygen would be preferentially desorbed as the temperature is increased, resulting in a decrease of selectivity. The decrease in oxygen coverage with increasing temperature, therefore, can be attributed to the loss of loosely bound oxygen. The amount of the loosely bound oxygen depends on how the catalyst is prepared or sintered, resulting in different selectivity for different catalyst at a given temperature. The unusual selectivity behavior discussed above is consistent with the explanation. The metastable oxygen is that portion of chemisorbed oxygen that remains adsorbed in the presence of oxygen but desorbs in the absence of oxygen. This indicates that the metastable oxygen is also a form of loosely bound oxygen. Thus, the selectivity would be unusually high, according to the explanation, if the majority of the chemisorbed oxygen is loosely bound, which is the case as shown in Table 3 for the unusual selectivity behavior. Thus, it might be postulated that the same site which is not responsible for the ethylene oxide formation at a lower temperature could become the site responsible for the ethylene oxide at a higher temperature. That is, the fraction of total sites responsible for the ethylene oxide formation could change with reaction temperature as the temperature excitation causes a change in the distribution of the sites responsible for the oxide formation.

IN CONCLUSION

We have shown that the selectivity of silver catalyst can be well characterized based on the oxygen chemisorption behavior. The fact that the results are applicable to the silver catalyst prepared, heat-treated, and sintered in a variety of ways indicates that it is quite possible to predict the selectivity based on the oxygen chemisorption. The results show that the selectivity depends mainly on the oxygen coverage with slight dependence of the maximum selectivity on the maximum amount of chemisorbed oxygen. The selectivity dependence on oxygen coverage and the role of metastable oxygen can be explained in terms of loosely bound oxygen, which is postulated to be responsible for the ethylene oxide formation.

The selectivity correlation presented here should not be confused with the temperature effect on selectivity. As indicated earlier, the selectivity could not be well correlated to temperature. Further, the temperature dependence of oxygen coverage was different for different catalyst. Experimental verification of the correlation at temperatures lower than the peak temperature was not possible because the catalytic activity was so low at these temperatures that the selectivity could not be determined with any confidence.

The dynamic method for the oxygen chemisorption yielded information that cannot be obtained from a static method, in particular the information on the metastable oxygen. This could be attributed to the fact that the dynamic method represents more closely the oxygen chemisorption behavior during reaction than the static method can.

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