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Formation of O_2^- radical anions on the adsorption of NO + O_2 and NO_2 + O_2 mixtures on ZrO_2 according to EPR data

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The O_2^- radicals are formed at the surface of ZrO_2 by the interaction of adsorbed NO or NO_2 with oxygen at coordinatively unsaturated Zr^{4+} cations.

The formation of O_2^- radicals during the adsorption of $H_2 + O_2$, H–X + O_2 and $CH_4 + O_2$ on MgO[1–4] and $C_3H_6 + O_2$ on Mo/MgO and V/MgO catalysts[5] has been well investigated. Moreover, the superoxide anion was also observed on the adsorption of NO + O_2 on CeO_2; however, this effect is little understood.[6]

We found the EPR signal of a complex after the adsorption of NO + O_2 and $NO_2 + O_2$ mixtures on thermally activated ZrO_2. The properties of the complex were investigated, and it was classified as the O_2^- radical adsorbed on the Zr^{4+} cation.

Zirconium dioxide in a tetragonal modification with a specific surface area of 100 m^2 g^{-1} was prepared from $Zr(NO_3)_4$ of analytical grade according to the published procedure.[7]

The EPR and temperature-programmed desorption (TPD) measurements were performed in EPR tubes in a vacuum using 35 mg samples. The test sample was pre-heated at 970 K and 10^{-4} Pa for 1 h. After the thermal treatment, the sample was cooled to room temperature, and a gas was adsorbed at $P = (0.5–10)\times10^2$ Pa for ~3 min. The EPR spectrum was measured at room temperature and 77 K using an ESR-V spectrometer (Institute of Chemical Physics) with a Diapason temperature-controlled attachment. The concentration of radicals was found by the double integration of the EPR spectrum with the use of $CuSO_4\cdot5H_2O$ as a reference sample.[8]

In the TPD experiments, a test gas was adsorbed for 5 min, and the system was then evacuated for 20 min. Next, the sample was heated at a rate of 12 K min^{-1} under continuous evacuation. The desorption spectrum was recorded on an MX-7303 mass spectrometer.

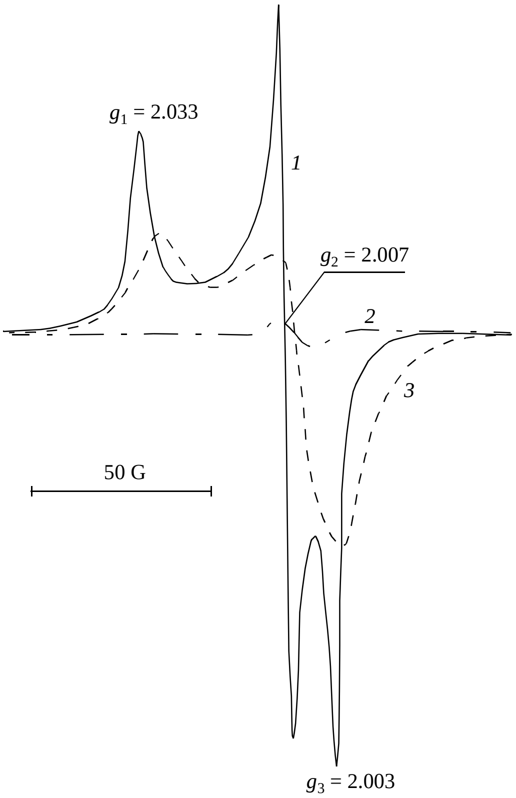

Figure 1 EPR spectra of complexes after the adsorption of NO and O_2 on ZrO_2 (*1*) in a vacuum or (*2*) in NO and (*3*) in O_2 atmospheres.

The adsorption of O_2, NO or NO_2 on ZrO_2 at room temperature was not accompanied by the appearance of EPR signals. However, an EPR signal was formed after the admission of NO (50 Pa) and then O_2 (2×10^2 Pa) (Figure 1, curve *1*). The spectrum remained unchanged after the gas was pumped out at 293 K, and the corresponding concentration of paramagnetic complexes is 6×10^{18} spin g^{-1}.

The spectrum of the complex almost disappeared in an NO atmosphere (2×10^2 Pa) and was broadened in O_2 (1×10^3 Pa) (Figure 1, curves *2* and *3*, respectively). The spectrum was completely restored by evacuating the gas. These changes resulted from the dipole–dipole interaction between complexes and paramagnetic molecules.

The following *g*-tensor values were found from the spectra recorded at 77 and 293 K: $g_1 = 2.033$, $g_2 = 2.007$ and $g_3 = 2.003$. An EPR signal (Figure 2) with the same parameters ($g_1 = 2.033$, $g_2 = 2.007$ and $g_3 = 2.003$), which corresponds to the O_2^- radical anion, was observed upon the photoadsorption of oxygen under illumination of the oxide with light from a DRSh-1000 mercury lamp at $P = 10^3$ Pa and $T = 293$ K.

The agreement between the spectra (Figures 1 and 2), the *g*-values and the published data[9] suggests that the O_2^- radical anion is formed in the adsorption of NO + O_2 on ZrO_2.

In accordance with the ion model,[9] the charge of a stabilising cation is equal to +4 for $g_1 = 2.033$. Consequently, the O_2^- radical is localised at the Zr^{4+} cation.

In the reaction of adsorbed NO_2 with oxygen on the oxide, an analogous O_2^- radical was observed; however, it was more weakly bound to the surface. The radical was detected only in an O_2 atmosphere and disappeared upon evacuating the gas.

We failed to detect O_2^- radicals after heating the sample in oxygen at 970 K followed by cooling in O_2 to room temperature or 77 K. However, the signal of O_2^- appeared immediately after the evacuation of oxygen and the admission of NO and then O_2. In the photoadsorption, the intensity of the O_2^- signal

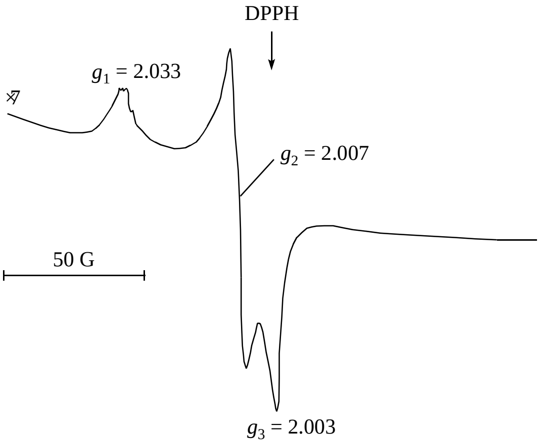

Figure 2 EPR spectrum of the O_2^- radical in a vacuum after the photoadsorption of oxygen.

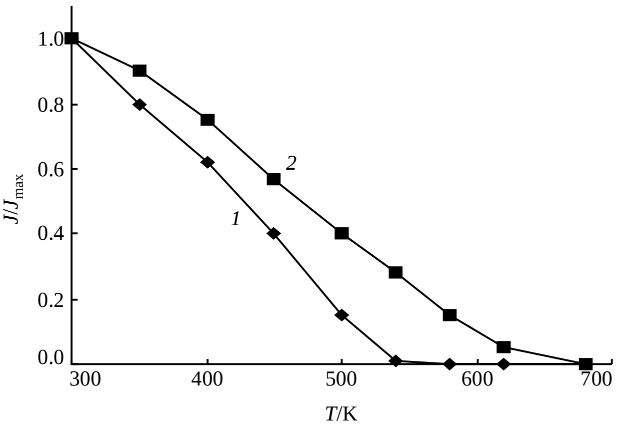

Figure 3 Intensities of the EPR spectra of O_2^- radical anions as functions of the temperature of heating samples with radicals in a vacuum for 5 min: (*1*) O_2^- (NO + O_2) and (*2*) O_2^- (UV + O_2^-).

slowly increased for 1 h and was lower than that after the adsorption of NO + O_2 by one order of magnitude. Consequently, the formation of the O_2^- (NO + O_2) radicals on ZrO_2 proceeds more effectively than that of the O_2^- (UV + O_2) radicals.

The amount of O_2^- radicals depends on the gas pressure. At an NO pressure lower than 10 Pa (O_2, 2×10^2 Pa), the amount of O_2^- radicals decreased. The O_2^- radicals were also formed on the admission of oxygen to the sample with adsorbed NO; however, the amount was 2×10^{18} g^{-1}. In this case, NO was adsorbed at 1×10^2 Pa for 3 min, and the gas was then pumped out for 20 min.

The amount of O_2^- radicals depends on the temperature (T_v) at which the sample was heated in a vacuum. It increased from 2×10^{17} to 6×10^{18} g^{-1} as the temperature was increased from 500 to 970 K.

The dependence of the O_2^- concentration on T_v and P_{NO} allows us to conclude that Lewis acid sites are formed during the dehydration of the ZrO_2 surface.[10–12] We estimated the concentration of coordinatively unsaturated Zr^{4+} cations from the EPR spectra of (NO–Zr^{4+}) complexes[13] formed on the adsorption of NO (1×10^2 Pa, 77 K) to be 2×10^{19} g^{-1}. This value is consistent with the concentration of O_2^- radicals 6×10^{18} g^{-1}. Thus, coordinatively unsaturated Zr^{4+} cations can paticipate in the formation of the anion radicals.

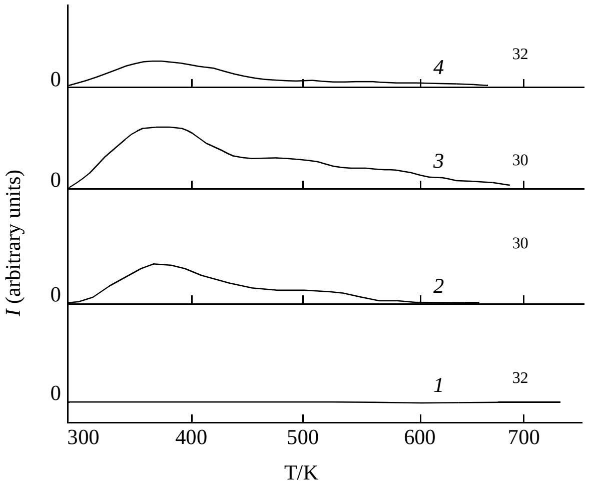

Figure 4 Spectra of TPD from zirconium dioxide after the adsorption of (*1*) oxygen and (*2*) NO and (*3*, *4*) after the formation of O_2^- radicals on the adsorption of NO + O_2.

Different species were observed during the adsorption of NO and NO_2 on Lewis acid sites of ZrO_2 at room temperature. The NO^+ species decomposed at $T < 650$ K, whereas nitrate and nitrite species decomposed at $T > 650$ K.[12]

Figure 3 shows that the O_2^- concentration decreases with temperature. Radicals were detected only below 550 K. After the treatment at 550 K, the activity of the oxide was fully regenerated. Consequently, the NO^+ and O_2^- species can be interrelated because the temperature ranges of NO^+ and O_2^- decomposition and regeneration of the oxide are coincident.

The decomposition of O_2^- radicals results in the desorption of O_2 and NO molecules (Figure 4). The activation energy of O_2 desorption is ~100 kJ mol^{-1}. This value is consistent with the heats of the O_2^- formation on the catalysts (80–100 kJ mol^{-1}).[9] The activation energy was estimated as described in ref. 14.

The coincidence of the spectra (Figures 1 and 2) and the temperature ranges of O_2^- decomposition (Figure 3, curves *1* and *2*) allows us to conclude that O_2^- (NO + O_2) and O_2^- (UV + O_2) radicals are adsorbed at similar Zr^{4+} surface sites.

The above data indicate that the superoxide anion is formed during the adsorption of an NO + O_2 mixture on thermally activated ZrO_2. The first step is the formation of an NO complex on coordinatively unsaturated Zr^{4+} cations or Zr^{4+}- - -O^- pairs. The second step involves intermolecular electron transfer from the NO complex to an oxygen molecule. The superoxide anion is stabilised at the Zr^{4+} cation beside the NO complex. However, the structure of the NO complex is unclear, and we cannot give an adequate explanation of the different stability of O_2^- (NO + O_2) and O_2^- (NO_2 + O_2) radicals.

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