JOURNAL OF CATALYSIS **159,** 313–322 (1996)
ARTICLE NO. 0093

Hydrogenation of Acetylene over $Ni/NiAl_2O_4$ Catalyst: Characterization, Coking, and Reaction Studies

J. A. Peña, J. Herguido, C. Guimon,[1] A. Monzón, and J. Santamaría[2]

Department of Chemical and Environmental Engineering, University of Zaragoza, 50009 Zaragoza, Spain

Received January 25, 1995; revised October 30, 1995; accepted November 24, 1995

$Ni/NiAl_2O_4$ catalyst has been used for the hydrogenation of acetylene to ethylene and ethane at temperatures between 423 and 493 K. The results presented include data on the physicochemical characterization of the catalyst, the evolution of its activity and selectivity and its coking behavior. These studies have been carried out on fresh catalyst and on catalyst samples subjected to an accelerated thermal aging process. The results show that the catalytic activity increases with time on stream (*activation period*), until a point is reached in which catalyst deactivation predominates (*deactivation period*). Catalyst aging in this system was found to reduce coke formation and to increase the hydrogenation activity observed.

INTRODUCTION

Ni-based catalysts are widely used in the chemical industry, mainly in hydrogenation, steam reforming, and methanation reactions. A major drawback with such catalysts is their tendency to form coke under the usual reaction conditions (1, 2). It has been known for some time (3) that coke deposits on Ni catalysts may be present in a variety of morphologies, i.e., amorphous, filamentary (whiskers), and graphitic. The effect of these coke deposits on the observed catalytic activity can be different, due to the fact that some morphologies do not directly block active sites. Thus, at least for some time, the fraction of coke present as whiskers allows the nickel crystallite to remain exposed to the reaction environment, thus retaining their activity. In addition, in some cases the process of whisker formation gives rise to fragmentation of large crystallites, therefore increasing the active surface area. This may produce an activation/deactivation behavior for the reaction of carbon formation, i.e., the rate of carbon formation initially increases until the active sites are deactivated at a greater rate than they are generated. This type of behavior has recently been reported for Ni-based catalysts (4, 5).

Most of the studies to date on Ni-based catalysts have been carried out using alumina or silica supports. However, there are other less studied supports such as $NiAl_2O_4$, which can provide a stabilizing effect, while maintaining a high degree of chemical inertia. If the metal is stabilized, its aggregation will be much slower, and lower coking rates can be expected, since it appears that carbon nucleation requires nickel ensembles of a certain size (6). Thus, for instance, Al-Ubaid and Wolf (7) found a much greater stability for Ni supported on the aluminate than on other supports, and Bhattacharyya and Chang (8) have recently proposed the use of a nickel aluminate spinel catalyst in order to reduce coke formation in CO_2 reforming of methane.

From the above, it seems interesting to study the behavior of a $Ni/NiAl_2O_4$ catalyst under strongly coke-forming conditions. Moreover $Ni/NiAl_2O_4$ catalysts are also interesting because of their versatility in terms of composition. This is due to the fact that the support includes the active metal, which makes it possible to tailor the pretreatment conditions (temperature and length of reduction) in order to obtain the desired amount of nonstoichiometric Ni in a partially inverted spinel catalyst (7, 9).

In this work, $Ni/NiAl_2O_4$ catalyst has been characterized and its performance in the hydrogenation of acetylene has been studied. This reaction was chosen as a test because of the facility of coke formation from acetylene in the presence of metallic Ni (3, 10, 11). Also, given the significant variations found in the kinetics of the coking and main reactions for fresh and aged catalysts in other catalytic systems (12), the behavior of $Ni/NiAl_2O_4$ catalyst after an accelerated aging process has also been studied and compared to that of the fresh catalyst.

EXPERIMENTAL

Catalyst Preparation

The $Ni/NiAl_2O_4$ catalyst used in this work was prepared in our laboratory by coprecipitating $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, following the method described by Al-Ubaid and Wolf (7). The resulting paste was dried overnight

---

[1] Laboratoire de Physico-Chimie Moléculaire, URA 474 du CNRS, University of Pau., 64000 Pau., France.

[2] To whom correspondence should be addressed.

0021-9517/96 $18.00

at 378 K and then calcined in air for 11 h, at temperatures between 1123 and 1173 K.

Catalyst Characterization

Temperature-programmed reduction (TPR) experiments were carried out in order to study the effect of several reduction pretreatments on the relative amounts of the different phases present in the catalyst. Whenever reduction pretreatments were carried out before TPR experiments, these were performed *in situ*, and consisted of heating at 10 K/min under a stream containing 70.6% H_2 in N_2 until the desired temperature was reached. The catalyst was maintained at this temperature until a total of 3 h of pretreatment was completed. The sample was then cooled down to the desired temperature under a nitrogen atmosphere before the start of the TPR experiment. TPR experiments were carried out using 5.66% H_2 in N_2, with a 10 K/min heating rate. The sample size was 200 mg, with catalyst particle diameters between 250 and 630 μm. The value of parameter P, defined as $\beta\ S_0/FC_0$ (13), was ca. 32.2 K, β being the heating rate, S_0 the initial amount of reducible species, and F and C_0 the total flow and the hydrogen concentration in the carrier gas, respectively. P gives an indication of the sensitivity of the analysis, which is higher as P decreases. In this case, a value of 32.2 was found to provide a sufficiently high resolution.

Some temperature-programmed oxidation (TPO) experiments were conducted in which the catalyst was partially regenerated by burning a fraction of the coke deposits. In these experiments, the catalyst was coked during reaction at 473 K until a coke loading near 30% by weight was reached. After coking, the temperature was brought up to 523 K and a gas stream containing 2% O_2 in N_2 was admitted into the system. The coke was burnt off under a temperature ramp from 523 to 623 K, and then the temperature was kept at 623 K until a certain amount of coke (usually 30% of the total coke deposited on the catalyst) was eliminated. The objective of keeping the temperature low was to burn only the most reactive coke (presumably the coke deposited directly in contact with the metal (14)) and to examine the effect of this partial regeneration on the coke deposition rate when coking was resumed.

The elementary analysis of fresh and aged catalyst samples was carried out in a Perkin–Elmer P-40 apparatus by plasma analysis (IPC). BET surface areas were determined using N_2/He mixtures in a Micromeritics Pulse Chemisorb 2700 apparatus. The catalyst was first pretreated as previously described, degassed in nitrogen at 250 K for 11 h, and then cooled to room temperature in flowing nitrogen.

Powder X-ray diffraction (XRD) patterns of the catalyst were obtained with a Rigaku/Max System diffractometer using Cu $K\alpha$ radiation. The patterns were recorded between 15° and 70° (2θ), using a scanning velocity of 0.02°/s.

X-ray photoelectron spectroscopy (XPS) studies were carried out at room temperature on a SSI spectrometer (Model 301), using Al$K\alpha$ radiation. The spectrometer was equipped with a high temperature reaction cell to carry out catalyst pretreatments. The samples were pretreated using analogous reduction procedures to those described above, and then transferred to the analysis chamber under an inert atmosphere. The sample was then turbopumped to a residual pressure of about 4×10^{-10} Torr. The adventitious C 1*s* line at a binding energy of 284.6 eV was used as an internal standard.

The catalyst surface was examined using a JEOL JSM 6400 scanning electron microscope. This allowed an assessment of the morphology of the coke deposits and of the extent of coke formation in whiskers, both on fresh catalysts and on catalyst samples subjected to an accelerated aging process.

Kinetic Experiments

The reaction studied was the hydrogenation of acetylene, carried out in a thermobalance unit (C.I. Electronics) acting as a differential reactor. The system was equipped with mass flow controllers for reactants and automatic temperature control. The sample was held in a stainless steel gauze basket, with a sieve opening of 125 μm. The catalyst sample was around 250 mg, with particle diameters between 250 and 500 μm. Weight data were automatically collected every 6 s with an accuracy of ± 0.001 mg, and sent to a personal computer for storage and analysis. In a typical run, more than 1200 data points relating coke weight, temperature, and time were collected. At the reactor exit, the gases could be analyzed by gas chromatography, which allowed simultaneous determination of the coke content of the catalyst and of the activities for the main and coking reactions.

Preliminary experiments were performed at the maximum temperature employed in order to ensure the absence of significant mass transfer resistances when the above particle diameter range and a total flow rate of 750 N cm^3/min were used. Also, in blank experiments it was found that the contributions of the stainless steel gauze basket to both the main and coking reactions could be neglected under the operating conditions used.

A typical kinetic experiment consisted of: (i) a drying stage from room temperature to 473 K, (ii) a reduction stage using a 3/1 H_2/N_2 stream under a 10 K/min temperature ramp up to 773 K, (iii) an isothermal period at this temperature until the 3 h reduction period was completed, as described above, (iv) adjustment of the temperature of the sample to reaction temperature under a N_2 stream and introduction of the feed. The reactor feed was a 60/25/15 $C_2H_2/N_2/H_2$ mass-flow controlled mixture. The reaction produced mainly C_2H_4, C_2H_6, and CH_4, which were analyzed by gas chromatography at regular intervals. Also, coke was produced in relatively large quantities, which could be continuously monitored by automatically collecting weight data. This system allowed simultaneous determination of the rates for the main and coking reactions, with an experimental setup similar to that used by Acharya and Hughes (15).

Catalyst Aging

In order to assess the magnitude of the changes introduced by thermal aging in the main and coking reactions, some experiments were also run after subjecting the catalyst to a process of accelerated aging, similar to that described in previous works (12, 16). It basically consisted of subjecting the catalyst to three reaction/regeneration cycles, using severe regeneration conditions in a separate 14 mm i.d., 300 mm long integral fixed bed reactor. Catalyst coking was carried out at 673 K for 30 min in this reactor, using the same reaction mixture as in the kinetic experiments. The regeneration was carried out at an initial temperature of 748 K, using a 33% O_2 in N_2 mixture. Under these conditions the water vapor produced and the high temperatures reached (up to 913 K) caused a rapid aging of the catalyst, giving rise to significant changes in its kinetic behavior as will be shown below. The aged catalyst particles were sampled from the exit zone of the reactor, where the highest temperatures were reached.

RESULTS AND DISCUSSION

Catalyst Characterization

BET analysis on freshly prepared catalyst samples after calcination yielded a specific surface area of 96.0 m^2/g, which was rather stable. Even after the accelerated aging process, the area obtained was only slightly lower, 89.2 m^2/g. The elemental analysis yielded a composition of 21.69% Ni by weight, which is well below the approximate 33% level required for the formation of a stoichiometric Ni spinel (7).

NiO interacts with Al_2O_3 at relatively low temperatures (673–723 K) to form nickel aluminate (9, 17). The amount of aluminate formed increases with temperature and time of calcination. In this work, the calcination temperature used is well above these values and therefore a significant amount of aluminate can be expected. Figure 1 shows the XRD patterns obtained for an unreduced or fresh catalyst (curve a), and for a catalyst subjected to a reduction treatment at temperatures up to 1173 K (curve b). It can be seen that both NiO and $NiAl_2O_4$ are present in the unreduced catalyst, while there is no significant amount of metallic Ni. However, after the reduction treatment is carried out (curve b), the $NiAl_2O_4$ phase has almost completely disappeared while metallic Ni is clearly present. Some NiO can also be observed in this case, possibly due to the room temperature passivation of the catalyst surface after the reduction treatment.

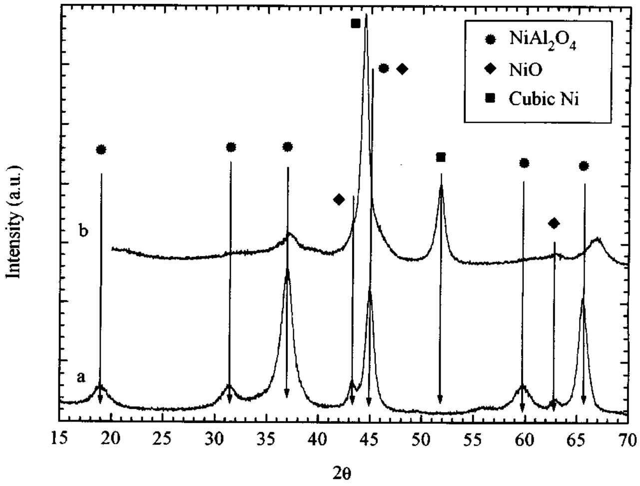

FIG. 1. XRD analysis showing the different phases present in the catalyst. (a) Fresh catalyst, (b) catalyst reduced under a 5.66% H_2/N_2 mixture, using a 10 K/min temperature ramp from room temperature to 1173 K.

The TPR experiments confirmed the above results. Thus, in Fig. 2 it can be observed that the unreduced catalyst presents a peak at approximately 1018 K, which can be attributed to the reduction of the nickel aluminate. A second peak, at approximately 778 K, corresponds to nickel oxides which are not completely integrated in the spinel structure, but have a certain degree of interaction with the support (18). The reduction treatments would be expected to cause a decrease in the area of the aluminate peak and the disappearance of the peak at 778 K. This can be observed in Fig. 2, where, even after the lowest temperature reduction treatment (773 K), the 778 K peak has disappeared. Also, after reduction at 773 and 873 K, respectively, the

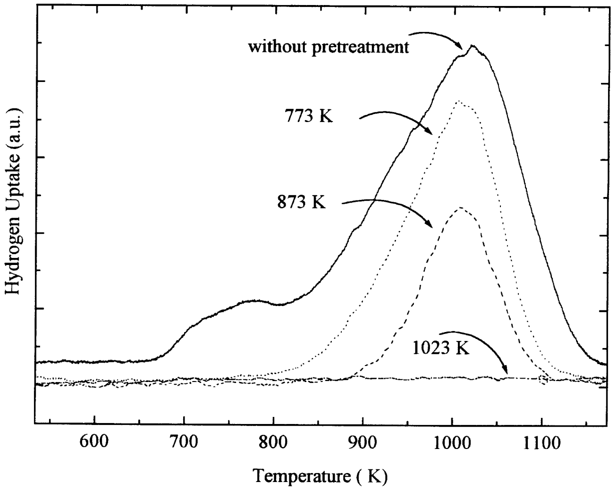

FIG. 2. Temperature programmed reduction of a Ni/NiAl$_2$O$_4$ catalyst without previous reduction and after reduction treatments of different intensity.

TABLE 1

XPS Results for Ni/NiAl$_2$O$_4$ Catalyst without Pretreatment and after Reduction Pretreatments at 773 and 873 K

	Binding energy (eV)			
	O (1s)	Al (2p)	Ni (2$p_{3/2}$) (%reduction)	Ni/Al
Without pretreatment	530.50	74.00	855.2 (100%)	0.28
$T_{\mathrm{reduction}} = 773$ K	531.00	74.60	851.6 (14%) 855.2 (86%)	0.24
$T_{\mathrm{reduction}} = 873$ K	530.80	74.40	851.7 (26%) 855.2 (74%)	0.17

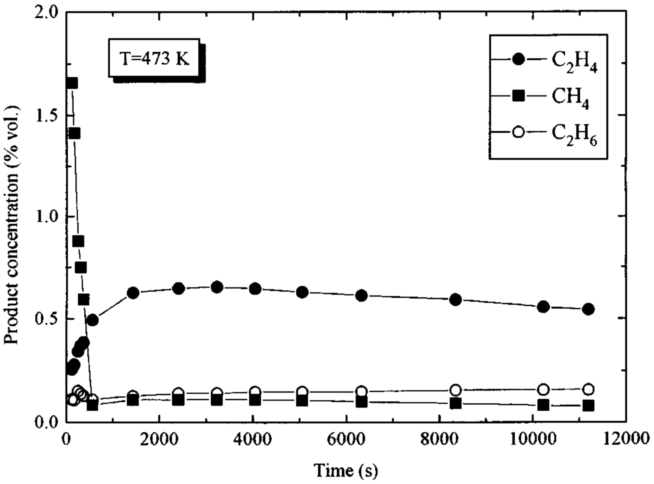

FIG. 3. Variation of the product distribution with time on stream at 473 K.

area of the peak at 1018 K is, respectively, 68 and 32% of the area in the curve corresponding to the unreduced catalyst, and with a reduction at 1023 K the peak completely disappears.

Table 1 shows the results obtained by XPS analysis of the unreduced catalyst as well as of those reduced at 773 and 873 K, respectively. It can be observed that the atomic Ni/Al ratio in the unreduced catalyst (0.28) decreases as the catalyst is reduced at higher temperatures, down to a level of 0.17 after a reduction treatment at 873 K. On the other hand, the increase in the signal around 851 eV in Table 1 also shows that the total amount of Ni^0 present on the surface increases. This fact suggests a sintering process of the nickel at the surface under a reducing atmosphere, which would explain the observed decrease in exposed surface nickel, and the increased proportion of Ni^0. These results are in line with the data reported by Bartholomew *et al.* (19), who found that after subjecting a Ni/NiAl$_2$O$_4$ catalyst to a H$_2$ atmosphere at 1123 K for 50 h there was a significant increase in the Ni crystallite size due to sintering, and at the same time a large increase in the H$_2$ uptake, which these authors attributed to the ability of the catalyst to create new nickel crystallites (Ni^0) via reduction of the support.

Kinetic Experiments

The variation of the activity and selectivity of the catalyst with reaction time was investigated in a series of reaction experiments at different temperatures. Figure 3 shows the variation with time of the concentration of CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ at the reactor exit at 473 K. A high methane concentration can be observed initially, followed by a rapid decrease to a very low value. On the other hand, the concentration of C$_2$H$_4$ starts at a very low value and increases with reaction time until a maximum value is reached at about 3200 s. From this time on, the concentration of C$_2$H$_4$ slowly decreases, while the concentration of C$_2$H$_6$ shows a slow monotonic increase after a few hundred seconds on stream. In addition, coke was formed rapidly on the catalyst surface at this reaction temperature, reaching levels around 10% by weight (mg coke/mg cat. × 100) in 5 min.

One of the factors that may contribute to the above behavior is the strong variation in the selectivity to gaseous products that takes place with time on stream. This can be seen in Fig. 4, where the total hydrogenation rate (i.e, the rate of C$_2$H$_4$ production plus twice the rate of C$_2$H$_6$ production) and the coking rate are represented together. Initially the rate of coke formation increases, reaching its maximum at about 180 s. During this stage, most of the carbon present in the converted acetylene goes to coke and methane, which can be considered as a by-product of coke formation in this case. The coke formation and the methane production rates decrease abruptly after the abovementioned maximum, reaching a relatively stable value at a low level after about 500–1000 s in both cases. The decrease in the coke

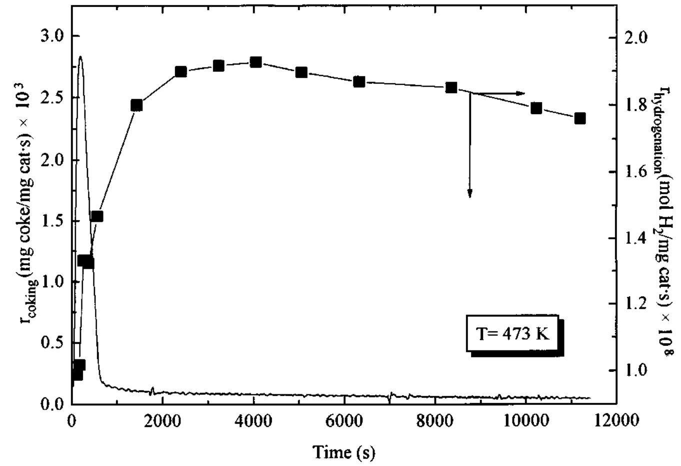

FIG. 4. Total hydrogenation rate and coking rate versus time on stream, at 473 K.

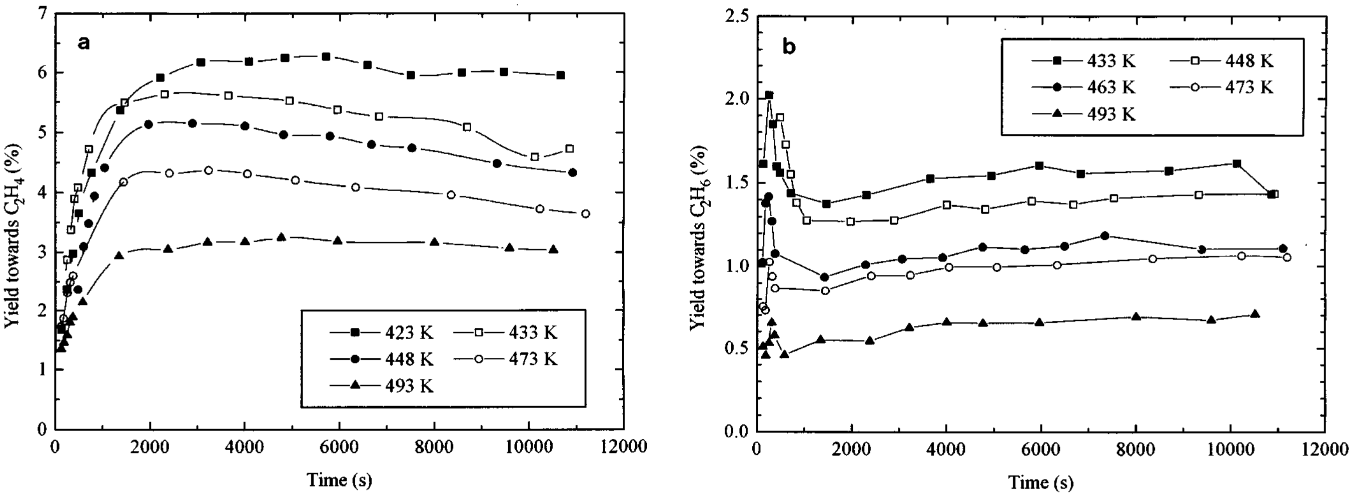

FIG. 5. Variation of the yield to ethylene (a) and ethane (b) with time at different temperatures.

formation rate increases the amount of acetylene available to give hydrogenation products, and therefore contributes to the observed increase in the yields to C_2H_4 and C_2H_6 observed in Fig. 3.

However, the results in Fig. 4 also indicate that the decrease in the coke formation rate cannot be the only reason to explain the increase in ethylene production. Thus, it can be observed that the hydrogenation rate increases significantly for a long time (about 3000 s) after the coke formation rate has decreased to a low level. This was a typical result of many reaction experiments carried out at different temperatures. The reason for the increase in the hydrogenation activity is very probably related to the continued formation of new active sites in the Ni/NiAl$_2$O$_4$ catalyst, in a similar fashion to the activation processes reported by McAllister and Wolf (4, 5) for a Ni-based catalyst. In the case studied in this work, however, the activation process appeared to be more intense due to the ability of the support to provide supplementary nickel.

Figure 5 shows the yield to ethylene (Fig. 5a) and ethane (Fig. 5b), defined as moles of a given product divided by moles of acetylene in the feed, at different temperatures. The same trend shown in Fig. 3 is repeated in Fig. 5a at other temperatures. It can be seen that the ethylene yield increases, reaches a maximum, and then slowly decreases. Also, as the temperature is increased, the ethylene yield decreases. Since the reaction products are far from the equilibrium concentration, the main reason for this behavior is the increased rate of coke formation that occurs at higher temperatures. Thus, for instance, after 4000 s of reaction at 493 K the coke content of the catalyst is 0.285 mg coke/ mg cat., while at 423 K the coke content is much lower 0.103 mg coke/mg cat. The faster coke coverage at the higher temperatures means that less active area is available, and explains the lower hydrogenation rates observed.

The results in Fig. 5b show an interesting behavior, with a fast initial increase in the rate of ethane production followed by a maximum and a sharp decrease to a lower level. In Fig. 4, it was shown that the coking and total hydrogenation rates behave very differently, with reaction rate maxima separated by long reaction periods. This suggests that different types of sites may be involved in the two types of reaction. Nevertheless, it must be noted that ethylene production is the reaction that accounts for most of the hydrogenation rate observed. Unlike ethylene production, the trend displayed by the ethane production rate is very similar to that obtained for the coking rate, with both rate maxima coincident in time. Thus, the most active hydrogenation sites that give rise to nearly all of the initial ethane production also seem to bear the main responsibility in promoting the fast initial coke formation. As a consequence, after the initial activation stage these sites undergo a rapid drop in activity to a lower level, while less strong hydrogenation sites are able to give increasing ethylene yields for at least 2000 s of reaction time.

Comparison of Fresh and Aged Catalysts

The XRD analysis of the aged catalyst (not shown) was coincident with that of the fresh catalyst (shown in curve a of Fig. 1). However, TPR analysis did show some differences, which are displayed in Fig. 6. The high-temperature peak (1018 K in the fresh catalyst) has a lower area and is slightly displaced toward higher temperatures in the aged catalyst. Also, the shoulder that appears at about 770 K is smaller in the aged catalyst. This means that the amount of nickel present in the spinel structure (high-temperature peak) and in interacting but not completely integrated nickel oxides (shoulder) has decreased. On the other hand, a new peak appears at a lower temperature (561 K), which is similar

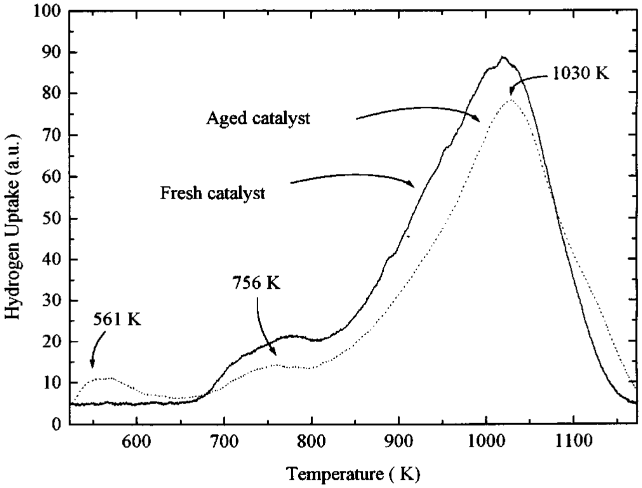

FIG. 6. Comparison of the temperature programmed reduction patterns of fresh and aged Ni/$NiAl_2O_4$ catalysts.

to the reduction temperature of unsupported nickel oxide (see, for instance, Ref. (20)).

Figure 7 compares the coking behavior of fresh and aged catalysts at two different temperatures. It can be observed that there are two different zones in each of the curves in the graph, the first one corresponding to a very fast coke formation, followed by a second zone of much slower coke growth. During this second period, the coke deposits on the catalyst grow at a quasiconstant rate, which is similar for all the temperatures studied, although different for fresh and aged catalysts. The slopes of the coke growth lines corresponding to the fast and slow coking periods are higher for the fresh catalyst, in which the transition between both periods is much sharper. As a consequence, at any temperature, the coke content is always considerably higher on the fresh catalyst. Thus, for instance, Fig. 7 shows that after 6000 s at 473 K the coke content on the fresh catalyst is 0.244 mg of coke per mg catalyst, while on the aged catalyst it is only 0.151 mg of coke per mg of catalyst.

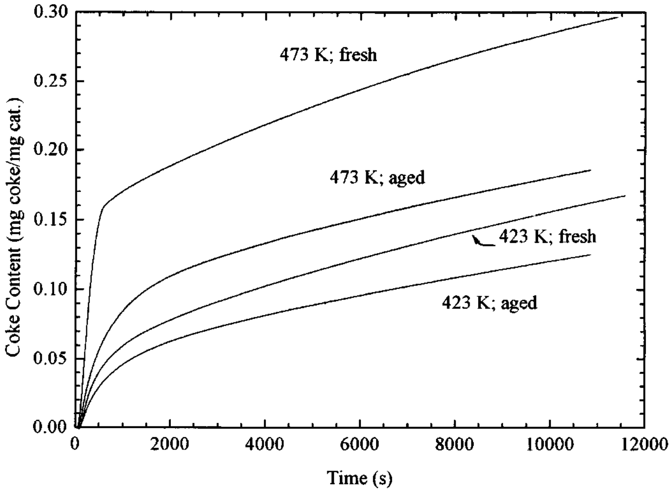

FIG. 7. Variation with time of the coke content at two different temperatures, for fresh and aged catalysts.

The examination of the catalyst surface by scanning electron microscopy (SEM) showed the presence of coke with two morphologies, namely coke in a two-dimensional layer or mantle, covering part of the catalyst surface, and coke in whiskers or filaments. The existence of coke in whiskers, which was expected for Ni catalysts under the conditions employed, is demonstrated in Fig. 8, where the characteristic corkscrew structure of coke whiskers can be observed. However, it may also be noted that, while carbon filaments do exist in this case, they are relatively scarce compared to other SEM studies in the literature of coke formation on nickel catalysts (e.g., 5, 21, 22). Given the large amounts of coke deposited, this result would indicate the dominance of two-dimensional, mantle coke in the system studied. Coke whiskers were even scarcer and very often absent from SEM micrographs of aged catalysts (not shown).

The comparison between the area of the two curves in Fig. 6 shows that the total amount of reducible nickel in the aged catalyst has decreased significantly. This is probably a consequence of the cyclic aging method, which may involve the loss of a significant proportion of the nickel crystallites detached from the surface by the carbon filaments when these are burnt. The nickel crystallites that are not lost by entrainment in the gas stream may return to the catalyst surface but in this case they would be expected to present a minimal interaction with the support, and to give TPR peaks in the same range observed for the low-temperature peak displayed by the aged catalyst. Also, the loss of Ni crystallites during aging would also mean a decrease in the number of sites capable of filament formation, which is consistent with the absence of whiskers in many of the micrographs corresponding to aged catalysts.

The aging process also gave rise to significant changes in the kinetic behavior of the catalysts, as shown in Fig. 9, where the total hydrogenation rate is plotted versus time at three different temperatures for fresh and aged catalysts. It can be seen that, at any temperature, the total hydrogenation rate is considerably higher for the aged catalyst. Since the aged catalyst produces coke at a much lower rate, the higher hydrogenation activities obtained with the aged catalyst could in principle be attributed to the differences in the coking kinetics induced by the aging process. However, significant differences in catalyst behavior persist, even when both catalysts are compared at the same coke level, as can be seen in Fig. 10, which plots the yield to ethylene versus coke loading for fresh and aged catalyst, at two different temperatures. It can be observed that, in all cases, the yield to ethylene increases simultaneously with the coke content up to a certain coke loading. This stage, termed

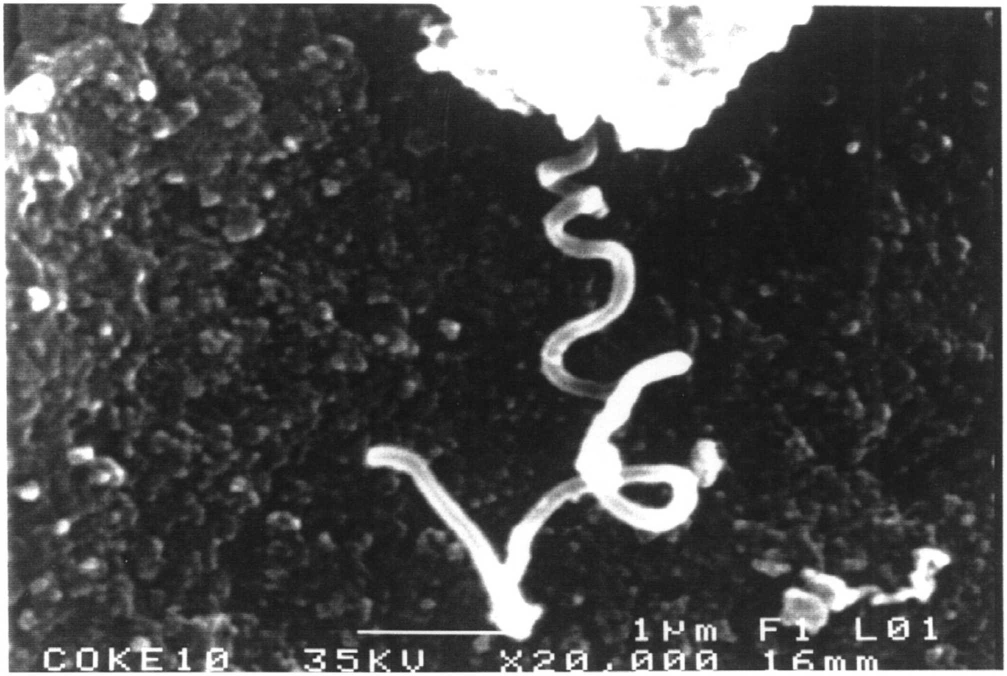

FIG. 8. SEM micrograph of a Ni/NiAl$_2$O$_4$ catalyst coked at 473 K.

the activation period, corresponds to the predominance of the generation of active sites on the catalyst surface, which initially overcomes the influence of catalyst deactivation by coke and sintering. During this period, the yield obtained at any temperature for a given coke content is always higher for the aged catalyst. Since different types of coke are possible with Ni-based catalysts, it could be speculated that the aging process gives rise to a less deactivating type of coke, such as coke in whiskers. In this case, for a given coke level, a higher proportion of deactivating coke would be present on the fresh catalyst. However, as has been shown above, the aged catalyst forms in fact less coke in whiskers than the fresh catalyst. Also, Fig. 10 shows that, after the maximum, both the fresh and aged catalysts tend to conform to the same curve of yield versus coke content, which indicates a similar deactivating effect of coke.

The explanation for the higher activity of aged catalysts is more likely to be related to the difference in the coking rate with respect to the fresh catalyst. Whether it takes place through the extraction of Ni from the support or through

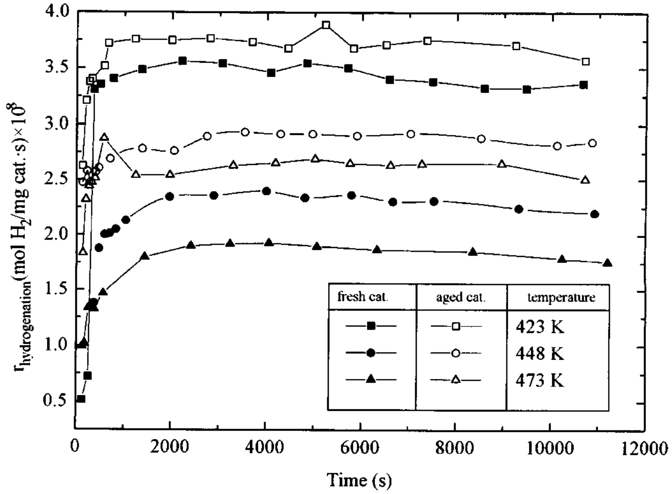

FIG. 9. Total hydrogenation rates for fresh and aged catalysts at three different temperatures.

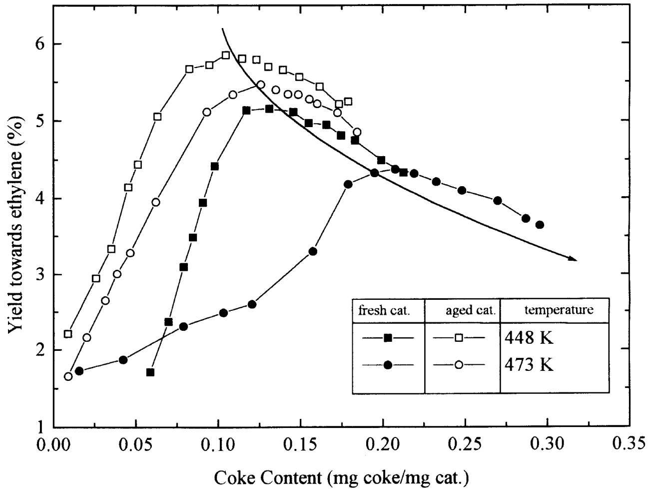

FIG. 10. Ethylene yield versus coke content for fresh and aged catalysts at two different temperatures.

the fragmentation of nickel crystallites or both, the activation process is necessarily of a limited scope. Initially, the activation proceeds at a high rate in easily accessible sites, but as these are depleted, the rate of generation of active surface sites accordingly decreases. At the same time, the deactivation process by coking (and possibly by sintering) is also taking place on the catalyst. When the activation and deactivation rates become equal, the net active site generation rate is zero, and the activity maximum is reached. From this point on, the total number of active sites (and therefore the activity) decrease.

Obviously, if a fast coverage of active sites takes place during the activation period, a lower number of active sites will be present when the maximum activity is reached (23). Although the time scale for the data in Fig. 10 is not shown, it is clear that the aged catalyst needs a longer time to attain a given coke level. Thus, for instance, at 473 K the aged catalyst reaches a 0.1 mg coke/mg cat. level in 1540 s, while the fresh catalyst needs a considerably shorter period (303 s). Hence, if comparable activation rates were assumed, a higher net site generation rate during the activation period would be obtained for the aged catalyst, which explains the higher activities observed.

Partial (Selective) Regeneration of the Catalyst

The above description of the observed coking behavior is consistent with the following scenario. Morphologically, at least two types of coke are present. One of them, termed two-dimensional or mantle coke, is formed directly on nickel sites firmly attached to the surface, while the other is able to separate crystallites from the surface and give rise to coke in whiskers. Both types of coke are formed simultaneously at the beginning, and both are likely to be affected by the activation process. As a consequence, the coking rate initially grows, following the increase in the total number of sites. However, since there is a finite number of sites that are available for activation, the fast formation of coke on the surface quickly leads to the coverage of most of the sites there, giving rise to the sharp decrease of the coking rates observed in Fig. 4. After most of the coking sites on the surface are covered, the residual coking activity is mainly provided by the whiskers, in which coking takes place without an associated loss of activity. This explains the "constant" coking rate zone as a period of filament growth. Finally, it should be noticed that the rate is slowly decreasing in the constant coking rate zone, i.e., the lines in this zone are slightly curved, with a gradually decreasing slope. This is in agreement with a progressive encapsulation of some of the crystallites by carbon, which puts an end to filament growth (10).

According to this scenario, the coke deposited directly on the surface would have a strong deactivating effect, while the coke deposited in whiskers would only cause a slow deactivation, as nickel crystallites become encapsulated by carbon. This explains why approximately stable hydrogenation rates are obtained (Fig. 9), in spite of considerable increases in the amount of coke deposited on the catalyst during the constant coking rate period, in which coke growth has been attributed to whiskers. To give further confirmation to this hypothesis a regeneration experiment was carried out under mild conditions, with the aim of selectively burning the coke deposited on filaments, while leaving largely intact the coke on the surface. This was based on previous experimental results (4, 10, 24), which showed the high reactivity of the carbon filaments toward gasification, a process catalyzed by the metal crystallite at the top of the filament, in a similar but reverse fashion to filament formation. In our case, preliminary TPO experiments (not shown) confirmed the existence of at least two zones of coke combustion. The most reactive coke was burnt in the first or low-temperature zone, exhibiting a substantial reaction rate at temperatures as low as 573 K, and a local maximum in the combustion rate at about 663 K.

For the selective regeneration experiments, the catalyst was coked in the thermobalance at 473 K under the usual reaction conditions until a coke loading of approximately 0.30 mg/mg of catalyst was achieved. This is shown in curve A of Fig. 11. The catalyst was then heated to 523 K under nitrogen, and at this temperature 2% of oxygen was introduced. A 1 K/min temperature ramp was then started to 623 K, and the catalyst was maintained at this temperature until 12.5 mg of coke were removed. This accounts for approximately

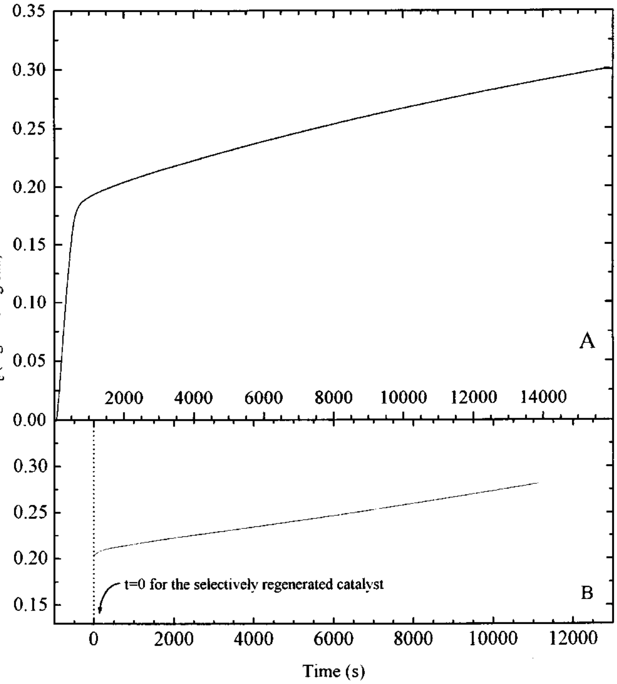

FIG. 11. Coking at 473 K of a fresh catalyst (A), and of a partially regenerated catalyst (B).

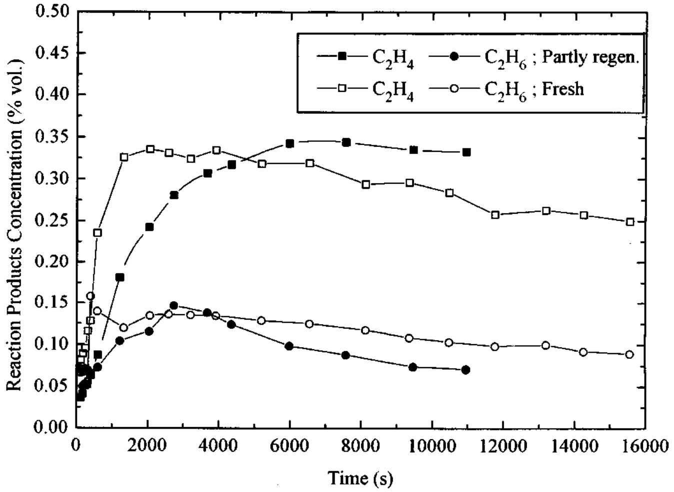

FIG. 12. Variation with time of ethane and ethylene concentrations at the reactor exit. Open symbols correspond to a fresh catalyst and full symbols to a partially regenerated catalyst.

45% of the coke weight corresponding to the linear growth period of curve A in Fig. 11. The catalyst was then cooled under nitrogen to 473 K and the reaction was restarted. Curve B of Fig. 11 shows that the coking behavior of the catalyst was practically identical to that obtained at the same coke level before regeneration. This strongly suggests that a selective regeneration has been achieved, since if the coke deposits on the catalyst surface had been burnt off, a much faster coking would have been obtained.

The evolution of the product concentrations at the reactor exit is shown in Fig. 12. It can be seen that, with some delay, a very similar behavior is reproduced after partial regeneration. Some degree of delay is logical since the fresh catalyst is already reduced at $t = 0$, while the partly regenerated catalyst has been subjected to an oxidizing atmosphere and needs some extra time for reduction. It must also be remembered that the regenerated catalyst starts with a coke loading of 0.20 mg/mg of catalyst. The fact that in spite of this high initial coke loading the behavior of the fresh catalyst is approximately reproduced confirms that, after the fast initial surface coverage has taken place (in approximately the first 500 s of the experiment in Fig. 11 A), the rest of the coke deposited has a much smaller effect on the observed activity.

CONCLUSIONS

The $Ni/NiAl_2O_4$ catalyst is able to hydrogenate acetylene to ethylene and ethane under relatively mild reaction conditions. The kinetic behavior of the catalyst is complex, which in part stems from the heterogeneity of the Ni species present on the catalyst surface: Ni, NiO, and $NiAl_2O_4$. The relative abundance of these species may vary considerably during the course of reaction. Thus, the catalyst is able to provide supplementary Ni sites from the reduction of the oxide and aluminate phases, but also Ni is lost during the operation/regeneration cycles, probably due to the entrainment of crystallites in the regeneration gas stream. The prediction of catalyst performance is further complicated by coke formation which, as in other Ni-based catalysts, may take place under different morphologies that have different deactivating effects. In addition, as has been shown above, the rate of coke formation undergoes substantial and rapid changes during the course of the reaction.

The key to understanding the observed catalytic behavior lies in the simultaneous consideration of the activation and deactivation processes that are taking place on the catalyst. All the curves that represent the activities of the different reactions (hydrogenation to ethylene, hydrogenation to ethane, coke formation) go through a maximum with time, thus indicating that, simultaneously with catalyst deactivation by coking and sintering, some kind of activation process is taking place in the catalyst. Initially, the net rate of active site generation is positive, and the activities for all of the above reactions increase with time. The sites that are generated on the catalytic surface are active for coking and hydrogenation, but not to the same extent. Thus, on the fresh catalyst, the activities for ethane production and coke formation follow a very similar evolution, with coincident maxima. Consequently, at least part of the sites responsible for coke formation also seem to be very active for ethane production. On the other hand ethylene formation follows a different pattern, and continues to increase for a considerable time after the maximum in the coking rate has taken place, which suggests the involvement of a different type of sites.

The heterogeneity of the sites on the catalyst surface was indirectly confirmed by the effect of aging on catalytic performance. Thus, a few coking/regeneration cycles are enough to cause significant changes in the kinetic behavior of the catalyst. These changes are selective in nature and decrease the coke formation rate, while increasing the total observed rates of hydrogenation to ethane and ethylene. As a consequence, the net rate of active site generation is higher for the aged catalyst, and a faster apparent activation rate is obtained. Also, because of the lower deactivation rates, a greater number of active sites are present when the activation and deactivation rates are balanced, and therefore higher maximum hydrogenation yields are obtained with the aged catalyst.

Finally, at least two types of coke morphologies are present on $Ni/NiAl_2O_4$ catalysts, namely an amorphous coke that covers the surface as a two-dimensional layer or mantle and coke in whiskers or filaments. These types of coke grow on different sites, have different gasification temperatures, and have different effects on the catalytic activity and selectivity. The formation of monolayer coke is fast, and its rate strongly depends on the number of active coking sites available on the surface. This number may increase considerably in the initial stages of the reaction, through an *in situ* reduction of the nickel species. The formation of coke in-whiskers is a much slower process, which takes place at an approximately constant rate. The effect of the coke in-whiskers and of two-dimensional surface coke on the activities for the main and coking reactions is markedly different. It is therefore essential to differentiate between the two types of coke on the catalyst when studying the activity-coke relationship.

ACKNOWLEDGMENT

This work has been carried out with financial support from DGICYT (Spain), Project PB94-0568.

REFERENCES

1. Hughes, R., "Deactivation of Catalysts." Academic Press, San Diego, 1984.
2. Rostrup-Nielsen, J. R., and Højlund Nielsen, P. E., *in* "Deactivation and Poisoning of Catalysts" (J. Oudar and H. Wise, Eds.). Dekker, New York, 1985.
3. Baker, R. T. K., Barber, M. A., Harris, P. S., Feates, F. S., and Waite, R. J., *J. Catal.* **26**, 51 (1972).
4. McAllister, P., and Wolf, E. E., *J. Catal.* **138**, 129 (1992).
5. McAllister, P., and Wolf, E. E., *Carbon* **30**, 189 (1992).
6. Rostrup-Nielsen, J., *J. Catal.* **85**, 31 (1984).
7. Al-Ubaid, A., and Wolf, E. E., *Appl. Catal.* **40**, 73 (1988).
8. Bhattacharyya, A., and Chang, V. W., *in* "Catalyst Deactivation, Studies in Surface Science and Catalysis Vol. 88" (B. Delmon and G. F. Froment, Eds.). Elsevier, Amsterdam, 1994.
9. El-Shobaky, G. A., Al-Noaimi, A. N., and Saber, T. M. H., *Bull. Soc. Chim. de France* **6**, 930 (1987).
10. Figueiredo, J. L., *in* "Progress in Catalyst Deactivation" (J. L. Figueiredo, Ed.), *NATO Adv. Science. Inst. Series, E: Applied Sciences,* Vol. 54. Kluwer Academic, Dordrecht/Norwell, MA, 1981.
11. Kopinke, F. D., Zimmermann, G., Reyniers, G. C., and Froment, G. F., *Ind. Eng. Chem. Res.* **32**, 56 (1993).
12. Peña, J. A., Monzón, A., Santamaría, J., and Fierro, J. L. G., *Appl. Catal.* **101**, 185 (1993).
13. Malet, P., and Caballero, A., *J. Chem. Soc. Faraday Trans. I* **84**, 2369 (1988).
14. Pieck, C. L., Jablonski, E. L., Parera, J. M., Frety, R., and Lefebvre, F., *Ind. Eng. Chem. Res.* **31**, 1017 (1992).
15. Acharya, D. R., and Hughes, R., *Appl. Catal.* **52**, 115 (1989).
16. Blasco, V., Royo, C., Monzón, A., and Santamaría, J., *AIChE J.* **38**, 237 (1992).
17. Zieliński, J., *J. Catal.* **76**, 157 (1982).
18. Jinxiang, L., Lixiu, Y., and Xuanzhen, J., *Thermochim. Acta* **178**, 9 (1991).
19. Bartholomew, C. H., Pannell, R. B., and Fowler, R. W., *J. Catal.* **79**, 34 (1983).
20. Medina, F., Salagre, P., Fierro, J. L. G., and Sueiras, J., *J. Catal.* **142**, 392 (1993).
21. Bokx, P. K. D., Kock, A. J., Boellaard, E., Klop, W., and Geus, J. W., *J. Catal.* **96**, 454 (1985).
22. Demicheli, M. C., Duprez, D., Barbier, J., Ferretti, O. A., and Ponzi, E. N., *J. Catal.* **145**, 437 (1994).
23. Agorreta, E. L., Peña, J. A., Santamaría, J., and Monzón, A., *Ind. Eng. Chem. Res.* **30**, 111 (1991).
24. Trimm, D. L., *Catal. Rev.-Sci. Eng.* **16**, 155 (1977).