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Kinetic modeling of the reoxidation of vanadia-based catalysts

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Abstract

The reoxidation kinetics of classical vanadia-based EL10V Eurocat catalysts are compared with those obtained on a new catalytic material, prepared by DC magnetron sputtering, by means of temporal analysis of products (TAP) at reduction and reoxidation temperatures from 723 to 823 K. After reduction to different degrees of reduction with multipulses of propane, the kinetics of reoxidation were obtained from single-pulse experiments. Irreversible dissociative chemisorption of di-oxygen allowed to describe the latter over the full range of investigated conditions for EL10V1 with a single pre-exponential factor, $A = 4.05 \times 10^2$ $kg_V m^3/mol^2$ s, and a single activation energy, $E_a = 33.41$ kJ/mol. In the case of the sputtered catalysts, investigated at 773 K only, a single rate coefficient also describes the reoxidation at different degrees of reduction for every V-loading. Its value increases with increasing V-loading up to a constant value of 1.09 ± 0.11 $kg_V m^3/mol^2$ s, but remains lower than the corresponding rate coefficient for the reoxidation for EL10V8 which amounts to 13.30 $kg_V m^3/mol^2$ s.

Keywords: Vanadia-based catalysts; Reoxidation; Kinetic modeling; TAP

1. Introduction

Supported vanadium oxide catalysts, containing surface vanadia species on oxide supports, are succesfully used for oxidative dehydrogenation (ODH) of light alkanes to olefins. As the ODH reaction has been reported to proceed through the Mars—van Krevelen (redox) mechanism [1], the reduction and reoxidation of the V_2O_5/TiO_2 catalyst can be studied separately. Although the kinetics for the propane oxidative dehydrogenation on V_2O_5/TiO_2 catalysts have been investigated under steady-state reaction conditions where propane and oxygen are fed together [2–4], only few studies report the kinetics of the separated processes or for different degrees of reduction [5,6]. Since, the catalyst surface is sensitive to the gas phase composition, the catalyst may behave differently under transient than under steady-state operating conditions. This paper presents the results of a transient kinetic study performed on the reoxidation of some reduced vanadia-based catalysts. The main goal was to investigate the influence of the degree of reduction on the reoxidation kinetics. With the TAP reactor, the transient kinetics can be determined by analysis of single-pulse experiments of di-oxygen.

2. Experimental

2.1. Catalysts

DC magnetron sputtering in an argon/oxygen atmosphere was applied as deposition technique, and inert beads (ZrO_2 granulates embedded in SiO_2) of 250–425 μm diameter 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 were heated ex situ up to 350 °C for 1 h in air. Reactive sputtering was applied in order to favor fully stoichiometric deposition of the oxides. Different catalysts were obtained by varying the sputter time (5, 15, 60, 150 and 330 min, respectively), and are referred to as Ti_HV5_H, Ti_HV15_H, Ti_HV60_H, Ti_HV150_H and Ti_HV330_H [7]. As a reference, the Eurocat EL10V1 and EL10V8 catalysts were investigated. These catalysts were prepared by Rhône–Poulenc and contain 1 and 8 wt.% of V_2O_5, respectively, [8].

2.2. TAP measurements

The TAP reactor system has been described in detail elsewhere [9]. Two types of experiments were carried out:

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Nomenclature

Symbols

A	pre-exponential factor ($kg_V\, m_r^3\, mol^{-2}\, s^{-1}$)
C_{O_2}	gas phase concentration of oxygen ($mol\, m_r^3$)
C_*, C_{O*}	concentration of reduced, respectively, oxidized free active sites ($mol\, kg_c^{-1}$)
C_t	total concentration of free active V-sites ($mol\, kg_c^{-1}$)
D^c_{eff,O_2}, D^i_{eff,O_2}	effective Knudsen diffusion coefficient for oxygen in the catalyst, respectively, inert bed ($m_r^2\, s^{-1}$)
E_a	activation energy ($kJ\, mol^{-1}$)
k_{diss}	dissociation rate coefficient ($kg_V\, m_r^3\, mol^{-2}\, s^{-1}$)
L_i, L_c, L_o	length of, respectively, the first inert bed, the catalyst bed and the second inert bed (m_r)
N_p	number of mols in the inlet pulse (mol)
R	molar gas constant = 8.314 ($J\, mol^{-1}\, K^{-1}$)
R^0	initial degree of reduction
S	cross-section of the reactor (m_r^2)
T, T_{ref}	temperature, respectively, reference temperature (K)
V_0	inlet volume of the reactor (m_r^3)
z	axial coordinate (m_r)

Greek symbols

ε_c	porosity of the catalyst bed
ρ_B	density of the catalyst bed ($kg_c\, m_r^{-3}$)
τ	time characteristic of the inlet pulse (s)

single-pulse and multipulse experiments. The number of molecules admitted per single-pulse was in the range of 10^{14}–10^{15} molecules, allowing the transport in the reactor to occur through Knudsen diffusion. Depending on the amount of catalyst loaded, the ratio of admitted oxygen during a single-pulse to the total vanadium loading, was always below 0.05. The catalyst samples (0.01–1.00 g) were packed between two layers of quartz of the same particle size.

2.2.1. Reoxidation of EL10V1

The catalyst was reduced at 723, 748, 773, 798 and 823 K to three different degrees of reduction by admitting, respectively, 2.5×10^{18}, 5.0×10^{18} and 7.5×10^{18} propane molecules over the oxidized surface. For each reduction temperature and degree of reduction, the reoxidation was carried out at 723, 748, 773, 798 and 823 K.

2.2.2. Reoxidation of the sputtered catalysts and EL10V8

The reoxidation was studied at 773 K after two consecutive reductions of the completely oxidized catalyst samples with 2.5×10^{18} and 7.5×10^{18} C_3H_8 molecules, respectively.

2.2.3. Degree of reduction

The degree of reduction, defined as the ratio of the number of oxygen atoms removed from the catalyst, leading to free reduced active sites, to the total deposited vanadia content (measured by inductively coupled plasma (ICP) [7]), was determined by titration of the reduced vanadyl species with O_2, assuming an O_2 to V chemisorption stoichiometry of 1:2. During the reoxidation of the catalyst no CO_2 and CO was observed hence no carbonaceous species were deposited on the surface. The oxygen that is consumed during the reoxidation of the catalysts is therefore exclusively used to reoxidize the surface.

3. Results and discussion

3.1. Kinetics of the reoxidation of EL10V1

The following model for the reoxidation was used: $O_2 + 2^* \xrightarrow{k_{diss}} 2O^*$.

The continuity equations with the initial and boundary conditions that are used to integrate the differential equations are shown below.

$$\varepsilon_c \frac{\partial C_{O_2}}{\partial t} = D^c_{eff,O_2} \frac{\partial^2 C_{O_2}}{\partial z^2} + \rho_B(-k_{diss} C_{O_2} C_*^2),$$

$$\frac{\partial C_*}{\partial t} = -2k_{diss} C_{O_2} C_*^2, \quad C_t = C_* + C_{O*}$$

Initial conditions

$$C^0_{O_2} = 0, C^0_* = R^0 C_t \quad \text{and} \quad C^0_{O*} = (1 - R^0)C_t,$$
$$t = 0, 0 \le z \le L_i + L_c + L_o$$

Boundary conditions

$$V_0\left(\frac{\partial C_{O_2}}{\partial t}\right) = -SD^i_{eff,O_2}\left(\frac{\partial C_{O_2}}{\partial z}\right) + \frac{N_p}{\tau^2} t \exp\left(-\frac{t}{\tau}\right),$$
$$t \ge 0, z = 0$$

$$(C_{O_2}) = 0, \quad t \ge 0, z = L_i + L_c + L_o$$

Different reoxidation models were considered. Kondratenko et al. [10] determined pre-exponential factors and activation energies for the most detailed model, accounting for reversible molecular adsorption of oxygen, followed by the reversible dissociation of molecular adsorbed oxygen to describe the oxidation of Na_2O/CaO, Sm_2O_3/CaO and Sm_2O_3 catalysts at 923 K. However, to describe the oxidation of V–Mg–Mo–Ga–O, V–Mg–Mo–Mn–Ga–O, V–Mg–Mo–Fe–Ga-O and V–Mg–O catalysts, Kondratenko et al. [11] only took into account the irreversible dissociation of oxygen. Some authors (Huang et al. [12], Dewaele et al. [13]) assumed extra steps in which the surface oxygen transformed into bulk oxygen or into another surface state. However, from our regression analysis it was clear that the dissociation of oxygen was the only kinetically relevant step on the time scale of a single-pulse TAP experiment for the EL10V1 catalyst. This is an expected result as the physical characterization of the catalyst led to the conclusion that almost all vanadia is on the surface, therefore, the oxygen bulk diffusion can be neglected. Moreover, purging of the reoxidized catalyst with inert gas did not result in any oxygen at the exit of the reactor. This suggests that desorption of oxygen should not be considered. Additionally, since the non-isothermal regression did not lead to meaningful adsorption enthalpy values, the reoxidation of the EL10V1catalyst is described by the irreversible dissociative chemisorption of di-oxygen, in contrast to Sack et al. [14], where the reoxidation of the Eurocat catalysts at only one temperature, 773 K, and for only one degree of reduction, 0.21, was better described (highest significance of the regression) by the reversible molecular adsorption of di-oxygen, followed by irreversible dissociation. Since, the reduction was performed by admitting the same number of propane molecules at different temperatures, the obtained degrees of reduction (R^0) are different. The initial degrees of reduction are shown in Table 1. By simultaneous regression of the single-pulse experiment responses obtained at temperatures from 723 to 823 K, the Arrhenius parameters A and E_a were estimated. C_t was kept constant and equals the value of the V-loading determined by ICP ($C_t = 0.1079$ mol/kg$_c$). The results are shown in Table 1. A large spreading for the pre-exponential factor A as well as for E_a can be observed if the different degrees of reduction are considered separately. If however, within one reduction temperature, the experiments at different degrees of reduction are regressed simultaneously with a single A and E_a, the corresponding confidence interval becomes mostly smaller while the significance of the regression, expressed as F-value, increases. Finally, a single combination of A and E_a is estimated for all experiments together. From Table 1 it is clear that the confidence interval in this case is very small while the F-value shows the highest value. Therefore, it can be concluded that the last regression is statistically more significant and that a single pre-exponential factor and a single activation energy describe the reoxidation at different degrees of reduction and for different reduction temperatures. Fig. 1 shows the fit between the experimental and the calculated oxygen responses for a reduction temperature of 723 K, a reoxidation temperature of 748 K and a degree of reduction of 0.11. It is clear that the difference between the responses calculated with A and E_a obtained after considering the different reduction temperatures and degrees of reduction separately, respectively, together is very small indeed.

Table 1
Estimates of the pre-exponential factor A and the activation energy E_a with their 95% confidence intervals and the F-value obtained by the regression of oxygen single-pulse experiments at 723, 748, 773, 798 and 823 K after reduction at 723, 748, 773, 798 and 823 K with propane to different degrees of reduction for EL10V1

T_{red} (K)	R^0	A (kg$_V$ m^3/mol^2 s)	E_a (kJ/mol)	F (10^5)
723	0.07[a]	$(2.19 \pm 0.07)\ 10^5$	74.55 ± 1.96	6.91
	0.11	$(3.15 \pm 0.06)\ 10^2$	33.06 ± 1.37	4.55
	0.13	$(5.81 \pm 0.15)\ 10^2$	35.95 ± 1.76	1.66
	All R^0	$(1.24 \pm 0.02)\ 10^3$	41.25 ± 1.04	8.84
748	0.10	$(0.41 \pm 0.01)\ 10^2$	20.98 ± 1.08	6.90
	0.13	$(0.38 \pm 0.01)\ 10^2$	19.10 ± 0.66	6.07
	0.16	$(3.96 \pm 0.05)\ 10^2$	33.75 ± 0.96	1.65
	All R^0	$(1.04 \pm 0.01)\ 10^2$	25.72 ± 0.58	9.04
773	0.15	$(3.60 \pm 0.04)\ 10^2$	35.12 ± 0.78	5.24
	0.17	$(7.40 \pm 0.06)\ 10^2$	37.28 ± 0.65	3.01
	0.20	$(1.42 \pm 0.01)\ 10^2$	26.35 ± 0.61	2.35
	All R^0	$(2.68 \pm 0.02)\ 10^2$	31.42 ± 0.57	4.58
798	0.17	$(1.22 \pm 0.02)\ 10^3$	41.91 ± 1.46	1.16
	0.21	$(7.14 \pm 0.05)\ 10^2$	36.85 ± 0.61	2.57
	0.24	$(1.69 \pm 0.01)\ 10^2$	27.07 ± 0.57	1.98
	All R^0	$(4.46 \pm 0.03)\ 10^2$	34.22 ± 0.62	3.14
823	0.18	$(1.49 \pm 0.01)\ 10^4$	55.32 ± 0.72	2.83
	0.24	$(5.90 \pm 0.04)\ 10^3$	48.58 ± 0.62	2.12
	0.25	$(8.20 \pm 0.06)\ 10^3$	49.95 ± 0.68	1.57
	All R^0	$(7.31 \pm 0.04)\ 10^3$	50.12 ± 0.46	4.70
All T_{red}	All R^0	$(4.05 \pm 0.02)\ 10^2$	33.41 ± 0.33	19.45

[a] This value was excluded from the regression of all degrees of reduction together.

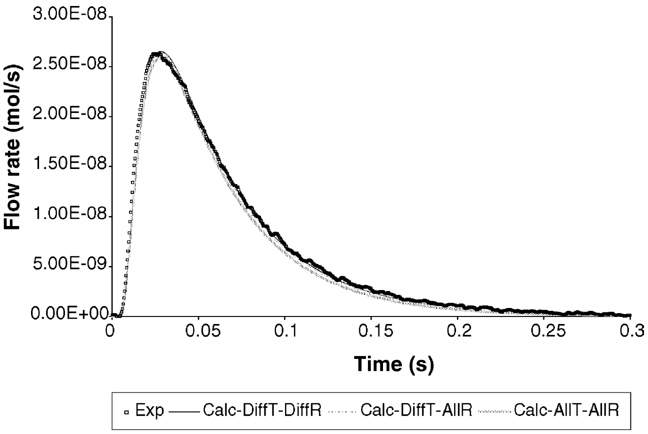

Fig. 1. Oxygen responses at 748 K after reduction at 723 K to a degree of reduction of 0.11. Dots: experimental oxygen response; full line: response calculated with parameters obtained for a reduction temperature of 723 K and a degree of reduction of 0.11; dashed line: response calculated with parameters obtained for a reduction temperature of 723 K and all degrees of reduction together; thick dashed line: response calculated with parameters obtained for all reduction temperatures and all degrees of reduction together.

3.2. Kinetics of the reoxidation of the sputtered catalysts and EL10V8

Irreversible dissociative chemisorption of di-oxygen was also assumed to estimate the kinetic parameters of the reoxidation of reduced sputtered and EL10V8 catalysts at 773 K. Therefore, the same continuity equations apply with the same boundary and initial conditions. Also here, C_t was kept constant and equals the value of the V-loading determined by ICP (Table 2). Pulsing the same amount of propane for the catalysts with low vanadia loadings as for the catalysts with high vanadia loadings led to some reduction of the anatase layer on the former and a full reduction of the vanadia layer. The estimated rate coefficients for the reoxidation kinetics, based on mass of vanadium, are shown in Table 2. A single rate coefficient for the different degrees of reduction was determined. From Table 2 it is clear that mostly the confidence interval becomes smaller, while the F-value is large so that the regression is statistically significant. Moreover, from Fig. 2 it can be seen that the rate coefficient increases with increasing V-loading, reaching a constant value of 1.09 ± 0.11 kg$_V$m^3/mol^2 s between catalysts Ti$_H$V60$_H$ and Ti$_H$V330$_H$. The increase

Table 2

Total concentration of deposited vanadium from ICP (C_t), initial degrees of reduction, estimates of the rate coefficients with their 95% confidence intervals and the F-value obtained by the regression of the oxygen single-pulse experiments at 773 K after reduction with propane to different degrees of reduction at 773 K for EL10V1, EL10V8, Ti_HV5_H, Ti_HV15_H, Ti_HV60_H, Ti_HV150_H, Ti_HV330_H

	Total V-loading from ICP = C_t (mol_V/kg_c)	R^0	k_{diss} (kg_Vm^3/mol^2 s)	F (10^5)
EL10V1	1.08×10^{-1}	0.23	9.19 ± 0.05	0.85
		0.11	10.40 ± 0.07	2.79
		0.09	14.40 ± 0.13	1.79
		0.22	6.87 ± 0.04	1.55
		All R^0	10.60 ± 0.10	1.39
EL10V8	8.56×10^{-1}	0.02	27.50 ± 0.29	2.33
		0.01	13.30 ± 0.48	2.16
		0.01	5.68 ± 0.69	2.39
		0.01	2.98 ± 0.19	5.12
		All R^0	13.30 ± 0.36	2.38
Ti_HV5_H	4.42×10^{-5}	1.00	0.46 ± 0.01	11.10
Ti_HV15_H	6.87×10^{-5}	1.00	0.62 ± 0.01	16.10
Ti_HV60_H	2.65×10^{-4}	1.00	1.80 ± 0.01	1.29
		0.68	0.68 ± 0.01	9.97
		0.40	1.04 ± 0.01	9.10
		0.41	0.87 ± 0.02	6.28
		All R^0	1.01 ± 0.01	3.23
Ti_HV150_H	7.17×10^{-4}	0.75	1.54 ± 0.01	1.18
		0.38	0.91 ± 0.01	15.10
		0.23	1.25 ± 0.02	13.10
		0.22	1.20 ± 0.02	9.03
		All R^0	1.20 ± 0.01	10.50
Ti_HV330_H	1.05×10^{-3}	0.63	1.09 ± 0.01	7.22
		0.37	1.37 ± 0.01	10.00
		0.26	1.63 ± 0.02	14.70
		0.49	0.59 ± 0.01	7.55
		All R^0	0.98 ± 0.01	5.40

of k_{diss} with increasing V-loading was observed for the Eurocat catalysts as well. Our former study on the reoxidation kinetics of sputtered catalysts with deposition time $\geq$ 1 h, reported k_{diss} values based on the total catalyst mass, while for C_t the total V- and Ti-loading was considered [14].

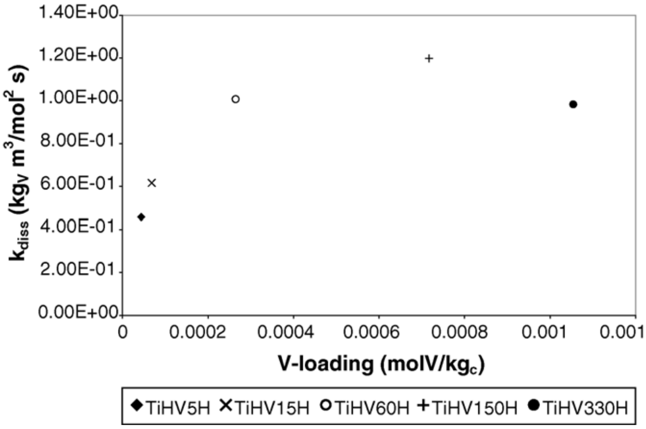

Fig. 2. Rate coefficients at 773 K as a function of V-loading for catalysts Ti_HV5_H, Ti_HV15_H, Ti_HV60_H, Ti_HV150_H and Ti_HV330_H.

4. Conclusions

The reoxidation of the (partially) reduced catalysts can be described in a statistically optimal way by kinetics corresponding to the irreversible dissociative chemisorption of di-oxygen. On the EL10V1 catalyst, a single pre-exponential factor and a single activation energy describe the reoxidation at different degrees of reduction and for different reduction temperatures. Therefore, it is sufficient to take into account changes of the initial concentration of reduced active sites, C_*^0, to describe reoxidation kinetics at different degrees of reduction. A single rate coefficient describes the reoxidation of the sputtered catalysts at every V-loading. Its value increases with increasing V-loading up to a constant value that is reached for catalysts having a deposition time higher than 60 min. This increase is also observed for the Eurocat catalysts.

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