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**Note**

# A THERMAL ANALYSIS STUDY OF $V_2O_5$ AND $Ag_{0.35}V_2O_5$

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Recently, we studied the activity of a silver–vanadium bronze catalyst for the oxidation of CO [1]. This catalyst, the formula of which can be represented as $Ag_{0.35}V_2O_5$ or more precisely as $Ag(I)_{0.35}V(IV)_{0.35}V(V)_{1.65}O_5$, is a non-stoichiometric solid solution of silver in $V_2O_5$. The silver atoms in the solid solution are singly ionised.

To elucidate the catalytic activity, a knowledge of the behaviour of the catalyst at different temperatures in reducing, and of the reduced catalyst in oxidising gas atmospheres is required. The following thermal analysis study (DTA, TG, DTG) was therefore performed.

## EXPERIMENTAL

Experiments were conducted on three different materials, viz. $V_2O_5$, a physical mixture of powders of metallic silver and $V_2O_5$ of a silver-to-$V_2O_5$ molar ratio of 0.35, and a sample of the silver–vanadium bronze which had previously been prepared by solid state synthesis [2]. The starting materials were purchased from Johnson Matthey and were of "Specpure" quality.

TG, DTG and DTA measurements were simultaneously performed using a Mettler TA-2 thermoanalyser (accuracy 0.02 mg). The data acquisition and data handling were computerised. The correction for gas flow and buoyancy effects and the (re)plotting were carried out on a Cyber 78/28 computer using a FORTRAN IV program. Details of the equipment and procedures can be found elsewhere [3]. The sample weight was approximately 70 mg and the heating rate was always 5°C $min^{-1}$. DTA was done with inert alumina as a reference. Pt/PtRh thermocouples were used.

Each of the three materials was investigated during the following sequence of treatments: dehydration/calcination at a temperature increasing up to about 600°C in an argon flow, reoxidation up to 600°C in an argon flow containing 10 vol % of oxygen, followed by reduction with a flow of 10 vol % $H_2$ in Ar, again up to a temperature of about 600°C.

Subsequently, the samples were subjected to one or more additional (re) oxidation–reduction cycles; they were always cooled down to room temperature in the original gas flow before changing the gas atmosphere, e.g. from reducing to oxidising.

## RESULTS AND DISCUSSION

Figure 1 shows the result of a reduction experiment performed on $V_2O_5$. The shoulder in the DTG curve at approximately 130 min. is caused by the transition in the temperature program from an increasing to a constant temperature.

The decrease in weight indicates a reduction from $V_2O_5$ to $V_2O_3$ within 1.0%. The onset temperature of the reduction is 503 ± 8°C based on a measurable change of the DTG signal. The effect on the DTG signal that can be discerned corresponds to a change in weight of 0.10 mg, which turned out to be the reproducibility of the mass-balance of the reaction. Van Dillen [4] reported the onset temperatue of reduction to be 456°C for $V_2O_5$. Though Van Dillen used a different TA apparatus, we do not feel that the difference in onset temperature is due to the apparatus. We rather believe that the type of $V_2O_5$ we used does indeed display a higher onset temperature of reduction than the $V_2O_5$ sample Van Dillen studied. The specpure $V_2O_5$ used in this work has been prepared by high temperature oxidation (ca. 550°C) of metallic vanadium, whereas the sample studied by Van Dillen was prepared by decomposition of $NH_4VO_3$ which leads to a relatively large amount of lattice-defects [5]. With the more stoichiometric material, the reduction temperature is enhanced because there are only a few "sites" available for the dissociation of hydrogen.

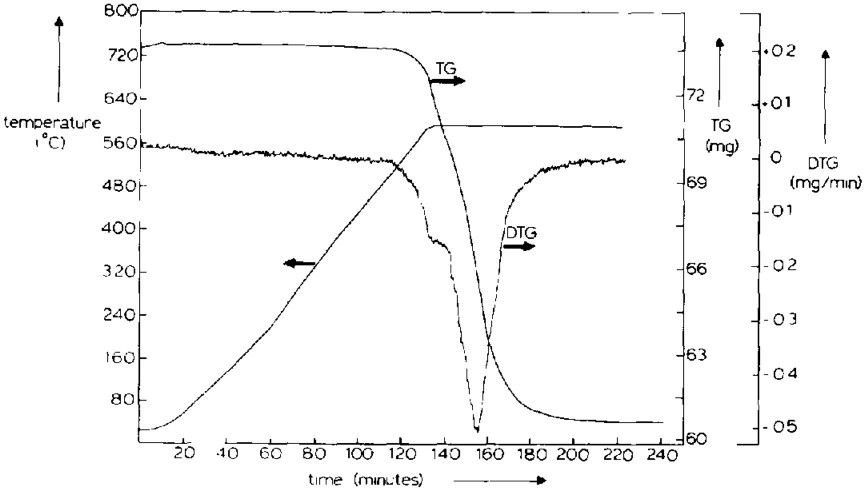

Fig. 1. First reduction thermal analysis experiment on $V_2O_5$.

The rapid reoxidation of $V_2O_3$ in our TG experiments leads to less ideally crystallised $V_2O_5$ particles. As a result the onset temperature for the second reduction of $V_2O_5$ dropped to $440 \pm 8°C$. The shoulder in the DTG signal has disappeared since the reduction was virtually complete during the stage where the temperature increased by 5°C $min^{-1}$. The smooth peak of the DTG signal indicates that the reduction of $V_2O_5$ to $V_2O_3$ proceeds in one step, at least under our experimental conditions. Reoxidation of $V_2O_3$ already proceeds at about 150°C [4] with a single DTG peak situated around 405°C.

Some DTG curves for the reduction experiments of the three samples are collected in Fig. 2. As is evident from this figure, reduction of $Ag_{0.35}V_2O_5$

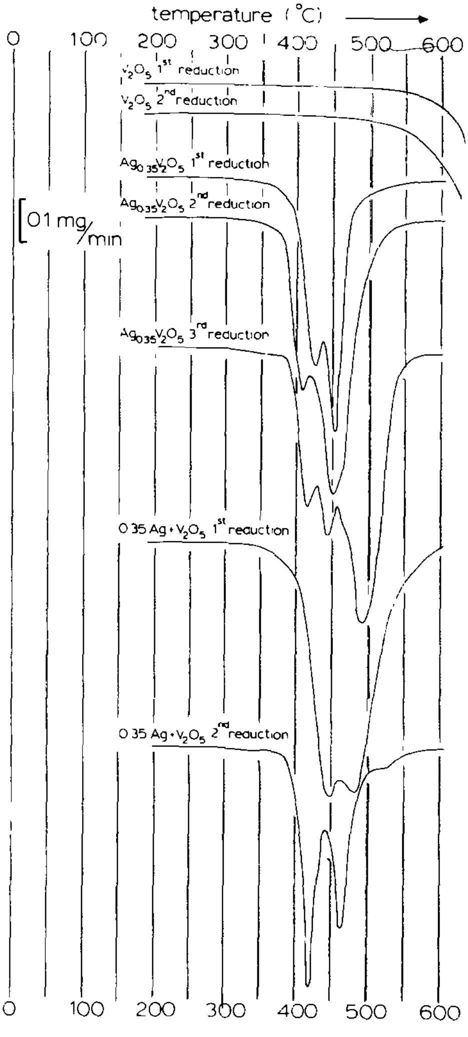

Fig. 2. Differential thermogravimetric curves for the reduction of $V_2O_5$, $Ag_{0.35}V_2O_5$ and a stoichiometric mixture of Ag and $V_2O_5$ with $Ag/V_2O_5$ equal to 0.35.

sets in at a significantly lower temperature (onset temperature 348 ± 6°C) than that of $V_2O_5$. Another difference with $V_2O_5$ is the time and thus the temperature range within which total reduction is attained, though the reduction proceeds at much lower temperatures. Probably the presence of silver in the $V_2O_5$ matrix not only lowers the onset temperature of reduction but also accelerates the reduction.

This is confirmed by the presence of two peaks in the DTG curves. The measured weight loss corresponds to silver and $V_2O_3$, most probably a mixture of these components, with a reproducibility better than 1%. In the region in the solid where the reduction proceeds, silver is expelled from the original matrix and is either deposited as free silver or accommodated in the bronze matrix to form a bronze of a higher silver content. Free silver will catalyse the reduction. The second maximum can thus be ascribed to the presence of free silver.

The dispersion of the metallic silver in the sample must affect the reduction rate. Therefore, the DTG pattern can be severely influenced by small differences in the experimental procedure, e.g. the length of the isothermal period at maximum temperature. This effect is most evident in reduction curve 3 for $Ag_{0.35}V_2O_5$ where three relative DTG maxima are displayed. The effect of the distribution of metallic silver is more pronounced with the stoichiometric mixture 0.35 $Ag + V_2O_5$. The temperatures at which the differential weight loss reaches a maximum during the first reduction are intermediate between those for $Ag_{0.35}V_2O_5$ and $V_2O_5$. This is caused by the inhomogeneous distribution of silver during dehydration and

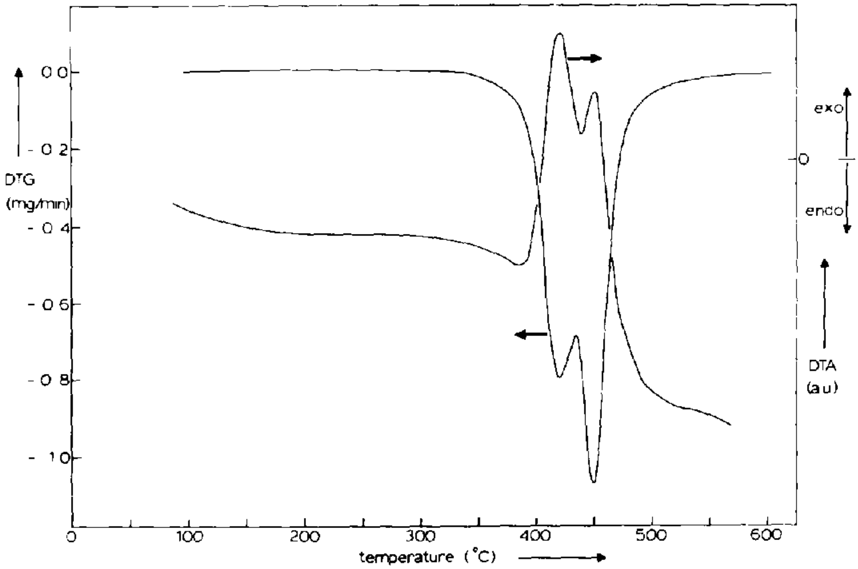

Fig. 3. DTA and DTG curves for the first reduction experiment on $Ag_{0.35}V_2O_5$.

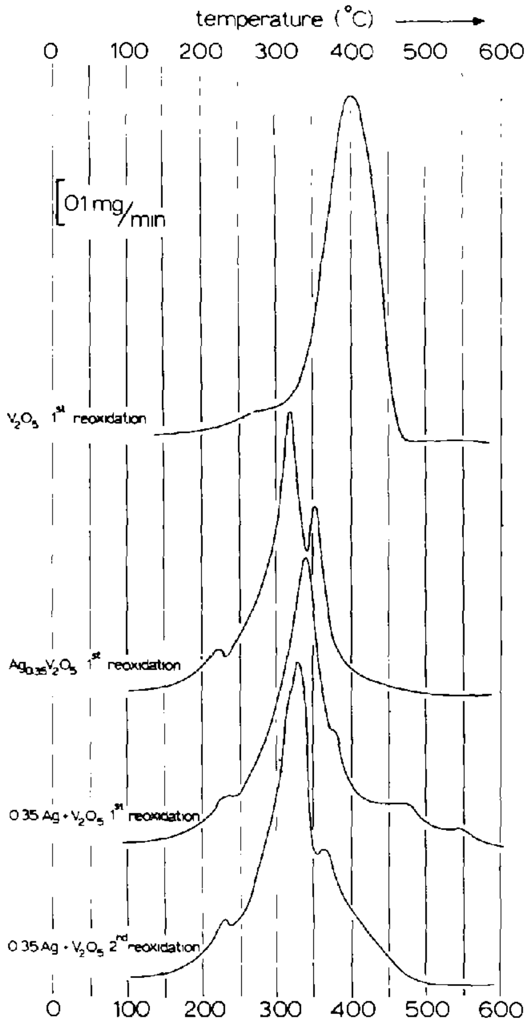

Fig. 4. DTG curves for the reoxidation of previously reduced samples.

reoxidation prior to the first reduction. As the number of oxidation–reduction cycles increased, the homogeneity of the sample improved. This is clearly indicated by the DTG pattern of the second reduction exhibiting lower DTG peak temperatures.

The DTA patterns for both the stoichiometric mixture and the silver–vanadium bronze excellently match with the corresponding DTG curves. An example is represented in Fig. 3.

For the reoxidation experiments of the reduced samples we refer to Fig. 4. The reoxidation of the Ag/$V_2O_3$ samples proceeds with three relative maxima in the DTG curves. All patterns show a great deal of similarity. Here, too, the catalytic action of silver is an important feature. The shoulder at

225°C is probably due to the formation and subsequent decomposition of $Ag_2O$. The DTG peak at 325°C corresponds to the silver-catalysed oxidation of $V_2O_3$ to $V_2O_5$ followed by bronze formation. The peak at 355°C, indicating an increase in oxidation rate, is also caused by oxidation of $V_2O_3$ to $V_2O_5$. Since this peak is also situated at a lower temperature than the DTG maximum for pure $V_2O_3$, the silver–vanadium bronze which is already formed at lower temperatures might catalytically accelerate the oxidation of $V_2O_3$.

Though similar in shape, the DTG curves for the reduced stoichiometric mixture do show a difference. The peak maxima are shifted to slightly higher temperatures. This is caused by a more inhomogeneous dispersion of silver than that resulting from reduction of the silver–vanadium bronze.

The DTA curves during reoxidation confirm the DTG results as was also observed with the reduction experiments.

In conclusion, we can state that DTG, especially, is a powerful technique in studying the reduction and (re)oxidation behaviour of oxidizing catalysts. Summarising our results, it is evident that the formation of a silver–vanadium bronze in the solid state, from Ag and $V_2O_5$, is a slow process. This observation was also made by Scholtens [2]. Several reduction–oxidation sequences up to 600°C are necessary to obtain DTG patterns equivalent to those found for a bronze sample. Furthermore, a remarkable observation is the catalytic action of silver in both the reduction and oxidation experiments.

A result which is of fundamental and practical importance in the field of heterogeneous oxidation catalysis, e.g. [4], is the fact that "doping" $V_2O_5$ with silver, leading to a relatively high concentration of V (IV) ions, has a significant effect on the onset temperature of reduction of the catalyst.

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