Mendeleev Commun., 2000, 10(3), 116–117

Thermal generation of singlet oxygen ($^1\Delta_gO_2$) on ZSM-5 zeolite

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10.1070/MC2000v010n03ABEH001187

Thermal generation of equilibrium $^1\Delta_gO_2$ in air at moderate temperatures and non-equilibrium thermal desorption of singlet oxygen from Ca–Cs/ZSM-5 zeolite were experimentally detected.

The participation of singlet oxygen ($^1\Delta_gO_2$) in the oxidation of hydrocarbons on heterogeneous catalysts was discussed previously.[1–3] Data on the thermal desorption of $^1\Delta_gO_2$ from the Li–Sn–P–O system[2] and V_2O_5 catalysts[3] were reported, and indirect evidence of the occurrence of $^1\Delta_gO_2$ at the surface of transition metal oxides was also obtained by EPR spectroscopy.[1] However, these results are inadequately reproducible, and until the present time there is no direct evidence of the participation of thermally generated $^1\Delta_gO_2$ in oxidation reactions (either homogeneous or heterogeneous), although the possibility of the direct thermal excitation of oxygen to a singlet state was considered by Turro.[4] Moreover, the thermal generation of $^1\Delta_gO_2$ in an equilibrium concentration at moderate temperatures according to the reaction

$$O_2 \rightleftarrows O_2(^1\Delta_g) \qquad (1)$$

(the reverse of the quenching of singlet oxygen) was not observed (probably, because of the absence of sensitive methods for the detection of $^1\Delta_gO_2$).

Previously,[5] a sensitive chemiluminescence (CL) technique for the determination of extremely low concentrations of singlet oxygen in a gas phase was developed. This technique allowed us to perform continuous measurements of equilibrium $^1\Delta_gO_2$ concentrations in air at relatively low temperatures and to examine non-equilibrium thermal desorption of $^1\Delta_gO_2$ from zeolites.

The generation of singlet oxygen took place in an air flow (pressure of 60 Torr and linear velocity of 1.2 m s^{-1}) passed through a heated zone of a quartz tubular reactor (30 mm in length and 5 mm internal diameter). At the reactor outlet, the gas was rapidly cooled to ambient temperature and then arrived at a CL detector (for experimental detail, see ref. 5). Because the time of singlet oxygen quenching in air is rather long (~1 s at 60 Torr and room temperature), the equilibrium $^1\Delta_gO_2$ concentration corresponding to the temperature of the heated zone of the reactor can be measured. In this case, the quenching of $^1\Delta_gO_2$ during the time it takes for air to be cooled and transferred to the CL detector is negligible.

The equilibrium $^1\Delta_gO_2$ concentration is determined by the expression [in the case of $C(^1\Delta_gO_2) << C(O_2)$][6]

$$C(^1\Delta_gO_2) = C(O_2)(g_1/g_2)\exp(-E/RT) \qquad (2)$$

where $C(^1\Delta_gO_2)$ is the equilibrium $^1\Delta_gO_2$ concentration in the gas phase at the temperature T; $C(O_2)$ is the ground-state oxygen concentration (total oxygen concentration); g_1/g_2 is the electronic statistical weight ratio for the singlet and ground triplet states of oxygen, $g_1/g_2 = 2/3$ (ref. 6); E is the excitation energy of the oxygen singlet state (the enthalpy of formation of $^1\Delta_gO_2$).

Indeed, the intensity of the thermal formation of equilibrium $^1\Delta_gO_2$ was essentially the same on various catalysts (Ca–Cs/ZSM-5, the Li–Sn–P–O system and V_2O_5) and in an empty reactor. Figure 1 demonstrates a typical curve for this process. The energy E calculated from these data using equation (2) is 88.6 kJ mol^{-1} (±10%), which is consistent with $E = 94.2$ kJ mol^{-1}, as found from spectroscopy data.[1] The corresponding preexponential factor $C(O_2)(g_1/g_2)$ is $\sim 6\times 10^{17}$ molecule cm^{-3} (the calculated value for air at 60 Torr and room temperature is 3.7×10^{17} molecule cm^{-3}, the difference may be due to incorrect independent calibration of the CL detector at low $^1\Delta_gO_2$ concentrations).

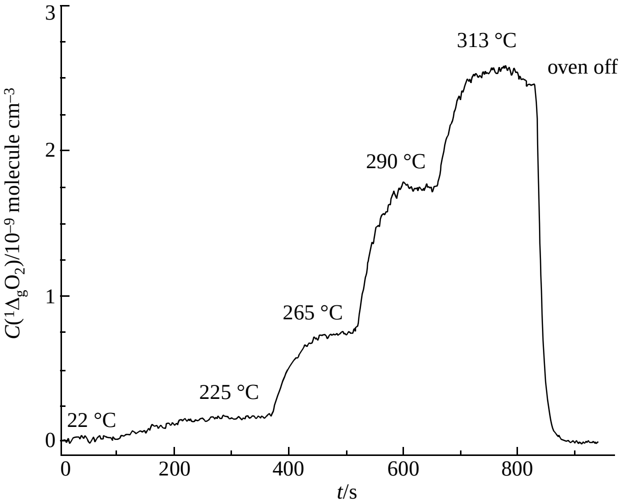

Figure 1 Thermal generation of equilibrium $^1\Delta_gO_2$ in an empty quartz reactor under conditions of a stepwise increase in the temperature (the detector was calibrated using a photochemical generator of $^1\Delta_gO_2$).

If a sufficient ballast volume or a glass filter was placed between the reactor and the CL detector, the signal vanished due to $^1\Delta_gO_2$ quenching. The same behaviour was observed in experiments when singlet oxygen was photochemically generated in a glass tube coated with methylene blue (in place of a heated reactor).

Taking into account all of the results, we can state with assurance that direct thermal generation of $^1\Delta_gO_2$ in equilibrium concentrations took place in our experiments. Note that a simple blank reactor can be used as a reliable standard source for calibration because the temperature dependence of $^1\Delta_gO_2$ concentration at the reactor outlet is determined by equation (2).

The Li–Sn–P–O and V_2O_5 catalysts generated $^1\Delta_gO_2$ only in equilibrium concentrations in our experiments. Thus, they exhibited no difference from an empty reactor.

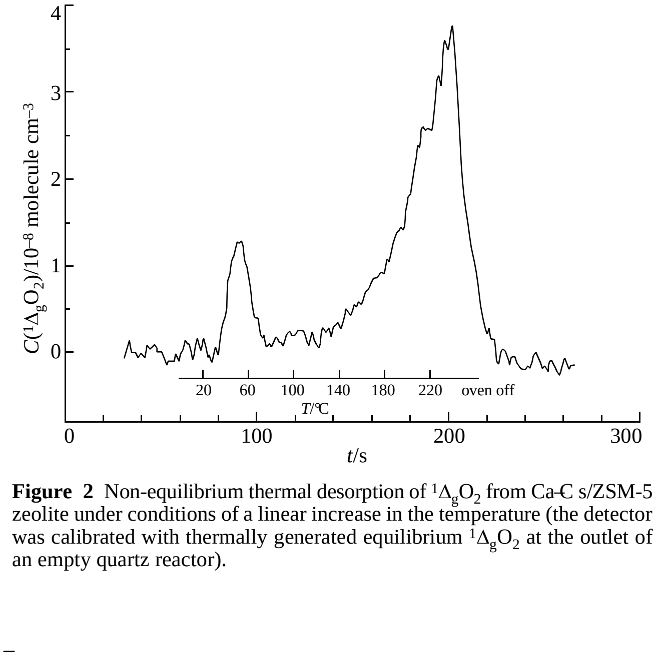

Figure 2 Non-equilibrium thermal desorption of $^1\Delta_gO_2$ from Ca–Cs/ZSM-5 zeolite under conditions of a linear increase in the temperature (the detector was calibrated with thermally generated equilibrium $^1\Delta_gO_2$ at the outlet of an empty quartz reactor).

The non-equilibrium generation of $^1\Delta_g O_2$ (*i.e.*, in higher than equilibrium concentrations) was observed only on zeolite samples (ZSM-5 exchanged with alkaline and alkaline-earth cations). Figure 2 demonstrates a typical plot of the thermal desorption of $^1\Delta_g O_2$ from Ca–Cs/ZSM-5 zeolite. The sample was prepared from H-ZSM-5 (Si/Al ratio of 80) by continuous ion exchange in a 0.1 M $CsNO_3$ solution and then in a 0.1 M $Ca(NO_3)_2$ solution. Next, it was calcined at 650 °C in air for 4 h and exposed to dry air at room temperature for 16 h prior to the use in experiments.

It can be seen in Figure 2 that, in addition to the thermal generation of equilibrium $^1\Delta_g O_2$, which is detectable at temperatures higher than 140 °C, the curve exhibits a low-temperature peak of non-equilibrium thermal desorption of $^1\Delta_g O_2$ (T_{max} = = 55 °C). This peak completely disappeared in the subsequent thermal desorption experiments. The capacity of the zeolite for non-equilibrium desorption of $^1\Delta_g O_2$ was restored after exposure to air at ambient pressure for 24 h.

It is obvious that, in this case, oxygen molecules adsorbed on the zeolite are the source of $^1\Delta_g O_2$. The reasons why the concentration of electronically excited $^1\Delta_g O_2$ in desorbed oxygen exceeds an equilibrium value are unclear. It is our opinion that the following factors can be responsible for this phenomenon: (i) stabilization of the $^1\Delta_g$ state of an adsorbed O_2 molecule as a result of splitting two degenerate π_g^*-orbitals[1] in strong electrostatic fields within zeolite channels ($\approx 10^{10}$ V m^{-1} in ZSM-5)[7] and (ii) differences in the activation energies of adsorption (and desorption) for the ground $^3\Sigma_g$ and excited $^1\Delta_g$ states of oxygen molecules, *e.g.*, at the surface of MgO, $E_{a\ ads}(^1\Delta_g O_2) = 0$, while $E_{a\ ads}(^3\Sigma_g O_2) > 0$ (ref. 8).

Anyway, this experimental fact is the first example of the non-equilibrium thermal production of $^1\Delta_g O_2$ over heterogeneous catalysts (with the exception of the results,[2,3] which were found to be irreproducible).

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Received: 8th July 1999; Com. 99/1515