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The Silver-Catalysed Decomposition of N_2O and the Catalytic Oxidation of Ethylene by N_2O over Ag(111) and Ag/α-Al_2O_3

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Single-crystal measurements show that N_2O decomposition is significantly activated on atomically clean Ag(111). The presence of preadsorbed atomic oxygen accelerates the process, as do small amounts of dissolved oxygen; larger amounts of dissolved oxygen have an opposite effect. Isotope distribution data show that the reaction tends to occur preferentially in the vicinity of preexisting surface oxygen atoms. Atomic oxygen deposited by N_2O decomposition is shown to be active for ethylene epoxidation in three different types of experiment, in each of which the effect of gaseous oxygen was negligible. These results provide strong support for the "atomic oxygen" mechanism of ethylene epoxidation.

INTRODUCTION

The chemisorption and catalytic decomposition of N_2O has been studied on a range of transition metal single-crystal surfaces of well-defined structure (*1–6*). At sufficiently low temperatures (300–900 K) dissociative chemisorption occurs, leading initially to the deposition of adsorbed oxygen atoms and the release of gaseous N_2. In the context of catalysts and catalysis, N_2O decomposition by metal oxides is a classical problem which has played an important role in the development of theories of catalysis (*7*). At a more practical level, N_2O is a useful reagent in the measurement of metal surface areas of supported catalysts; oxygen deposition by N_2O has been used to estimate the metal area of Ag/Al_2O_3 catalysts (*8*). From the point of view of reaction mechanism, a particular interest attaches to the use of N_2O when used as the oxidant in the oxidation of ethylene over silver catalysts.

The subject of ethylene epoxidation has been extensively reviewed (*9*) and much discussion has centered on the identity of the epoxidising species. It is well established that under appropriate conditions oxygen adsorption on silver can lead to the formation of both atomic (O(a)) and molecular (O_2(a)) species at the metal surface (*10–12*). Some authors have concluded that O_2(a) is the crucial epoxidising species (*13–17*) while others have assigned this role to O(a) (*18–22*). Recent and more direct experimental investigations have tended to support the latter view (*23–26*). In this connection, some workers have used N_2O as a test reagent because it is thought that at sufficiently high temperatures this molecule leads exclusively to the formation of O(a) at silver surfaces (*1–6, 27*). However, the results of such experiments (*28–31*) have been somewhat equivocal because of the possible occurrence of the following sequence of reactions:

$$N_2O(g) \rightarrow O(a) + N_2(g)$$
$$2O(a) \rightarrow O_2(g)$$
$$O_2(g) \rightarrow O_2(a) \rightarrow \text{epoxidation?}$$

This paper deals with the chemisorption and decomposition of N_2O at the atomically clean Ag(111) surface under pressure conditions which are pertinent to practical ca-

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talysis. The oxygen surface species are characterised, and the effect of temperature and varying levels of dissolved oxygen (O(d)) are investigated. The ethylene epoxidation activity of the single-crystal system is described for two types of experiment in each of which the possibility of interference from adventitious gaseous O_2 has been eliminated. Finally, we report on microreactor results for an Ag/α-Al_2O_3 catalyst operating in N_2O/ethylene at 2.3 atmospheres.

METHODS

The ultrahigh vacuum/pressure cell apparatus has been described previously (*24–26*). Surface characterisation of the single-crystal wafer was performed by LEED/Auger analysis in ultrahigh vacuum; the specimen could then be translated to the pressure cell for studies at elevated pressures. These were of two kinds, either (a) the specimen was retained in the pressure cell which was operated as a differential batch reactor or (b) after gas dosing it was returned to the ultrahigh vacuum chamber for temperature programmed reaction (TPR) or desorption (TPD) measurements. The sample itself was a 99.999% purity (111)-oriented Ag wafer with a favourably high face : edge ratio (7 : 1). *Both* specimen faces could be characterised before and after reaction measurements. Control experiments were carried out to check for oxygen contamination effects which might otherwise compromise interpretation of the TPD results which follow. It was shown that no decomposition of N_2O with subsequent O_2 evolution occurred on the Ta specimen support rods and wires. *In situ* mass spectrometric monitoring of the gas composition during N_2O dosing was used to ensure that the O_2 level was maintained at 0.01% under these conditions; thanks to the low sticking probability of O_2 on Ag(111), the rate of surface oxygen accumulation due to O_2 chemisorption was therefore entirely negligible.

The microreactor system used was constructed out of $\frac{1}{4}$-in.-o.d. stainless-steel tubing and is shown schematically in Fig. 1. Gas sampling was achieved by an on-line Perkin–Elmer Sigma 300 gas chromatograph with an air-activated gas sampling valve, Porapak N and Molecular Sieve 13X columns in a series-bypass configuration.

The catalyst used consisted of an α-alumina support impregnated with 14% by weight of silver. One gram of this catalyst was used in the reactor, where it was securely held in place by glass wool plugs. The reactor was encased in a 30-cm-long

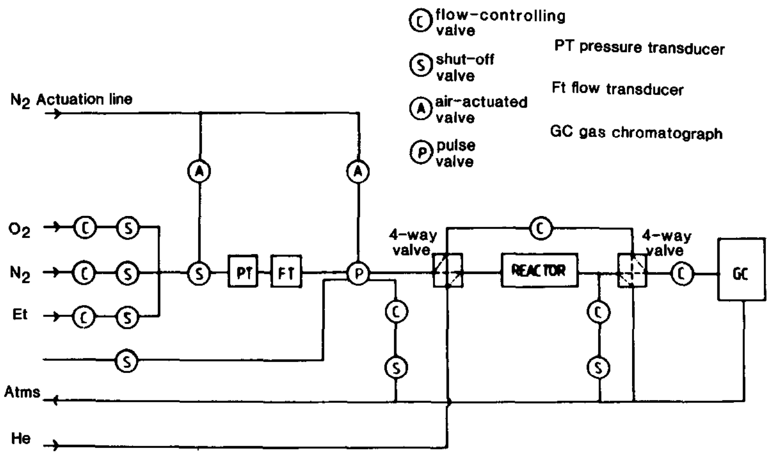


FIG. 1. Schematic diagram of microreactor.

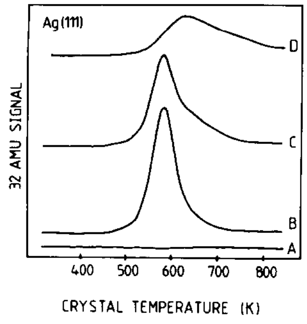


FIG. 2. Temperature programmed desorption of O_2 after heating in 2 Torr N_2O for 30 s at (A) 400 K, (B) 520 K, (C) 640 K, (D) 760 K.

insulated heating block and tempeature measurement of the catalyst bed was achieved by embedding a stainless-steel-encapsulated T1/T2 thermocouple in the middle of the bed. Control experiments showed that in this mode of operation there were temperature variations of no more than 2 K between any two points along the bed.

The reaction mixture consisted of ethylene and nitrogen (purity > 99.9%) and research grade N_2O (purity > 99.99%). Sufficiently high flowrates were maintained in the reactor to ensure that the reaction was not diffusion-controlled (GHSV $\geq$ 2000 (*32*)).

RESULTS

N_2O Decomposition on Ag(111)

Room-temperature dosing of the specimen with large exposures of N_2O at 2 Torr led to no detectable adsorption. Doses of up to 6×10^7 L (1 L = 1 L 10^{-6} Torr s) showed no adsorbate signals in the Auger spectrum and TPD measurements showed no gas evolution at 28, 32, and 44 amu (N_2, O_2, N_2O, respectively). However, heating the specimen in 2 Torr of N_2O did lead to oxygen uptake; Fig. 2 shows the result of TPD measurements at 32 amu made after heating for 30 s to various temperatures, followed by cooling to 300 K and evacuation. It can be seen that there is a negligible interaction at 400 K, substantial uptake at 520 K (the temperature at which ethylene epoxidation is typically carried out), and that a different type of oxygen species is formed at higher temperatures. The 580 K desorption peak is known to be due to O(a) (*33–35*) and we have previously shown that the higher temperature feature (Figs. 2C, D) is due to the presence of subsurface oxygen (*26*). These results show that N_2O decomposition on Ag(111) is a significantly activated process which gives rise to O(a) and O(d) species, both of which are significant in the partial oxidation of ethylene (*21, 23, 25*). They also demonstrate that N_2O dosing does *not* give rise to the dioxygen species (O_2(a)) which results from dosing with O_2 itself and which is characterised by a desorption peak at 380 K (*12, 33*).

The effect of preadsorbed surface atomic oxygen on the decomposition of N_2O was examined in the following way. The clean surface was first dosed with 2×10^6 L of $^{18}O_2$ at 0.2 Torr and 300 K; this exposure is insufficient to saturate the clean Ag(111) surface (*33*). The specimen was then heated carefully to 400 K, a procedure which selectively removes the $^{18}O_2$(a) dioxygen species leaving only ^{18}O(a) on the surface and without any formation of ^{18}O(d) (*26, 33*). This incomplete atomic overlayer was then exposed to 4×10^6 L of $N_2{}^{16}O$ *at 300 K*. Figure 3 shows the results of a subsequent multi-mass TPD measurement in which the signals at 32, 34, and 36 amu were monitored simultaneously. Two conclusions may be drawn from these data. First, it is evident that in the presence of preadsorbed O(a), N_2O decomposition is no longer an activated process; dissociative chemisorption now proceeds quite readily at 300 K. Second, the isotopic distribution in the desorbing O_2 is very far from the statistically expected result. The majority species are $^{18}O^{18}O$ and $^{18}O^{16}O$ with relatively little $^{16}O^{16}O$; as discussed below, this observation is thought to be significant to the mechanism of N_2O decomposition.

The effect of varying levels of O(d) was investigated by a similar procedure. Heating the crystal at 425 K for 2 h in a 6:1

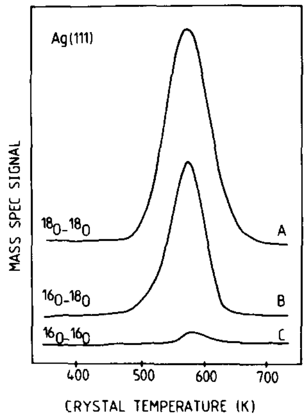


FIG. 3. Multi-mass TPD after predosing with $^{18}O(a)$ and subsequent saturation with $N_2{}^{16}O$ at 300 K (see text). (A–C) 36, 34, 32 amu, respectively. Heating rate 11 K s^{-1}.

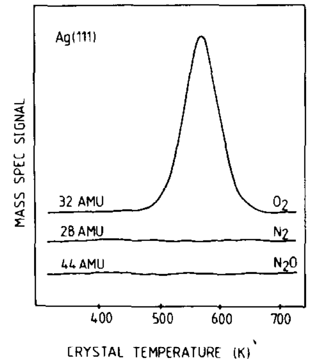


FIG. 4. Multi-mass TPD after dosing an O(d)-loaded surface with 0.2 Torr N_2O for 15 s at 300 K.

ethylene : oxygen mixture at 10 Torr results in a level of subsurface oxygen which gives rise to selective oxidation activity (*25*). A surface thus prepared was then heated briefly to 900 K to remove O(a), leaving an O(d) level which under standard conditions (*26*) gave rise to an oxygen (KLL) Auger intensity 1% that of the Ag (356 eV) transition. Dosing this surface with 3 × 10^6 L of N_2O at 0.2 Torr and *300 K* gave rise to the TPD results shown in Fig. 4; once again, nonactivated decomposition of N_2O has occurred. We recently reported (*26*) that repeated coadsorption/desorption experiments with Cl_2 and O_2 on Ag(111) gave rise to dramatically increased levels of subsurface oxygen. This procedure was used to generate a heavily oxygen-loaded subsurface (O(KLL): Ag (356 eV) Auger intensity ratio = 6.2%); after removal of O(a) by desorption, the specimen was used to study N_2O decomposition. It was now found that this reaction was once again a significantly activated process; TPD revealed no detectable dissociative chemisorption at 300 K. However, heating to various temperatures in 2 Torr of N_2O as before, subsequent TPD experiments showed features in the 32 amu spectra whose appearance was dependent on the crystal temperature during dosing (Fig. 5). It thus appears that relatively low levels of O(d) act to enhance the catalytic decomposition of N_2O, whereas sufficiently high levels of O(d) have an opposite effect. (In both cases (Figs. 4, 5) LEED/Auger measurements confirmed an absence of facetting, reconstruction, or residual chlorine on the surfaces prepared for N_2O decomposition in the manner described.)

Catalytic Oxidation of Ethylene by N_2O over Ag(111): TPR and Reactor Measurements

A surface condition corresponding to Fig. 5C was prepared by dosing the speci-

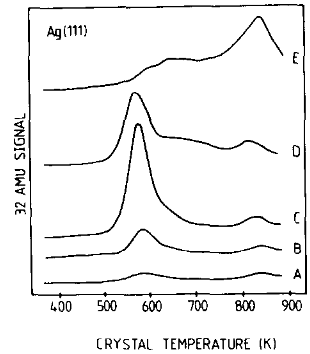


FIG. 5. TPD of O_2 from Ag(111) in presence of a high level of O(d) after various heating treatments in N_2O (2.0 Torr) following a 300 K exposure of 6 × 10^7 L N_2O at the same pressure. (A) After flashing briefly to 543 K. (B–E) After 30 s heating to 468, 543, 653, and 883 K, respectively.

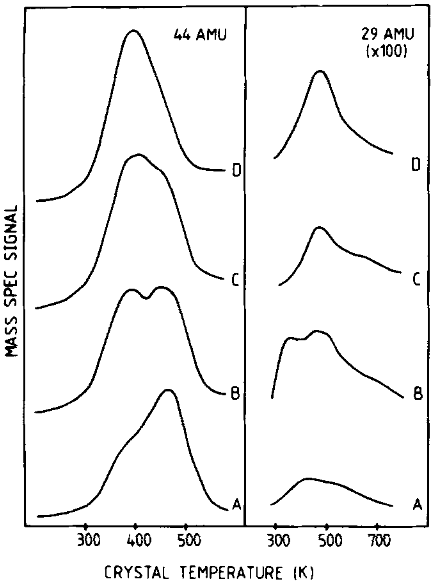


FIG. 6. Temperature programmed reaction spectra for CO_2 (44 amu) and ethylene oxide + acetaldehyde (29 amu) after dosing with 6×10^7 L N_2O (543 K, 2 Torr) followed by varying doses of ethylene at 300 K. (A–D) refer to ethylene doses of 3, 6, 12, and 24×10^7 L, respectively.

men (O(KLL): Ag (356 eV) Auger intensity ratio = 6.2%) with 6×10^7 L of N_2O at 543 K, i.e., selective deposition of O(a) and O(d) in the absence of O_2(a). This was followed by dosing with ethylene at 300 K, evacuation, and a TPR scan. Fig. 6 shows the 29 and 44 amu spectra (CHO^+, CO_2^+) obtained for varying doses of ethylene. (The CHO^+ signal contains contributions from both ethylene oxide and its isomerisation product, acetaldehyde (*24–26*)). It can be seen that ethylene oxide is indeed generated from an oxygen chemisorbed layer produced by N_2O decomposition and which contains no O_2(a).

Reactor studies with the single crystal were carried out with a 1 : 2 N_2O : ethylene mixture at a total pressure of 6 Torr. Table I shows the resulting activity data for ethylene oxide production at 580 K. It is important to note that the $O_2 : N_2O$ partial pressure ratio was monitored during these experiments and was always $<1 : 10^4$. The possibility that the observed ethylene oxide rate could be due to the O_2 impurity level can therefore be completely ruled out. The selective oxidation rate due to such a level of O_2 would be *at least* four orders of magnitude smaller than the observed value. For the purposes of comparison, Table I shows rate data obtained using an oxygen/ethylene mixture under similar conditions. The ethylene oxide selectivity in these latter experiments was ~10%; it was somewhat lower in the N_2O case.

Epoxidation by N_2O was also investigated over an Ag/α-Al_2O_3 catalyst in the flow microreactor under the following conditions:

$$N_2 : \text{ethylene} : N_2O = 52 : 37 : 11$$
$$\text{Total pressure} = 2.3 \text{ atm}$$
$$\text{GHSV} = 4700$$
$$\text{Temperature} = 537 \text{ K}.$$

Control experiments were carried out to check on possible decomposition of N_2O with subsequent O_2 evolution at the hot walls of the reactor. It was found that in the absence of the catalyst, the O_2 level in the N_2O outlet flow was ~0.004%. This level of oxygen cannot possibly account for the ethylene oxide rates observed in the presence of the catalyst. Once again, it appears that ethylene oxide can be directly produced from N_2O without the intervention of ad-

TABLE I

Comparison of the Rate of Ethylene Oxide (EO) Production on Ag(111) from Ethylene with Nitrous Oxide and Oxygen

Reaction conditions	EO turnover frequency (molecules/cm²/s)
2 Torr N_2O 4 Torr C_2H_4 580 K	3.4×10^{13}
2 Torr O_2 2 Torr C_2H_4 580 K	21.0×10^{13}

TABLE II

Production of Ethylene Oxide (EO) and Carbon Dioxide over Ag/α-Al_2O_3 in the Microreactor from Ethylene with Nitrous Oxide and Oxygen

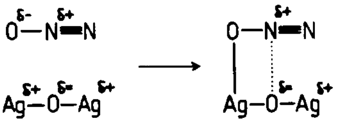
Reaction mixture	EO turnover frequency (molecules/ cm^2/s)	CO_2 turnover frequency (molecules/ cm^2/s)	Selectivity (%)
N_2:Et:N_2O = 2.0:37.0:11.0	0.8×10^{13}	0.4×10^{13}	79
N_2:Et:O_2 = 60.0:37.5:2.5	11.0×10^{13}	22.3×10^{13}	50

ventitiously formed gaseous O_2. Rate and selectivity data are presented in Table II along with comparison data obtained with an N_2:ethylene:O_2 mixture under similar conditions. Note that, as with the single crystal, N_2O leads to rates which are about 10 times lower than the rate observed with oxygen under similar conditions. In this case, however, the selectivity appears to be *higher* with N_2O. We return to both points under Discussion.

DISCUSSION

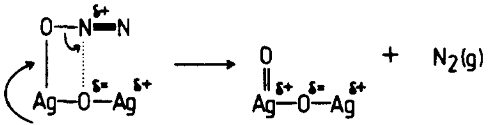
Catalytic Decomposition of N$_2$O

The finding that N_2O does not decompose at 300 K over clean Ag(111) is in agreement with the low-pressure studies of Goddard and Lambert (*36*). Our results (Fig. 2) also agree with earlier reports on the activated decomposition found at elevated temperatures on Ag wires, powder, and supported catalysts (*8, 27, 31, 32, 37*). The present work has shown clearly that the presence of O(a) (or of relatively low levels of O(d)) leads to an enhanced rate of dissociative chemisorption. Given these observations and the electronic structure and dipole moment of N_2O (*5, 38*) a plausible model for the interaction of N_2O with an oxygenated silver surface would be



(A)

Thus the formation of oxygen-induced Ag$^{\delta+}$ sites should enhance the interaction and therefore the coverage of the adsorbed molecular N_2O state on the surface; this acts as the precursor to dissociative chemisorption. The latter process can be thought to result from electron transfer to the adsorbate from the metal (a formally analogous process is invoked in the case of N_2O decomposition by metal oxides (*39*)). Formally, one may write



(B)

The striking isotopic distribution which was found in the experiments using $^{18}O(a) + N_2{}^{16}O(g)$ is at least consistent with this model which predicts that N_2O should preferentially adsorb and decompose in the vicinity of preexisting O(a) sites. If adatom mobility was restricted (*11*) then for a surface partially precovered with $^{18}O(a)$ one would expect a strong positional correlation between $^{18}O(a)$ and subsequently deposited $^{16}O(a)$ (from N_2O). The observed preponderance of $^{16}O^{18}O$ and $^{18}O^{18}O$ molecules is then to be expected (Fig. 3).

The preceding discussion has emphasised the possible catalytic role of O(a); an essentially similar view could be put forward to account for the way in which relatively low levels of O(d) could also enhance the decomposition rate. This leaves the question of how it is that sufficiently high levels of O(d) can actually inhibit the decomposition reaction. Recourse to the theory of N_2O decomposition on oxides (*39*) by thinking of the surface layer as "Ag_2O-like" does not appear to be helpful. Ag_2O is a *p*-type semiconductor (*40*) and in terms of the above theory it should therefore be a rather efficient catalyst for N_2O decomposition. It does however seem rather unrealistic to regard our oxygen-loaded Ag as Ag_2O-like since the *p*-type behaviour of the latter is the result of cation vacancies. A possible explanation is that at high oxygen levels the second step (B) in our proposed mechanism becomes rate-limiting. Whatever the case, this experimental result can provide at least a partial explanation for the reduced activity of N_2O relative to O_2 in the catalytic oxidation of ethylene both in the single crystal case and over the $Ag/\alpha\text{-}Al_2O_3$ catalyst. The argument is based upon the relative dissociation probabilities of N_2O and O_2. Under epoxidation conditions (~500 K) in the presence of high partial pressures of N_2O (or O_2) the subsurface becomes extensively oxygen-loaded. This inhibits further N_2O decomposition and thus retards the rate of O(a) uptake (often thought to be rate-limiting in this reaction) leading to the low conversion rate of ethylene. In the case of O_2, however, the presence of high levels of O(d) does *not* appreciably affect the dissociation rate (*11*) and a correspondingly higher catalytic rate is therefore to be expected.

Catalytic Oxidation of Ethylene by N_2O

All three types of reaction measurements clearly point to the conclusion that O(a) deposited by the dissociative chemisorption of N_2O is catalytically active in the formation of both CO_2 and ethylene oxide from ethylene. This O(a) species appears to be identical with that which results from the dissociative chemisorption of O_2 itself. Therefore an important aspect of these results is that they add considerable weight to recently accumulating evidence (*23, 26*) in favour of the hypothesis that O(a) is the crucial chemical species which leads to both partial and total oxidation of ethylene over silver.

The single-crystal data and the supported catalyst data are in good agreement regarding the relative total activities of N_2O and O_2 as oxidants. This is in agreement with earlier work (*29–31*); note, however, that the single-crystal selectivities are significantly lower than with the $Ag/\alpha\text{-}Al_2O_3$ catalyst. This may be straightforwardly understood as follows. Practically any foreign species markedly suppresses the ethylene burning activity of Ag, with a concomitant increase in selectivity. High-area supported catalysts expose unknown and uncontrollable amounts of contaminated metal surface leading to a relatively high selectivity. With our low-area single-crystal specimen, essentially the entire metal surface area is chemically characterised and maintained free of unwanted foreign species; higher burning activity and lower selectivity are therefore to be expected.

A potentially more interesting question concerns the substantially higher selectivity which is observed with the supported catalyst when N_2O rather than O_2 is employed. A possible explanation is that this effect might be due to the presence of very small amounts of higher nitrogen oxides in the N_2O feed gas used in these microreactor experiments. It is known that ppm levels of these oxides can exert a pronounced favourable effect on the selectivity of ethylene oxidation catalysts (*41*). Current work in our laboratory on single-crystal Ag(111) indicates that very small amounts of higher nitrogen oxides *do* in fact favourably affect the selectivity of silver towards the partial oxidation of ethylene (*42*).

CONCLUSIONS

(1) N_2O decomposition is significantly activated on atomically clean Ag(111). The presence of preadsorbed O(a) markedly enhances the rate of dissociative chemisorption; isotope data reveal a strong correlation between the location of O(a) species and reaction sites for N_2O decomposition.

(2) Relatively low levels of O(d) exert a similar positive influence on the decomposition rate; high levels of O(d) have an opposite effect.

(3) TPD and TPR data show that O(a) deposited by N_2O is active in ethylene epoxidation. This O(a) species appears to be identical with that resulting from the chemisorption of O_2 itself.

(4) Both single-crystal batch reactor results and flow microreactor data for Ag/

α-Al_2O_3 demonstrate that the use of N_2O can lead directly to the formation of ethylene oxide *without* the intervention of adventitiously produced gaseous oxygen. The "atomic oxygen hypothesis" thereby appears to be more firmly established.

(5) The relative activities of N_2O and O_2 as oxidants can be straightforwardly understood; likewise one can understand the relative selectivities of atomically clean Ag(111) and a practical Ag/α-Al_2O_3 catalyst.

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