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Catalysis Today 91–92 (2004) 149–153

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TAP studies on the reoxidation of some partially reduced vanadia-based catalysts

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Abstract

The interaction of oxygen with partially reduced vanadia-based catalysts was investigated by Temporal Analysis of Products (TAP) transient technique in order to determine the degree of reduction and its effect on the reoxidation process. The well-defined Eurocat catalyst EL10V1 was chosen as reference catalyst and, based on the results obtained by oxygen titration (oxygen adsorption capacity), its degree of reduction was determined at different reaction temperatures. The values were in good agreement with those obtained by propane titration. The reducibility increases by increasing the temperature. The degree of reduction of a new class of vanadium oxide catalysts, obtained by magnetron sputter deposition, was also determined and the values were compared with those obtained on EL10V1, when a number of propane molecules equivalent of a degree of reduction of 21% for EL10V1 was pulsed over all samples. For the sputtered catalysts, the oxygen uptake at 773 K decreased from 0.94 to 0.68 μmol O_2/m^2 with increasing deposition time from 1 to 5.5 h. The degree of reduction of another well-defined Eurocat catalyst, EL10V8, was also determined. At the same temperature the oxygen uptake increased from 0.18 μmol O_2/m^2 on EL10V8 to 1.17 μmol O_2/m^2 on EL10V1. Reversible molecular adsorption of oxygen, followed by irreversible dissociation, allows to describe the single-response TAP data for EL10V1 and EL10V8. For the sputtered catalysts a one-stage irreversible dissociative adsorption of oxygen provides the best description of such single-response TAP data.

Keywords: Vanadia-based catalysts; Reduction; Reoxidation; Adsorption capacity; Reaction kinetics; TAP; Degree of reduction

1. Introduction

Vanadia-based catalysts are used in various partial oxidation reactions of hydrocarbons [1]. If the oxidation process is carried out in a fixed bed reactor, adding oxygen to the feed, the production capacity can be limited because of the explosion limits. To improve the former, as well as the selectivity, a moving bed technique can be used. The catalyst and the hydrocarbon then move together through the reactor, the catalyst being reduced and the hydrocarbon oxidized by consuming oxygen from the catalyst lattice. After separation of the products, the catalyst is reoxidized in a regenerator. The continuous transport of the catalyst between reactor and regenerator requires that it is abrasion-resistant. It is known that highly adhesive thin films can be deposited by sputter deposition. Therefore, a consecutive deposition of (i) a layer of anatase TiO_2 and (ii) a layer of V_2O_5 onto an inert carrier was performed [2]. In this paper, such sputtered catalysts are compared to well-defined catalysts in order to verify their suitability as selective oxidation catalysts. In particular, the kinetics of reoxidation of the partially reduced catalysts are investigated.

2. Experimental

2.1. Catalysts

DC magnetron sputtering in an argon/oxygen atmosphere was applied as deposition technique, and inert beads (ZrO_2 coated with SiO_2) of 250–495 μm diameter with a BET surface area of 0.21 m^2/g served as support. The beads were introduced into a vacuum system with a rotating drum to be coated first with TiO_x for 3 h, using a plasma sprayed rutile target, and then with VO_x, using two-plane ceramic V_2O_3 targets. Between the two coatings and at the end, the beads

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doi:10.1016/j.cattod.2004.03.024

Table 1
Some characteristics and degree of reduction of the investigated samples

Catalyst	V/Ti surface atomic ratio[a]	Surface V loading (μmol/m^2)	Total V loading (μmol/g) [from ICP]	BET surface area (m^2/g)	Degree of reduction[b] (%)
EL10V1	0.16[c]	5.49	107[c]	10.1	21.0
EL10V8	0.43[c]	39.90	844[c]	11.0	0.45
S1	0.11	6.61[d]	1.41	0.205	14.0
S2	0.27	15.70[d]	3.53	0.204	4.0
S3	0.61	36.36[d]	–[e]	0.568	1.5

[a] Obtained from XPS measurements.

[b] Degree of reduction after pulsing 7.5×10^{18} propane molecules corresponding to 21% reduction of EL10V1 at 773 K.

[c] Average value from Ref. [6].

[d] Determined from XPS measurements.

[e] Due to heterogeneous deposition, no reproducible results were obtained.

were heated *ex situ* up to 350 °C for 1 h in air. Reactive sputtering was applied in order to favor fully stoichiometric V/Ti (1:1) deposition. Three different catalysts were obtained by varying the sputter time (1, 2.5 and 5.5 h, respectively) and are referred to as S1, S2 and S3 [2]. BET surface area measurements and XPS measurements were carried out and the results are shown in Table 1. XRD measurements showed that the sputtered catalysts were amorphous. As a reference, the Eurocat EL10V1 and EL10V8 catalysts were investigated. These catalysts were prepared by Rhône-Poulenc [3], by deposition of 1 wt.%, respectively 8 wt.% of V_2O_5 onto TiO_2. The EL10V1 catalyst is considered to consist of islands of monolayer of vanadia onto titania, while the EL10V8 catalyst consists of more than a monolayer and contains even crystallites [4]. BET surface area measurements [5] as well as XPS measurements [6] were also carried out on these two catalysts and results are shown in Table 1.

2.2. Temporal Analysis of Products (TAP) measurements

The TAP reactor system has been described in detail elsewhere [7]. Three types of experiments were carried out: single-pulse, alternating pulse and multipulse experiments. The number of molecules admitted per single pulse was in the range 10^{14}–10^{15} molecules, allowing the transport in the reactor to occur through Knudsen diffusion only. The catalysts were packed between two layers of quartz beads having the same particle size. Each sample was pretreated by pulsing 3×10^{18} oxygen molecules at reaction temperature in order to reach a completely oxidized state.

To study the interaction of oxygen with partially reduced EL10V1, 0.100 g of catalyst was used, which corresponds to a surface area of 1.0 m^2. The reduction and reoxidation of the EL10V1 catalyst were investigated at three temperatures: 723, 773 and 823 K. A standard reduction was performed by admitting multipulses of propane over a completely oxidized catalyst. The number of propane molecules varied from 0 to 100% of the amount of VO_x species on a monolayer, corresponding to a number of 7×10^{18} VO_x/m^2 [8]. Because the volume of sputtered catalysts for a surface area of 1.0 m^2 was higher than the microreactor capacity, the comparison of the sputtered catalysts with EL10V1 and EL10V8 is based on experiments performed on 0.10 m^2 surface area for all samples. The same surface area was chosen because catalyst samples containing the same amount of vanadia do not necessarily have the same amount of surface vanadia. Moreover, for a low surface area, a single-pulse experiment of oxygen over partially reduced catalysts can be used to determine the kinetics of the reoxidation. On the contrary, when the surface area is 1.0 m^2, the oxygen conversion after reduction is 100% during the first single-pulse experiment, resulting in a flat response, which does not allow to determine the kinetics properly. For EL10V8, S1, S2 and S3 catalysts the study was limited to one temperature, 773 K, for both reduction and reoxidation. A 21% reduced EL10V1 catalyst was taken as a reference to compare the reducibility of the different catalysts over which the same number of propane molecules as for EL10V1 was pulsed.

2.3. Degree of reduction

The degree of reduction, defined as the ratio of the number of oxygen molecules taken up by the catalyst to the surface vanadia content, was determined as follows. The reduced vanadyl species were titrated with O_2, assuming an O_2 to V chemisorption stoichiometry of 1:2 and considering that no carbonaceous species were burned off and that all oxygen was used to reoxidize the surface. On the other hand, a fully oxidized catalyst was titrated with propane, and the oxygenated products were followed. Since it was very difficult to measure H_2O directly, the amount of H_2O molecules was calculated from the amount of propene and CO_2 formed, taking into account the kinetics of the oxidative dehydrogenation [9].

3. Results and discussion

3.1. Interaction of oxygen with the partially reduced EL10V1 catalyst—degree of reduction

The interaction of oxygen with the partially reduced EL10V1 was investigated by multipulse experiments of

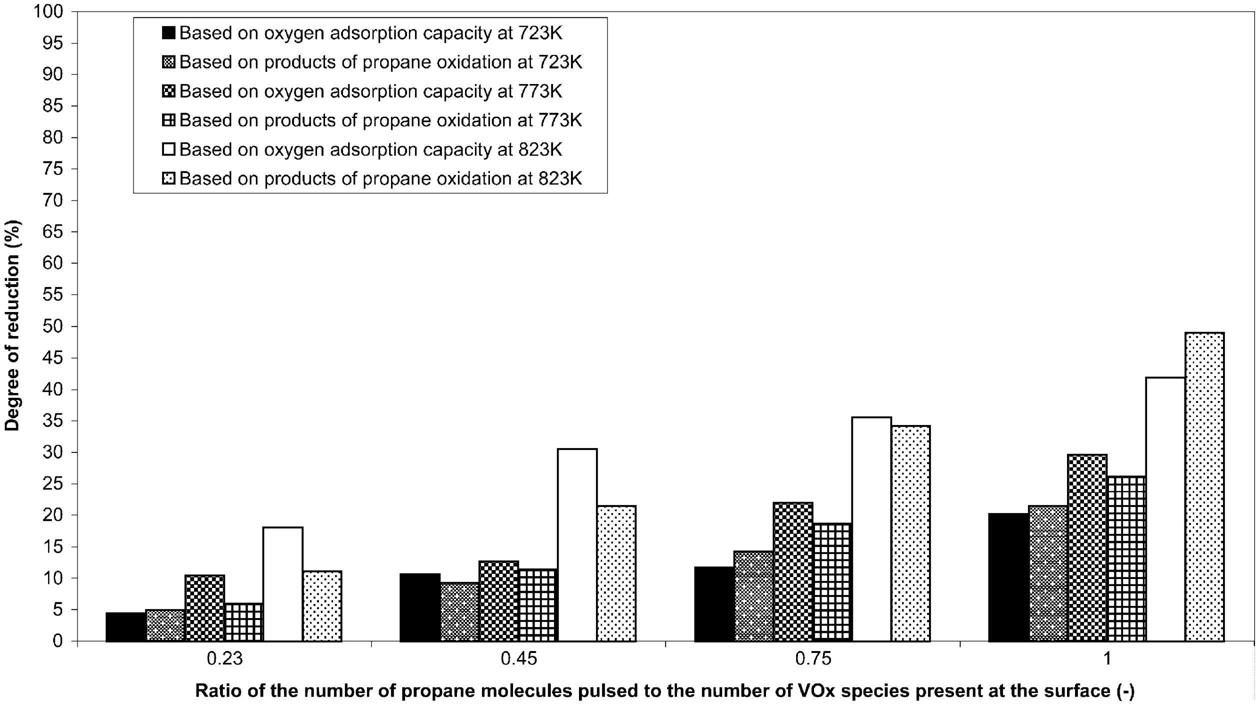

Fig. 1. Degree of reduction of EL10V1 for different temperatures and number of propane molecules pulsed as calculated by two different methods: (1) oxygen adsorption capacity and (2) products of propane oxidation.

oxygen. The surface area of the individual oxygen responses initially increases and finally remains constant. The initial increase is attributed to oxygen, which is strongly interacting with the reduced catalyst surface. As the reduction was performed in the absence of any gas-phase oxygen, the oxygen species could be considered to replace the oxygen consumed from the lattice. Following the procedure presented in Section 2.3, the degree of reduction was determined and compared with its calculated value from the balance of the oxygenated products formed during reduction of the catalyst. The two values show a good agreement except for some cases (Fig. 1). The differences appear because the oxidation–reduction cycle is not completely reversible. As expected, the reducibility increases with increasing temperature.

During reoxidation, CO_2 and H_2O responses were also followed. H_2O could be detected at 773 and 823 K only. The response was very broad with a large tail indicating the very slow formation and desorption of H_2O. The number of CO_2 molecules that were formed during the reoxidation is very small and decreases with temperature and degree of reduction. This observation confirmed one of the assumptions made in Section 2.3, namely that the amount of oxygen consumed to burn off carbonaceous species can be neglected.

3.2. *Role of adsorbed oxygen species*

To check the presence of molecular adsorbed oxygen species, O_2^*, and to understand their role in the oxidation of propane, alternating pulse experiments, in which the oxygen pulse preceded the propane pulse, were performed. At $T \leq 723\,K$, CO_2 is formed on the oxygen as well as on the propane pulse. The number of CO_2 molecules formed on the oxygen pulse was constant irrespective of the time interval between the oxygen and the propane pulse. On the other hand, the number of CO_2 molecules formed on the propane pulse decreased with increasing time interval to a constant value at time intervals $\geq 0.5\,s$. At $T \geq 723\,K$, no CO_2 was formed on the oxygen pulse, while the number of CO_2 molecules on the propane pulse was constant for all time intervals. It seems that at $T \leq 723\,K$ weakly bound oxygen species with a life time $\leq 0.5\,s$ are present which promote total oxidation. This is shown by the decrease of the number of CO_2 molecules formed on the propane pulse with increasing time interval between the two pulses. Moreover, at $T \leq 723\,K$, readsorption of the reaction products formed on the propane pulse occurs, indicated by the CO_2 response on the oxygen pulse. Propene was formed only on the propane pulse. As its amount was constant at all temperatures and time intervals, it seemed that only lattice oxygen was involved in the selective oxidation. Therefore, the adsorbed products and the different oxygen species influence the reduction and reoxidation in a dynamic way so that the model of the active surface can be assumed [10].

3.3. *Degree of reduction of EL10V8, S1, S2 and S3, compared with EL10V1*

The reoxidation process was carried out by admitting multipulses of oxygen. The oxygen adsorption capacity for

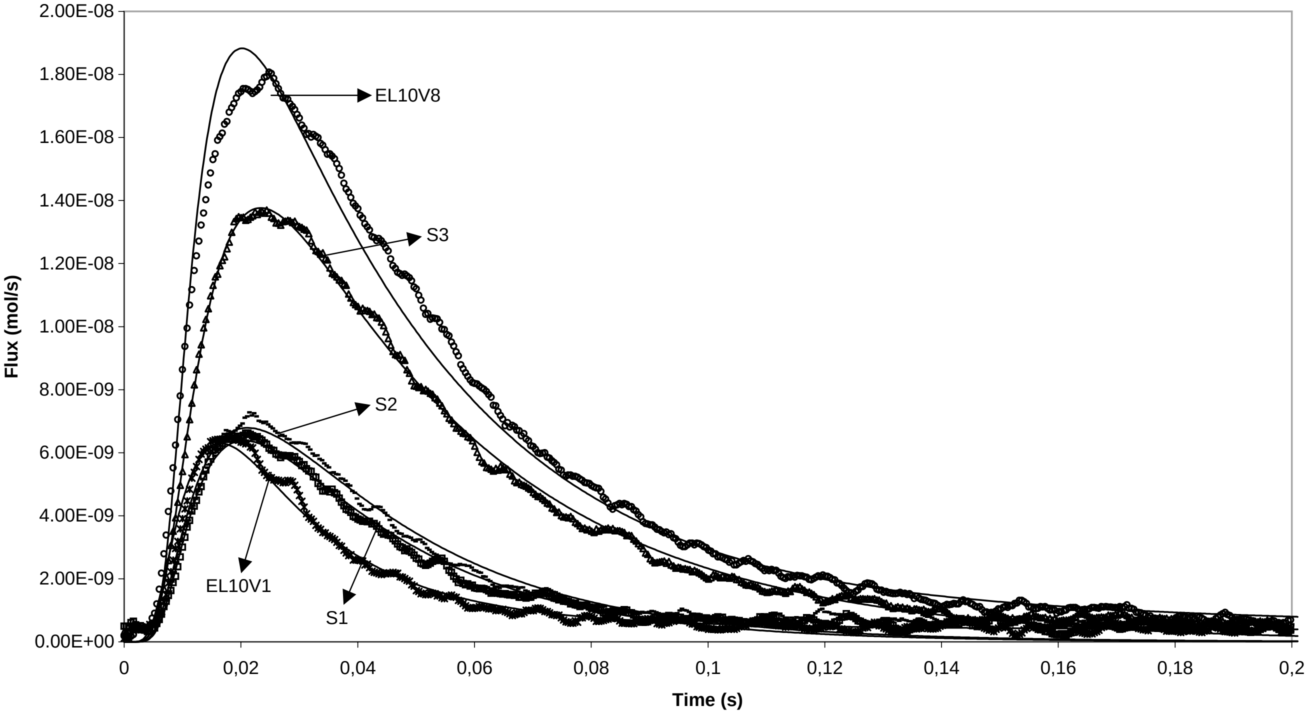

Fig. 2. Oxygen responses at 773 K after reduction with 7.5×10^{18} propane molecules yielding 21% reduction of EL10V1 at 773 K. Dashed line: experimental oxygen response; full line: calculated with the parameters given in Table 2.

EL10V1, S1, S2, S3 and EL10V8 was respectively 1.17, 0.94, 0.68, 0.54 and 0.18 μmol O_2/m^2. From the oxygen adsorption capacity and the vanadium loading on the surface (Table 1), the degree of reduction of S1, S2, S3 and EL10V8 was calculated and compared to that of EL10V1 (Table 1). EL10V8 shows the lowest reducibility, followed by S3, S2 and S1, while EL10V1 has the highest reducibility under the same conditions. A correlation between the reducibility and V loading is seen (Table 1).

The oxygen response to the single-pulse experiment of oxygen over the reduced catalysts sharpens from EL10V1 to EL10V8 over S1, S2 and S3. The initial oxygen conversion was calculated and shows the following order: 78.72% (EL10V1) > 73.98% (S1) > 66.63% (S2) > 32.59% (S3) > 31.45% (EL10V8). The results obtained by the single-pulse experiment of oxygen thus confirm the already stated order of reducibility.

3.4. Kinetic model of reoxidation

Taking into account the experimental results, a model for the reoxidation process was proposed and the kinetic parameters were estimated. For EL10V1 and EL10V8, reversible molecular adsorption of oxygen (1), followed by irreversible dissociation of the adsorbed species (2) described the results in the best way (Fig. 2):

$$O_2 + {}^* \underset{k_2}{\overset{k_1}{\leftrightarrow}} O_2^* \tag{1}$$

$$O_2^* + {}^* \xrightarrow{k_3} 2O^* \tag{2}$$

The degree of reduction is taken into account in the mass balance for the total molar concentration of the active sites. The estimated values of the rate coefficients and of the concentration of the active sites (C_t) are shown in Table 2. It is clear from Table 2 that on EL10V8 the molecular adsorption of oxygen can almost be neglected ($k_3/k_1 = 85$). Therefore, most of the adsorbed species immediately dissociate. This can be attributed to the presence of a large amount of crystallites, which are more easily reoxidized [11]. For the sputtered catalysts, a one-stage irreversible dissociative adsorption of oxygen (3) described the experimental results in the best way (Fig. 2):

$$O_2 + 2^* \xrightarrow{k} 2O^* \tag{3}$$

The estimated values of the rate coefficients and of the concentration of active sites (C_t) are also shown in Table 2. The reaction rate coefficient increases with increasing vanadia loading.

According to the kinetic modeling, two oxygen species are present on EL10V1 and on EL10V8 during reoxidation, namely (i) molecular adsorbed oxygen (O_2^*), although in very low amount on EL10V8, and (ii) lattice oxygen (O^*). For EL10V1 this result was confirmed by observations from alternating pulse experiments. The data obtained on EL10V8 can also be described by the one-stage irreversible dissociative adsorption of oxygen (k_3 in Table 1). However,

Table 2
Estimates with their 95% confidence intervals for the kinetic parameters obtained by the regression of the oxygen single-pulse experiments after reduction with 7.5×10^{18} propane molecules corresponding to 21% reduction of EL10V1 at 773 K

Catalyst	k_1 (10^4 m^3/mol s)	k_2 (1/s)	k_3 (10^5 kg/mol s)	k (10^8 kg m^3/mol^2 s)	C_t (10^{-5} mol/m^2)
EL10V1	3.35 ± 0.07	0.64 ± 0.09	0.26 ± 0.18		1.09 ± 0.01
EL10V8	10.13 ± 1.97	3.17 ± 0.43	85.37 ± 17.09		7.80 ± 0.30
S1				1.73 ± 0.18	1.17 ± 0.04
S2				2.91 ± 0.26	3.12 ± 0.09
S3				27.18 ± 1.85	7.27 ± 0.06

reversible molecular adsorption, followed by dissociation of the adsorbed species described the results even better.

4. Conclusions

The degrees of reduction determined (1) by titration with oxygen of partially reduced EL10V1 or (2) by titration with propane of completely oxidized EL10V1 show a good agreement. Two types of oxygen species are present on the surface of EL10V1 during reoxidation: lattice oxygen (O^*), responsible for selective oxidation, and molecular oxygen (O_2^*), responsible for total oxidation. The reducibility of the sputtered catalysts is in between the reducibility of EL10V1 and EL10V8, while for the sputtered catalysts, the reducibility decreases with increasing vanadia loading. Reversible molecular adsorption of oxygen, followed by irreversible dissociation of the adsorbed species described the results in the best way for EL10V1 and EL10V8, while for all sputtered catalysts, irreversible dissociative adsorption of oxygen shows the best fitting. The TAP technique proved to be a suitable technique to characterize new catalytic materials used for selective oxidation and to better understand the catalytic processes.

Acknowledgements

This work was performed in the framework of a Concerted Research Action (GOA) financed by the Ghent University, and of the Belgian Programme on Interuniversity Poles of Attraction initiated by the Belgian State, Prime Minister's Office, Science Policy Programming. The scientific responsibility is assumed by its authors. The sputter deposition was performed in a chamber sponsored by the action "Equipment for Materials Investigation 1997–2000" from the Flemish government. We also would like to thank Mrs. Mihaela Florea and Mrs. Anne Iserentant from Université Catholique de Louvain for respectively the BET measurements and the ICP analysis of the samples.

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