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ESR Investigations of Sulfuric Acid Catalyst Deactivation

The industrial catalyst for oxidation of SO_2 to SO_3—the key step in sulfuric acid production—is a Supported Liquid Phase (SLP) catalyst. Molten vanadium containing alkali metal pyrosulfates is here dispersed on an inert support. The catalyst is well described by the liquid–gas system $M_2S_2O_7/V_2O_5$–$SO_2/O_2/SO_3/N_2$, where M is a mixture of about 80% K and 20% Na. Recently cesium has also been added to decrease the deactivation temperature of the catalyst to below 420–450°C (depending on the partial pressure of SO_2). The deactivation leads to an increase of the apparent activation energy from about 75 to 150–200 kJ/mol. It was assumed for a long time that the deactivation was due to the precipitation of a vanadium-containing crystalline phase. This was, however, only very recently proved by Boghosian *et al.* (*1*), who investigated the catalytic activity and compound formation in unsupported model melts containing V_2O_5 and $M_2S_2O_7$ (M = Na, K, Cs). During catalysis V(V) is partly reduced to V(IV) and probably also to V(III). Below the temperature of deactivation crystalline V(IV) and V(III) compounds of Na, K, and Cs could be isolated. The V(IV) compound isolated from the $K_2S_2O_7/V_2O_5$–$SO_2/O_2/SO_3/N_2$ system (below the temperature of deactivation) was $K_4(VO)_3(SO_4)_5$. Structure and vibrational spectra of this compound have been published by Fehrmann *et al.* (*2*).

In the present note we describe the results of an ESR (Electron Spin Resonance) investigation of an industrial SLP catalyst.

The investigated catalyst was VK38 from Haldor Topsøe A/S, Denmark. This catalyst consists of ca. 6% V_2O_5 on kieselguhr and the alkali metal to vanadium mole ratio is about 3.8 (0.8 Na/V + 3.0 K/V). ESR investigations of the catalyst are feasible because V(IV) with the electron configuration $[Ar]3d^1$ is paramagnetic and possible ESR-active impurities in the support do not interfere at the microwave frequencies used.

The ESR spectrometer was a slightly modified JEOL JES-ME-1X apparatus equipped with a Bruker ER4114HT high temperature cavity operating up to 1000°C. The ESR reactor cell made of quartz is shown in Fig. 1. The cell consists of two concentric tubes where the synthesis gas enters at (A) and leaves at (B) after being in contact with the catalyst sample contained in the inner tube at (C). The lower narrow part of the cell is inserted in the Dewar of the cavity, placing all of the sample inside the sensitive part of the cavity. A VK38 pellet was gently crushed and about 25 mg was placed in the inner tube between two plugs of quartz wool. To assure a chemically uniform catalyst bed, the space velocity was adjusted so that the reactor was differential (conversion of SO_2 less than 5% at 500°C). The gas composition before and after the reactor was analyzed after absorption of SO_3 in 96% H_2SO_4 on a GC (Shimadzu GC-8APT with a 4 m stainless steel column containing Supelco Chromosorp 102). Helium was used as the carrier gas.

It can be seen from the data of Boghosian *et al.* (*1*) that the VK38 deactivates at 440°C in an unconverted gas of 10% SO_2, 11% O_2, and 79% N_2. The activation energy above the break point is 77 kJ/mol; below it is 149 kJ/mol. Spectrum A in Fig. 2 shows the catalyst at 504°C in pure oxygen. Under these conditions the vanadium is completely oxidized to ESR-inactive V(V)-species. The minor absorption is most probably due to

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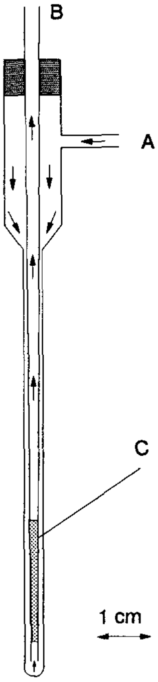

FIG. 1. ESR-reactor cell. (A) Inlet of synthesis gas, (B) outlet of partly converted gas, (C) catalyst bed. Arrows indicate direction of gas flow during operation.

impurities in the support, since an ESR spectrum of the support alone at 500°C shows similar features. Switching to a gas with the composition 9.4% SO_2, 11% O_2, and 79.6% N_2, a very broad isotropic line appears (spectrum B) with badly resolved hyperfine structure arising from the coupling to the ^{51}V nucleus ($I = 7/2$). We find $g = 1.985 \pm 0.005$ and a hyperfine structure constant in the low field region of about 95 ± 10 Gauss. These are typical features for V(IV)-species in solution as earlier observed by Mastikhin *et al.* (*3*), Boreskov *et al.* (*4*), and others. When the temperature decreases, it is seen that the signal intensity increases (spectra C and D). This is only partly due to a change in the Boltzmann distribution. At 442°C a sharp slightly anisotropic line appears and becomes very intense at 437°C (spectra E and F). Since Boghosian *et al.* (*1*), under similar conditions, observed a drastic decrease of the catalytic activity of VK38 below this temperature, this line is most probably due to the formation of the deactivation compound. In order to investigate whether this compound actually is $K_4(VO)_3(SO_4)_5$ at high temperature and in the environment of a strongly ionic melt, we recorded a spectrum (spectrum G) of this salt—obtained as earlier described (2)—at 450°C. The close agreement of spectra F and G with respect to the line shape, the *g*-value, and the line width strongly indicates that the compound $K_4(VO)_3(SO_4)_5$ is formed in VK38 below the temperature of deactivation. Finally the catalyst was reheated to 492°C, leading to the complete dissolution of the precipitated V(IV) compound (spectrum H). A comparison between spectrum H and spectra B and C indicates complete reversibility in good

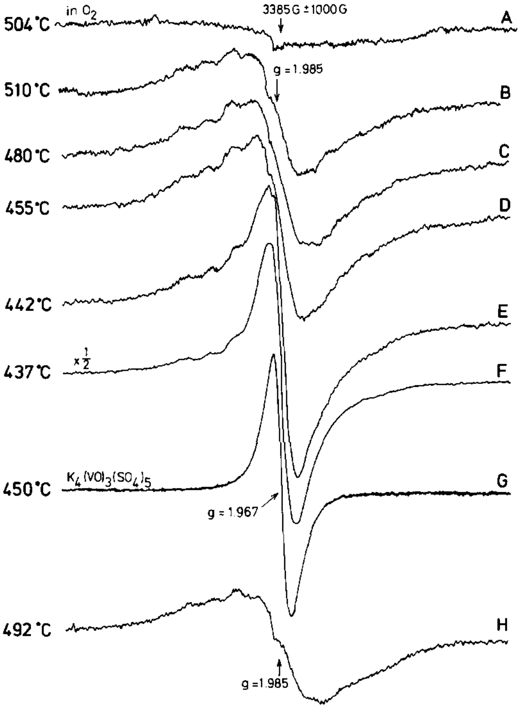

FIG. 2. ESR spectra of the catalyst VK38 (Haldor Topsøe A/S) in 100% O_2 (A) and in 9.4% SO_2, 11% O_2, and 80% N_2 (B–F and H). The spectrum of $K_4(VO)_3(SO_4)_5$ was recorded in air (G). The magnetic field (in Gauss), temperatures, and *g*-values are indicated in the figure.

accordance with the industrial experience that a heat treatment of a deactivated catalyst at 460–480°C restores the catalytic activity (*5*).

To determine very accurately the ESR characteristics for $K_4(VO)_3(SO_4)_5$, we recorded a sample at room temperature together with an internal Mn(II) standard. From this spectrum we find $g = 1.967 \pm 0.001$ and the line width $\Delta H = 72 \pm 2$ Gauss.

During deactivation of the VK38 catalyst V(III) compounds may also be formed but they are difficult to detect by ESR. However it seems to be V(IV) compounds that dominate the precipitates formed during catalytic deactivation of $M_2S_2O_7$–V_2O_5 melts with low mole ratios of M/V (*1*). Since $M/V = 3.8$ for VK38 it seems likely that V(IV) compounds primarily are formed during the deactivation.

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