

E.S.R. Evidence for the Photo-formation of N_2O^- and the Electron Transfer from It to O_2 at 77 K on Titanium Oxide Grafted onto Porous Vycor Glass

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E.s.r. studies have shown that u.v. irradiation of titanium oxide grafted onto porous Vycor glass in the presence of N_2O leads to formation of N_2O^- anion radicals, their electrons being easily transferred to added O_2 molecules to produce O_2^- anion radicals even at 77 K.

As an approach to utilization of solar energy, photocatalysis with metal oxides, especially powdered TiO_2 , has recently been investigated by a number of workers.¹ Although it is well established that co-ordinative unsaturation at the surface plays a significant role in the heterogeneous catalysis, the role of surface ions with low co-ordination in the photocatalysis is still unclear. To investigate this, grafted TiO_2 can be used where it is easy to control the degree of co-ordinative unsaturation at the surface. In this work we report on e.s.r. studies of the photo-formation of O_2^- and N_2O^- anion radicals, and on electron transfer from the N_2O^- to added O_2 molecules at 77 K on titanium oxide grafted onto porous Vycor glass.

The grafting was performed *via* the reaction of titanium(IV) chloride with the surface hydroxy groups of porous Vycor glass (Corning Co., No. 7930, surface area $150 \text{ m}^2/\text{g}$) in the gas phase, followed by treatment with water vapour to replace the chlorine atoms. The number of surface hydroxy groups on the Vycor glass was stabilised at $4.0 \text{ OH}/\text{nm}^2$ by degassing at 773 K. N_2O (or O_2) gas was introduced onto the grafted catalyst which had been heated in oxygen at 773 K and then degassed at 500 K. U.v. irradiation was carried out with a 500 W mercury lamp equipped with water and colour filters ($\lambda > 290 \text{ nm}$) at 77 K in the e.s.r. cavity. E.s.r. spectra were measured using a JES-ME-1 (X-band) spectrometer. Mn^{2+} in MgO powder was used for *g*-values and sweep calibrations.

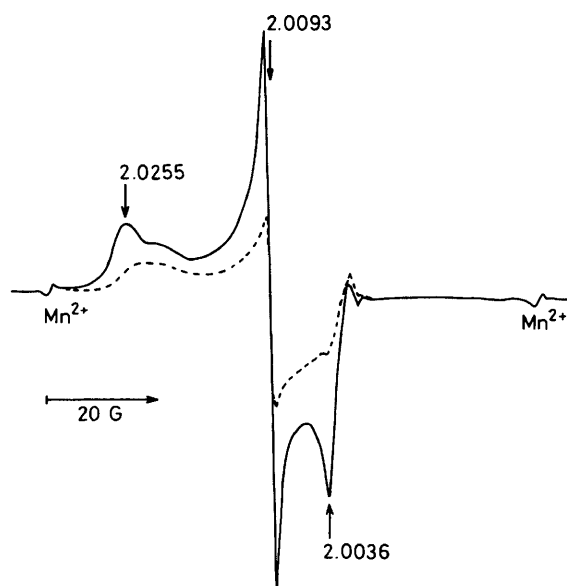


Figure 1. E.s.r. spectra of photo-formed O_2^- anion radicals on grafted titanium oxide at 77 K (—: after u.v. irradiation, initial O_2 pressure 4.0 Torr, amount of the O_2^- anion radicals = $5.54 \times 10^{-6} \text{ mol}$; - - -: after degassing at 333 K, amount of the O_2^- anion radicals = $1.99 \times 10^{-6} \text{ mol}$).

The grafted titanium oxide exhibits an absorption spectrum having a peak at *ca.* 310 nm, in good agreement with that of other TiO_2 spectra reported by Lyashenko *et al.*² As shown in Figure 1, u.v. irradiation of the grafted titanium oxide in the presence of O_2 at 77 K gave rise to a signal having $g_1 = 2.0255$, $g_2 = 2.0093$, and $g_3 = 2.0036$, its intensity increasing with increasing irradiation time. This signal could be attributed to the formation of O_2^- anion radicals since the *g*-values and shape of the peak are in agreement with those of O_2^- on TiO_2 .³

U.v. irradiation of the grafted titanium oxide at 77 K in the presence of N_2O molecules was found to give a new signal having $g = 2.00196$, as shown in Figure 2. The intensity of the signal increased with increase in u.v. irradiation time, being stable at 77 K. On raising the temperature to *ca.* 300 K,

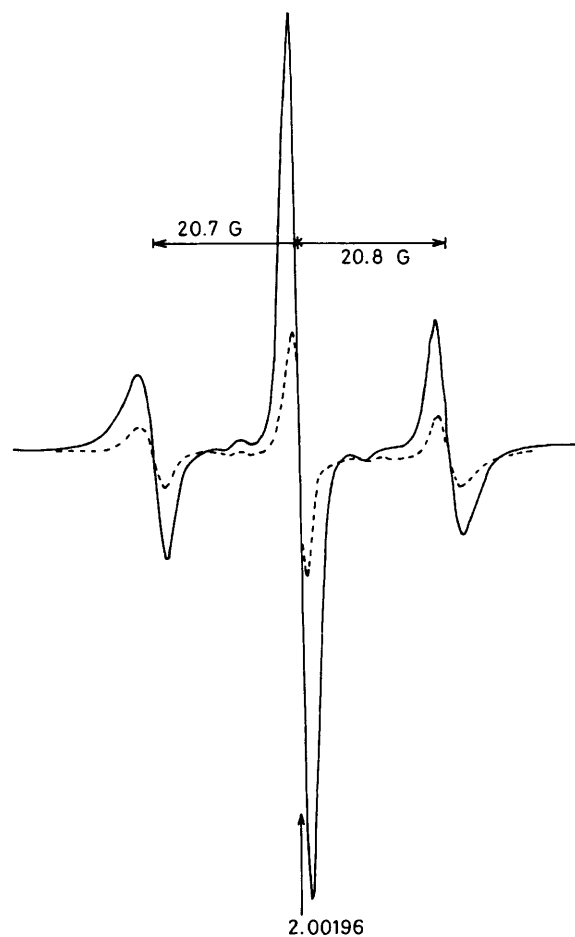


Figure 2. E.s.r. spectra of photo-formed N_2O^- anion radicals on grafted titanium oxide at 77 K (amount of the N_2O^- anion radicals: — $8.62 \times 10^{-6} \text{ mol}$; - - - $2.62 \times 10^{-6} \text{ mol}$).

however, it immediately disappeared. The signal consists of three lines with an intensity ratio of *ca.* 1:4:1, depending on the N₂O pressure and the temperature. It is also characterized by hyperfine splitting of *ca.* 21 G.† Such a value suggests that the hyperfine splitting is caused by one nitrogen atom. It is well known that three lines with different intensities are observed with hyperfine splitting from one nitrogen atom in the spectra of adsorbed species or of frozen solutions.⁴

The signal disappeared immediately on the addition of O₂ molecules at *ca.* 100 Torr at 77 K. Simultaneously, the appearance of the O₂⁻ anion radicals described above took place. The concentration of the O₂⁻ anion radicals was approximately equal to that represented by the replaced signal. Since the electron affinity of O₂ molecules is *ca.* five times larger than that of N₂O molecules, the O₂⁻ anion radicals are probably formed by an electron transfer reaction between the N₂O⁻ species and O₂ molecules.

It is well known that the N₂O molecule is dissociated on activated oxide surfaces to produce an O⁻ species, which results from electron transfer from the catalysts to N₂O molecules. There has been no report on e.s.r. evidence for the formation of N₂O⁻ as the precursor on the oxides though detection of N₂O⁻ was reported by Mishra and Symons in 1972.⁵ E.s.r. signals showing hyperfine interaction with two nitrogen atoms have been reported by Naccache *et al.*,⁶ Che *et al.*,⁷ and Lunsford *et al.*,⁸ none of them being attributed to N₂O⁻ species. Formation of the N₂O₂⁻ species proposed by Lunsford *et al.*⁸ seems unlikely in the present system, since electron transfer from the N₂O⁻ species to the added O₂ molecules occurs efficiently.

Thus, we conclude that we have detected a new signal probably arising from N₂O⁻ anion radicals formed by electron transfer from excited titanium oxide to the N₂O molecules adsorbed on it.‡ It should be noted that the electron transfer reaction occurs with high efficiency even at 77 K on the grafted titanium oxide.

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† 1 G = 10⁻⁴ T.

‡ U.v. irradiation of grafted titanium oxide at 300 K in the presence of N₂O molecules led to the formation of N₂ molecules.