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Luminescence During N_2O Interaction with Thoria

We have reported the occurrence of a luminescence [called "adsorboluminescence" by previous authors (*1*)] during the adsorption of oxygen on thoria surfaces (*2–4*), and shown lately that when observed with other gases (CO, N_2, H_2), it was due to oxygen traces (*5*), so that the question is whether or not the phenomenon is specific to oxygen. Another question of interest is whether a "cataluminescence," i.e., a luminescence occurring during a catalysis, could be observed. It seemed that using nitrous oxide as an adsorbate would give a hint of the answers to both questions, according as nitrous oxide is decomposed or not on the surface of thorium oxide. In fact, as we shall see, the behavior of N_2O allows a deeper insight into that of adsorbed oxygen species.

The experiments have been carried out with nitrous oxide taken from a cylinder provided by "L'Air Liquide." Its impurities amount to 0.5% by volume ($N_2 < 0.5\%$, $O_2 < 50$ volume per million (vpm), $H_2O < 20$ vpm, $CO < 2$ vpm, $H_2 < 1$ vpm) and it is purified further by a vacuum condensation at 77 K, after which the molar fraction of uncondensable gases is less than 1 vpm. Thorium oxide is prepared from thorium nitrate decomposition followed by a standard procedure which includes an intermediate treatment of the surface with hydrogen (*2*). Praseodymium-doped thoria samples have also been prepared.

The setup used is a conventional one for the study of a catalytic rate: it basically consists of a batch reactor connected to a recirculation loop, in which the moving of the gas is ensured by a pump of a conventional design (*6*). A differential pressure monitor (A.C.B. Schlumberger 262 H) allows a continuous reading of the pressure inside the reactor circuit. When necessary, the composition of the gas can be analyzed with a mass spectrometer (A.E.I., MS 10 type), which can detect oxygen amounts above 20 vpm in the presence of N_2O.

During the course of the reaction, the light emitted can be simultaneously recorded by observing the apparent surface of the catalyst with a photomultiplier, followed by an amplifier and a recorder as already described (*2*). An optical filter (M.T.O. D.H. 485 B) cuts off the radiation emitted by the furnace, when the temperature of the latter is higher than 250°C. The spectral distribution of the emitted light can be obtained by setting a Huet M 25 type grating monochromator in front of the photomultiplier.

The results show that two temperature domains are to be considered:

1. At Temperatures Below 200°C

No pressure variation can be detected. Nevertheless, decomposition does occur, since mass spectrometry reveals the production of 10^{-5} moles of nitrogen when N_2O is left in contact with 3.5 g of ThO_2 at 166°C during 45 min. No oxygen, however, can be detected in the gas phase, a fact which is in agreement with the total pressure constancy.

During the experiments, a light emission occurs, as shown by Fig. 1. After an initial peak the intensity decrease is well represented by the relation:

$$I = \frac{k'}{t + t_0},$$

where k' and t_0 are constants. The intensity level is too low to allow the recording

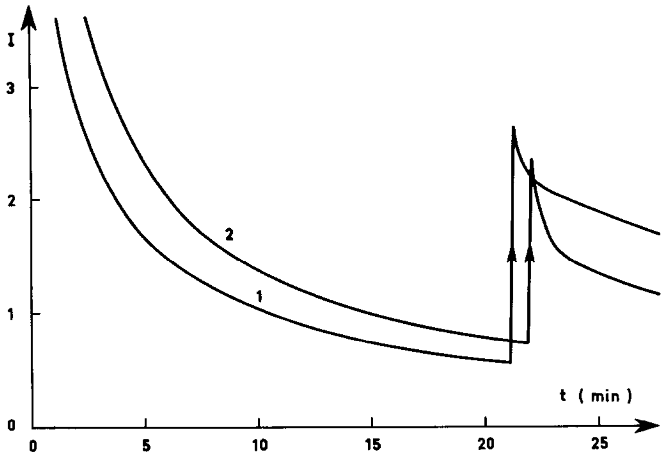

FIG. 1. Luminescence during N_2O admission on thoria surface at lower temperatures: (1) $T = 154°C$, $P_0(N_2O) = 125$ Torr; (2) $T = 169°C$, $P_0(N_2O) = 127$ Torr; intensity I in arbitrary units.

of the spectral distribution. A remarkable feature is that the luminescence undergoes a sharp increase on evacuation.

2. *At Temperatures Above 250°C*

The pressure increase proves the occurrence of catalysis. If x is the ratio of the number of moles of nitrogen produced at time t to the number of moles of nitrous oxide initially introduced, $\ln[1/(1-x)]$, is a linear function of t (Fig. 2), which means that the order with respect to N_2O is equal to one. Plotting the logarithm of the slope k of these straight lines against the reciprocal of the absolute temperature gives a straight line which corresponds to an apparent activation energy of 19.5 kcal/mole.

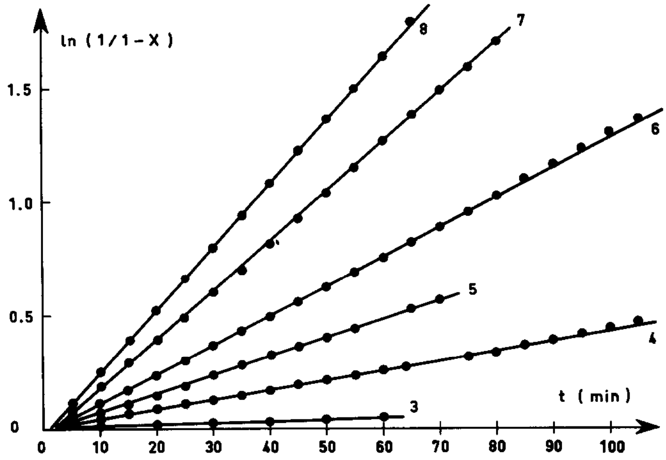

FIG. 2. Kinetic curves for higher temperature decomposition of N_2O on thoria surfaces:

	T (°C)	P_0 (N_2O) (Torr)
(3)	250	130
(4)	300	129
(5)	326	133
(6)	339	130
(7)	355	130
(8)	371	140

The luminescence curves obtained during catalysis are depicted, with the corresponding numbers, in Fig. 3. As shown, they exhibit, after the initial peak, a second maximum, which is shifted towards shorter times when the temperature increases. The spectrum of the emitted light is similar to that observed during oxygen admission: it consists of a broad band, peaking at about 640 nm. Using Pr-doped thoria allows a better comparison since the two separated bands found at 635 and 710 nm in the case of oxygen adsorption are again found at the same locations with N_2O.

All the foregoing results establish the occurrence of the N_2O decomposition on thoria surfaces. At lower temperatures, only nitrogen is detectable in the gaseous phase. This means that the gaseous oxygen concentration is less than the mass spectrometer sensitivity, i.e., 20 vpm of oxygen, which corresponds to a partial pressure of 2.5×10^{-3} Torr in the presence of 125 Torr of nitrous oxide. At these lower temperatures, most of the oxygen could remain chemisorbed, as already found for instance in the case of low temperature decomposition of N_2O on ZnO (*7*). It can be easily shown in our case that the oxygen capacity of the surface is far from being reached in our experiments. The saturation of the surface at 250°C can be estimated from a previous study (*8*) at 0.8 mg/g of thoria, i.e., 17.5×10^{-5} moles of oxygen atoms for 3.5 g of thoria, which is much higher than the 10^{-5} moles of nitrogen yielded by N_2O decomposition at a lower temperature.

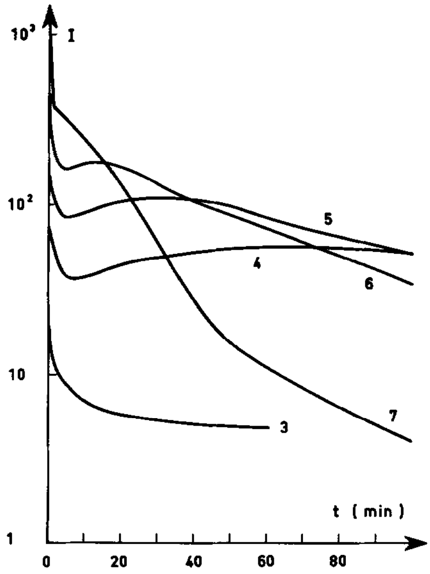

FIG. 3. Intensity of luminescence (in arbitrary units) observed during higher temperature decomposition of N_2O on thoria surfaces.

Thus, in all cases, oxygen species are formed at the surface, and the luminescence spectrum, when recordable, coincides with that given by the adsorboluminescence of oxygen alone. Therefore, it is logical to ascribe the observed light emission to the same oxygen species, which could be O_2^- in the adsorbed phase, or singlet gaseous oxygen, as supposed in an earlier publication (*9*). It is worth noting at this point that photoluminescence due to O_2^- ions trapped in alkali halides has been shown to occur with a spectral distribution peaking in the same wavelength range as ours (*10*). Evidence that O_2^- is formed during N_2O decomposition on thoria has been directly provided by ESR experiments, carried out between −100 and +100°C (*11*), and it has been previously shown that O_2^- is still present on thoria surfaces at 250°C (*8*). The following mechanism would be in agreement with the occurrence of O_2^- as an intermediate of N_2O decomposition:

$$N_2O_g + e^- \rightleftharpoons N_2O^-_{ads}, \qquad (1)$$

$$N_2O^-_{ads} \longrightarrow N_2 + O^-_{ads}, \qquad (2)$$

$$2\,O^-_{ads} \overset{a}{\underset{b}{\rightleftharpoons}} O^-_{2_{ads}} + e^- \qquad (3)$$

$$O^-_{2_{ads}} \overset{a}{\underset{b}{\rightleftharpoons}} O^-_{2_g} + e^-, \qquad (4)$$

e^- being an electron from the solid surface. It can be assumed, which is generally agreed, that (2) is the rate determining step, the other ones being in quasi-equilibrium. Contrary to previous work on the same catalysis (*12,13*), our kinetic results do not allow us to check precisely the rather complex rate expression which can be derived from such a mechanism, since first order kinetics result from any mechanism involving weak adsorption by N_2O and O_2. However, the assumption that oxygen species resulting from N_2O decomposition are involved in the reversible reactions (3) and (4) explains why a luminescence flare is observed when the surface is evacuated, since these equilibria are then shifted in the forward direction, i.e., the rate of the luminescent reaction (3a) is enhanced.

Consideration of the adsorption of pure oxygen, as already reported (*2–5,9*), is relevant. The equilibria (3) and (4) can be considered also in this case, together with the equilibrium of direct formation of O^- ions from gaseous oxygen:

$$O_{2g} + 2\ e^- \underset{b}{\overset{a}{\rightleftharpoons}} 2\ O^-_{ads}, \qquad (5)$$

so that gaseous oxygen can be adsorbed both in a dissociative way according to the forward direction (5a) and in a nondissociative way, according to the backward reaction (4b). Such a scheme has been proposed as early as 1960 by Barry and Stone (*14*) for the adsorption of oxygen on ZnO. In such a scheme, the reactions leading to O_2^- would produce luminescence. Consideration of these equilibria would explain most of the facts previously known on the transformations of oxygen species on thoria surfaces, and among them, on the one hand, that as shown by ESR O_2^- is formed by oxygen adsorption, transformed further into other species, and that it disappears during desorption (*8*), and, on the other hand, that when oxygen is evacuated from a thoria surface, the adsorboluminescence does not always fall abruptly to zero, but may decrease slowly, or even exhibit a sharp peak before decreasing.

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