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Deactivation by Coke of a Cr_2O_3/Al_2O_3 Catalyst during Butene Dehydrogenation

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The coking data obtained during the dehydrogenation of *n*-butene on a Cr_2O_3/Al_2O_3 catalyst have been successfully fitted using a model which considers simultaneously coke deposition directly on the surface (monolayer coke) and on multiple layers. The variation of the monolayer and multiple-layer coking rates with time, temperature, and hydrogen partial pressure have been investigated. The results obtained in this work show that the relevant deactivation variable for this system is the amount of monolayer coke, rather than the total coke content of the catalyst. © 1993 Academic Press, Inc.

INTRODUCTION

In spite of the many studies devoted to catalyst coking, there appears to be no general agreement on whether coke deposition always results in reduced catalytic activity, or in the extent of deactivation caused by a certain level of coking on a catalyst. Thus, after a rapid initial coke deposition, a slow coking frequently occurs, and it is sometimes found that the catalyst retains a significant and steady catalytic activity after the fast coking stage. The intrinsic activity–coke relationship is often obscured by the fact that coke deposits, in addition to covering surface sites, may also result in reduced pore cross-sectional area, and may ultimately cause pore blockage. Also, poisoning and sintering may take place simultaneously with coke deposition.

The complex nature of coking and its interactions with other deactivation phenomena has given rise to the appearance of many kinetic models aimed to deal with some of the problems involved in catalyst deactivation by coke. The objective of the models in this field usually includes both the prediction of the amount of coke deposited on the catalyst given a certain time-on-stream and particular operating conditions, and the extent of the deactivation caused by the coke deposits.

Thus, Klingsman and Lee (*1*) have proposed a model for coke growth in multiple layers in which they establish the activity–coke relationship for a given number of coke layers. In this work the activity versus time and coke versus time functions were not obtained. However, the model of Klingsman and Lee allows the estimation of the amount of coke in a monolayer, which is an important parameter in order to quantify the catalytic activity.

A different approach was followed by Dadyburjor and Liu (*2*), who developed a kinetic model for coke growth which considers two types of coking: the first involves only bare sites, while the second involves bare and covered sites simultaneously. With these considerations, a three-parameter equation was obtained which predicts the total amount of coke for a given time and reaction conditions. Dadyburjor and Liu (*2*) showed that this equation can, in fact, accommodate a number of empirical equations previously used to fit coke versus time data. In this work, however, no equation is postulated to relate catalytic activity and coke concentration.

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Dumez and Froment (*3*) studied the dehydrogenation of *n*-butene to 1,3-butadiene over a Cr_2O_3/Al_2O_3 catalyst. From the kinetic data obtained with fresh catalyst a LHHW mechanism was proposed for the main reaction with two active sites taking part in its controlling step ($m = 2$). They concluded that in this reaction coke is formed from both butene and butadiene, and that the coke formation step involves two sites ($h = 2$). Finally, they established an empirical exponential activity–coke relationship ($a = \exp(-\alpha C)$), both for the activities of the main and of the coking reaction, in which the α parameter does not depend on temperature or concentrations. Acharya and Hughes (*4*) used the kinetics proposed by Dumez and Froment (*3*) to carry out an extensive analysis of the behaviour of the system at the catalyst particle and industrial reactor levels.

Later, Marin *et al.* (*5*) used the models developed by Beeckman and Froment (*6, 7*) to interpret the data obtained by Dumez and Froment (*3*). They found a good agreement with the assumptions of instantaneous coke growth followed by growth of coke at a finite rate. Also, using the assumption of one active site taking part in the controlling step of the main reaction ($m = 1$), they obtained a somewhat better fit than that of Dumez and Froment (*3*).

In the present work a dual coke growth model which contemplates coke formation directly on the catalyst surface (monolayer coke) and coke formation on coke previously deposited (multilayer coke) is employed to describe the coking of a Cr_2O_3/Al_2O_3 catalyst during the dehydrogenation of *n*-butene. This model, thereafter termed the monolayer–multilayer coke growth model (MMCGM) was first proposed by Nam and Kittrell (*8*) and later generalized by Corella and Monzón (*9*). The model does not take into account the internal structure of the catalyst, and therefore its application is limited to the cases in which pore blockage is not significant. This obviously means relatively low coke concentrations. However, as shown later for the system studied in this work, the MMCGM gives a good fit of the experimental data for all the range of coke deposition levels investigated, which extends up to 8% by weight.

Coking Kinetics

According to the MMCGM, the variation of coke deposition on the catalyst with time can be described by considering simultaneously coke formation directly on the catalyst surface (first layer or monolayer coke) and coke growth on previous coke layers (multilayer coke). As mentioned above, this model has already been described in the literature and therefore it will only be dealt with briefly in this section.

The model considers separate kinetics for coke formation on the catalyst surface or monolayer coke (C_m), and coke formation in multiple layers (C_M). Thus, the overall coking rate is given by

$$\frac{dC}{dt} = \frac{dC_m}{dt} + \frac{dC_M}{dt}. \qquad (1)$$

Different mechanisms can be envisaged to describe the simultaneous growth of monolayer and multilayer coke. In general, the formation of monolayer coke includes the adsorption of a reactant or product on the catalyst surface, which gives rise to the formation of the coke precursor and then to coke. This coke formed on the surface may evolve towards other structures, for instance through graphitization processes. On the other hand, the multilayer coke grows on top of previously existing coke. This can take place directly at an activated point in a coke layer or by diffusion through a metallic entity such as in the case of coke formation in whiskers. Thus, coke formation in multiple layers may start as soon as there is monolayer coke available, and the completion of the equilibrium monolayer is not a prerequisite for multiple-layer coke growth. In any case, the rate of formation of monolayer coke is proportional to the fraction of bare sites on the catalyst surface, whereas the rate of formation of multiple-layer coke is proportional to the fraction of sites covered on the first layer. (Nam and Kittrell (*8*); Corella and Monzón (*9*)). Thus, we can write

$$\frac{dC_m}{dt} = C_{max}\,\psi_m\left(1 - \frac{C_m}{C_{max}}\right)^h \tag{2}$$

$$\frac{dC_M}{dt} = \psi_M C_m, \tag{3}$$

where

$$C_{max} = \frac{M_c L}{h}. \tag{4}$$

In the above equations h is the kinetic order of the coking reaction, which is related to the number of sites involved in the controlling step of the deactivation reaction, and ψ_m and ψ_M are, respectively, the monolayer and multiple layer coking functions. Both ψ_m and ψ_M are in general functions of temperature and of the partial pressures of reactants and/or products. For a differential reactor (which is the case considered in this work), the effect of the partial pressures would be mitigated and thus the main dependence of ψ_m and ψ_M would be on temperature. Accordingly, Arrhenius-type parameters can be calculated for ψ_m and ψ_M. The total rate of coke formation is given by the sum of the contributions of Eqs. (2) and (3). It should be noted that the model allows the discrimination of the coke in a monolayer and in multiple layers for any reaction time. This is important, since monolayer coke directly eliminates active sites, while multiple-layer coke can do this only through pore blockage, which is not considered in this work.

ψ_m and ψ_M are obtained as:

$$\psi_M = A_M^0 \exp\left[-\frac{E_M}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{5a}$$

$$\psi_m = A_m^0 \exp\left[-\frac{E_m}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right], \tag{5b}$$

where T_m is the reparametrization temperature employed (833 K).

Given the usual definition of activity for the main reaction, we can write (9)

$$a = \frac{r_1}{r_0} = \left(1 - \frac{C_m}{C_{max}}\right)^m. \tag{6}$$

From the above equations (2), (3), and (6), we can obtain upon integration the coke–time and activity–coke relationships. Thus, for $h = 1$ we obtain:

Coke–time:

$$C = C_{max}\frac{\psi_m - \psi_M}{\psi_m}[1 - \exp(-\psi_m t)] + C_{max}\psi_M t; \tag{7}$$

Activity–coke:

$$C = C_{max}\frac{\psi_m - \psi_M}{\psi_m}(1 - a^{1/m}) - C_{max}\frac{\psi_M}{m\psi_m}\ln a; \tag{8}$$

Coking rate vs time:

$$r_c = \frac{dC}{dt} = C_{max}(\psi_m - \psi_M)\exp(-\psi_m t) + C_{max}\psi_M; \tag{9}$$

and for $h = 2$:

Coke–time:

$$C = C_{max}\left(1 - \frac{1}{1 + 2\psi_m t}\right) + 2C_{max}\psi_M t - C_{max}\frac{\psi_M}{\psi_m}\ln(1 + 2\psi_m t); \tag{10}$$

Activity–coke:

$$C = C_{max}(1 - a^{1/m}) - C_{max}\frac{\psi_M}{\psi_m}(1 - a^{-1/m}) + C_{max}\frac{\psi_m}{2\psi_M}\ln a; \tag{11}$$

Coking rate vs time:

$$r_c = dC/dt = C_{max}\psi_m/(1 + 2\psi_m t)^2 + C_{max}\psi_M - \frac{C_{max}\psi_M}{(1 + 2\psi_m t)}. \tag{12}$$

In the above equations C_{max} represents the maximum surface coverage attainable under a given set of operation conditions (amount of coke deposited directly on the catalyst surface at time equal to infinity). From the above equations (9) and (12), it is clear that the initial coking rate can be obtained as the product of $C_{\max}$ and ψ_{m}.

EXPERIMENTAL

The experiments were carried out in a thermogravimetric unit (C.I. Electronics) which was used under differential reactor conditions. Weight data were automatically collected, averaged over a certain time interval (usually 15 s) and sent to a personal computer for storage and analysis (as is shown in Fig. 1).

A commercial Cr_2O_3/Al_2O_3 catalyst (Harshaw) was used for the dehydrogenation of n-butene. The catalyst had 19 wt% Cr_2O_3, with a BET area of 50 m^2/g and a pore volume of approximately 0.28 cm^3/g. The original 4-mm-diameter cylindrical pellets were crushed to an appropriate size.

Blank experiments were carried out to ensure that the contribution of the stainless-steel gauze basket to both the main and the coking reactions was negligible. It was found that, after several coking/regeneration cycles in the balance, the contribution from the basket would become significant. Therefore a new basket was used in each of the experiments performed. Previous experiments were also carried out to ensure the absence of internal and external diffusion resistances. As a result, a particle size between 250 and 630 μm and a total gas flow rate of 750 standard cm^3/min were selected.

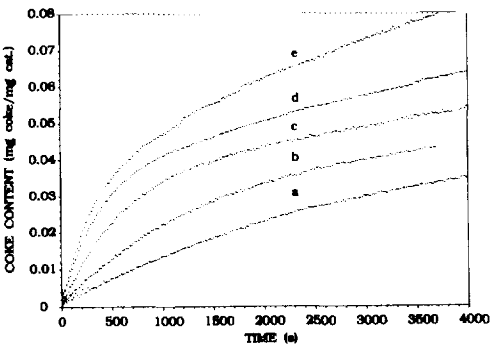

FIG. 1. Coke deposited on the catalyst versus time at several temperatures. Key: (a) 793 K; (b) 813 K; (c) 833 K, (d) 853 K, and (e) 863 K.

The feed stream contained 50% of 1-butene, and variable proportions of nitrogen and hydrogen. The flows were automatically regulated by means of mass flow controllers (Brooks). A supplementary flow rate measurement was provided at the reactor exit to check total flowrates. The same mass of catalyst (202 mg) was used in all the experiments performed.

Experiments were carried out in an isothermal mode, at temperatures between 793 and 873 K. In each experiment the catalyst sample was brought up to the reaction temperature in a nitrogen stream. The reacting mixture was then introduced using a four-way valve, and the exit gases were sampled for GC analysis at regular intervals. The main reaction products were *cis*- and *trans*-2-butene, 1,3-butadiene, and hydrogen, although small amounts of ethane, ethylene, and butane were also detected. Since weight data were also collected simultaneously, the activities for coking and for the main reaction could be related to the coke content of the catalyst at any given time. A recent example of this type of approach is the work by Acharya *et al.* (*10*).

RESULTS AND DISCUSSION

The change of the coke content of the catalyst is represented in Fig. 1 for different temperatures. It can be seen that the rate of coking increases strongly with temperature. In fact, an Arrhenius plot of the initial coking rate at the five temperatures gives a good fit ($r = 0.9954$). Also, the figure shows that the rate of coking decreases markedly as the catalyst becomes coked. Thus, the coking reaction deactivates itself, although a certain level of coking activity seems to be retained for long times, as will be shown later.

As the coke content increases, the activity of the catalyst for the main reaction de-

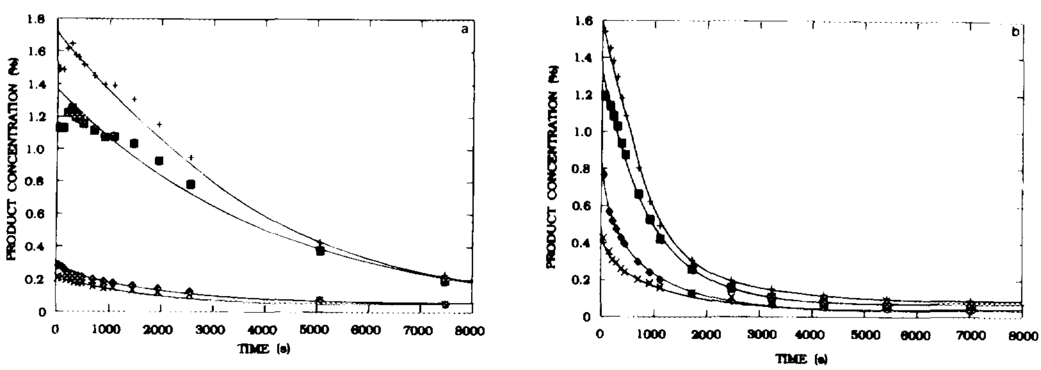

FIG. 2. (a) Product concentration versus time at 793 K. (b) Product concentration versus time at 833 K. Key: (♦) hydrogen, (×) 1,3 butadiene, (+) *trans*-2-Butene, and (■) *cis*-2-butene.

creases. Figure 2 shows the evolution of the main reaction products with time at 793 (a) and 833 K (b). At other temperatures similar trends were observed. It can be seen that, although the temperature has a relatively small effect upon the initial rates of production of butene isomers, the concentration of butadiene (the desired product) and hydrogen change considerably with temperature. For any of these products, however, a decrease in their concentration can be observed with time on stream, due to coke build-up on the catalyst. The decrease is steeper at 873 K owing to the faster coke formation at this temperature.

The concentrations of butadiene and hydrogen at the reactor exit are represented as a function of coke concentration at two different temperatures in Fig. 3. It is interesting to note that the hydrogen concentration is initially higher than the butadiene concentration, and that this situation continues until a coke concentration of about 4–4.5% is reached, when the butadiene and hydrogen production rates are approximately the same. This can be explained by the high initial rate of coke production, which implies a considerable evolution of hydrogen. The small amounts of ethane and ethylene detected would also contribute towards hydrogen production, especially in early stages of the process, in which the catalyst shows some cracking activity.

The coke versus time data given in Fig. 1 have been fitted with the model described earlier. The parameter values obtained for $h = 1$ and $h = 2$ are given in Table 1. The MMCGM gives an excellent multivariable fit of the coke versus time data at the different temperatures investigated. The table also shows that although the parameters are defined with high precision in both cases, the fitting obtained for $h = 2$ is better. Thus, the results would support the findings of Dumez and Froment (*3*) regarding the number of sites involved in the deactivation reaction. The narrow range of variation obtained in this work for the kinetic parameters is a consequence of the large number

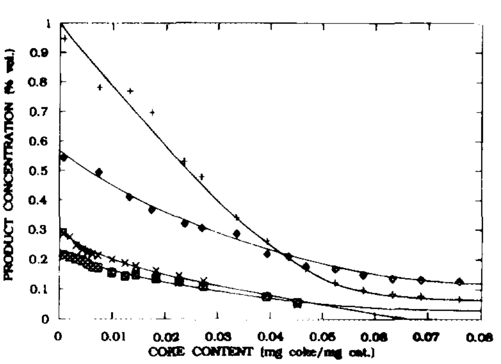

FIG. 3. Butadiene and hydrogen concentration vs. coke concentration at 793 K and 833 K. Key: (+) hydrogen at 833 K; (♦) 1,3 butadiene at 833 K, (×) hydrogen at 793 K, and (■) 1,3 butadiene at 793 K.

TABLE 1

Parameter Values Obtained from the Fit of the Coke versus Time Data with the MMCGM Model

Parameter	Value	Standard error	*t*-Test
	$h = 1$		
$C_{\max}$ (mg coke/mg cat.)	0.045	$\pm 0.293 \times 10^{-4}$	1527.29
A^0_{m} (s^{-1})	$0.112 \cdot 10^{-2}$	$\pm 0.446 \times 10^{-5}$	251.73
$E_{\mathrm{a,m}}$ (kJ/mol)	158	± 0.70	226.81
A^0_{M} (s^{-1})	$0.649 \cdot 10^{-4}$	$\pm 0.536 \times 10^{-6}$	121.09
$E_{\mathrm{a,M}}$ (kJ/mol)	183	± 1.32	139.02
S.S.R.	$2.91 \cdot 10^{-3}$		
	$h = 2$		
$C_{\max}$ (mg coke/mg cat.)	0.062	$\pm 0.330 \times 10^{-4}$	1874.66
A^0_{m} (s^{-1})	$0.486 \cdot 10^{-3}$	$\pm 0.202 \times 10^{-5}$	240.13
$E_{\mathrm{a,m}}$ (kJ/mol)	155	± 0.50	308.52
A^0_{M} (s^{-1})	$0.151 \cdot 10^{-4}$	$\pm 0.179 \times 10^{-6}$	84.58
$E_{\mathrm{a,M}}$ (kJ/mol)	210	± 2.16	96.98
S.S.R.	$1.93 \cdot 10^{-3}$		

of experimental points (several hundred) taken during any experiment, which increases the reliability of the statistics obtained.

The activation energies given in Table 1 ($h = 2$) are, respectively, 155.4 and 210 kJ/mol for monolayer and multiple-layer coking. The activation energy for monolayer coking is lower, which could be expected for coke which forms directly on the catalyst surface. The comparison of these activation energy values to those in the literature is difficult in view of the large spread of the reported values. However, values in the region of 125 and 165 kJ/mol have often been reported for coking during dehydrogenation reactions (e.g., Pal *et al.* (*11*); Dumez and Froment (*3*)), and thus the above value of activation energy for monolayer coking would fit well in that range.

According to the model, most of the coke is deposited directly on the surface during the early stages of coking. Then, multilayer deposition occurs, and the fraction of the coke deposited as coke in multiple layers increases. Figure 4 shows the predicted coke distributed at 853 K. It can be observed that in this case after the initial stage the amount of monolayer coke increases very slowly. In fact, at 5000 s the calculated amount of monolayer coke is already 0.0562 mg/mg of catalyst, which represents approximately 91% of the asymptotic maximum concentration of monolayer coke $C_{\max}$, given in Table 1.

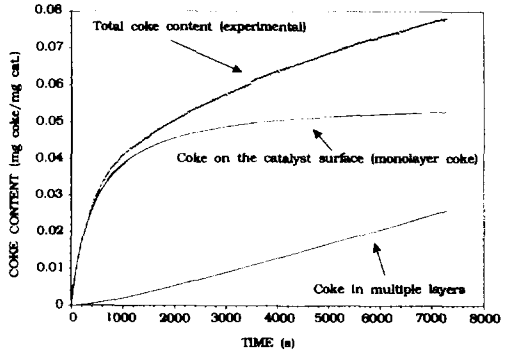

FIG. 4. Variation with time of coke distribution at 853 K.

The physical meaning of the model parameters given in Table 1 for $h = 2$ is also consistent with the experimental observations, since the model predicts a constant activity (which corresponds to multiple-layer coke growth), when the maximum coke concentration in a monolayer is reached. This can be observed in Fig. 5 from experimental data at 853 K. In this figure, the measured coking activity (defined as the rate of coking at a given time

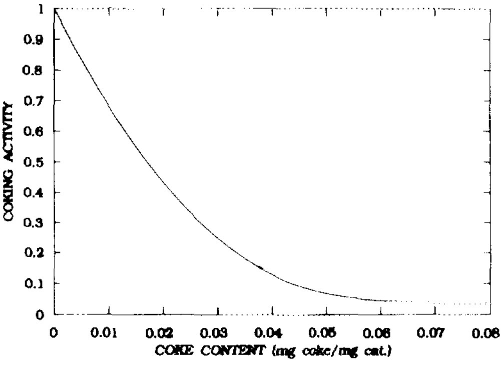

FIG. 5. Theoretical coking activity versus coke concentration at 853 K.

divided by the initial rate of coking) is represented as a function of the total coke content of the catalyst. It can be seen that a plateau in the coking activity (corresponding to about 7.5% of the initial coking rate) appears for a total concentration of about 0.065 mg coke/mg of catalyst. At this point the model predicts (Fig. 4) that the monolayer growth is virtually complete (96.6% of C_{max} has been reached), which is in agreement with the observed constant rate of coke growth. Although it is clear that the observed residual activity for coking will cease to be constant when the multilayer coke build-up reaches a level which causes significant pore blockage, this condition does not seem to be reached under the conditions investigated (up to 8% coke concentration by weight).

The examination of the parameters in Table 1 shows several interesting features. Thus, all the experiments at the different temperatures can be fitted using the same value of C_{max} ($h = 2$) within a narrow range: $0.062 \pm 0.33 \times 10^{-4}$ mg coke/mg catalyst. This indicates that the final coverage of the active surface would be the same for all the temperatures investigated. This, however, may be altered if the reaction atmosphere changes (e.g., if the hydrogen concentration increases). Another interesting feature is the higher activation energy found for the growth of coke in multiple layers. This means that an increase in the reaction temperature would favour the multilayer coke formation, and is consistent with the lower influence of the catalytic surface that would be expected for the formation of multilayer coke, compared to coke formation directly on the catalyst surface.

In their analysis of coking during butene dehydrogenation on a Cr_2O_3/Al_2O_3 catalyst, Marin *et al.* (*5*) used a value of 3.8×10^{-6} kmol sites/kg cat. as the concentration of active sites on the catalyst. This value was derived from literature data based on oxygen uptake for this catalyst. These authors used a model which described catalyst deactivation in terms of coverage of active sites and blockage of pores. The model contemplated instantaneous coke growth followed by growth of the coke at a finite rate. With the above value of concentration of active sites and the assumption of one site involved in both the main and the coking reactions, their model allowed them to calculate several coking parameters. Among these, a value of 1.196×10^4 kg coke/kmol coke was calculated as the molecular mass of coke. This value can be compared to the value of M_c which can be obtained from the results in this work. If we take the values for $h = 1$ in Table 1 (since Marin *et al.* (*5*) assume one single site in their model), and accept the value proposed for concentration of active sites (L), then from Eq. (4) it follows that M_c is equal to 1.176×10^4, which is in very good agreement with the value calculated by Marin *et al.* (*5*).

Relationship between Activity and Coke Content

The variation of the butadiene production rate with time differs widely at the different temperatures investigated, as shown in Fig. 2. However, if the activities are calculated as (r/r_0) and plotted against the coke concentration, a curve with relatively little spread is obtained. This is shown in Fig. 6. The curve also shows a tendency towards a residual activity, i.e., although the coke

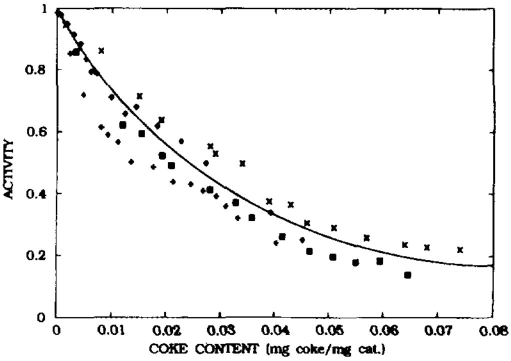

FIG. 6. Activity for butadiene production versus total coke content at several temperatures. Key: (◆) 793 K, (+) 813 K, (■) 833 K, and (×) 853 K.

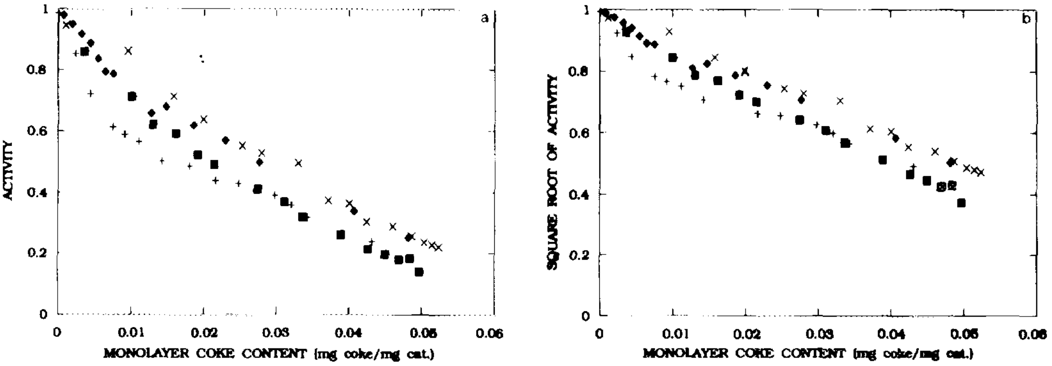

FIG. 7. (a) Activity for butadiene production versus monolayer coke content, at several temperatures. Key: (◆) 793 K, (+) 813 K, (■) 833 K, and (×) 853 K. (b) Square root of activity for butadiene production versus monolayer coke content at several temperatures. Key: (◆) 793 K, (+) 813 K, (■) 833 K, and (×) 853 K.

concentration is still increasing, the activity seems to tend asymptotically to a value which is different from zero.

If the coking behaviour of the system studied in this work is adequately described by the monolayer–multilayer coke growth model, the relationship between activity and coke content would be given by Eq. (6), i.e., the activity would decrease with the amount of coke deposited in the first layer, while coke deposition in multilayers would not affect the catalytic surface (and therefore the activity), as long as pore blockage does not take place.

From Eq. (6), if $m = 1$, the activity would decrease linearly with monolayer coverage, while if $m = 2$, a straight line would be obtained from the plot of the square root of the activity versus monolayer coke content. Both representations are shown in Figs. 7a and 7b, respectively. It can be seen that the behaviour of the kinetic data is considerably more consistent with the assumption of $m = 2$. This is also in agreement with the results of Dumez and Froment (*3*). Also, the Figure indicates that the amount of coke in a monolayer is a relevant parameter to quantify the deactivation in this system, since the data at the different temperatures in Fig. 7b display a linear behaviour.

Regarding the monolayer coke concentration, it has been stated above that the value obtained for $C_{\max}$ is the same in all the experiments performed with a 50% butene/nitrogen feed, in spite of the wide temperature range, from 793 to 873 K. $C_{\max}$ represents the asymptotic amount of coke deposited directly on the catalyst surface. It does not necessarily mean the amount of coke deposited at complete surface coverage. In fact, the existence of a residual activity after the monolayer coke growth has virtually stopped would indicate that the surface is not completely covered. Therefore, it seems interesting to investigate the variation of the monolayer coverage with the reaction conditions. In particular, in a dehydrogenation reaction the hydrogen produced would partially hinder coke formation as noted by Dumez and Froment (*3*). To verify this, coking experiments were carried out at 853 K with different levels of hydrogen in the feed. The corresponding coke concentration versus time curves are shown in Fig. 8. It can be observed that the presence of hydrogen effectively slows coke deposition. Thus, for instance, at 2500 s on stream, the amount of coke produced with a 50 : 30 : 20 butene/hydrogen/nitrogen feed is roughly half of that obtained with a 50% butene/hydrogen feed.

The monolayer–multilayer coke growth model was used to fit the data obtained with the different hydrogen concentrations. The

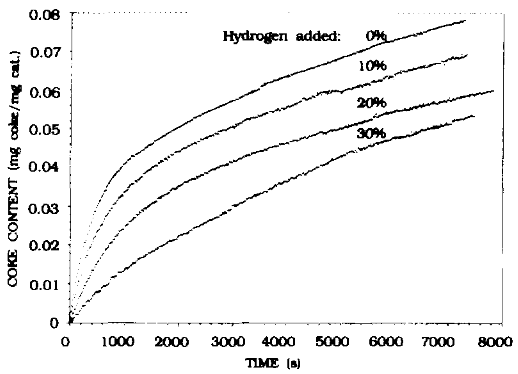

FIG. 8. Variation of coke deposition at 853 K for different values of hydrogen concentration in the feed.

results are given in Table 2 and in Figs. 9a to 9c. It can be observed that the maximum monolayer coke concentration reached in any experiment decreases as the hydrogen concentration increases. The initial coking rate and the monolayer coking function also decrease, while there is little effect of the hydrogen concentration on the multilayer coking function. This would indicate that hydrogen can interact with the surface preventing coke deposition to a certain extent, whereas the coke deposited in multiple layers away from the surface is not affected by hydrogen. This was confirmed by experiments in which a previously coked Cr_2O_3/Al_2O_3 sample was subjected to a feed containing 50% H_2 in N_2 with time at 853 K for 90 min. There was no measurable weight loss, which indicates that hydrogen was not able to gasify coke under these conditions.

CONCLUSIONS

The monolayer–multiple layer coke deposition model successfully describes the coking behaviour of a Cr_2O_3/Al_2O_3 catalyst during the dehydrogenation of 1-butene up to coke concentrations of 8% by weight.

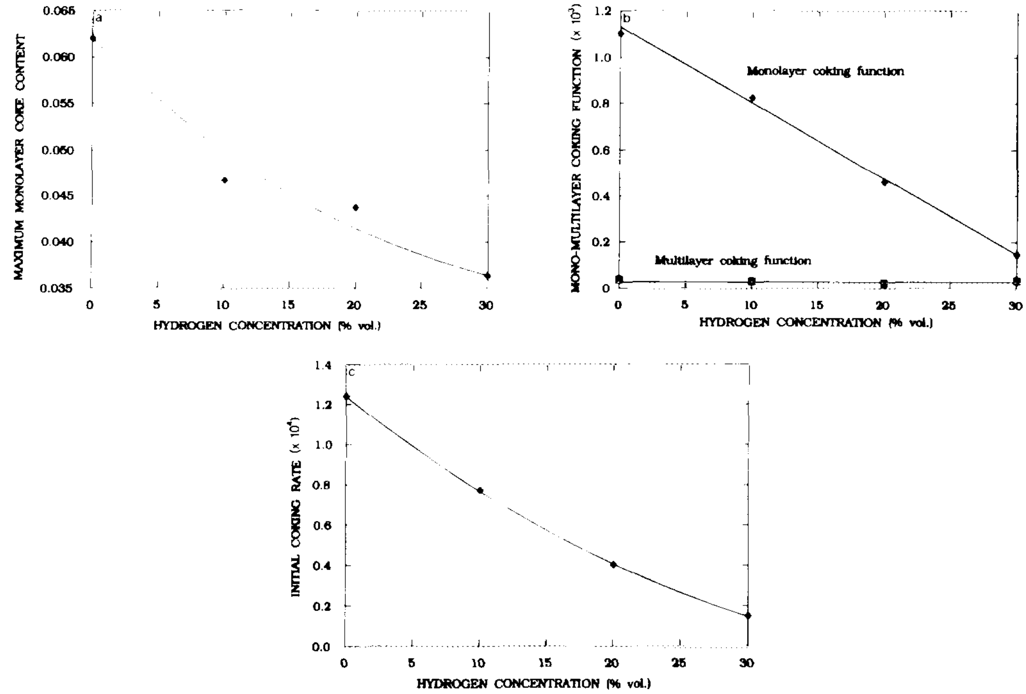

FIG. 9. (a) Maximum coke concentration in a monolayer versus hydrogen concentration in the feed. (b) Monolayer (ψ_m) and multilayer (ψ_M) coking functions versus hydrogen concentration in the feed. (c) Initial coking rate in a monolayer versus hydrogen concentration in the feed.

TABLE 2

Influence of the Hydrogen Content of the Feed on the Coking Parameters

% H_2	$\psi_m \times 10^3$ (s^{-1})	$\psi_M \times 10^4$ (s^{-1})	Initial coking rate (mg coke/s mg cat) × 10^4	C_{max} (mg coke/mg cat)
0	1.102	0.387	1.237	0.062
10	0.825	0.314	0.771	0.047
20	0.460	0.246	0.402	0.044
30	0.147	0.350	0.149	0.036

The best statistical fit was obtained by assuming two active sites taking part in the controlling steps of the main and of the deactivation reactions. This is coincident with previous results of other authors (*3*) for this system. It must also be noted that, regarding coke concentration, a good fit was also obtained with other assumptions of reaction orders.

The catalyst is active for butene dehydrogenation and isomerization. Both activities decline strongly with coking. There is a faster drop in the rate of hydrogen production than in that of butadiene production, due mainly to the fact that hydrogen is also produced during coking, which occurs at a high rate in the initial stages of the reaction.

Coke formation also undergoes deactivation as coking proceeds, until a constant coking activity is reached, which corresponds to the maximum coke concentration in a first layer C_{max} under a given set of reaction conditions.

The most relevant deactivation parameter appears to be the amount of coke deposited on the first layer on the catalytic surface, i.e., the surface coverage. Coking in multiple layers beyond the first one does not have a large effect upon the catalytic activity for butadiene production. A plot of the square root of activity at different reaction temperatures versus the coke concentration on the first layer gave a linear behaviour with relatively little spread. This indicates that the coke content in the first layer, rather than the total coke content, is the relevant deactivation parameter.

The value of C_{max} depends on the hydrogen partial pressure, decreasing for higher values of the latter. The monolayer function and the initial coking rate also decrease, while the multilayer function does not seem to be much affected. Thus, higher hydrogen concentration would imply higher residual activities at long reaction times.

APPENDIX: NOTATION

a	activity
A_m^0	Monolayer coking parameter calculated at the average temperature (833 K) (s^{-1})
A_M^0	Multilayer coking parameter calculated at the average temperature (833 K) (s^{-1})
C	Total coke content of the catalyst (mg coke/mg catalyst)
C_m	Monolayer coke content of the catalyst (mg coke/mg catalyst)
C_M	Multilayer coke content of the catalyst (mg coke/mg catalyst)
C_{max}	Equilibrium coke content on a monolayer (mg coke/mg catalyst)
$E_{a,m}$	Activation energy for monolayer coking (kJ/mol)
$E_{a,M}$	Activation energy for multilayer coking (kJ/mol)
h	Kinetic order of the coking reaction
L	Total concentration of active sites (mol active sites/g catalyst)
m	Kinetic order of the main reaction
M_c	Average molecular weight of coke (g coke/mol coke)
p_i	Partial pressure of species i (atm)

r_t	Rate of dehydrogenation at a given time (mol/s g catalyst)
r_0	Rate of dehydrogenation at $t = 0$ (mol/s g catalyst)
S.S.R.	Sum of squared residuals
t	Time (s)

Greek Symbols

ψ_m	Monolayer coking function (s^{-1})
ψ_M	Multilayer coking function (s^{-1})

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