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# The Decomposition of Nitrous Oxide on Polycrystalline Platinum

The decomposition of $N_2O$ on polycrystalline platinum has recently been studied extensively by Takoudis and Schmidt (*1*). It appears to be of general interest to compare their results with results in the earlier literature, since one expects observations to be reproducible at least in a rather simple system such as $N_2O/Pt$.

The range of experimental conditions which have been studied previously is listed in Table 1.

Some of the results obtained prior to 1960 may have been affected by impurities in the platinum metal employed as catalysts. Such impurities can cause irregularities in the kinetics of $N_2O$ decomposition, as shown by Riekert and Staib (*7*).

All studies agree that the rate of $N_2O$ decomposition is retarded by oxygen. In order to compare the results of different authors in a quantitative way, it is expedient to consider the probability $b_{N_2O}$ of reaction of $N_2O$ molecules, colliding with the platinum surface at a given temperature. The $b_{N_2O}$ can be computed from the rate laws observed, extrapolating to zero oxygen partial pressure. As can be seen from Table 2 the reaction probability $b_{N_2O}$ is independent of reactant partial pressure over 8 orders of magnitude of $p_{N_2O}$; a median of $b_{N_2O} = (2.1 \pm 0.9) \times 10^{-3}$ at 1200 K is obtained from the results of 4 independent investigations between 1963 and 1974. On the basis of data presented by Takoudis and Schmidt (*1*),

TABLE 1

Investigations of $N_2O$ Decomposition on Platinum

| Form of catalyst | $p_{N_2O}$ (mbar) | $p_{O_2}$ (mbar) | T (K) | Year | Ref. |
|---|---|---|---|---|---|
| Wire | 67–530 | Up to 265 | 873–1473 | 1925 | (*2*) |
| Wire | 0.13<br>$10^{-4}$ | Up to 0.1<br>Up to $2 \times 10^{-4}$ | 1000–1800<br>900–1100 | 1930<br>1932 | (*3*) |
| Wire | 80–270 | Up to 80 | 773–1473 | 1931 | (*4*) |
| Wire | 20–265 | Up to 200 | 1320–1550 | 1932 | (*5*) |
| Sponge | 26–665 | Up to 665 | 760–843 | 1934 | (*6*) |
| Wire<br>Foil | 4–9<br>130–400 | Up to 3.5<br>Up to 70 | 973–1473<br>950 | 1962 | (*7*) |
| Wire<br>Foil | 6.7–53<br>133–400 | Up to 53<br>Up to 190 | 873–1473<br>773–850 | 1963 | (*8*) |
| Wire | 0.027–5.3 | Up to 2.1 | 820–1100 | 1963 | (*9*) |
| Wire | $3.7 \times 10^{-5}$ | Up to $2 \times 10^{-3}$ | 1200–1300 | 1964 | (*10*) |
| Ribbon | $<10^{-7}$[a] | — | 300, 500<br>>1100 | 1974 | (*11*) |
| Ribbon | $4 \times 10^{-5}$–$4 \times 10^{-4}$ | — | 300–1100 | 1980 | (*12*) |

[a] UHV, exact value not given.

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TABLE 2

Reaction Probability of $N_2O$ Decomposition at 1200 K

| | $b_{N_2O}$ | | | | |
|---|---|---|---|---|---|
| | $1.3 \times 10^{-3}$ | $2.3 \times 10^{-3}$ | $1.9 \times 10^{-3}$ | $3.3 \times 10^{-3}$ | $1.8 \times 10^{-3}$ |
| $p_{N_2O}$ (mbar) | 13.33 | 0.13 | 0.13–2.66 | $4.9 \times 10^{-5}$ | $<10^{-7}$ |
| Ref. | (*8*) | (*1*) | (*9*)[a] | (*10*) | (*11*) |

[a] Extrapolated from results obtained at 1100 K.

who were apparently unaware of the earlier work, one obtains $b_{N_2O} = 2.3 \times 10^{-3}$ at 1200 K. It can therefore be concluded that the observations regarding the $N_2O$–Pt system are quite reproducible. However, the values of $b_{N_2O}$ in Table 2 are based on observations in the presence of oxygen by extrapolating the observed rate laws to the hypothetical condition of zero oxygen pressure. They pertain nevertheless to surfaces which could have been at least partially covered by chemisorbed oxygen.

On a *clean* platinum surface, on the other hand, nitrous oxide decomposes even at room temperature (*11*) into gaseous nitrogen and chemisorbed oxygen. The values of the initial reaction probability of $N_2O$ are as high as $4.7 \times 10^{-2}$ at 300 K and $6.8 \times 10^{-3}$ at 500 K on the clean surface. These values are more than 7 orders of magnitude higher than the values obtained by extrapolation of rate laws observed in the presence of $O_2$ to zero oxygen partial pressure.

TABLE 3

Reaction Probability of $N_2O$ Decomposition at 873 K

| | $b_{N_2O}$ | | |
|---|---|---|---|
| | $1.8 \times 10^{-4}$ | $1.3 \times 10^{-4}$ | $3.3 \times 10^{-3}$ |
| $p_{N_2O}$ (mbar) | 0.13 | 0.026–0.76 | $8 \times 10^{-5}$ |
| Ref. | (*1*) | (*9*)<br>(913 K) | (*12*) |

The platinum surface can be maintained oxygen-free under reducing conditions. Table 3 shows reaction probabilities extrapolated from the data of Takoudis and Schmidt (*1*) and Redmond (*9*) which were obtained in the presence of free oxygen in the gas phase and a value obtained in the presence of CO as a reducing agent (*12*). The difference in $b_{N_2O}$ between oxygen-free and oxygen-covered surface is much less pronounced at 870 K than at 500 K due to the temperature coefficient of $b_{N_2O}$, which is slightly negative for the clean surface.

Thus the conditions of oxygen-free and oxygen-covered surface have to be distinguished in this system: otherwise the reproducibility of kinetic observations may be obscured.

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