

Temperature-programmed reduction and oxidation experiments with V_2O_5/TiO_2 catalysts

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Temperature-programmed reduction (TPR) and oxidation (TPO) experiments were performed with V_2O_5/TiO_2 catalysts with vanadia loadings of 1 wt.% (Eurocat EL10V1) and 8 wt.% (Eurocat EL10V8) and with unsupported V_2O_5 . It was possible to correlate the redox properties with the presence of different vanadia species: crystalline and polymeric vanadia species known to be present on EL10V8 were found to be the most difficult to reduce but the easiest to reoxidize. Monomeric vanadyl species known to be present on EL10V1 were the easiest to reduce but the most difficult to reoxidize. In a further set of experiments toluene was used as reducing agent under isothermal conditions at 623 K to probe the catalytic properties of the various vanadia species. In the subsequent TPO experiments the oxygen mass balance including O_2 , CO, CO_2 and H_2O was solved thus allowing us to distinguish between the oxidative degradation of adsorbates and the reoxidation of the catalyst. The O_2 consumption at lower temperatures was shown to originate from the total oxidation of adsorbates, observed for all three samples, whereas the O_2 consumption at higher temperatures, observed only for EL10V8 and V_2O_5 , was caused by the reoxidation of these catalysts. Thus, monomeric vanadyl species were able to adsorb toluene dissociatively, but no oxygenated products were released into the gas phase. In contrast, fast oxygen insertion into toluene and desorption of oxygenates occurred when crystalline and polymeric vanadia species were present.

1 Introduction

A large variety of temperature-programmed experiments are applied in heterogeneous catalysis to characterize the activation and the reactivity of catalysts.^{1,2} In particular, temperature-programmed reduction (TPR) has proved a powerful tool to analyze the reduction kinetics of oxidic catalyst precursors.³ This technique consists of heating the catalyst with a linear temperature ramp in a flow of hydrogen while monitoring the hydrogen consumption. In this way, fingerprint profiles are obtained which allow one to study the influence of the support and of promoters on the reducibility. Furthermore, the amount of reducible species in the catalyst and their degree of reduction can be derived from the integrated hydrogen consumption, and lumped kinetic parameters can be estimated if an adequate model of the reduction process exists. Similarly, the oxidation behavior of a catalyst can be studied by temperature-programmed oxidation (TPO) experiments which are less frequently applied. The advantage of this method which uses oxygen as reactant is that it allows one to monitor the oxygen uptake directly. TPR experiments are sometimes complemented with TPO experiments in order to study the reversibility of reduction/reoxidation cycles. However, structural changes of the catalyst which may occur when heating to elevated temperatures in a hydrogen atmosphere have to be avoided.

It is often not possible to correlate the reducibility in hydrogen, as obtained by TPR, with the catalytic performance in selective oxidation reactions with hydrocarbons as reducing agents. In this case, the reduction of the catalyst cannot be seen isolated from the preceding adsorption of the reactant, and the overall reducibility of the catalyst is determined by the sum of both the adsorption and the redox properties. Thus, it seems to be appropriate to use the reactant molecule

itself as the reducing agent. In a similar way, TPO was applied by Dias *et al.*⁴ to analyze the carbon residue deposited on the catalyst surface during *o*-xylene oxidation, and in a recent publication by Bulushev *et al.*⁵ to study irreversibly adsorbed toluene. Reduction in a hydrocarbon atmosphere supplies additional information because not only catalyst reduction, but also product formation and deposition of strongly bound adsorbates on the catalyst surface may occur, resulting in complex TPO profiles. Also, this type of study is experimentally more demanding as several different products which need to be quantified may be formed.

The objective of the present work was to examine the effect of hydrogen and toluene as reducing agents on subsequently obtained TPO profiles over V_2O_5/TiO_2 catalysts in order to develop a combined *ex situ* method which allows one to extrapolate to the redox behavior of the catalyst under reaction conditions. V_2O_5/TiO_2 (anatase) was chosen as a test system, since it is an oxidation catalyst which has been extensively studied and which exhibits catalytic activity in a large variety of reactions. Eurocat samples were used because of the vast amount of information available.⁶ Highly dispersed surface species in strong interaction with the support are assumed to predominate on the catalyst with the low loading of vanadia (1 wt.% V_2O_5 , Eurocat EL10V1) and polymeric and crystalline vanadia on the sample with the high loading of vanadia (8 wt.% V_2O_5 , Eurocat EL10V8). In the first part of this study, conventional TPR experiments using hydrogen as the reducing agent were conducted and complemented with TPO experiments. In the second part, a feed stream of diluted toluene in nitrogen was used as the reducing agent. The reduction of the catalyst was performed isothermally, again followed by a TPO experiment which served to reoxidize the catalyst and also to burn off hydrocarbons deposited on the catalyst surface. In this way, information about the

reducibility as well as about the formation of oxygenates on the catalyst surface was obtained.

2 Experimental

2.1 Samples

The samples used in this study were the Eurocats EL10V1 and EL10V8 kindly supplied by J. C. Védrine, the nominal vanadia content being 1 and 8 wt.%, respectively. BET surface areas were $10 \text{ m}^2 \text{ g}^{-1}$ (EL10V1) and $11 \text{ m}^2 \text{ g}^{-1}$ (EL10V8). The samples were prepared by wet impregnation of the TiO_2 (anatase) support with vanadyl oxalate solution, drying and calcining for 4 h at 450°C . The preparation and characterization of these samples is described in detail in ref. 7. V_2O_5 (purity > 99.6%, $S_{\text{BET}} = 2 \text{ m}^2 \text{ g}^{-1}$) obtained from Janssen Chimica was used as reference material.

2.2 Temperature-programmed experiments

The experiments were carried out in a flow apparatus consisting of a versatile feed system and a quartz reactor of 6 mm inner diameter based on the design by Monti and Baiker⁸ and Cvetanovic and Amenomiya.⁹ The former consisted of four stainless-steel gas lines equipped with mass flow controllers. Feed gases were Ar (purity 99.9995%, Air Products) and gas mixtures (Messer Griesheim) of H_2 (4.2%; purity 99.999%) in Ar (purity 99.999%) and O_2 (9.87%; purity 99.995%) in Ar (purity 99.999%). The calibration of the instruments was also performed with these gases. The calibration of the TCD was checked by using CuO which is known to be reduced completely to Cu^0 . The mass spectrometer was calibrated for O_2 , CO , CO_2 and H_2O using gas mixtures of known composition by referring to Ar as internal standard. A N_2 stream (purity 99.999%, Messer Griesheim) saturated with toluene at room temperature was fed to the reactor. The resulting toluene concentration of 3.5% was checked by GC analysis. The reactor effluent passed through a dry ice/isopropanol trap (200 K) prior to passing through the detectors which were chosen by a multiposition valve. A paramagnetic detector (Advance Optima Magnos 16, Hartmann und Braun) was used to monitor the O_2 concentration and a thermal conductivity detector (TCD) (Hydros 100, Rosemount) was used to monitor the H_2 concentration. Additionally, a slip stream of the reactor effluent was analyzed with a quadrupole mass spectrometer (Omnistar, Pfeiffer).

Prior to each reduction experiment, the samples were pretreated at 673 K in flowing dry and purified air (in the case of the TPR experiments) or in 9.87% O_2/Ar (in the case of reduction with toluene) for 1 h. Both procedures are known to achieve the V^{5+} oxidation state. The experimental conditions for a TPR experiment were a flow rate of 85 Nml min^{-1} ($\text{Nml} = \text{normal ml}$, i.e. ml at 0°C and 1013 mbar), a hydrogen concentration of 4.2%, a heating rate of 10 K min^{-1} , a final temperature of 1073 K, and a sample weight of 200 mg (supported catalysts) or 50 mg (V_2O_5). In TPR–TPO cycles, the final temperature in TPR was 873 K for Eurocat samples in order to prevent structural changes. The corresponding conditions in TPO were a flow rate of 107 Nml min^{-1} , an oxygen concentration of 9.87%, a heating rate of 15 K min^{-1} , a final temperature of 723 K (supported catalysts) or 873 K (V_2O_5) and a sample weight of 200 mg (supported catalysts) or 50 mg (V_2O_5) unless specified otherwise. Again, the conditions were chosen in such a way that at V^{5+} oxidation state was achieved. It is known from IR studies with these samples that no adsorbates remain on the surface after heating to 673 K in O_2 .¹⁰ Reduction in toluene was performed by exposing the sample to a stream of 3.5% toluene in N_2 (80 N ml min^{-1}) at a constant temperature of 623 K for 5 min. It is known that TPR is very sensitive to the experimental parameters. Thus, care was taken to achieve a K number (defined as the ratio of reducible substance (mol) divided by the hydrogen flow (mol

s^{-1})) within the range of 55–140 s, as proposed by Monti and Baiker,⁸ whenever experimentally possible.

3 Results and discussion

3.1 Temperature-programmed reduction in H_2

When reducing unsupported V_2O_5 in the temperature range up to 1123 K (inset in Fig. 1, Fig. 2), five peaks were resolved, the assignment of which has been established in the literature.¹¹ Using a heating ramp of 10 K min^{-1} (trace C in Fig. 2), the TPR peaks were found to be located at 910, 932, 971, 1044 and 1102 K. The peaks correspond to intermediate oxides in the transformation of V_2O_5 to V_2O_3 . Their composition can be deduced from the measured hydrogen consumption. The assignment based on reaction stoichiometry was confirmed in the literature by XRD analysis.¹¹ The first peak corresponds to the formation of V_6O_{13} , the second to VO_2 , and with the completion of hydrogen consumption V_2O_3 is reached. The integrated H_2 consumption, the degree of reduction α obtained for each peak and the corresponding temperatures are summarized in Table 1.

The reduction behavior of Eurocat samples has been extensively described in the literature.¹² In the Eurocat study, a

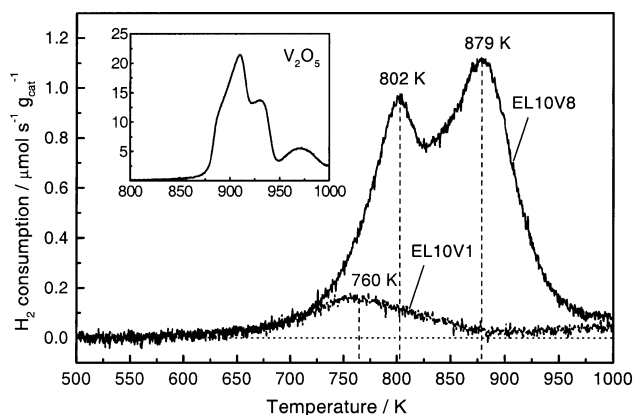


Fig. 1 TPR profiles obtained for Eurocat samples by reduction with H_2 . Pretreatment: 1 h at 673 K in air. Experimental conditions: heating rate 10 K min^{-1} , final temperature 1073 K, sample weight 200 mg, flow rate 85 Nml min^{-1} , 4% H_2/Ar . The inset shows the TPR profile of V_2O_5 (50 mg, 10 K min^{-1}) for comparison.

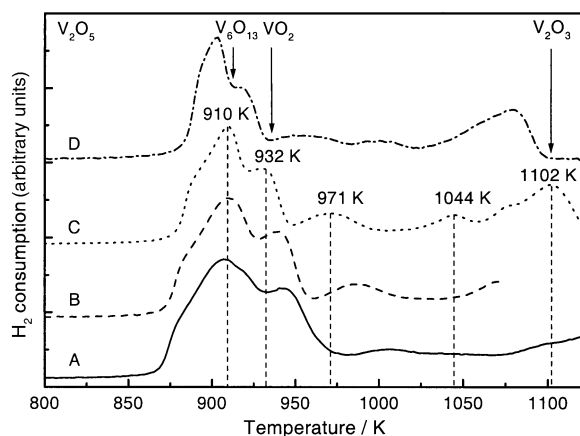


Fig. 2 Normalized TPR profiles obtained with V_2O_5 at different heating rates: (A) 20, (B) 15, (C) 10 and (D) 5 K min^{-1} . The arrows indicate transitions between different vanadium oxides as concluded from the degree of reduction. Pretreatment: 1 h at 673 K in air. Experimental conditions: final temperature (A, C, D) 1123 K or (B) 1073 K, sample weight 50 mg, flow rate 85 Nml min^{-1} , 4% H_2/Ar .

Table 1 Results of H₂ TPR experiments with $\beta = 10 \text{ K min}^{-1}$, 4.2% H₂ in Ar, $Q = 85 \text{ Nml min}^{-1}$. H_2^{calc} is the calculated H₂ uptake expected for complete reduction of V⁵⁺ to V³⁺. Total H₂ is the measured total consumption of H₂. For the TPR peaks, the degree of reduction α and T_{max} are shown assuming $\alpha = 100\%$ for V⁵⁺ to V³⁺

Sample	H_2^{calc} /mmol g ⁻¹	Total H ₂ / mmol g ⁻¹	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
EL10V1	0.11	0.125	114% 760 K				
EL10V8	0.86	0.92	41% 802 K	107% 879 K			
V ₂ O ₅	11.0	11.0	36% 910 K	51% 932 K	63% 971 K	74% 1044 K	100% 1102 K

standardized procedure has been established for TPR experiments in order to ensure the comparability of the results. The T_{max} values (temperature at maximum H₂ consumption rate) obtained under similar conditions in this study for EL10V8 are 802 and 879 K (Fig. 1) which agree well with literature data on the same catalyst sample. Values in the range 793 to 833 K ($T_{\text{max},1}$) and 878 to 913 K ($T_{\text{max},2}$) have been reported.¹² For sample EL10V1, 760 K was found, compared to literature values ranging from 776 to 788 K.¹² This discrepancy might be related to the larger sample amount (8 times more) used in the Eurocat study in order to cope with the very small vanadia content. This might also be the reason why in two cases in the Eurocat study a shoulder was observed in the TPR experiments with EL10V1 which was not found in other studies. All samples were reduced to the oxidation state V³⁺.

In the V₂O₅/TiO₂ system different vanadia species such as monomeric, polymeric and crystalline VO_x species may coexist at the surface.^{13–16} Thus, the peaks do not necessarily represent different steps of reduction of the same species but should rather be considered to result from a superposition of different reduction steps of several species.¹⁷ The TPR profile of the high-loading catalyst EL10V8 exhibits two distinct peaks. Compared to unsupported V₂O₅, the reduction of V₂O₅/TiO₂ catalysts is found to be shifted to lower temperatures by about 100 K. This enhanced reducibility of the catalyst is generally ascribed to the interaction with the support. Based on results for samples with different vanadia contents, the high-temperature peak at 879 K is usually ascribed to the reduction of highly polymeric or crystalline vanadia, since the EL10V8 sample is known to contain V₂O₅ crystallites which can be detected by XRD. This peak is absent in the TPR profile of the EL10V1 sample which exhibits one single peak at 760 K due the reduction of one type of species. At this low loading, the majority of the vanadia species are obviously present as a monolayer in strong interaction with the support. The integrated hydrogen consumption corresponds to a complete reduction of V⁵⁺ to V³⁺, as observed for other V₂O₅ samples. It is noteworthy that the TPR trace does not reach the baseline at high temperatures. When reducing pure TiO₂, a slight H₂ uptake was observed at high temperatures which increased with rising temperature up to the end of the temperature ramp.

In order to gain further information on the kinetics of the reduction process, TPR profiles were recorded with different heating rates (Fig. 2 and Fig. 3). The peaks are generally shifted to higher temperatures with increasing heating rates. In the case of unsupported vanadia (Fig. 2), no further shift of the first peak is observed when increasing the heating rate from 15 to 20 K min⁻¹. It has to be taken into account that this temperature region is close to the melting point of V₂O₅ at 963 K. In the case of sample EL10V8, the first peak is also not shifted when the heating rate is raised to 20 K min⁻¹. This might be an indication of structural changes of the starting material, since Nogier *et al.*¹⁸ observed the phase transition of the support and changes in the BET surface area at 833 K. From the dependence of the temperature of the peak

maximum T_{max} on the heating rate, an apparent energy of reduction can be calculated. The apparent activation energies of reduction of the EL10V8 sample derived from the slopes of the Arrhenius plot shown in the inset of Fig. 3 amount to 209 kJ mol⁻¹ for the first step and to 129 kJ mol⁻¹ for the second step. Consequently, the observed higher rate of reduction of the monomeric species at lower temperatures must originate from a significantly higher apparent preexponential factor. The quantitative results are summarized in Table 2.

3.2 Temperature-programmed oxidation after TPR with H₂

The reoxidation behavior of the catalysts after TPR used to generate the V³⁺ oxidation state was analyzed by TPO. The V₂O₅/TiO₂ samples were pretreated as follows in order to avoid structural changes: the TPR temperature ramp was stopped at 873 K and that temperature was maintained until the hydrogen consumption reached the baseline. No phase transition of the anatase support was found to be induced by such a treatment, as confirmed by XRD and Raman spectroscopy.¹⁰ The final TPR temperature was at 1073 K for unsupported V₂O₅ in order to achieve the V³⁺ oxidation state also

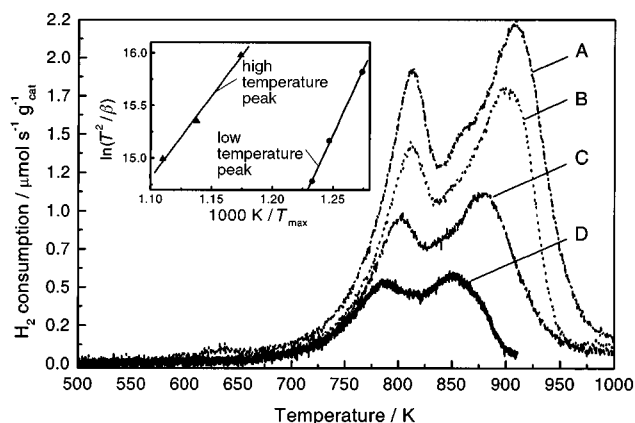


Fig. 3 TPR profiles obtained with EL10V8, variation of the heating rate: (A) 20, (B) 15, (C) 10 and (D) 5 K min⁻¹. Pretreatment: 1 h at 673 K in air. Experimental conditions: final temperature (A–C) 1023 K or (D) 873 K, sample weight 200 mg, flow rate 85 Nml min⁻¹, 4% H₂/Ar. The inset shows the determination of the apparent activation energy from T_{max} of both peaks obtained for different heating rates (5–15 K min⁻¹).

Table 2 H₂ TPR results obtained with EL10V8. Variation of the heating rate and calculation of an apparent activation energy E_a from the shift of T_{max} for β ranging from 5 to 15 K min⁻¹

$\beta/\text{K min}^{-1}$	5	10	15	20	$E_a/\text{kJ mol}^{-1}$
Peak 1	785 K	802 K	811 K	(812 K)	209
Peak 2	852 K	879 K	901 K	(908 K)	129

with this sample. Then, after cooling to room temperature in Ar, a TPO experiment was conducted. The TPO profiles are shown in Fig. 4. The TPO profile of unsupported V_2O_5 (trace C) exhibits two separate peaks, the low-temperature peak being rather broad and the high-temperature peak being very sharp. The T_{\max} values were 751 and 843 K, respectively. Hence, oxidation occurs at lower temperature than reduction with hydrogen. The TPO profile resembles the envelope of the TPR profile viewed from higher to lower temperatures. This suggests that the transitions observed in the TPR experiments with V_2O_5 are reversed in TPO experiments. Two steps can be distinguished: according to the integrated oxygen consumption, the peak at 751 K corresponds to the transition of V_2O_3 to VO_2 , the second sharp peak to the formation of V_2O_5 . The TPO profile of EL10V8 (trace B) shows a peak at 647 K with a shoulder at 562 K. Reoxidation of the low-loading sample EL10V1 (trace A) with predominantly vanadia species in strong interaction with the support occurred at somewhat higher temperatures yielding a peak at 668 K.

Obviously the same transitions that were observed in TPR are also seen in TPO, being inversely related. Repetition of several TPR–TPO cycles did not lead to major changes. Thus, the process can be assumed to be roughly reversible. Compared with unsupported V_2O_5 , the supported vanadia catalysts are easier to reduce and also easier to reoxidize indicating that the support promotes both reduction and reoxidation. These results furthermore suggest that polymeric and crystalline vanadia species present on EL10V8 are easiest to reoxidize but most difficult to reduce, whereas highly dispersed vanadia species present on EL10V1 are easiest to reduce but most difficult to reoxidize. This is in agreement with the results obtained by Majunke and Baerns¹⁹ who observed a higher degree of reduction for EL10V1 than for EL10V8 when the same reduction treatment was used.

3.3 Temperature-programmed oxidation after reduction with toluene at constant temperature

The reduction with toluene was carried out at a moderate temperature unlikely to induce structural changes but relevant for selective oxidation reactions. Thus, the catalysts were exposed to toluene at a constant temperature of 623 K which was found to be sufficiently high to achieve a significant conversion of toluene. Using H_2 as reducing agent, hardly any reduction occurs at this temperature, as shown by the preceding TPR data. The O_2 consumption measured during the TPO experiment (referred to as total O_2 consumption, O_2^{total}) corresponds to the overall amount of O_2 necessary both to

reoxidize the catalyst and to burn off the adsorbate. When the burnt-off products are quantified, the amount of oxygen contained in these products can be balanced against the total O_2 consumption. The difference yields the O_2 uptake of the catalyst itself (O_2^{cat}), i.e. the amount of oxygen required for reoxidation. Furthermore, the total amount of CO_x detected in the product stream provides information about the capacity of the catalyst to adsorb hydrocarbons and about their stability on the surface.

The TPO profiles corresponding to the total O_2 consumption (O_2^{total}) obtained after reduction with toluene are shown in Fig. 5. The overall amount per sample weight is lowest for unsupported vanadia, for EL10V1 an intermediate value is found while the highest O_2 consumption is observed for EL10V8. Further experiments showed that pure TiO_2 did not interact with toluene. Furthermore, the catalysts differ in the temperature range of the oxygen uptake. The profile of EL10V8 shows peaks at 593 and 650 K, in contrast to the profile of unsupported V_2O_5 with a broad peak at 645 K. Sample EL10V1 exhibits one single peak centered at 578 K. In Fig. 6 the formation rates of the oxidation products are shown as a function of temperature. Degradation of the oxygenates leads to the formation of CO_x and water, with CO_2 being the main product. Minor amounts of maleic acid anhydride (MAA) were also detected in the case of the V_2O_5/TiO_2 samples indicating the oxidative degradation of the aromatic ring. CO_x and water formation accounts for the major part of the total O_2 consumption of the supported catalysts (Fig. 6b and c) whereas catalyst reoxidation dominates for unsupported V_2O_5 (Fig. 6a) as may be concluded from the oxygen balance. Calculating the oxidation numbers from O_2^{cat} yields 4.8 for EL10V1 and 4.6 for EL10V8, indicating that the supported catalysts were only partially reduced by the exposure to toluene. These values are in good agreement with the oxidation state of the active catalyst under reaction conditions which has been reported to be 4.7–4.8 in *o*-xylene oxidation.²⁰

The calculated trace of catalyst reoxidation (O_2^{cat}) obtained for EL10V8 (Fig. 6b) passes through a small maximum at 560 K, then decreases to negative values and finally forms a high peak at about 650 K. This can be rationalized as follows: a positive peak, i.e. an oxygen uptake, is obtained when the adsorbate is oxidized but remains on the catalyst surface. When the oxidized adsorbate is released after further oxidation at higher temperatures, more oxygen is found in the products than is consumed from the gas phase at the same time resulting in a negative peak.

The peak at about 650 K (O_2^{cat} , EL10V8) is not accompanied by CO_x formation. Such an O_2 uptake peak which is

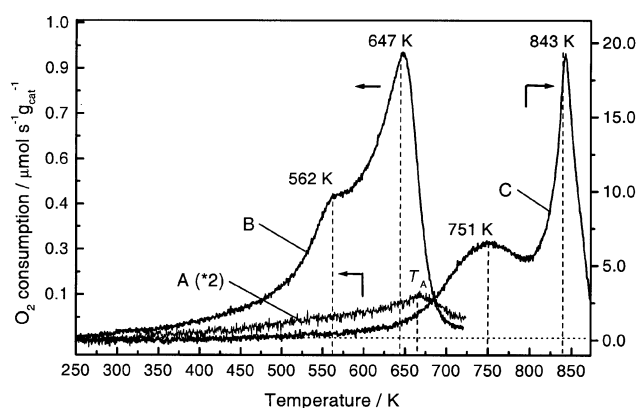


Fig. 4 TPO profiles obtained subsequent to TPR experiments. TPR conditions were such that the V^{8+} oxidation state was achieved. (A) EL10V1 (consumption of O_2 multiplied by 2), (B) EL10V8, (C) V_2O_5 . The temperature of maximum O_2 consumption (T_A) is at 668 K in case of EL10V1. Experimental conditions: heating rate 15 K min^{-1} , final temperature (A,B) 723, (C) 873, sample weight (A,B) 200 mg, (C) 10 mg, flow rate 107 Nml min^{-1} , 10% O_2/Ar .

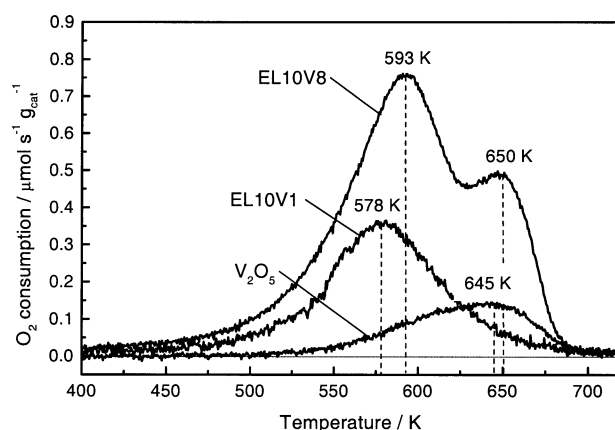


Fig. 5 TPO profiles (total O_2 consumption) after reduction with toluene. Pretreatment: 1 h at 673 K in air followed by reduction at 623 K by exposing to 3.5% toluene/ N_2 for 5 min and cooling to ambient temperature in Ar. TPO conditions: heating rate 15 K min^{-1} , final temperature 723 K, sample weight 200 mg.

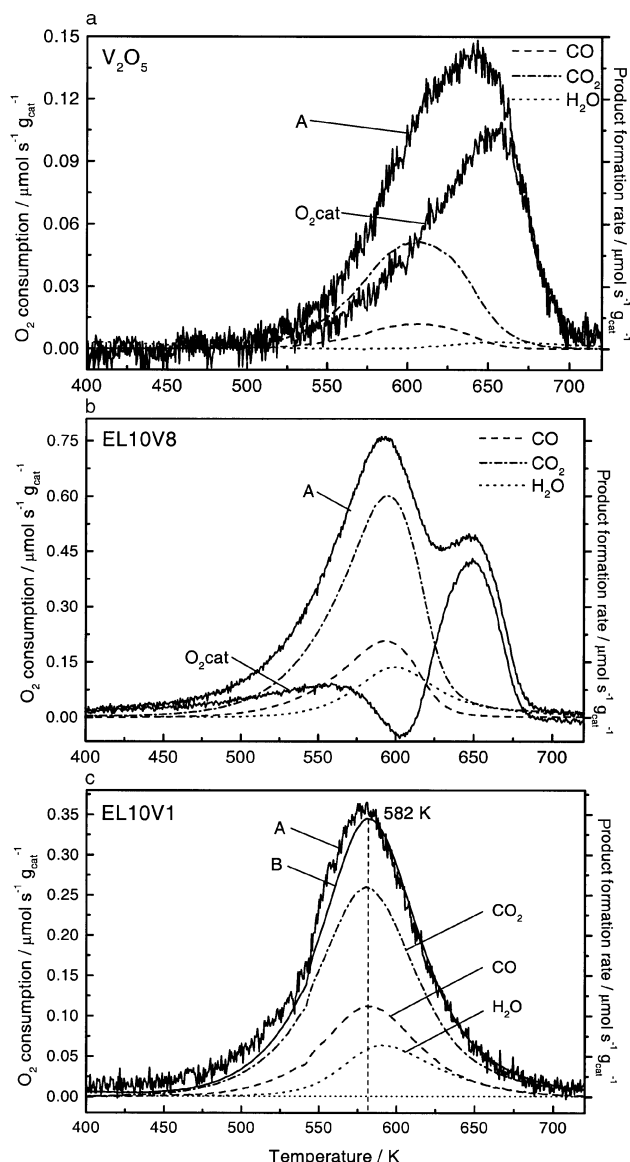


Fig. 6 Rates of O_2 consumption and product formation during TPO after reduction with toluene, (A) denotes total oxygen consumption (from Fig. 5). a and b: O_2^{cat} corresponds to the portion of the total O_2 consumption which actually reoxidizes the catalyst, as calculated from the oxygen balance. c: (B) is the calculated total amount of oxygen detected in the products (stoichiometric sum of CO_2 , CO , H_2O).

solely due to reoxidation of VO_x species is also observed for V_2O_5 at about the same temperature. Thus, the vanadia species giving rise to this reoxidation peak are most probably crystalline species, known to be present on sample EL10V8. The interaction of toluene with crystalline vanadia obviously leads to the formation of oxygenates that, upon desorption, leave behind oxygen vacancies and, as a consequence, reduced vanadia species. For sample EL10V1, on the other hand, the total O_2 consumption during the TPO experiment appears to be used exclusively for the degradation of the oxygenates, since no distinct reoxidation peak is seen. Instead, the stoichiometric sum of the oxygen contained in the products does not only yield nearly the same integrated value as the total O_2 consumption but also shows essentially the same temperature dependence. Thus, the interaction of toluene with the monomeric vanadyl species present on sample EL10V1 mainly results in the formation of oxygenates that remain on the catalyst surface in the absence of gas-phase oxygen. This is presumably due to a low tendency to create oxygen vacancies by transferring oxygen from the vanadyl species into desorbing oxygenated products.

As a result, a high capacity for oxidative adsorption can be ascribed to highly dispersed vanadia species in strong interaction with the support. The oxygen consumption of the first peak, which is assigned to such species, was three times higher for sample EL10V1 than for sample EL10V8 when referred to the total vanadia content. These results are in agreement with a previous *in situ* diffuse reflectance IR FT spectroscopy (DRIFTS) study of adsorption products formed on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts upon exposure to toluene which indicated the same functions of the different vanadia species.¹⁰ Monomeric vanadyl species were found to be the sites responsible for oxidative adsorption, whereas oxygen insertion and desorption of oxidation products only occurred when polymeric and crystalline vanadia species were present.

The DRIFTS experiments also showed the same adsorbate structure on both EL10V1 and EL10V8, in agreement with similar CO_2 , CO and H_2O profiles observed in the present study when further oxidizing the adsorbed oxygenates during the TPO experiment.¹⁰ Interestingly, the formation of MAA has only been detected for the $\text{V}_2\text{O}_5/\text{TiO}_2$ samples. It is the product which desorbs at the highest temperatures. According to the small amount of water formed, the oxygenates contain a significantly lower amount of hydrogen than toluene. As known from IR studies, the interaction with toluene first leads to the abstraction of hydrogen atoms from the methyl group, whereas the aromatic system of the adsorbate is still intact at the conditions used here for the isothermal reduction with toluene (see *e.g.* ref. 21–23).

Selective oxidation reactions of alkyl aromatics are known to follow a Mars–van Krevelen mechanism.²⁴ As lattice oxygen is inserted into the molecule, the reaction can occur in the absence of gas-phase O_2 . The desorption of oxidation products creates oxygen vacancies which are replenished from gas-phase O_2 in a subsequent step. According to the present study, monomeric vanadyl species cannot react in this way, since adsorbates formed in the absence of gas-phase oxygen on monomeric vanadyl species cannot be desorbed. Thus, the capability of oxygen insertion is associated with the presence of crystalline and polymeric vanadia species. Konietzki *et al.*²⁵ report results from a mechanistic study in high vacuum using the *temporal analysis of products* (TAP) reactor on toluene oxidation over amorphous microporous mixed oxides exhibiting homogeneously distributed isolated vanadyl centers. They observed irreversible adsorption on isolated vanadia centers when toluene was pulsed in the absence of gas-phase oxygen but did detect benzaldehyde, CO_x and water when V_2O_5 was used. However, the microporous mixed oxide proved to be an active and selective catalyst for benzaldehyde formation when the feed gas mixture contained both toluene and oxygen. By using isotopically labeled $^{18}\text{O}_2$, Konietzki *et al.*²⁵ were able to show that the active oxygen being transferred to benzaldehyde originated from the vanadyl species. Adsorbed oxygen species were identified as hydrogen acceptors and as reoxidizing agents for the reduced vanadyl sites. Further studies in our laboratory are in progress using the TAP reactor to elucidate the mechanism of the selective oxidation of toluene over $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts in the presence and in the absence of gas-phase O_2 .

4 Conclusions

The investigation of the redox behavior of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst by performing sequences of TPR and TPO experiments in H_2 and O_2 , respectively, showed that these supported samples are not only easier to reduce than unsupported V_2O_5 but also exhibit oxygen consumption maxima at about 100 K lower temperatures, thus indicating an easier exchange of lattice oxygen. The experiments revealed substantial differences in the behavior of the samples with high and low vanadia

loading which point to the particular role of crystalline and polymeric vanadia species on the one hand (EL10V8) and monomeric species in strong interaction with the support (EL10V1) on the other hand. Crystalline vanadia is most difficult to reduce in H_2 but easiest to reoxidize, whereas monomeric vanadyl species are easiest to reduce in H_2 but most difficult to reoxidize.

A modified method using toluene as the reducing agent was also applied. Toluene proved to be a more efficient reducing agent than hydrogen, in particular with V_2O_5 : no hydrogen consumption was observed with this sample below 873 K whereas treatment with toluene at 623 K did lead to a partial reduction. Crystalline and polymeric vanadia species were reduced when exposed to toluene, as indicated by the reoxidation peak observed in consecutive TPO experiments, and are thus capable of oxygen insertion. Monomeric vanadyl species, on the other hand, formed adsorbed oxygenates which remained on the catalyst surface until they were burnt off in the presence of gas-phase oxygen during the subsequent TPO experiment. Our results therefore indicate that monomeric vanadyl species represent the sites for oxidative adsorption in toluene oxidation on V_2O_5/TiO_2 catalysts. For the formation of desorbing oxygenated products in the absence of gas-phase oxygen, however, polymeric and crystalline vanadia species have to be present.

In summary, the combined application of TPR and TPO experiments using H_2 and toluene as reducing agents is considered a fast and quantitative method to detect the presence of different vanadia species on supported VO_x catalysts and to probe their catalytic properties. Further studies are in progress in our laboratory applying this method to elucidation of the role of the promoters in V_2O_5/TiO_2 catalysts.

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