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DEACTIVATION PROPERTIES OF A HIGH-PRODUCTIVE VANADIA-TITANIA CATALYST FOR OXIDATION OF O-XYLENE TO PHTHALIC ANHYDRIDE

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Abstract - The behavior of a high-productive V_2O_5-TiO_2 (anatase) supported O 4-28 catalyst for oxidation of o-xylene to phthalic anhydride was investigated in the first three years of its exploitation in industry. By using a suitable mathematical model, an identification problem was solved and activation profiles of the catalyst along a fixed bed located in the tubes of an industrial reactor were determined. Experimental temperature regimes and yields of the main and side products for different periods of the catalyst life were used. The proper technological regimes providing for a maximum yield according to the requirements of the catalyst producer company were defined.
Keywords: Catalyst deactivation; Experimental; Fixed-bed; Identification problem.

INTRODUCTION

Serious interest in the deactivation problems of various catalysts used in industry has recently been shown in the scientific literature (Monzón, Romeo and Borgna, 2003; Ar and Balci, 2002; Gayubo et al., 2003; Mónzon, Garetto and Borgna, 2003; Aguayo et al., 2003; Heinrichs et al., 2003; Vieira Soares et al., 2003; Vogelaar et al., 2003; Florea et al., 2003; Wang et al., 2003; Wood and Gladden, 2003; Belyaeva et al., 2002; Bal'zhinimaev et al., 2001; Ozava et al., 2003). This is doubtlessly due to the substantial changes of the catalyst properties in the course of its exploitation, with the corresponding aggravation of the technological regime indicators. Hence, the importance of any quantitative information related to this problem on the different catalytic processes known as "gas-solid catalyst". In some scientific investigations the causes of deactivation have been determined (Vieira Soares et al., 2003; Vogelaar et al., 2003). In other ones, the influence of the process conditions on deactivation has been studied (Florea et al., 2003; Wang et al., 2003), whereas there are papers suggesting kinetic models of the deactivation of various catalysts used in different catalytic processes (Monzón, Romeo and Borgna, 2003; Ar and Balci, 2002; Gayubo et al., 2003; Monzón, Garetto and Borgna, 2003; Ozava et

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al., 2003). The latter are the most important ones from the chemical engineer's point of view.

The V_2O_5-TiO_2 (anatase) supported catalysts for oxidation of o-xylene to phthalic anhydride also undergo essential reversible and irreversible deactivation during the time of their exploitation (Bond and König, 1982; Galantowicz et al., 1994, Dias et al., 1997). As it is known (Dias et al., 1997), phthalic anhydride is one of the main products of organic synthesis. The importance and the unabated interest in this oxidation process (Boger and Menegola, 2005), as well as the trend to use high-productive catalysts in industry (Verde and Neri, 1984a), are worthy of the studies dedicated to the deactivation of the above-mentioned catalysts. Based on these considerations, in a previous paper (Anastasov, 2003a) we made an attempt to evaluate quantitatively the deactivation of the O 4-26 catalyst during the complete cycle of its exploitation in the industrial reactor. It is a vanadia-titania catalyst, and it operates with an inlet o-xylene concentration of up to 60 g/m^3 (STP). Its producer is BASF Company. This paper is an extension of the above-mentioned study (Anastasov, 2003a), and it deals with the behavior of another, more modern and productive catalyst for oxidation of o-xylene to phthalic anhydride. It is named O 4-28 and it is also a V_2O_5-TiO_2 (anatase) supported catalyst produced by the same company. The load of this catalyst reaches 80 g/m^3(STP). As it is expected, the purpose of this study is identical with that one exposed in Anastasov (2003a). It consists in determining the activity profiles along the bed, which give the best approximation to the experimental temperature regimes, phthalic anhydride yields and side products obtained in the industrial reactor during different periods of catalyst use. Actually, this activity distribution as a function of time (Heinrichs et al., 2003) affects directly the kinetic model of the oxidation process as it corrects it in accordance with the catalyst deactivation. It is assumed that the activity change is one and the same for all chemical reactions included in the kinetic scheme.

The above goals are achieved by solving an identification problem while using a suitable mathematical model, experimental temperature profiles, and yields of the various products obtained in an industrial multi-tubular reactor of a fixed catalyst bed. Both the reactor and installation for phthalic anhydride production were built by BASF in ORGAHIM Chemical Plants, Rousse, Bulgaria. Certainly, the main idea of this study is to define expedient changes of the technological regime, depending on the catalyst age, if necessary.

We hope that the results reported here and in Anastasov (2003a) will contribute to implementing useful practical tasks concerning the deactivation of the modern V_2O_5-TiO_2 (anatase) supported catalysts for phthalic anhydride production. As it was mentioned, these results are based on experimental data obtained directly in an industrial apparatus during regular operation. Having in mind the modest claims of this study, we would like to mention here the remarkable paper by Wood and Gladden (2003). These authors had the opportunity to use special technique for studying the deactivation of hydroprocessing catalysts, which were operated in an industrial reactor for up to 4 years.

EXPERIMENTAL SECTION

The Catalyst

The experimental data used in this study refer to a V_2O_5-TiO_2 (anatase) supported catalyst, named O 4-28 and operating with a maximum o-xylene load of up to 80 g/m^3 (STP). But this inlet concentration is rarely reached in industry. Usually, it varies between 55 and 75 g/m^3 (STP) (Anastasov, 2003 b). The weight ratio of the V_2O_5 active phase to the TiO_2 catalyst support in its anatase form is about 0.06 (Galantowicz, 1996), while the promoters are P and Rb. The carriers of the active mass, the thickness of which is about 0.1 mm, are porcelain rings 6 mm high and of external and internal diameters of 8.4 and 4.6 mm, respectively. The fixed bed bulk density is about 1500 kg/m^3 with porosity of 0.4. A single contact tube in the reactor is loaded with about 2.100 g of catalyst.

The Industrial Reactor

As it was already mentioned, BASF Company manufactured both the industrial reactor and installation for phthalic anhydride production in ORGAHIM Chemical Plants, Rousse, Bulgaria. The apparatus is a shell-and-tube exchanger, where the catalyst is located in the tubes, while the cooling agent, a molten salt of $NaNO_2$ and KNO_3 (weight ratio 43:57) circulates in the shell side. The number of the contact tubes is 10550; the length and the inner diameter of each one are 3,250 mm and 26 mm, respectively. The steam generator is installed outside the apparatus. The height of the fixed bed is about 280 cm, while the temperature in it is measured in nine contact tubes arranged in a definite way in the bundle. The NiCr-Ni mobile measuring

thermocouples are 300 cm long each, and they are mounted in a jacket located in the centre of the tube; they enable the operator to measure the temperature along the whole bed length. It is determined as the arithmetic means of the readings of all thermocouples, with an accuracy of 1.5°C. The temperature profiles in the different tubes are reported continuously. The reactor scheme has been presented in our paper Nikolov et al. (1991).

Analyses

The analyses of o-xylene (o-XL), the desirable phthalic anhydride (PA) product and the side substances o-toluyl aldehyde (o-TA) and phthalide (PH) have been made by means of gas chromatography. The product maleic anhydride (MA), accompanying the oxidation process, has been determined polarographically. The analyses discussed have been performed on the reactor outlet at definite time intervals.

THE MATHEMATICAL MODEL

In order to determine the activation profiles along the bed, we used a two- dimensional mathematical model interpreting the behaviors of the gas phase and the catalyst. It is Froment (1974) who has suggested this model that consists of incomplete mixing along the bed radius for the gas as well as transfer of mass and heat between the two phases.

The model is considered the most suitable one for studying high exothermic catalytic processes with chemical reactions occurring on the external surface of the catalyst element (Lapidus and Amundson (eds.), 1977), Kershenbaum and López-Isunza, 1982; Quina and Ferreira, 1999). For a stationary regime, the model equations describing the process taking place in a single contact tube of cylindrical form are as follows:

Gas Phase:

$$D_{r,i}\left(\frac{\partial^2 C_i}{\partial r^2}+\frac{1}{r}\frac{\partial C_i}{\partial r}\right)- V_b\frac{\partial C_i}{\partial l}+k_{gp,i}a\left(C_{p,i}-C_i\right)=0 \quad (1)$$

$$\lambda_r\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)- V_b C_g\frac{\partial T}{\partial l}+h_{gp}a\left(T_p-T\right)=0 \quad (2)$$

with boundary conditions:

$$l=0;\qquad C_i=C_{0,i};\qquad T=T_0 \quad (3)$$

$$r=0;\qquad \frac{\partial C_i}{\partial r}=0;\qquad \frac{\partial T}{\partial r}=0 \quad (4)$$

$$r=R;\qquad \frac{\partial C_i}{\partial r}=0;\quad -\lambda_r\frac{\partial T}{\partial r}=h_{gc}\left(T-T_c\right) \quad (5)$$

Solid phase (catalyst):

$$k_{gp,i}a\left(C_i-C_{p,i}\right)+ W_{p,i}\left(C_{p,i},T_p,F_A(l)\right)\rho_p\left(1-\varepsilon\right)=0 \quad (6)$$

$$h_{gp}a\left(T-T_p\right)+ \sum_{m=1}^{s} r_{p,m}\left(C_{p,i},T_p,F_A(l)\right)\rho_p\left(1-\varepsilon\right)\left(-\Delta H_m\right)=0 \quad (7)$$

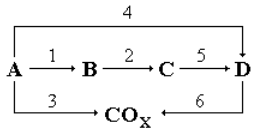
The system equations (1)-(7) is approximated by an implicit finite-difference scheme and solved iteratively by using the false-transient method. The method of solution has been exposed in detail in our paper Nikolov and Anastasov (1992a).

The model coefficients: D_r, λ_r, k_{gp}, h_{gp} and h_{gc} are specified by using the dependencies presented in Anastasov et al. (1988), while some concrete values are given in Anastasov (2003a).

KINETICS

In this investigation, as well as in all our more important studies concerning the simulation of the oxidation process (Anastasov, 2003a, 2003b; Nikolov and Anastasov, 1992a, 1992b; Anastasov et al., 1988; Anastasov and Nikolov, 1998; Anastasov, 2002), we use the kinetics proposed by Calderbank et al. (1977). A doubtless and very important merit of this kinetics is the reporting of phthalide, whose content determines the quality of the final product. Unfortunately, regarding the maleic anhydride generated in the oxidation process (about 2-3 mol %) (Galantowicz, 1996; Skrzypek et al., 1985) as combustion product is a substantial disadvantage.

So, the network suggested by Calderbank et al. (1977) is:



where A, B, C and D are o-XL, o-TA, PH and PA. The oxidation of PA to products of combustion is insignificant and can be neglected (Calderbank et al., 1977).

The kinetic equations by stages expressed in partial pressures according to Calderbank et al. (1977) are:

$$r_{p,1} = K_1 \alpha P_A \tag{8}$$

$$r_{p,2} = K_2 \alpha P_B \tag{9}$$

$$r_{p,3} = K_3 \alpha P_A \tag{10}$$

$$r_{p,4} = K_4 \alpha P_A \tag{11}$$

$$r_{p,5} = K_5 \alpha P_C \tag{12}$$

where:

$$\alpha = \frac{K_C P_{ox}}{K_C P_{ox} + \left(K_1 + 6.5K_3 + 3K_4\right) P_A + K_2 P_B + K_5 P_C} \tag{13}$$

The value of $K_c P_{ox}$ with air and at near atmospheric pressure is 0.722 10^{-5} kmol/kg s (Calderbank et al., 1977).

As the authors of the kinetics shown state, it can be successfully used to interpret the behaviors of various commercial V_2O_5-TiO_2 (anatase) supported catalysts. According to our industrial and pilot investigations (Nikolov and Anastasov, 1992a, 1992b; Anastasov and Nikolov, 1998), the kinetic dependencies discussed, together with the kinetic parameters suggested (Calderbank et al., 1977), describe quite satisfactorily the oxidation process carried out by the low-productivity catalyst O 4-25. This catalyst too is a vanadia-titania one, but it operates with inlet reagent concentration of up to 40 g/m^3 (STP). Until recently, it was used in the installation for phthalic anhydride production in Bulgaria. In fact, our position on the ability of the original kinetics to predict the operation of the low-productivity catalysts complies with the results presented in the papers of Kershenbaum and López-Isunza (1982) and López-Isunza et al. (1987).

Unfortunately, things are not the same with the high productive O 4-26 (inlet o-xylene concentration of up to 60 g/m^3 (STP)) and O 4-28 ($C_{A,0}$=80 g/m^3 (STP)) catalysts. It was found (Anastasov, 2003b) that the original pre-exponential factors and energies of activation were not able to describe adequately the experimental temperature profiles, the PA yields and the contents of the side products while using the catalysts indicated above. This made us search for new kinetic parameters that should be suitable for both the high-productive catalysts O 4-26 and O 4-28 (Anastasov, 2003b). The kinetic model and scheme remain unchanged (Anastasov, 2003 b).

The new parameters valid for O 4-28 catalyst are shown in Columns 3 and 4 of Table 1. They predict very well the real picture in a fixed bed composed of a fresh sample of O 4-28. As a comparison, in Columns 1 and 2 of the same table, the original pre-exponential factors and energies of activation, which Calderbank et al. (1977) have suggested, have been presented.

So, this investigation was carried out while using the new kinetic parameters (Table 1, Columns 3 and 4) and the original kinetic model of Caldebank et al. (1977). It should be mentioned here that if modern catalysts are used (loading 80 and over 80 g/m^3(STP)), the industrial fixed bed is usually composed of two forms of different activities. In order to improve the process effectiveness (Anastasov and Nikolov, 1998), the lower activity form is loaded in the front part of the bed, while in its rear, where the reagent is practically exhausted and the temperature is low, the more active sample is placed. A similar organization of the fixed bed is also observed for O 4-28 catalyst. In this case, the first 160 cm of the bed contain a sample of an activity assumed as one relative unit, while the remaining 120 cm are composed of a catalyst that is 1.35 times as active (Anastasov and Nikolov, 1998).

Table 1: Original kinetic parameters according to Calderbank et al. (1977) and specified for O 4-28 catalyst.

Stage	Original kinetic parameters according to Calderbank et al. (1977)		Specified for catalyst O 4-28	
#	K_0	E_m	K_0	E_m
	(kmol kg^{-1} s^{-1} Pa^{-1})	(kJ/kmol)	(kmol kg^{-1} s^{-1} Pa^{-1})	(kJ/kmol)
1	3.7779 10^{-5}	61420	1.5090 10^{-5}	69417
2	5.4870 10^{-6}	46473	2.2690 10^{-6}	46473
3	3.5330 10^{-6}	51205	1.4010 10^{-6}	56312
4	1.2780 10^{-5}	54512	5.1610 10^{-6}	52586
5	3.1482 10^{-5}	57945	1.2632 10^{-5}	38519

RESULTS AND DISCUSSION

Profiling the Catalyst Activity Along the Bed

It was mentioned that the determination of the activity profiles was directly related to a possible revision of the technological regime. Such a revision should compensate for the negative influence of the deactivation phenomena upon the reactor productivity. The solution to the mathematical model with a deactivation profile included informs on how close the process characteristics are to the requirements and whether a change in the technological regime is necessary. The final objective is to maintain the highest yield of the desirable product, with the minimum content of the main contaminant, phthalide, irrespective of the catalyst age. Certainly, an appropriate temperature regime with a maximum temperature not higher than 500^{o} C is also necessary. It is known (Calderbank et al., 1977) that over 500^{o}C the catalyst undergoes a fast irreversible deactivation and loses practically its qualities.

Profiling the activity along the bed as a function of time was performed while solving an identification problem. It was mentioned that the activity distribution giving the best approximation to the experimental temperature profile, PA yield and PH contents for a catalyst at a particular age was searched for. An optimization procedure was used, based on the method of the "fortuity search" (trial and error approach) with a minimization of the sum of the squares of the differences between the experimental and calculated temperatures and yields. In this method, random numbers are used as directional derivatives of a vector in whose direction the minimum of the optimization function is searched. The activation profile achieved at a definite iteration was changed in the search process until the minimum of the optimization function was reached. The experimental temperature profiles investigated were for a catalyst operated for 6, 12, 24 and 36 months under industrial conditions. These periods concerned the first 36 months of the whole catalyst life (about 60 months). The full time of catalyst use was not studied, as the last experimental data available were for a catalyst that would be exploited for about 2 more years in industry. This will be done immediately when information on the complete cycle of the catalyst operation is obtained.

One can see in Fig. 1 the temperature regime produced by a one-month-old O 4-28 catalyst that can be considered absolutely fresh. The profile has been obtained while using the kinetic parameters determined in Anastasov (2003b) and shown in Columns 3 and 4 of Table 1. What impresses here is the perfect compliance of the experimental results with the predicted (Curve 1) ones in the region of the first hot spot, as well as the good compliance in terms of the second temperature maximum. It should be remembered that the temperature peak in the second half of the bed is a result of the higher activity (by 1.35 times) of the catalyst located after 160 cm, which was commented above. The experimental (81.6 mol %) and predicted (82 mol %) PA yields are almost identical. There are certain differences between the experimental and predicted results with respect to the PH content, but they are not significant (experiment 0.01 mol %, calculation 0.06 %). The systematic deviation between the experimental temperatures and the model prediction in the region after 80 cm should be commented. Unfortunately, we were not able to make the same excellent prediction of the experimental regime in the remaining part of the bed, as that in the first hot spot area. In our opinion, the main reason for this was some disadvantages of the kinetics suggested by Calderbank et al. (1977), which do not report the formation of maleic anhydride. But the adequate description of the hot spot behavior and of the products yields is sufficient evidence that the new kinetic parameters predict correctly the operation of the fresh catalyst. Hence, they can be successfully used for studying the deactivation processes in the catalyst.

Fig. 2 presents the behavior of a 6-month-old catalyst. This catalyst is expected to undergo certain slight deactivation, which can be seen in the figure. Curve 2 shows that in the first 50 cm the sample keeps its initial activity (assumed as 1), but in the region 50-160 cm it drops down to 0.9 relative units. After 160 cm, the more active catalyst in the dual catalyst bed system also deactivates slightly. Its activity decreases from 1.35 down to 1.30 relative units. The activation profile determined in this way (Curve 2) predicts precisely (Curve 1) the experimental temperatures in the zone up to 120 cm. The predicted hot spot (425.8^{o}C) is only 0.8^{o} C higher than the experimental one, while there is no difference in the locations of both hot spots. It is worth noting that in this and the next figures the calculated temperatures are the arithmetic means of the temperatures of the gas and solid phases. They refer to the centre of the bed (r = 0), where the thermocouples that read the experimental temperatures are located. Like the fresh catalyst (Fig. 1), in this case too the predicted temperature regime (Fig. 2, Curve 1) shows temperatures that are a little bit higher in comparison with the experimentally

registered ones in the zone after 120 cm. In our opinion, this is due to the reasons commented above. We shall not discuss here and in the next three figures (Fig. 3-5; periods of catalyst use 12, 24 and 36 months) the correspondence between the predicted PA yield and the yield BASF Company requires. This is done below, in the section referring to the definition of the technological regime. As to the phthalide content, the calculations show that for the whole period investigated (3 years) it was below 0.1 mol %, within the necessary limits (between 0.01 and 0.1 mol %).

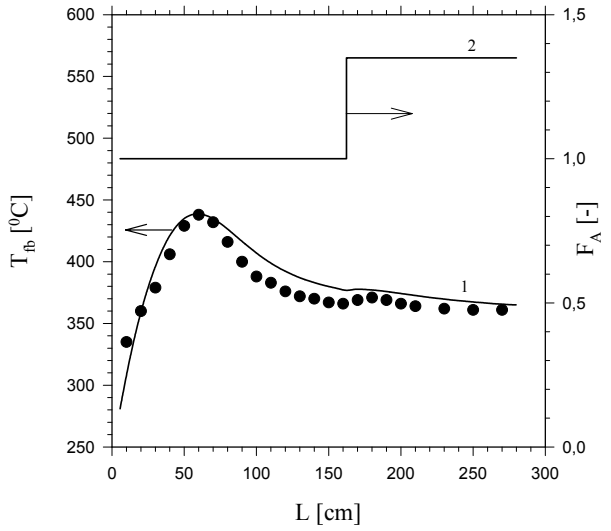


Figure 1: Temperature regime and activity of a fresh O 4-28 catalyst (age 1 month). Technological conditions: $V = 3.3$ m^3(STP) h^{-1}, $C_{A,0} = 59.3$ g m^{-3}(STP), $T_c = 358^oC$, $T_0 = 250^oC$. Circles – experimental temperatures in the bed centre ($r = 0$); curves – model predictions under the same conditions. Curve 1 – predicted temperature profile; Curve 2 – activity profile.

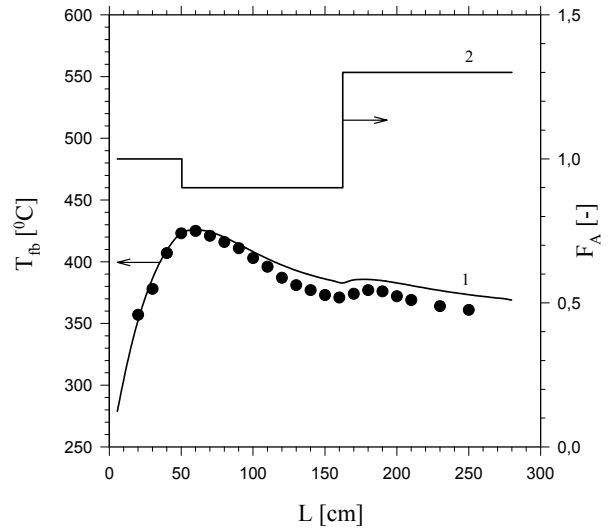


Figure 2: Behavior of a catalyst operated for 6 months in the industrial reactor. Technological conditions: $V = 4.0$ m^3 (STP) h^{-1}, $C_{A,0} = 63.4$ g m^{-3} (STP), $T_c = 358^oC$, $T_0 = 250^oC$. Circles – experiments; curves – model predictions under the same conditions. Curve 1 – calculated temperature profile; Curve 2 – activity profile along the bed.

With the progress of the catalyst use (Fig. 3; 12 months) the deactivation processes in the sample intensify. In comparison with the 6-month-old catalyst (Fig. 2), the activation profile (Curve 2) giving the best approximation (Curve 1) to the experimental temperatures (points) shows a reduction of the activity from 0.9 (Fig. 2, Curve 2) down to 0.65 (Fig. 3, Curve 2) in the hot spot region (0-50 cm) and in the next 110 cm of the bed (to 160 cm). The more active second bed, located after 160 cm, decreases its activity considerably less – from 1.30 down to 1.25 relative units. The predicted hot spot temperature of 437.6°C (Curve 1) does not differ from the experimental one (437°C), but a certain difference in their locations is observed. The calculated hot spot is situated about 10 cm deeper in the bed. It makes an impression that the sample used for 12 months (Fig. 3) shows an experimental hot spot temperature (437°C) higher than that produced with a younger and more active catalyst (Fig. 2, 425° C). This can be explained with the lower inlet gas temperature of the older catalyst (Fig. 3, age 12 months, T_0 = 240°C) in comparison with that of a sample used for 6 months only (Fig. 2, age 6 months, T_0 = 250°C). The dependence observed is completely in compliance with our experimental investigations and theoretical conclusions shown in Nikolov and Anastasov (1992a) and Anastasov (2002). According to these papers the reduction of the inlet gas temperature below the coolant temperature increases the hot spot temperature.

The next figure (Fig. 4) shows the temperature regime of an O 4-28 catalyst exploited for 24 months under industrial conditions. Curve 1 represents the solution to the mathematical model with the activation profile given by Curve 2. It is interesting that the sample has kept its activity unchanged in the zone 50-160 cm in comparison with the catalyst used for a two times shorter period (Fig. 3). For both catalysts (12 and 24 months old) it remains equal to 0.65 relative units. It seems that the deactivation processes in this region slow down considerably, which confirms the results of Ozawa et al. (2003) and Heinrichs et al. (2003). But an enlargement of the zone of lower activity towards the beginning of the bed is observed. The sample keeps its initial characteristics in the first 35 cm only, where the temperatures are lower. At the same time the deactivation of the second catalyst bed located after 160 cm continues. In relation to the one-year-old sample, the catalyst in this zone decreases its activity by 0.1 more relative units, regardless of the low operation temperatures (about and below 400°C). There the deactivation is most probably reversible and due to the deposition of residual tar products over the active catalyst surface. The authors of papers Dias et al. (1994, 1996) and Cheng et al. (1996) also confirm such an assumption.

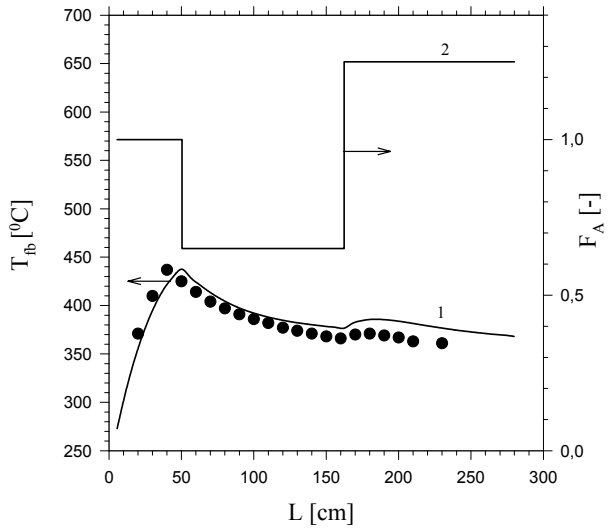


Figure 3: Experimental and predicted temperature regimes and degree of deactivation of a catalyst aged 12 months. Technological conditions: V = 3.3 m^3(STP) h^{-1}, $C_{A,0}$ = 58.7 g m^{-3}(STP), T_c = 358°C, T_0 = 240°C. Points – experiments; curves – model solutions under the same conditions. Curve 1 – predicted temperature profile; curve 2 – activity profile.

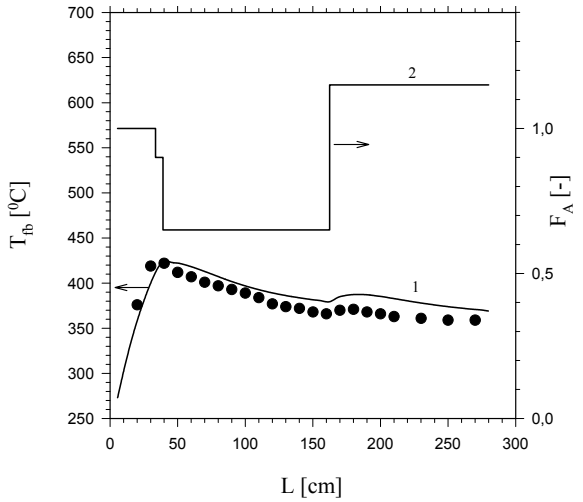


Figure 4: Results shown by a catalyst used 2 years in the industry. Technological conditions: V=3.3 m^3(STP) h^{-1}, $C_{A,0}$ = 62.4 g m^{-3}(STP), T_c = 358^{o}C, T_0 = 240^{o}C. Points – experiments; curves – model predictions under conditions as in the experiments.

As it was mentioned above, the last experimental data on the catalyst studied refer to a 3-year-old sample. Their treatment is presented in Fig. 5. It can be definitely stated that the model solution (Curve 1) with the deactivation determined (Curve 2) is quite adequate for the experimental temperature profile. The compliance of the experiments with the predictions in the important region of the bed up to 110 cm is perfect – the calculated curve passes through the experimental points. Here the strong deactivation of the catalyst operating under the highest temperatures in the hot spot region (30 to 60 cm) is remarkable. The sample located there decreases its initial activity by more than two times (from 1 to 0.45 relative units). The authors Galantowicz et al. (1994), who studied the same process, have reported similar changes of this activity. In our opinion, the phenomena observed is due to an irreversible thermal deactivation (sintering) caused by the high temperatures; it substantially reduces the active catalyst surface. Galantowicz (1996) and Wellauer (1985) also shared this same opinion on the processes of oxidation of o-xylene to PA and n-butane to maleic anhydride, respectively. Just the irreversible deactivation in the region of the high temperatures removes the hot spot in the depth of the bed, in the case of longer (over 3 years) catalyst exploitation. Nikolov et al. (1987) have found this fact experimentally, for a low productive V_2O_5-TiO_2 catalyst ($C_{A,0}$ = 40 g/m^3 (STP)).

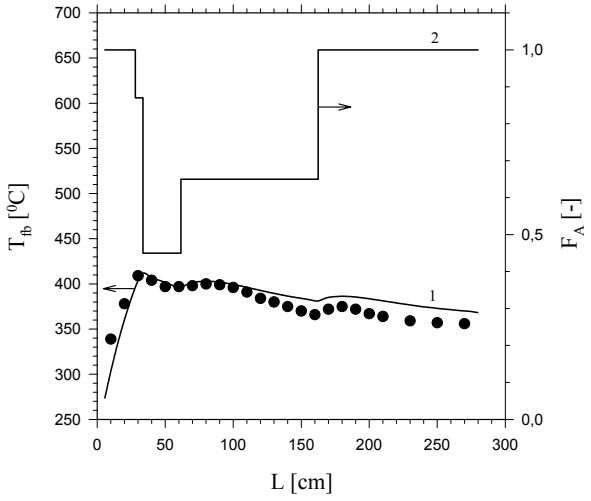


Figure 5: Status of a catalyst exploited for 36 months. Technological conditions: V = 3.1 m^3(STP) h^{-1}, $C_{A,0}$ = 62.4 g m^{-3}(STP), T_c = 357^{o}C, T_0 = 240^{o}C. Points – experiments; curves – model solutions under the same conditions. Curve 1 – temperatures determined by the model; curve 2 – catalyst activity along the bed.

It is stated in some recent studies (Belyaeva et al., 2002; Bal'zhinimaev et al., 2001) that the irreversible deactivation of a vanadia catalyst for oxidation of SO_2, operated at high temperatures, is due to crystallization processes in the active component V_2O_5. It should be noted that the conclusions of these authors comply with ours, regarding the activity of the crystal and amorphous forms of V_2O_5. These conceptions have been discussed at some length in our paper Nikolov and Anastasov, (1992b) devoted to the pre-treatment of a low productive catalyst for oxidation of o-xylene.

In order to explain the behavior of the 36-month-old catalyst it is still necessary to say that, in comparison with the younger samples (12 and 24 months), the deactivation processes in the front part of the bed (from 30 to about 60 cm) go on, while in the zone from about 60 to 160 cm they do not develop. The catalyst activity in this area remains the same (about 0.65 relative units) for all the three catalysts, regardless of their ages (12, 24 and 36 months). But the more active bed continues to worsen its characteristics, and three years later its activity equals that of the fresh sample loaded in the first part of the dual catalyst bed system (Fig. 5, Curve 2, L = 160-280 cm, F_A = 1). The fact that, at a constant inlet temperature of the reaction mixture, the hot spot temperature decreases with the increase of the catalyst age, and lower temperatures characterize the thermal regime (Fig. 3-5), draws the attention.

In order to give a better idea of the activity changing with time, the profiles represented by curves 2 in Fig. 1-5 are shown in Fig. 6. To our thinking, Fig. 6 gives better information on how the different bed regions deactivate in the course of time. It can be seen how the zones of lower activity expand gradually and what parts of the bed are most seriously affected by the deactivation processes. It is impressive that, after the initial slight deactivation in the zone 60-160 cm (10 % for 6 months), in the next 6 months (1-year-old catalyst) the activity drops down to 0.65 relative units and remains unchanged in the following two years. In the course of time the deactivation of the second, more active catalyst located after 160 cm in the DCB system, accelerates continuously. As it was discussed above, in our opinion the low temperatures in this region lead to deposition of residual products, blocking reversibly the active surface. In contrast to the O 4-26 catalyst operating at an inlet reagent concentration of up to 60 g/m^3 (STP) (Anastasov, 2003a), the activity in the beginning of the bed (to about 30 cm) remains unchanged and equal to 1 during the whole three-year period. But having in mind that, at the end of the sixth month, this region was 50 cm long (Figs. 2 and 6) and, subsequently, it reduced its length by about two times (Figs. 5 and 6) for 30 months, it could be expected that, in the course of time (2 more years to the replacement of the catalyst with a new batch), it would fade away completely.

It is difficult here to give an explanation for the step-wise changing of the activity along the bed observed in all activation profiles. It is important to note here that Lyubarskii et al. (1981) have reported a similar activity distribution in the same process, but unfortunately without any discussion. At the same time, we think the stepwise fashion of the activity profiles is not due to the performance of the "fortuity search" method used. The initially assumed form of the activity profile during the solution of the identification problem was an uninterrupted function. However, this function gives a worse agreement with the experiments than a terraced distribution of the activity.

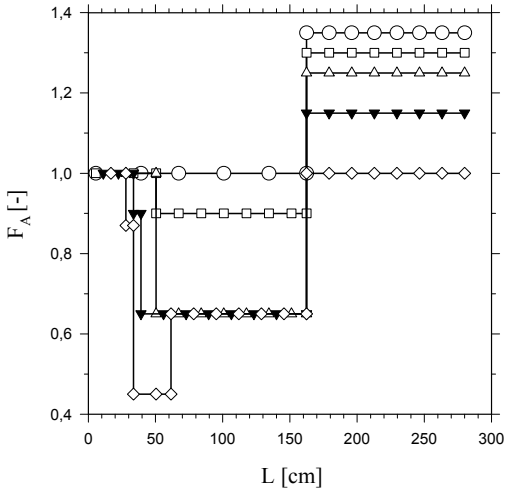


Figure 6: Calculated activity profile for all periods investigated under the conditions in Fig. 1 to 5. ○ - fresh catalyst used for 1 month in the industry, □ - catalyst aged for 6 months, △ - catalyst aged for 12 months, ▼ - catalyst used for 24 months, ◇ - catalyst used for 36 months

Definition of a Technological Regime Corresponding to the Variations of the Catalyst Activity

The catalyst producer company has provided strictly defined requirements for phthalic anhydride yields, depending on the time of catalyst use. In our study Anastasov (2003a), these are discussed in detail. The dependence of the maximum and minimum yields of the main product demanded by BASF on the catalyst whole lifetime, until the replacement of the catalyst with a new batch, is also shown. Therefore, we think that it is not necessary to present this information again. But it is important to only note that, for the exploitation periods of 6, 12, 24 and 36 months studied here, the pairs of minimum and maximum PA yields are 80.8/81.6, 80.6/81.5, 79.8/81.1 and 78.9/80.5 mol %, respectively. But it is surprising that the technological regimes applied in industry in the different periods of the catalyst life were not able to secure PA yields within the above-mentioned limits. Obviously, the regime parameters differ significantly from the optimal ones. This makes us search for values to meet the producer's requirements for a maximum PA yield corresponding to the catalyst age. It should be remembered that, in order to achieve this objective, suitable changes of the technological parameters are necessary. These concern the coolant temperature T_c, the inlet gas temperature T_0, the reacting mixture flow rate V, and the inlet reagent concentration $C_{A,0}$. It is most convenient to vary T_c and/or T_0, as the change of the contact time (flow rate V, respectively) or the inlet reagent concentration $C_{A,0}$ might be hazardous for the reactor productivity. By means of the mathematical model and the activity profiling along the bed the coolant temperatures leading to a maximum PA yield were determined. Of course, the restriction that the catalyst temperature should be below the tolerable value of 500° C was observed. In Table 2, one can see the optimum values of the coolant temperature T_c, as well as the most important indicators of the technological regime, namely the temperature and the location of the hot spot, the PA yield, and the PH content.

Table 2: Parameters and characteristics of industrial and recommended regimes.

Time of use	Technological conditions								Technological characteristics							
	V		$C_{A,0}$		T_c		T_0		T_{hs}		L_{hs}		Y_C		Y_D	
	m^3(STP)/h		g/m^3(STP)		°C		°C		°C		cm		mol %		mol %	
months	ind.	opt.	ind.	opt.	ind.	opt.	ind.	opt.	ind.	opt.	ind.	opt.	ind.	opt.	ind.	opt.
6	4.0	4.0	63.4	63.4	358.0	372.0	250.0	250.0	425.8	457.2	61.6	56.0	0.097	0.077	76.8	81.6
12	3.3	3.3	58.7	58.7	358.0	367.0	240.0	240.0	437.6	460.0	50.4	50.4	0.086	0.074	78.5	81.5
24	3.3	3.3	62.4	62.4	358.0	369.0	240.0	240.0	424.0	450.6	39.2	39.2	0.093	0.078	77.3	81.1
36	3.1	3.1	62.4	62.4	357.0	370.0	240.0	240.0	411.9	441.9	33.6	33.6	0.099	0.083	75.6	80.5

The results given in Table 2 show that the coolant temperatures used in the industrial reactor (357-358° C) are rather low. According to the industrial experience of a number of researchers (Galantowicz, 1996; Skrzypek et al., 1985; López-Isunza and Kershenbaum, 1992; Verde and Neri, 1984b), as well as our studies Anastasov (2003a) and Nikolov and Anastasov (1992b, 1989), this temperature varies between 360 and 380° C, but it should not fall below the lower limit (360° C). Usually, it is between 370 and 375° C. This is valid for both the low- and high-productive catalysts for o-xylene oxidation. Indeed, it can be seen in Table 2 that if T_c rises up to about 367-372° C, the PA yield increases considerably and falls in compliance with the maximum one demanded by BASF. These temperature increases are not dangerous for the temperature regime in the reactor, as in all technological regimes recommended (Table 2) the hot spot temperature does not exceed 460° C. At the same time the phthalide content varies between 0.074 and 0.083 mol % and completely meets the requirements.

CONCLUSIONS

The deactivation processes occurring in a high-productive V_2O_5-TiO_2 (anatase) supported O 4-28 catalyst during a three-year period of exploitation in an industrial reactor can be systematized as follows:

1. Activity profiles along the fixed bed are determined. They predict very well, in some cases perfectly, the behavior of the catalyst during the first three years of its use. This refers to both the temperature regime (temperature and location of the hot spot) and the yields of the main and side products. The profiles can be used to specify the optimum technological regime as a function of time.
2. The different bed zones decay at different rates. In the region of the moderate temperatures (60-160

cm) the activity remains unchanged for a long period (about 2 years).
3. It seems that the deactivation of the second, more active catalyst accelerates with time because of the deposition of residual volatile products caused by the comparatively low temperatures in this region.
4. In the zone of the first hot spot (from about 30 to 60 cm) a significant thermal irreversible deactivation of the catalyst is observed. The sample located there reduces its activity by over two times during a three-year period of use. This fact complies with other studies.
5. For 36 months the deactivation process does not affect the first 30 cm of the bed.
6. The progress of the deactivation process in the catalyst reduces the temperatures in the bed.
7. Suitable technological regimes depending on catalyst exploitation time are determined. By using these, the maximum PA yield required by the producer company can be achieved, with no risk of thermal destruction of the catalyst.

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NOMENCLATURE

a	specific external surface area of pellets	$m^2\ m^{-3}$
C	concentration of component in gas phase	$kmol\ m^{-3}$
C_g	heat capacity of gas	$J\ m^{-3}\ K^{-1}$
C_p	concentration of component on the surface of pellets	$kmol\ m^{-3}$
C_0	inlet concentration of component in gas phase	$kmol\ m^{-3}$, $g\ m^{-3}$ (STP) m^3 (STP) defined as m^3 at 0^0C and 101.325 kPa
D_r	coefficient of effective mass diffusivity in radial direction for gas	$m^2\ s^{-1}$
E	energy of activation	$kJ\ kmol^{-1}$
F_A	dimensionless factor accounting for in a formal way the catalyst activity along the bed	
h_{gc}	heat transfer coefficient between gas (bed) and cooling agent	$W\ m^{-2}\ K^{-1}$
h_{gp}	heat transfer coefficient between gas and catalyst pellets	$W\ m^{-2}\ K^{-1}$
ΔH	heat effect of corresponding reaction	$J\ kmol^{-1}$
k_{gp}	mass transfer coefficient between gas and catalyst pellets	$m\ s^{-1}$
K	reaction rate constant	$kmol\ kg^{-1}\ s^{-1}\ Pa^{-1}$
K_C	rate constant of catalyst reoxidation	$kmol\ kg^{-1}\ s^{-1}\ Pa^{-1}$
K_0	pre-exponential factor	$kmol\ kg^{-1}\ s^{-1}\ Pa^{-1}$
l	axial coordinate	M
L	length of bed	Cm
L_{hs}	position of hot spot along the bed length according to model predictions	Cm
P	partial pressure of component	Pa
P_{ox}	partial pressure of oxygen	Pa
r	radial coordinate	M
r_p	reaction rate by steps on catalyst pellets	$kmol\ kg^{-1}\ s^{-1}$
R	tube radius	M
s	number of reactions by steps	(-)
T	temperature of gas	K
T_c	temperature of cooling agent (accepted as equal to temperature of tube wall)	K, ^{0}C
T_{fb}	temperature in bed (^{0}C); measured experimentally, as well as mean temperature (obtained from arithmetic means of temperatures of gas and solid phases) for model predictions	^{o}C
T_{hs}	hot spot temperature for model predictions (obtained from arithmetic means of hot spot temperatures of gas and solid phases)	^{0}C
T_p	temperature of catalyst pellets	K
T_0	inlet temperature of reaction mixture	K, ^{o}C
V	flow rate of reaction mixture per single tube	m^3(STP) h^{-1}
V_b	gas velocity with respect to full cross section of tube	$m\ s^{-1}$

W_p	reaction rate by component on catalyst pellets	kmol kg^{-1} s^{-1}
Y	yield of component	mol %

Greek Symbols

α	defined in equation (13),	Dimensionless
ε	bed porosity,	Dimensionless
λ_r	coefficient of effective conductivity in radial direction for gas	W m^{-1} K^{-1}
ρ_p	density of catalyst pellets	kg m^{-3}

Subscripts

A	*o*-xylene	(-)
B	*o*-tolualdehyde	(-)
C	phthalide	(-)
D	phthalic anhydride	(-)
i	component;	1=*A*; 2=*B*; 3=*C*; 4=*D*
m	reaction step	(-)

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