Electron Tunneling in Heterogeneous Catalysis. Superoxide Anion Radical Decay on Palladium Promoted Yttria

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Ionic forms of palladium stabilized in yttria enhance the decay of superoxide radicals, localized on Y^{3+} cations, in reducing media by means of electron tunneling

An investigation of the elementary steps in catalytic transformations on the surface of solids is of importance in heterogeneous catalysis. Electrophilic oxygen species (O_2^-, O_2^{2-}, O^-) present on the surface of catalysts are likely to provide the latter with a susceptibility to total oxidation.[1] For Pd/CeO_2 the rate of O_2^- decay was dependent on Pd loading and correlated with activity in the low-temperature oxidation of CO.[2] Charge transfer through the conduction bands of ceria was assumed to be the reason for the observed phenomena.[3] Obviously, for the refractory unreducible rare-earth oxides doped with transition metals the acceleration of O_2^- decay could not occur because of their insulating properties. Here we present evidence that for Pd/Y_2O_3 this acceleration is possible.

Yttria was chosen as it provides a minimal width of ESR signals. Y_2O_3 was doped with Pd using a citrate amorphous-precursor decomposition method[4] and by coprecipitation. After calcination in air flow at 1070 K for 4 h, pressing and grinding, *ca.* 0.1 g of the catalyst was placed into an ESR tube, evacuated at 870 K for 3 h, oxidized at 870 K for 1 h and evacuated at 870 K for 0.75 h.

Oxygen adsorption at 293 K on Pd/Y_2O_3 yielded intense O_2^- signals with a g tensor typical for O_2^- on pure yttria,[5] hence Y^{3+} ions were in the first coordination sphere of O_2^-. Subsequent hydrogen admission at 293 K led to the decay of O_2^- and formation of Pd^+ ions with $g_\perp = 2.055$ and $g_\parallel = 2.45$ stabilized in the bulk, reactions (1) and (2).

$$\tfrac{1}{2}H_2 + O^{2-} \rightarrow OH^- + e \qquad (1)$$

$$Pd^{2+} + e \rightarrow Pd^+ \qquad (2)$$

Reaction (1) is confirmed by the formation of intense bands in the region of 3000–3600 cm^{-1}. In contrast to pure Y_2O_3, in which adsorbed O_2^- species were quite stable at 293 K in hydrogen, the decay of O_2^- in H_2 on Pd/Y_2O_3 was measurable at 200 K. Fig. 1 shows O_2^- decay kinetics at 293 K in excess H_2 at various Pd loadings. An enhancement of O_2^- decay with increase in Pd content may be noted.

ESR measurements showed that all Pd^+ ions which appeared in the course of the reduction vanished after evacuation at 870 K for 30 min. This may be assigned to the disproportionation reaction (3).

$$2Pd^+ \xrightarrow{\text{vacuum},870K} Pd^{2+} + Pd^0 \qquad (3)$$

Increasing the reduction time with subsequent evacuation at 870 K makes it possible to vary the Pd^0/Pd^{2+} ratio. After oxygen adsorption samples with different Pd^0/Pd^{2+} ratios provide O_2^- signals identical to those on standard treated samples. Kinetic curves for O_2^- decay on samples with different Pd^0/Pd^{2+} ratios in hydrogen are presented in Fig. 2. Apparently, the increase in metallic palladium content does not enhance O_2^- decay. Therefore, hydrogen spillover is not an essential step in the superoxide reduction.

Oxygen adsorption at 77 K on the reduced samples evacuated at 293 K leads to the formation of O_2^- with the simultaneous disappearance of Pd^+ ions, reaction (4).

$$Pd^+ + O_{2(ads)} \rightarrow O^-_{2(ads)} + Pd^{2+} \qquad (4)$$

Table 1 Kinetic parameters for O_2^- decay as a function of palladium content

Pd:Y	$B^a.10^4$	Pd^+, spin/10^{18}g	a/Å	ν_{eff}/s^{-2}	$R(t)^b$/Å
1:29	8.84	3.8	6.1	10.0	61
1:44	6.62	2.3	6.6	6.0	59
1:58	5.90	1.6	7.1	1.8	59

[a] $B = \frac{4}{3}\pi a^3 c$, see eqn.(6). [b] Reaction radius as calculated using the equation: $R(t) = a[f(\nu_{eff}t)]^{1/3}$ at $t = 1000$ s, the highest O_2^- concentration $\simeq 2 \times 10^{16}$ spin g^{-1}.

Increase of the oxidation temperature and/or concentration of Pd^+ ions may cause second electron transfer which results in the formation of peroxide, reaction (5).

$$Pd^+ + O^-_{2(ads)} \rightarrow O^{2-}_{2(ads)} + Pd^{2+} \qquad (5)$$

Reaction (5) may account for the acceleration of O_2^- decay when ionic forms of palladium are present on the surface of yttria because Pd^+ ions are formed immediately on hydrogen addition. Bearing in mind that Pd^+ ions and O_2^- species are separated by the dielectric media, electron transfer in reaction (5) at ambient and low temperatures should proceed by an electron tunneling (ET) mode. An additional argument in favour of this hypothesis is that all detectable Pd^+ species are coordinatively saturated. We could not detect the formation of paramagnetic adducts with molecules such as CO, NO or H_2O. The same phenomenon was supported by FT-IR measurements. In contrast to the Pd/Y_2O_3 system for Ni/Y_2O_3, adducts of Ni^+ and Ni^{2+} ions with CO and NO are readily detected by ESR and IR spectroscopy.[5] No Pd^+ ion adducts were detected for another doped basic oxide, MgO system.[6] Since Pd^+ species are coordinatively saturated, so the probability of their contact with O_2^- is negligible.

The easiest way to examine this hypothesis was to perform kinetic analysis of the decay curves. Indeed, ET recombination kinetics typical of chaotically distributed donors and acceptors[7] in a rigid dielectric medium was preferred for all experimental data over the whole time span, eqn. (6),

$$I(t)/I(0) = \exp\{-\frac{4}{3}\pi a^3 c f(\nu_{eff}t)\} \qquad (6)$$

where $I(t)/I(0)$ is the relative intensity of the O_2^- signal and $f(\nu_{eff}t)$ is the Inokuti–Hirayama functions,[7] eqn. (7).

$$f(\nu_{eff}t) = (\ln\nu_{eff}t)^3 + 1.732(\ln\nu_{eff}t)^2 + 5.934\ln(\nu_{eff}t) + 5.445 \qquad (7)$$

In eqn. (7), c is the concentration of donors (Pd^+ ions) and a and ν_{eff} are kinetic parameters characteristic of the ET process. Curves based upon a theoretical analysis are shown in Figs. 1–2 by solid lines. Table 1 contains quantitative data for the curves presented in Fig. 1. Tunnelling radii are in line with data from the ET recombination of defects in ionic crystals.[9–10] The ν_{eff} values are rather low, although theoretically there is no lower limit for the ν_{eff} values.[7]

Tunneling phenomena may be important in heterogeneous catalysis; *e.g.*, the formation of oxygen vacancies due to ET has been proposed to be the key factor in methanol synthesis

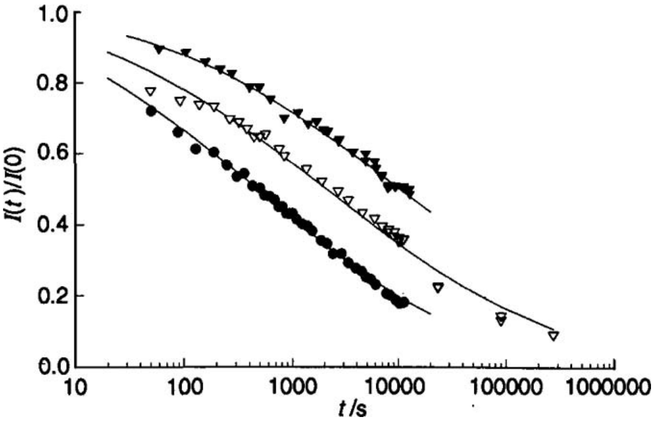

Fig. 1 Decay kinetics for the superoxide anion radicals in hydrogen (P_{H_2} 5.3 kPa) at 295 K for various Pd loadings. The solid curves were calculated using eqns. (6)–(7). Kinetic parameters for these curves are presented in Table 1. The vertical axis corresponds to the normalized intensity of the O_2^- signal. ▼ Pd: Y = 1.58, ▽ Pd: Y = 1.44, ● Pd: Y = 1.29.

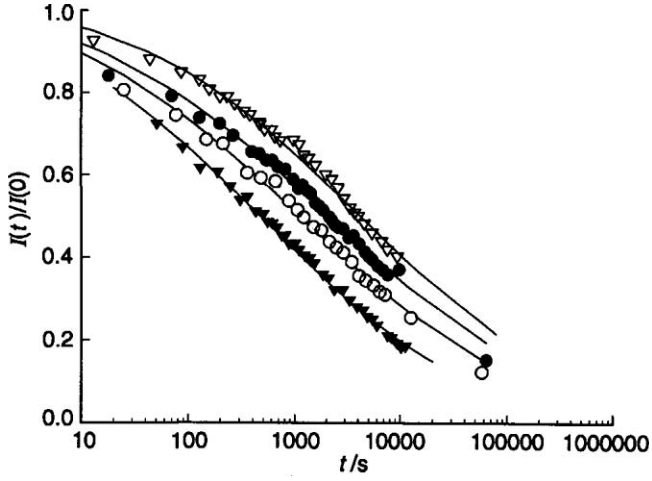

Fig. 2 Decay kinetics for the superoxide anion radicals in hydrogen (P_{H_2} 5.3 kPa) at 295 K for varying Pd^0/Pd^{2+} ratios (r); the solid curves were calculated using eqns. (6)–(7). The vertical axis corresponds to the normalized intensity of the O_2^- signal. ▽, $r = 0.679$; ●, $r = 0.325$; ○, $r = 0.113$ and ▼, $r \approx 0$.

catalysts.[9] At the same time it is necessary to admit that superoxide decay by the ET mode presented in this communication is rather a slow process and certainly a number of reaction paths may take place: *e.g.* interaction between chemisorbed species or between chemisorbed species and molecules in the gas phase. These reactions may also occur in the system studied for minor quantities of very reactive O_2^- species stabilized on certain Y^{3+} cations. The displacement of certain ligands on the Pd^+ ion by O_2^- particles seems to be quite improbable since it would lead to noticeable changes in the g tensor.

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