

ESR of SO_2^- and SO^- Anion-Radicals Adsorbed on Supported Vanadium Silica Gel Catalysts

The anion-radicals SO_2^- formed on the surface of various catalysts during the adsorption of SO_2 were studied previously (1-6). Sometimes it is believed that they can be the intermediate active species in the reactions of the oxidation of SO_2 to SO_3 and of the reduction of SO_2 to SO . Earlier (7) it was shown that after thermovacuum treatment of supported vanadium-silica gel catalyst tetrahedrally coordinated V^{4+} ions are formed on the surface. These ions are the centers for the adsorption of various molecules, including SO_2 . Upon adsorption this molecule stabilizes in the first coordination sphere of the tetrahedrally coordinated V^{4+} ion and changes its symmetry to distorted octahedral. The formation of SO_2^- anion-radicals was not previously observed, although in the case of analogous titanium- and molybdenum-containing supported samples these species usually appeared after SO_2 adsorption (3,6).

In the present work the properties of the supported vanadium-silica gel catalysts relating to the SO_2 adsorption have been studied in detail.

The supported vanadium-containing samples were prepared as previously (7) by impregnation of the silica gel ($S = 350 \text{ m}^2/\text{g}$) with aqueous NH_4VO_3 solutions, followed by drying at 70-80°C and calcining at 500°C. The vanadium content was about 2 wt%. The samples were placed into quartz ampoules for ESR measurements and heated in oxygen for 15 min at 700°C, as distinct from the temperature of 500°C used earlier (7). Then they were evacuated for 1 hr at 500°C (10^{-5} - 10^{-6} Torr), reduced by hydrogen for 10 min at

500°C and finally evacuated for 1 hr at the same temperature.

Supported vanadium-sulfide samples were prepared by impregnation of silica gel with aqueous $(\text{NH}_4)_3\text{VS}_4$ solution, followed by drying and decomposition in vacuum at 100°C. This method is usually used for bulk V_2S_5 preparation. The reduction was carried out at 400°C in vacuum.

The ESR spectra were recorded at liquid nitrogen temperature using an X-band spectrometer.

The properties of vanadium-silica gel catalysts with respect to SO_2 adsorption depend on the degree of their reduction and the temperature of the oxidizing pretreatment. Adsorption of SO_2 at room temperature on the samples pretreated in oxygen at 700°C and then reduced in a high pressure of hydrogen (500 Torr) leads to a change in the form of the original V^{4+} spectrum due to the formation of the distorted octahedral coordination. The same result was reported earlier (7). But in contrast to the work (7), a new signal (signal I), Fig. 1a, also appears on the background of the V^{4+} spectrum with parameters: $g_{\parallel} = 2.010 \pm 0.001$ and $g_{\perp} = 2.002 \pm 0.001$. Annealing of these samples *in vacuo* at 80-100°C leads to a decrease of the intensity of signal I and the appearance of another signal (signal II) with the following parameters:

$g_1 = 2.043 \pm 0.001$, $g_2 = 2.031 \pm 0.001$, $g_3 = 2.004 \pm 0.001$ and $a_1 = 6.5 \pm 0.3 \text{ G}$; $a_2 = 4.9 \pm 0.3 \text{ G}$; $a_3 = 2.4 \pm 0.3 \text{ G}$, Fig. 1b. After annealing at 300°C only signal II remains in the spectrum, Fig. 1c.

The adsorption of SO_2 at room temperature on the samples reduced in 10 Torr of

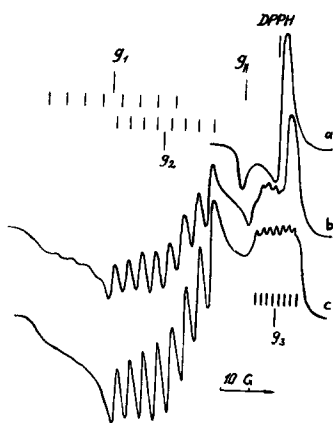


FIG. 1. a. Spectrum of SO_2^- ; b. spectrum of SO_2^- and SO^- ; c. spectrum of SO^- .

hydrogen also leads to the appearance of signal I but its intensity is small. On increasing the temperature this signal disappears without the appearance of signal II.

In the case of the samples pretreated in the same way as in the earlier work (7), namely, annealed at 500°C in oxygen before reduction in hydrogen, the formation of signal I takes place only after reduction in a high pressure of hydrogen (300–500 Torr). But even in this case its intensity is small and the annealing of the samples does not lead to the appearance of signal II. The form of the spectra of V^{4+} ions in all cases was the same as in (7).

The g -values of signal I are close to those reported for SO_2^- anion-radicals adsorbed on the surface of other solids (1–6). Since it appears after adsorption of SO_2 molecules on the reduced samples there is no doubt that it belongs to the adsorbed SO_2^- species. It is impossible to make any definite conclusions about the nature of the stabilization center for SO_2^- because hyperfine splitting from the ^{51}V nucleus is not observed and the g -values for SO_2^- are insensitive to the structure of the adsorption center (5). The absence of the hyperfine splitting does not mean, however, that the SO_2^- anion-radicals are not stabilized on

the surface vanadium ions because the hyperfine splitting constants may be small.

Signal II has hyperfine splitting from one vanadium nucleus but it cannot belong to the vanadium ion itself because the g -values are more than two. This signal cannot belong to O^- , O_2^- , O_3^- anion-radicals, nor to S_3^- , SSO^- , SO_3^- and SO_4^- anion-radicals. The former have different spectra on the surface of the vanadium-silica gel catalysts (8–10). The ESR spectra of the second group are known only for the species stabilized in matrices (11–17) but their parameters are also different from the parameters of signal II and cannot depend on the structure of the adsorption center to any great extent because they have a nondegenerate ground state.

Signal II, similar to the spectrum of O_2^- adsorbed on the same catalyst (9), has three g -values and three hyperfine splitting constants; moreover, as for O_2^- the largest constant corresponds to the largest g -value and the least one corresponds to the smallest g -value. Taking into account these points, it is natural to ascribe signal II either to SO^- or to S_2^- anion-radicals which are isoelectronic with O_2^- anion-radicals. The large g -tensor anisotropy value may be caused by the larger spin-orbit constant of sulfur compared with oxygen. To choose between these two species we investigated oxygen adsorption on the reduced silica supported vanadium-sulfide samples. At 300°C the appearance of signal II was also found. This fact and the fact of appearance of signal II after SO_2 adsorption on the vanadium-silica gel samples allow us to ascribe it to the species containing both sulfur and oxygen, namely to the SO^- anion-radical.

Thus the adsorption of SO_2 molecules on the reduced vanadium-silica gel catalyst gives rise to SO_2^- and SO^- anion-radicals. They are stabilized on the surface of the catalyst since they disappear after the adsorption of NH_3 molecules at room

temperature. It is important to note that reduction of the samples is essential for the formation of these species. We did not observe them previously (7) during SO₂ adsorption because of insufficient reduction of the samples.

REFERENCES

1. Machenko, A. I., Parijsky, G. V., and Kazansky, V. B., *Kinet. Katal.* **9**, 151 (1968).
2. Machenko, A. I., Parijsky, G. B., and Kazansky, V. B., *Kinet. Katal.* **8**, 704 (1967).
3. Vorotyntsev, V. M., Shvets, V. A., and Kazansky, V. B., *Kinet. Katal.* **12**, 1249 (1971).
4. Adachi, M., Imanaka, T., and Teranishi, S., *J. Chem. Soc. Jap. Pure Chem. Sect.* **90**, 445 (1969).
5. Schoonheydt, R. A., and Lunsford, J. H., *J. Phys. Chem.* **76**, 323 (1972).
6. Shvets, V. A., and Kazansky, V. B., *Kinet. Katal.* **4**, 935 (1971).
7. Vorotyntsev, V. M., Shvets, V. A., and Kazansky, V. B., *Kinet. Katal.* **12**, 678 (1971).
8. Shvets, V. A., Vorotyntsev, V. M., and Kazansky, V. B., *J. Catal.* **11**, 378 (1968).
9. Shvets, V. A., Vorotyntsev, V. M., and Kazansky, V. B., *J. Catal.* **15**, 214 (1969).
10. Nikisha, V. V., Shelimov, B. N., Shvets, V. A., Griva, A. P., and Kazansky, V. B., *J. Catal.* **28**, 230 (1973).
11. Schneider, J., Dischler, B., Rauber, A., *Phys. Status Solidi* **13**, 141 (1966).
12. Morton, J. R., in "Colloque Ampère." Vol. 15, p. 299. North-Holland, Amsterdam, 1969.
13. Wieschowski, A., *Phys. Status Solidi* **42**, 125 (1969).
14. Von Hofmann, U., Herzenstiel, E., Schonemann, E., and Schwarz, K. H., *Z. Allg. Anorg. Chem.* **367**, 119 (1969).
15. Chantry, G. W., Horsfield, A., Morton, J. R., Rowland, J. R., and Whiffen, D. H., *Mol. Phys.* **3**, 233 (1962).
16. Morton, J. R., *J. Phys. Chem.* **71**, 89 (1967).
17. Hariharan, N., and Sobhanadri, J., *Mol. Phys.* **17**, 507 (1968).

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