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Characterisation by thermal techniques

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Abstract

Differential thermal analysis and thermogravimetric analysis have been used to study EUROCAT-2 OXIDE (TiO_2–V_2O_5–WO_3). It has been found that water is removed at low temperature, and SO_2 removal and surface reduction (O_2 evolution) take place at high temperature, both for a fresh and a used catalyst. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal analysis is widely used for catalysts characterisation. In addition to insight in the knowledge of a catalyst, it is important to ascertain the temperature ranges where different phases are stable, in order to determine the optimal temperature range where a given reaction will take place preferentially, depending on the catalyst phases.

Although many different thermal techniques are commonly used, in the present report we will refer exclusively to differential thermal analysis (DTA) and thermogravimetric analysis (TG). The application of these techniques to EUROCAT oxide catalysts has been described previously [1]. In these techniques, the catalyst is heated (usually at a linear heating rate), and changes in its temperature (DTA) due to endothermic or exothermic processes (dehydration, phase transition, melting, etc.) with respect to an inert material, or changes in its weight (TG) due to removal of volatile species, in both cases as a function of temperature are determined. In some cases, the nature of gases evolved is analysed by gas chromatography (GC) or mass spectrometry (MS). The methods are usually quantitative, and so correlations can be concluded. On the other hand, the different apparatus commercially available follow different methods (volumetric, gravimetric or chromatographic) to perform all these determinations.

In this report, results are provided on the application of these techniques to the so-called EUROCAT OXIDE-2 catalysts, constituted by V_2O_5–WO_3–TiO_2. The samples (*fresh* and *used* catalysts) had been previously calcined at high temperature, and so weight losses or thermal effects expected, if any, should be very weak; desorption of gases through reaction with the environmental gas during analysis is, however, possible. In addition, removal of reagents or reaction products chemisorbed on the surface of the used catalyst is also possible.

2. Experimental

Two samples have been studied: an original, fresh catalyst, and the same catalyst used for 9000 h in the

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SCR reaction (the Mitshubishi process) [2]. Preparation of the catalyst [2] and results on elemental chemical analysis [3] have been reported. The catalysts were provided as honeycomb *monoliths*, and in some cases they were *crushed* and gently hand-ground to perform the measurements.

Simultaneous TG/MS analysis were performed in Laboratory CH-1 on a Netzsch STA409 thermobalance coupled with a heated capillary to an MS from Balzers QMG 420 using ca. 200 mg catalyst and a heating rate of 5°C/min in the temperature range 30–1100°C using He (50 ml/min) as carrier gas.

DTA profiles were recorded in Laboratory E-2 using a Perkin-Elmer DTA-1700 apparatus at a heating rate of 10°C/min and flowing dry air (60 ml/min), and α-alumina as reference. TG profiles were recorded in a Perkin-Elmer TGS-2 thermobalance, using ca. 30 mg of sample and a heating rate of 10°C/min, with dry air (60 ml/min) flowing through the sample.

Simultaneous DTA–TG analyses were performed (Laboratory F-3) in He using a Setaram TGA 62 instrument and ca. 30 mg sample. After equilibration at room temperature, the temperature was linearly (10°C/min) increased up to 1000°C; mass spectrometric analysis of the gases evolved were carried out with a Balzers quadrupole mass spectrometer QMG 420.

DTA and TG studies have been performed in Laboratory F-5 on a Netzsch STA 409 instrument, using samples of ca. 40 mg in a Pt crucible and heated from room temperature to 1000°C at 5°C/min under a flow of dry air.

Laboratory F-1 performed DTA and TG studies on a Setaram TGA-92 instrument controlled by a TG-ATD-92 unit; ca. 30 mg catalyst were used in a Pt crucible, and heated at 5°C/min under nitrogen or air (20 ml/min).

Finally, TG–DTG tests were performed in Laboratory I-4, using a Netzsch TA209 thermoanalyzer, in the 20–1000°C temperature range at a heating rate of 5°C/min. While in all other cases, the crushed samples were used, Laboratory I-4 performed their studies on the monoliths, uncrushed samples.

3. Results and discussion

X-ray diffraction data on these samples [3] have shown that they are mainly composed by the three nominal oxides, i.e., tungsta, vanadia and titania. So, only small weight losses, due to removal of adsorbed water or to condensation of surface hydroxyl groups, are expected, together with gases adsorbed during the catalytic cycles in the case of the used catalyst. However, under non-oxidizing conditions, also some reduction at high temperature, and oxygen loss, could be expected.

Table 1
Summary of TG results: weight losses (%) recorded for the fresh and used catalysts (crushed, unless otherwise stated)

Laboratory	Fresh		Used	
	<500°C	<1000°C	<500°C	<1000°C
CH-1	0.9	1.6	n.m.[a]	n.m.[a]
E-2	1.6	2.0	1.0	1.5
F-1	2.1	3.1	1.5	2.4
F-3	0.9	1.6	0.7	1.9
F-5	1.5	2.0	0.5	1.0
I-4	3.6[b]	4.2	2.2[b]	3.0

[a] Not measured.
[b] Up to 400°C.

The weight loss recorded in the different experiments was always lower than 5%; values summarized in Table 1 correspond to average of 2–3 measurements. In all cases, an almost continuous weight loss from room temperature to 1000°C is observed. No clear *plateaux* separating consecutive weight losses were recorded in any case. However, up to three different zones can be envisaged: from room temperature to ca. 120°C, from 120 to 650°C and from 650 to 1000°C (390, 650, and 800°C, according to Laboratory I-4). Main weight losses are recorded in the first and the third zones, while in the second zone the plots correspond to almost horizontal lines or extremely small losses. Differential thermogravimetric analysis (Laboratory F-3) shows that main weight losses take place at ca. 110°C (70°C according to Laboratory F-1) and 570–1000°C (685°C according to Laboratory F-1), these maxima coinciding with endothermic peaks in the DTA profiles recorded in all cases. Deviations in values reported from the different laboratories may be due to different water adsorption from the atmosphere during sample handling. Nevertheless, water is mostly physisorbed, and it is mainly desorbed at rather low temperatures. Differences between the fresh and the used catalysts are not either large.

Mass spectrometric monitoring of gases evolved indicates (Laboratories F-3 and CH-1) that water is mainly responsible for the weight loss in the low temperature region, while at higher temperatures oxygen is evolved from catalyst *fresh*, but SO_2 ($m/e = 48$) from catalyst *used* (355–580°C). Also, removal of oxygen is observed at ca. 744°C in Laboratory CH-1 (from 650°C upwards, according to Laboratory I-4) when the analysis is performed in the presence of He, i.e., under non-oxidizing conditions. Removal of sulphate species has been claimed [4] to be the origin of the second and the third weight losses in both monolith forms of the *fresh* and *used* catalysts, according to results reported by Laboratory I-4. After using the monolith catalysts in SCR and SO_2 oxidation tests, the same features have been observed (Laboratory I-4) in the TG–DTG curves, but it is relatively more pronounced than in the initial samples, likely due to sulphation during SO_2 oxidation, and the preset temperature shifts to lower values (390°C).

The DTA curves obtained at Laboratory F-5 shows, in addition to a broad endothermic effect at ca. 100°C due to removal of water (in agreement with results above, and also with MS monitoring of gases evolved, performed by other laboratories), very weak endothermic effects at 670–675 (also reported by Laboratory E-2) and 805–810°C, which can be related, for both catalysts, to phase transformations in the solid. However, it should be noted that X-ray diffraction results [3] on the used catalyst shows only minor differences with that of the fresh catalyst.

4. Conclusions

Both the *fresh* and the *used* catalysts characterised in this study show rather poor DTA and TG features, as in both cases the solids had been previously calcined at high temperatures and in the case of the used catalyst, reaction had taken place at 1000°C. Even though, water vapour is removed at low temperature (ca. up to 250–300°C), probably arising from physisorbed water and also condensation of surface hydroxyl groups. At higher temperatures (up to 1000°C) a weaker weight loss is ascribed to removal of SO_2 species (mainly in the used catalyst), or O_2, probably through surface reduction, when the analysis is carried out in an inert (He) atmosphere.

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