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Catalysis Today 56 (2000) 347–355

CATALYSIS TODAY

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Characterization by temperature programmed reduction

M.A. Reiche (CH-1), M. Maciejewski (CH-1), A. Baiker (CH-1) *

ETH-Zentrum, Swiss Federal Institute of Technology, Laboratory of Technical Chemistry, 8092 Zurich, Switzerland

Contributors: M.A. Reiche, M. Maciejewski, A. Baiker (CH-1); H. Berndt, U. Kürschner, A. Brückner, M. Baerns (D-1); M. del Arco, C. Martín, V. Rives (E-2); J.Ph. Nogier (F-2); H. Praliaud, B. Pommier, J. Varloud (F-3)

Abstract

Fresh and used EUROCAT Oxide-2 catalyst made up of V_2O_5, WO_3 and TiO_2 with SiO_2, Al_2O_3 and CaO as main additives have been studied by means of temperature programmed reduction (TPR). As in the EUROCAT Oxide-1 project (V_2O_5/TiO_2 catalysts) for similar conditions similar profiles were obtained in the different laboratories. In contrast to the V_2O_5/TiO_2 catalysts (EUROCAT Oxide-1 project), where the vanadia content could be determined by TPR with reasonable reliability, the exact determination of the vanadia and tungsta loading for the ternary catalysts is not possible because of the occurrence of several superimposed phenomena (reduction of vanadia, tungsta and titania and formation/reduction of $CaWO_4$, reactions are not completed at maximal temperature reached), which are not discernible by TPR.

Keywords: EUROCAT oxide; Vanadia-tungsten-titania; Temperature programmed reduction

1. Introduction

Temperature programmed reduction (TPR) with hydrogen is a widely used technique for the characterization of reducible solids and catalysts. The application of this technique in the frame of the EUROCAT Oxide-1 project has been reported previously [1]. In TPR, a reducible catalyst or catalyst precursor is exposed to a flow of a reducing gas mixture (typically a few vol.% of hydrogen in an inert gas) while the temperature is linearly increased. The rate of reduction is continuously followed by measuring the composition (H_2 content) of the reducing gas mixture at the outlet of the reactor. The experiment permits the determination of the total amount of hydrogen consumed, from which the degree of reduction and thus, the average oxidation state of the solid after reduction can be calculated. A detailed description of the underlying physical principles of the TPR method is presented in pertinent reviews and papers [2–6]. The aim of this study was to compare the results obtained on the fresh and used EUROCAT Oxide-2 catalysts in different research laboratories and to investigate whether it is possible to determine the vanadia and tungsta loading of the catalysts with sufficient accuracy.

2. Experimental

A typical apparatus for TPR measurements has been described earlier [1]. Table 1 shows the experimental parameters used by the different laboratories for the TPR-measurements. It should be noted that the conditions used, such as mass of catalyst, kind of pretreat-

* Corresponding author. Tel.: +41-1632-3153; fax: +41-1632-1163.
E-mail address: baiker@tech.chem.ethz.ch (A. Baiker (CH-1)).

0920-5861/00/$ – see front matter
PII: S0920-5861(99)00294-1

Table 1
Parameters for TPR measurements of EUROCAT 2 samples

Laboratory	F-3			E-2	D-1		CH-1		F-2
	Set 1	Set 2	Set 3		Set 1	Set 2	Set 1	Set 2	
Amount (g)	≈0.14	≈0.24	≈0.24	≈0.014	0.1	0.1	≈0.24	≈0.75	0.5
Grain size (mm)	Unknown [a]			Unknown[b]	0.125–0.4		0.3–0.5		Unknown[b]
Pretreatment									
Gas and flow rate (ml/min)	O_2			–	5% O_2 in He, 30		O_2, 75		O_2
Heating rate (K/min)	5			–	20		15		
Oxidation temperature (K)	573			–	673		573		673
Oxidation time (h)	2			–	0.5		2		1
Further treatment, gas, flow rate (ml/min)	–	–	–	–	Ar, 50		–	–	–
Temperature (K)	–	–	–	–	673		–	–	–
Time (h)	–	–	–	–	0.5		–	–	–
Cooling to RT	In O_2			–	In Ar		In O_2		In O_2
Purging, gas, time (min)	Ar, 90			–			He, 30		N_2
TPR									
Vol.% H_2 in carrier gas (F3: He, others: Ar)	0.97	5	5	5	5		5		5
Stabilizing under flux at ambient (min)				30	25		30		
Flow rate V^* (ml/min)	≈16	≈17.5	≈75	60	50		75		75
Heating rate β (K/min)	10			10	10		10		10
Start temperature (K)	RT			RT	RT		RT		RT
Maximum temperature (K)	1273			≈1173	873	1273	1273	885	1073
Isothermal hold (min)	50			–	60	30	30–90		–
Water trap after reactor (K)	–	–	–	195	[c]	[c]	195		195
Detector	MS			TCD	TCD		TCD		TCD
Characteristic number K (s)[d]	2220	875	174	18	111		174	525	254
Calibration	Standard mixtures			CuO	Ar-pulses		CuO		CuO

[a] Small monolith particles.
[b] Crushed.
[c] Trapping by molecular sieve 5 Å.
[d] Calculated assuming a reduction of V^{5+}–V^{3+} and W^{6+}–W^0.

ment, hydrogen concentration and flow rates, differ considerably. Similar conditions were applied in the experiments D-1 Set 1, F-3 Set 3 and CH-1 Set 1.

Another TPR-experiment (TG combined with MS) has been performed under more severe conditions (0.2 g sample, 20% H_2 in He, flow 50 ml/min, heating rate 5 K/min, maximum temperature ca. 1373 K) in laboratory CH-1.

In laboratory D-1 isothermal reduction and reoxidation experiments of the catalysts have been performed at 623 and 773 K using a thermobalance.

As discussed in Chapter 3.5 of the EUROCAT Oxide-1 project [1], such conditions for TPR measurements have been proposed which meet the recommendations of Monti and Baiker [3] and Malet and Caballero [5]. They propose a characteristic number K in the range of 55–140 s or the criterion $P \leq 20$ K, respectively. In the case of TPR curves that include several reduction steps an inadequate selection of the TPR-parameters leads to distorted profiles [5]. The characteristic number K is defined as $K\,(\mathrm{s}) = S_0/(V^* c_0)$, where S_0 (μmol) is the amount of reducible species, V^* ($\mathrm{cm^3\,(NTP)\,s^{-1}}$) the total volumetric inlet flux, and c_0 ($\mu\mathrm{mol\,cm^{-3}}$) is the hydrogen concentration in the carrier gas. Taking into account the influence of the heating rate β, Malet and Caballero [5] have proposed the characteristic number P, given by $P\,(\mathrm{K}) = (\beta\, S_0)/(V^* c_0) = \beta\, K$. However, in the described experiments [3,5] the catalyst contained only one reducible oxide and the reduction occurred in the relatively narrow range of 300 K, whereas in the current project the samples contained two reducible oxides and the reduction occurs in a range greater than 600 K. The conditions used in the experiments D-1

Set 1, F-3 Set 3 and CH-1 Set 1 will be referred to as reference conditions ($K = 110$–175). Lower (higher) K-values will be referred to as more severe (milder) conditions. Comparison of the K values, calculated assuming a reduction of V^{5+}–V^{3+} and W^{6+}–W^{0} (V- and W-content determined with chemical analysis by laboratory F-3, see chapter on chemical analysis [7]) show that they change by two orders of magnitude (see Table 1).

3. Results

Data reported by the different laboratories are summarized in Table 2 (temperatures of peak maxima and corresponding hydrogen consumption). In laboratory F-3 MS analysis of the evolving gases has been performed; so during TPR, both the signals at $m/z = 2$ (H_2^+) and $m/z = 18$(H_2O^+) have been monitored. Beside the H_2O-signals due to reduction additional peaks are also recorded due to the water removal at low-temperatures, in agreement with DTA/TG data reported in the chapter on thermal analysis of this issue. Also very weak peaks due to SO_2 ($m/z = 64$, 48) and H_2S ($m/z = 34$) have been reported for both samples. In the experiments carried out by laboratories D-1, E-2 and CH-1 only consumption of hydrogen has been monitored through TCD analysis.

Reduction profiles are presented in Figs. 1 and 2. In general, the profiles are similar, in all cases two

Table 2
Summary of TPR data

Laboratory	Sample	First peak		Second peak		Total H_2 (μmol/g)
		T (°C)	H_2 (μmol/g)	T (°C)	H_2 (μmol/g)	
F-3 (Set 1)[a]	EO2-F	953	519	1213	120	639
	EO2-U	953	613	1213	238	851
(Set 2)[a]	EO2-F	853	731	1168	1010	1741
	EO2-U	853	730	1163	1001	1731
(Set 3)[a]	EO2-F	841	762[b]	1133	1021[c]	1783[d]
	EO2-U	848	833[b]	1130	944[c]	1777[d]
E-2	P25	797	30	1103	10	40
	EO2-F	802	699	1032	928	1627
	EO2-U	798	657	1024	1101	1758
D-1 (Set 1)[a]	P25	845	40	1275	50	90
	EO2-F	834	570[b]	1120	1070[c]	1640[d]
(Set 2)[e]	EO2-F	840	480			
	EO2-U	817	490			
CH-1 (Set 1)[a]	P25	848	47	–	37	84
	EO2-F	849	602[b]	1139	944[c]	1546[d]
	EO2-U	840	664[b]	1133	1002[c]	1664[d]
(Set 2)[f]	EO2-F	851	559			
	EO2-U	844	581			
F-2[g]	EO2-F	883	459 ± 50[h]			
	EO2-U	893	548			

[a] Isothermally held at 1273 K.
[b] Values are calculated for the temperature range until 995 K, without any baseline correction.
[c] Values are calculated for the temperature range 995–1273 K, without any baseline correction.
[d] Values are calculated without any baseline correction and without taking into account the isothermal run at 1273 K.
[e] Isothermally held at 873 K.
[f] Isothermally held at 875 K.
[g] TPR until 1073 K.
[h] Three measurements.

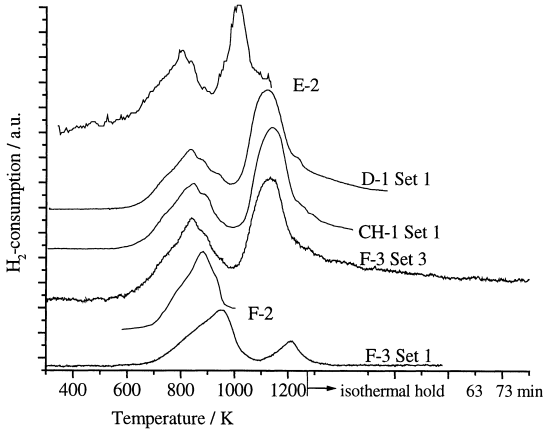

Fig. 1. TPR profiles of the fresh EUROCAT oxide catalyst. Curves D-1 Set 1, F-3 Set 3 and CH-1 Set 1 are measured under similar conditions, whereas for E-2 and F-3 Set 1 different conditions are used (see Section 2).

reduction peaks can be discerned. The low-temperature peak exhibits two shoulders, at temperatures approximately 100 K lower and 40 K higher than the main peak, respectively. The shoulder at lower temperature is more pronounced for the used catalyst, than for the fresh catalyst (Fig. 2).

The temperature of the first maximum of hydrogen consumption depends on the number K and shifts due to its increase from 800 ± 5 K (laboratory E-2) to 850 ± 30 K (laboratories CH-1, D-1, F-2, F-3 Set 2 and 3) and finally to 955 K (laboratory F-3 Set 1).

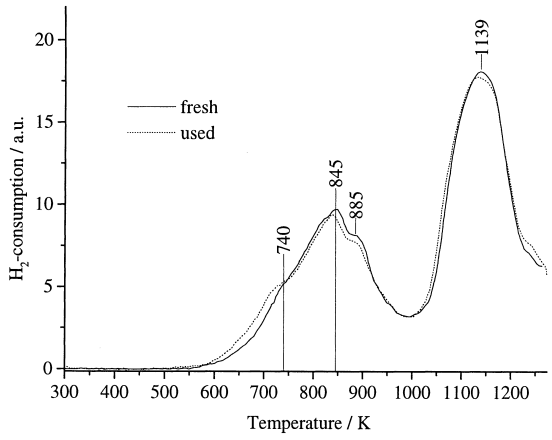

Fig. 2. Comparison of the TPR profiles of fresh and used EUROCAT oxide catalyst up to 1273 K, measured in laboratory CH-1.

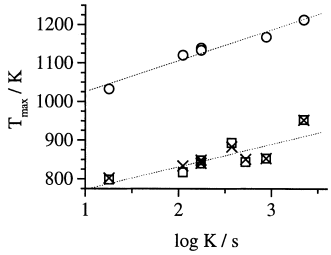

Fig. 3. The dependence of the temperature of the respective TPR-peak maxima on the logarithm of the characteristic number K ((×), and (□) first peak for EUROCAT fresh and used, respectively; (○), second peak for EUROCAT fresh).

A similar shift is observed for the second peak from 1032 K (E-2) through 1130 K (CH-1, D-1, F-3 Set 3) and 1165 K (F-3 Set 2) to 1213 K (F-3 Set 1) (see Table 2). The dependence of the temperature at the peak maxima on the characteristic number K is presented in Fig. 3. Note the agreement between the values of the maxima when similar conditions have been applied (see Table 2: CH-1 Set 1, D-1 Set 1 and F-3 Set 3).

The hydrogen consumption corresponding to the first peak varies between 460 μmol/g (F-2) and 833 μmol/g (F-3 Set 3) (Table 2). Note that the hydrogen consumption does not reach the baseline after the first peak. In all experiments the amount of consumed hydrogen is higher than necessary for the reduction of V_2O_5–V_2O_3, which would correspond to 400 (440) μmol H_2/g_{cat} according to the vanadia content determined by chemical analysis (3.6 (4.0) wt.% V_2O_5 for the fresh (used) catalyst, as shown in the chapter on chemical analysis [7]). The hydrogen consumption during the second stage of the reduction varies distinctly from 120 to 1101 μmol/g, depending on the measurement conditions used. Note, that also here the baseline is not reached, even after 83 min reduction at 1273 K (Fig. 1). The total hydrogen consumption for experiments with characteristic numbers $K \leq 174$ s amounts to 1546–1783 μmol H_2/g_{cat} (fresh) and 1664–1777 μmol H_2/g_{cat} (used) if the isothermal run at 1273 K is not taken into account and the baseline is assumed not to shift (Table 2). A TPR of P25 (TiO_2) performed up to 1473 K shows a continuously increasing reduction. A similar reduction of titania is also reported in the literature [8]. This is confirmed by another experiment of the

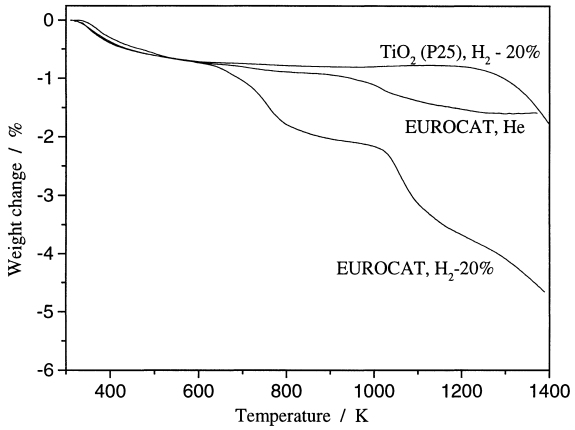

Fig. 4. Reduction of fresh EUROCAT sample and P25 studied by TG–MS. Curves resulting from heating in 20% H_2 and in He are shown.

EUROCAT fresh sample under more severe conditions up to 1390 K (20% H_2 in He, flow 50 ml/min, heating rate 5 K/min) carried out by means of TA/MS. The TG curve indicates a continual weight loss up to 1390 K (Fig. 4). The corresponding calculated amounts of reacted oxygen for three different temperature ranges are listed in Table 3. The XRD measurements of the reduced samples (Fig. 5) show diffraction patterns not being characteristic for any titania phase (Anatase, Rutile, Brookite or Srilankit), but of Magneli-type phases (Ti_nO_{2n-1}, $4 \leq n \leq 9$) [9]. Reduction of P25 under the same severe conditions up to 1400 K results in a similar XRD-spectra (Fig. 5), here the (110) reflection of rutile is nearly completely absent. The weight loss for P25 between 1165 and 1400 K is 1.00 wt.%, corresponding to the formation of titanium oxide with the stoichiometry of $TiO_{1.947}$ or $Ti_{18}O_{35}$. Powder XRD analysis of the samples after TPR runs up to 1173 K (laboratory E-2) show a lesser extent of phase transition with respect to the titania support. The anatase content, which before TPR amounted to 100% for both catalyst samples decreased to 43% for the fresh and 34% for the used catalyst after TPR analysis. This was determined from changes in the integrated areas of the main diffraction peaks due to both crystallographic forms of titania.

During the reduction of pure titania (P25) under TPR conditions a maximum at 800 K (E-2) or 845 K (D-1, CH-1) is reported, corresponding to the consumption of 30 and 45 μmol H_2/g, respectively. A second stage of reduction starts around 1050 K and is not finished until the maximum temperature is reached (E-2: 1140 K, D-1: 1273 K, CH-1: 1473 K).

Reduction of bulk vanadia (laboratory E-2) takes place in three steps, with two sharp reduction maxima at 900 and 925 K and a broader peak around 1073 K, the total consumption being 10 293 μmol H_2/g V_2O_5. Hydrogen consumption in these three steps is consistent with the following sequence of the V^{5+} reduction [10]: $V^{5+} \rightarrow V^{4.33+} \rightarrow V^{4+} \rightarrow V^{3+}$.

Reduction of bulk tungsta under the same experimental conditions (laboratory E-2) takes place in two steps, with maxima at 1005 and 1113 K. Hydrogen consumption amounts to 11 477 μmol H_2/g WO_3, indicating an 88% reduction extent from W^{6+} to metallic W^0. Reduction has not been completed probably due to too low a temperature being reached (ca. 1173 K). Vermaire and Berge [8] reported a strong shift of reduction to higher temperature for bulk WO_3 with increasing sample size.

Table 3
Amount of reacted oxygen calculated from the corresponding weight losses for the TG-MS experiments (20% H_2 in He, flow 50 ml/min, heating rate 5 K/min) carried out in laboratory CH-1

Sample	Temperature range	[K]	600–960	960–1273	1273–1373
Eurocat fresh	Oxygen	[μmol O]	852	1163	369
	cumulated	[μmol O]	852	2015	2384
P25	Oxygen	[μmol O]	57	69	374
	cumulated	[μmol O]	57	126	500
Difference	Oxygen	[μmol O]	795	1094	−5
	cumulated	[μmol O]	795	1889	1884

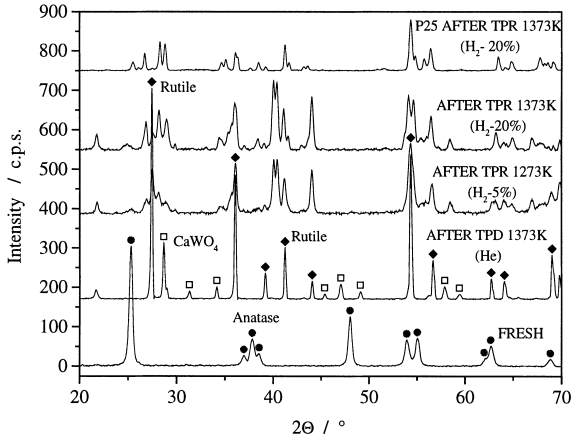

Fig. 5. XRD-pattern of fresh and reduced EUROCAT sample and reduced P25 measured in laboratory CH-1.

3.1. Isothermal reduction and reoxidation

Isothermal gravimetric reduction and reoxidation experiments (laboratory D-1) performed at 623 and 773 K show a higher rate of reduction for the used sample than for the fresh one at both temperatures (Fig. 6). At 773 K the reduction is much faster, a weight loss of 0.2% (without taking into account the buoyancy effect due to replacement of He by H_2) is already reached after 1–2 min, whereas at 623 K 154 min for the fresh or 57 min for the used sample is necessary. In all cases the reoxidation is almost instantaneous. The reduction is not completely reversible.

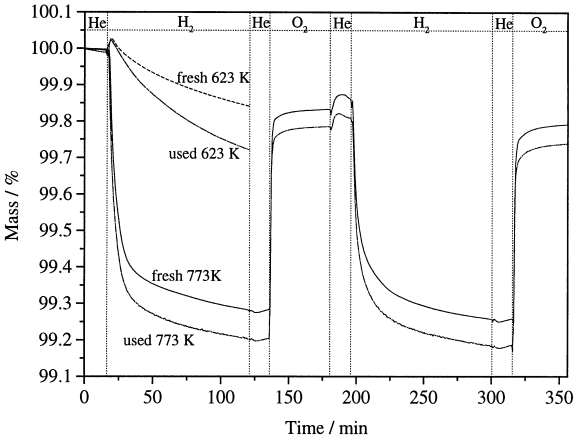

Fig. 6. Isothermal reduction and reoxidation TG-experiments performed in laboratory D-1.

4. Discussion

The different temperatures of maximal hydrogen consumption in the various measurements can be well explained by the different conditions applied, which are mirrored in the characteristic number *K*. The lowest temperatures for both maxima are observed in laboratory E-2. Here the characteristic number is low ($K = 18$), due to the low sample weight, which resulted in the low reduction temperature and decreasing signal–noise ratio compared to the other measurements. For laboratory F-3 Set 1 the characteristic number *K* is the highest, due to low hydrogen concentration (ca. 1%) and flow rate. This increases the reduction temperature. The use of higher hydrogen concentration (5%) shifts the temperatures of maximum hydrogen consumption markedly towards lower temperatures (F-3 Set 2). A further, but less pronounced shift is observed by increasing also the flow rate (F-3 Set 3). These effects are in agreement with the literature [3,6]. The results obtained by laboratory F-3 Set 3 are in good agreement with the results of laboratories D-1 and CH-1, where similar TPR-conditions have been applied. Furthermore it must be stated, that in spite of the different pretreatment used in the laboratories CH-1 (300 K, O_2) and D-1 (400 K, first 5% O_2, then He) no remarkable difference in the reduction profiles are observed.

Different amounts of hydrogen consumed during first stage of the reduction are reported (Table 2). This is, among others, due to the fact, that after the first step the hydrogen signal does not reach the baseline and therefore the integrated area of the first peak, being influenced by the experimental conditions used, is additionally dependent on the way of integrating (choice of baseline, choice of temperature range for integrating).

The hydrogen consumption represented by the low-temperature peak is higher than necessary for the reduction of V^{5+}–V^{3+}. This indicates that also tungsta is partly reduced in this temperature range. Partial reduction of tungsta at lower temperatures for binary WO_3/TiO_2 catalysts has already been observed in the literature [8,11]. Comparison with ternary V_2O_5–WO_3/TiO_2 catalysts indicates that the high-temperature shoulder of the first maxima around 880 K can be due to the reduction of tungsta species [12].

Since vanadia supported on titania is reduced at lower temperatures than bulk vanadia (reduction of V_2O_5/TiO_2 is generally complete below 973 K and WO_3/TiO_2-catalysts exhibit maxima above 1000 K [8,11]) the reduction maximum at higher temperature can be mainly attributed to the reduction of WO_3. The rate of reduction of WO_3 reaches a maximum between 1033 K (E-2) and 1213 K (F-3 Set 1). At this temperature different competing reactions occur. In addition to the reduction of WO_3, the reduction of TiO_2 starts. Since the reduction of TiO_2 is not complete at 1273 K, different results reported by the various laboratories for the amount of consumed hydrogen are likely to originate from the experimental conditions used and the time of the isothermal run at 1273 K and hence the integrating procedure. For experiments under similar conditions and identical integration procedures (no baseline correction, isothermal run not taken into account; Table 2) similar values of total hydrogen consumption are reported (fresh: 1656 ± 119 μmol H_2/g_{cat}; used: 1721 ± 80 μmol H_2/g_{cat}). For the TPR in laboratory E-2 under more severe conditions ($K = 18$) up to ca. 1173 K similar values (1627 and 1758 μmol H_2/g_{cat}, respectively) are obtained.

XRD of a sample of fresh V_2O_5–WO_3/TiO_2 after TPD in He till 1373 K (TG–MS experiment, Fig. 4) indicates the formation of calcium tungstate $CaWO_4$, as shown in Fig. 5. This occurs in addition to the reduction of WO_3 and TiO_2 at higher temperatures, and can be responsible for the fact that the high-temperature peak for the TPR run under 1% H_2 is smaller than the low-temperature peak, contrary to the other measurements. It seems that under these milder reduction conditions the formation of $CaWO_4$ is favored compared to the reduction of WO_3. A TG–MS experiment under 20% H_2 with the sample previously heated in He to 1373 K resulted in an additional weight loss due to reduction of 2.42 wt.%. The total weight loss (TPD + TPR) is 4.02 wt.%, compared to 4.55 wt.% for the TPR up to the same temperature. The smaller weight loss indicates the lower reducibility of $CaWO_4$ compared to WO_3.

Table 3 shows the amount of reacted oxygen for the TG–MS runs under more severe conditions (20% H_2, 5 K/min) calculated from the weight loss in the corresponding temperature range (see also Fig. 4). These conditions (high hydrogen concentration, low heating rate) shift the reduction towards lower temperature. Comparison of the EUROCAT fresh sample and P25 reveals that in the temperature range 1273–1373 K an identical weight loss is found. This leads to the conclusion that under these conditions reduction of V_2O_5 and WO_3 is finished at 1273 K and only titania is reduced at temperatures above 1273 K. XRD indicates that $CaWO_4$ is not formed (Fig. 5). Since the other components of the catalyst (SiO_2, Al_2O_3, CaO) are not reduced at these temperatures, the weight loss is due to the reduction of V_2O_5 and WO_3 which, after subtraction of the hydrogen consumption due to the support reduction, amounts to 1884 μmol H_2/g_{cat}. This value is very close to the one calculated from the vanadia and tungsta amount (2 wt.% V, 9.35 wt.% W) determined from laboratory F-3 by chemical analysis (see chapter on chemical analysis [7]), which would result in a hydrogen consumption of $392\ (V^{5+} \rightarrow V^{3+}) + 1527\ (W^{6+} \rightarrow W^0) = 1919$ μmol H_2/g_{cat}.

For all other measurements ($c(H_2) \leq 5\%$, $\beta = 10$ K/min) lower values of hydrogen consumption are obtained when the isothermal run at 1273 K is excluded (Table 2). An explanation is, as discussed above, that the reduction under the milder conditions is not complete up to the maximum experimental temperature of 1273 K. Also for P25 in the range 1273–1373 K a lower degree of reduction is observed under reference TPR conditions than under severe conditions. The milder the conditions (increasing characteristic number *K*) the lower is the degree of reduction until 1273 K.

4.1. Comparison of fresh and used EUROCAT sample

The shoulder at ca. 740 K of the first TPR-peak is more pronounced for the used EUROCAT sample than for the fresh sample. This indicates that partly the vanadia of the used sample is more easily reduced. The isothermal reduction/reoxidation experiments show that the rate of reduction at 623 and 773 K is in both cases greater for the used than for the fresh sample, whereas the rate of reoxidation in all cases is very fast and does not differ for fresh and used samples. Alemany et al. [13] suggested that the higher reducibility of V_2O_5–WO_3/TiO_2 samples is responsible for the higher reactivity of the ternary catalysts compared to the binary ones. Thus the greater ease of reduction

for the used sample might be an explanation for the higher activity of the used sample in the SCR reaction [14].

In previous investigations of titania supported vanadia catalysts [1,15–17] it was reported, that for low loadings (up to four theoretical monolayers) only a single peak occurred in the TPR profile, while for higher loadings an additional peak developed at high-temperature. This was because at low loadings the vanadia is in close contact with the support, whereas for high loadings crystalline vanadia becomes prevalent, and this is reduced at higher temperatures. In the EUROCAT Oxide-2 samples the vanadia loading is less than a theoretical monolayer (corresponding to about 0.1 wt.% V_2O_5/m^2), but the titania surface is additionally covered by other components such as WO_3. The better reducibility of the vanadia species for the used catalyst could be explained by a restructuring phenomenon, which occurs during the SCR-reaction. The vanadia could come into closer contact with the titania support, which leads to the higher reducibility observed.

5. Conclusions

The application of similar experimental conditions leads to satisfying agreement of the TPR results obtained in different laboratories. Changes in experimental conditions can result in different reduction temperatures and cause difficulties in proper quantification of the observed signals.

As a general conclusion one can state that the exact determination of catalyst loading in the multicomponent system vanadia/tungsta/titania is rather difficult by the TPR method. In the EUROCAT Oxide-1 project dealing with V_2O_5/TiO_2 in the temperature range of the vanadia reduction the reduction of titania was not significant and the vanadia content could be determined by TPR. In contradiction to this in the present project the exact determination of the vanadia and tungsta loading for the ternary catalysts is not possible due to the following factors:

1. *Low-temperature region*: The hydrogen consumption during the first stage of reduction is not only due to the reduction of vanadia, but also the partial reduction of tungsta.
2. *High-temperature region*: The second stage of reduction at higher temperature is influenced by different competing reactions:
1. Reduction of tungsta.
2. Reduction of titania.
3. Formation of $CaWO_4$, reduction of which is more difficult than that of tungsta.
4. For a heating rate of 10 K/min and a hydrogen concentration $\leq$5% the reduction of tungsta is not complete until 1273 K, being generally the upper limit of the TPR experiments. This leads to very imprecise quantification of the high-temperature TPR-peak due to the fact that the TPR signal does not come back to the baseline, which on the other hand can have at high-temperature a significant deviation from the straight-line course. Both these factors significantly can decrease the accuracy of the quantification.

Only if severe conditions are used, so that reduction is complete until the maximal experimental temperature is reached, and the amount of hydrogen consumed by reduction of the pure support is determined and taken into account, values of hydrogen consumption consistent with the loading determined by chemical analysis can be obtained. However, according to point 1, from the TPR alone no differentiation between vanadia and tungsta can be made.

Differences in the reduction behavior between the fresh and the used EUROCAT sample can indicate a restructuring process, which results in an increased reducibility of the vanadia for the used sample.

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