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The Effects of Coke Deposition on $NiMoO_4$ Used in the Oxidative Dehydrogenation of Butane

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The effects of coke deposition on the $NiMoO_4$ catalyst used for oxidative dehydrogenation of *n*-butane have been investigated. The coke deposition rate and the catalyst changes during this process were studied by TG, FTIR, and XRD. Coke deposition induces segregation of the $NiMoO_4$ into MoO_3 and NiO. It was observed that the coke elimination in He/air flow for 30 min is not complete and the catalyst recovers only partially its structure. On the other hand, it was observed that coke deposition pretreatments lead to stabilization of the $NiMoO_4$ β-phase at room temperature. If the coke is totally eliminated, the β-phase is again unstable. The expected catalyst deactivation with coke deposition was not observed. To the contrary, the conversion increases about 40% after such treatments, and the selectivity to dehydrogenation products also increases. Especially, the butadiene selectivity is more than twice higher. The increase of conversion and selectivity is ascribed to coke catalytic activity and β-phase stabilization.

INTRODUCTION

Catalyst coking is a phenomenon which involves the deposition of carbonaceous species on a catalyst surface. Materials deposited may include elementary carbon, high-molecular-weight polycyclic aromatics, and high-molecular-weight polymers which may originate in the gas phase, on the catalyst, on the support, or elsewhere in the system. Coke is used as a general term to define this heterogeneous material (1).

Chemically, coke could be represented by the empirical formula CH_n, where n varies between 0.1 and 2 depending on the origin and history of the coke deposit. The reactivity of the coke increases with hydrogen content and heat produced by combustion. Morphologically, coke may be divided into different types according to the degree of metal-to-carbon or carbon-to-carbon bonding (2), and coke structure is traditionally characterized by various spectroscopic techniques (3–5).

Coke deposition on the catalyst surface is one of the more common causes of catalyst deactivation. Industrially, catalyst deactivation occasions important economic losses, not only due to catalyst regeneration or cost of new catalyst, but also to production stops. The catalyst activity can be recovered, at least partially, by the elimination of coke. One of the more frequently used procedures is coke combustion in N_2/air or N_2/steam. However, an excessive increase of temperature can occur if the regeneration conditions are not appropriate, leading to catalyst sinterization or uncontrolled reaction (6, 7). Nonetheless, the carbonaceous materials formed on inorganic oxides in the course of oxidative dehydrogenation of etylbenzene to styrene have been considered to be catalytically active substances for this reaction (8, 9).

Increasing industrial interest in direct oxidative dehydrogenation of alkanes into alkenes has led to the development of several catalytic systems for this reactions. Nickel molybdate shows high catalytic activity and stability for oxidative dehydrogenation of butane, with good selectivity to dehydrogenation products (10). No results were found in the literature about the effects of coke on $NiMoO_4$ catalysts used for oxidative dehydrogenation of low alkanes.

The aim of this paper is to study the deposition of coke on $NiMoO_4$ catalysts used for oxidative dehydrogenation of *n*-butane and to investigate the effects produced in the catalyst properties, the consequences of the carbonaceous deposits on the dehydrogenation process, and the efficiency of the regeneration processes by coke gasification in He/air flow for both activity and selectivity of the catalyst.

EXPERIMENTAL

A stoichiometric α-$NiMoO_4$ catalyst was obtained by coprecipitation following the method described by Mazzocchia *et al.* (11). Characterization of the catalyst was carried out by inductively coupled plasma spectroscopy (ICP), atomic absorption (AA), XRD, IR, and XPS.

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Experimental details and results are described elsewhere (10). All the results showed an atomic ratio Mo/Ni = 1. The catalyst surface area (44.1 m^2/g) was determined by N_2 adsorption using the BET method with a Micromeritics ASAP 2000 apparatus.

Activity for oxidative dehydrogenation of butane was tested in a fixed-bed continuous flow tubular quartz reactor (I.D. 20 mm, length 600 mm) with a coaxially centered thermocouple. The catalyst charge was 0.4 g (grain size <0.25 mm) without inert diluent. The reaction was studied at 570°C and the feed was a mixture of butane, oxygen, and helium (5% butane, 10% O_2, and 85% He), the total flow being 12 liter/h. Analyses of the reactants and products were carried out by an on-line Schimadzu GC-8A gas chromatograph with two columns: (I) molecular sieve 13X (60–80 mesh, 2 m × 1/8″ ss); (II) dimethylsulpholane on Chromosorb P (60–80 mesh, 6 m, 1/8″ ss).

Coke deposition on the catalyst surface was forced by heating the catalyst to 530°C in He + butane flow ($Q_{\mathrm{He}} = 5.7$ liter/h and $Q_{\mathrm{but}} = 0.6$ liter/h) for 30 min. Before coke deposition, the reactor was purged with He flow until the air peak in the chromatogram practically vanished. In this way, the product distribution obtained in this process can be attributed only to the activity of the catalyst surface oxygen. Catalyst regeneration was carried out later by combustion of the deposited coke in He + air flow ($Q_{\mathrm{He}} = 5.7$ liter/h and $Q_{\mathrm{air}} = 5.7$ liter/h) also for 30 min. Temperature changed from 530 to 600°C as a consequence of the combustion process and finally stabilized at 560°C. After regeneration, in order to evaluate its effects, the catalyst was tested again in the experimental conditions described previously at 570°C.

Study of the coke deposition rate and effects of the deposits on the catalyst was performed while stopping the coke deposition process at 10, 20, 30, and 60 min. The coked catalysts were recovered and studied by thermogravimetric analysis (TG-DTG) with an Electronics Ltd. thermobalance and heating at 20°C/min in air flow (200 ml/min); XRD with a Rigaku apparatus with Cu$K\alpha$ radiation (Ni filtered) from 10 to 70°, at 2°/min; FTIR with a Perkin–Elmer 1600 spectrometer using KBr. Similar experiments were also performed with the samples obtained after 30 min coking and 30 min of combustion, in order to know the degree of coke elimination and the catalyst state after these treatments.

RESULTS AND DISCUSSION

Coke Deposition and Gasification

During coke deposition, an increase in the reactor pressure was observed, more important in the first 10 min, with no significant changes in temperature. A typical evolution of temperature and pressure during coke deposition is showed in Fig. 1. The $NiMoO_4$ catalyst is a yellow powder, but after this treatment the catalyst bed is a compact, hard, and black mixture of catalyst and coke, difficult to recover from the reactor. The coke particles act as a cement between the catalyst particles, blocking the interparticle voidage and thereby producing an increase in the reactor pressure.

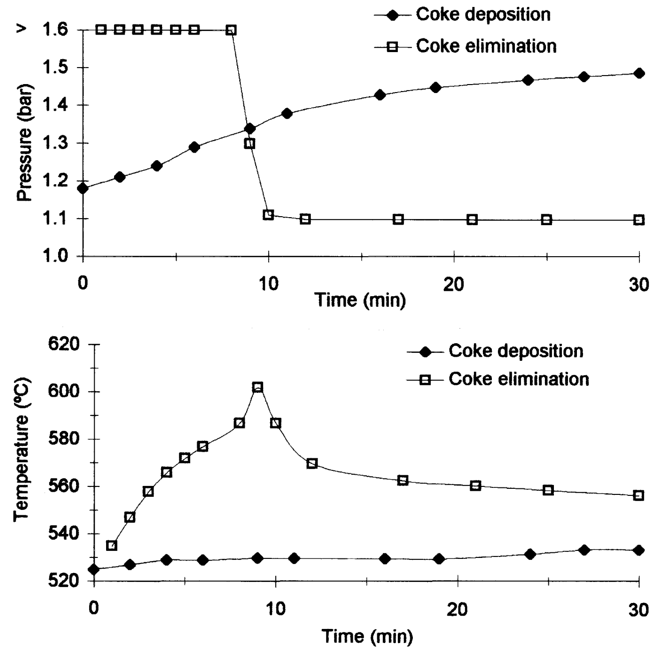

FIG. 1. Typical evolution of the pressure and temperature in the catalytic bed during coke deposition [He (5.7 liter/h) + butane (0.6 liter/h) flow] and gasification [He (5.7 liter/h) + air (5.7 liter/h) flow] pretreatments.

Elimination of this coke was carried out for 30 min in He/air flow maintaining the other experimental conditions. As a consequence of the combustion process, temperature increased mainly in the first 10 min of combustion (Fig. 1), decreasing later to the working temperature. Simultaneously, a strong decrease in the reactor pressure was observed. In fact, during the first 10 min of the run, the pressure is always greater than 1.6 bar. However, the reactor pressure decreases very quickly (in 20–30 s) after about 10 min of regeneration, and stabilizes around the normal working pressure (1.10 bar).

Thermogravimetric Analysis

Coke deposition was monitored while stopping the deposition process at different run times (10, 20, 30, and 60 min). The coked catalyst was withdrawn from the reactor and analyzed by TG in air flow. The results of these experiments shown in Table 1 confirm that the coke deposition takes place principally during the first 10–15 min of reaction, and only a small increase of coke deposition was recorded after 20 min of reaction.

Figure 2 presents the DTG profiles recorded for the coked catalysts during the treatment in air flow. In all cases, the coke gasification starts at bout 400°C. The curves show

TABLE 1

Burn-Off Percentage of Coked Catalysts by TG

Sample	B.O. (%)
$NiMoO_4 + 10$ min coke deposition	13.4
$NiMoO_4 + 20$ min coke deposition	18.8
$NiMoO_4 + 30$ min coke deposition	19.0
$NiMoO_4 + 60$ min coke deposition	19.1
$NiMoO_4 + 30$ min coke deposition $+ 30$ min coke gasification	7.2
$NiMoO_4$ after 50 h reaction	0.8
$NiMoO_4 + 2$ cycles coke deposition–gasification $+ 30$ h reaction	2.2

two minima; the first is observed around 440°C and the second one around 500°C. The percentage of coke eliminated below 470°C increases from 20% in the 10-min coked catalyst to about 40% for longer coke deposition times. Thus, although the total amount of coke does not increase significantly with coke deposition time after 20 min, it is clearly evidenced that its chemical nature changes with time of deposition.

It is not in the objectives of this paper to characterize the coke nature. However, it seems possible to have some understanding of the DTG results. During the first 10–15 min of coke deposition, the butane reacts with a clean catalyst surface, and a large proportion of coke which is gasified at 525°C is produced. After this process, the butane–catalyst interaction becomes weaker and a more reactive type of coke (because it gasifies at lower temperatures) is formed. This second type of coke must have weaker C–C bonds and higher hydrogen content which favors its reactivity (12, 13). Although the deposited amount and the nature of the deposit depend on the catalyst, the reactants, and the operating conditions, the formation of carbons deposits with different reactivity (α-carbon and β-carbon) on an Ni-alumina catalyst was described by McCarty and Wise (14).

The efficiency of the gasification process was checked in the case of 30 min of coke deposition and 30 min of coke gasification. The catalyst was withdrawn from the reactor and analyzed by TG. The loss of weight percentage recorded was 7.2%. This means that coke elimination is not complete after a 30-min gasification.

X-Ray Analysis

The original catalyst presents at room temperature a well-defined α-$NiMoO_4$ structure with octahedral Mo coordination (ASTM-standard 33-948); after 15 min at

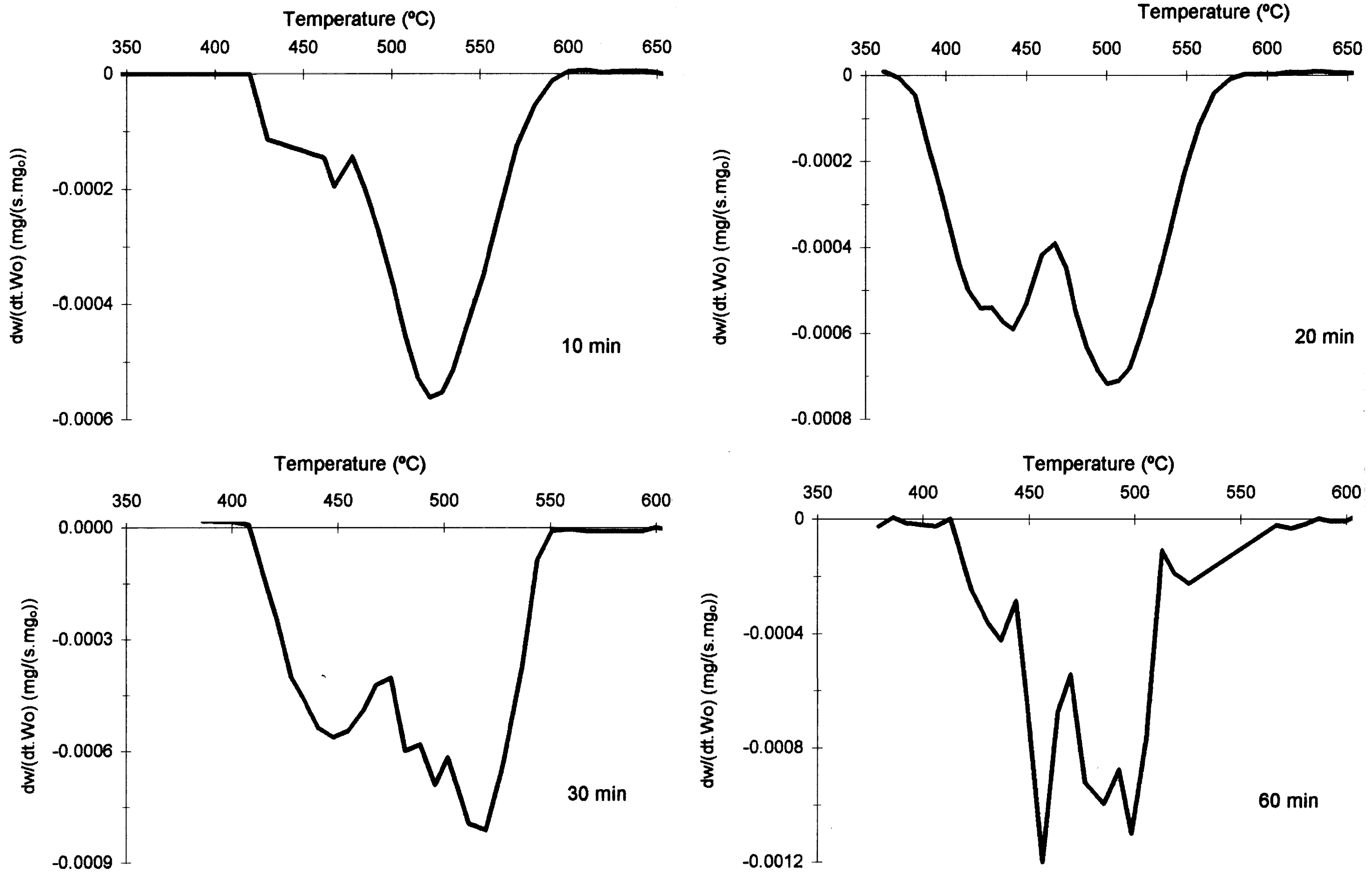

FIG. 2. DTG combustion profiles of coke formed at different deposition times.

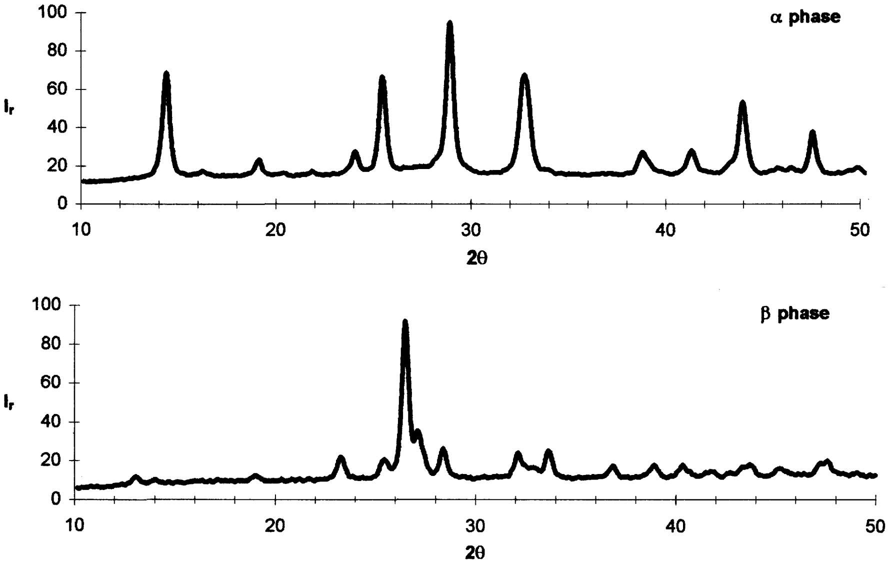

FIG. 3. XRD diffractograms of the α- (at room temperature) and β-phases (after 10 min at 710°C in air flow) of $NiMoO_4$.

710°C in air flow the transition to β-phase (tetrahedral Mo coordination) is complete (Fig. 3). The influence of coke deposition on catalyst structure was studied by XRD. These experiments show (Fig. 4) that this process leads to segregation of the $NiMoO_4$ into NiO and MoO_3. In fact, after coke deposition and independently of deposition time, the characteristic peaks of the original structure disappear and one only finds those corresponding to NiO ($2\theta = 37.3^\circ$, 43.3°, and 62.9°) and MoO_3 (ASTM 35-609; $2\theta = 23.4_{77}^\circ$, 25.7_{38}°, 25.9_{31}°, 27.4_{100}°, 33.7_{26}°, 39.1_{21}°, 50.0_{10}°, 52.8_{13}°, and 53.2_{10}°).

No peaks assignable to crystalline coke (graphitic coke) were found. However, the presence of such large amounts of amorphous coke produces widening of the peaks and so, in the case of the MoO_3 which has close peaks, only two bands at 23°–29° and 50°–54° have been assigned. It is also noteworthy that all the peaks of both oxides become better defined when deposition time increases, and therefore, in this sense, must increase their crystallinity. Moreover, observing NiO peaks, it is visible that the first and third peaks increase with respect to the second one. This fact evidences a possible transformation of the NiO structure from rhombohedral (ASTM 22-1189; $2\theta = 37.3_{60}^\circ$, 43.3_{100}°, and 62.9_{35}°) to a full symmetrical cubic structure (NaCl type)) ASTM 4-835; $2\theta = 37.3_{91}^\circ$, 43.3_{100}°, and 62.9_{57}°).

When coke is gasified, the catalyst recovers its yellow color, although the coke gasification is not complete or homogeneous, some portions of the catalytic bed remain black colored. Structurally, the catalyst recovers some α-$NiMoO_4$ structure (Fig. 4), but the β-phase is also observed at room temperature, and significant amounts of MoO_3 and NiO still remain.

It is well known that strongly bonded species, containing carbon or sulfur, may induce complex changes in the structure of a metallic substrate. In general, these phenomena are reversible and upon removal of the surface impurity the surface recovers its original structure (2). Extensive studies were performed about the influence of carbon on the stability of nickel (15, 16). For nickel-oxide-based systems, and in particular for the Al_2O_3-supported Ni/V/Sb/O system, Talyshinskii *et al.* (17) found that the catalyst consisting initially of a mixture of $Ni(VO_3)_2$, $Ni(SbO_3)_2$, and $SbVO_4$ during *n*-butane ODH partly decomposed, with formation of NiO, $Ni(VO_3)_2$, V_5O_9, and amorphous Sb oxide. Regeneration of the samples did not restore completely the original state. For the NiO–MoO_3 system, no references were found in literature on such behavior. In our case, as mentioned above, the nickel and molybdenum oxide segregation that occurred during coke deposition is almost reversible, and after coke gasification the catalyst recovers the initial structure. The presence of the different phases can play an important role both in the catalytic behavior and in β-phase stabilization because this phase is highly selective for ODH reactions (18–20).

Similar XRD experiments carried out with catalysts after 30 h of oxydehydrogenation of butane, with and without previous coke deposition–gasification processes before the reaction, evidence important structural differences between them (Fig. 5) specially in what concerns to the stabilization of the β-phase.

In the catalyst without coke deposition–gasification pretreatments, the oxydehydrogenation reaction during 30 h does not produce strong structural changes with respect to the fresh catalyst. A well defined α-$NiMoO_4$ structure is observed although, the peak corresponding to I_{100} of β-$NiMoO_4$ structure is now visible at room temperature. The X-ray diffractogram of the catalyst after 50 h of

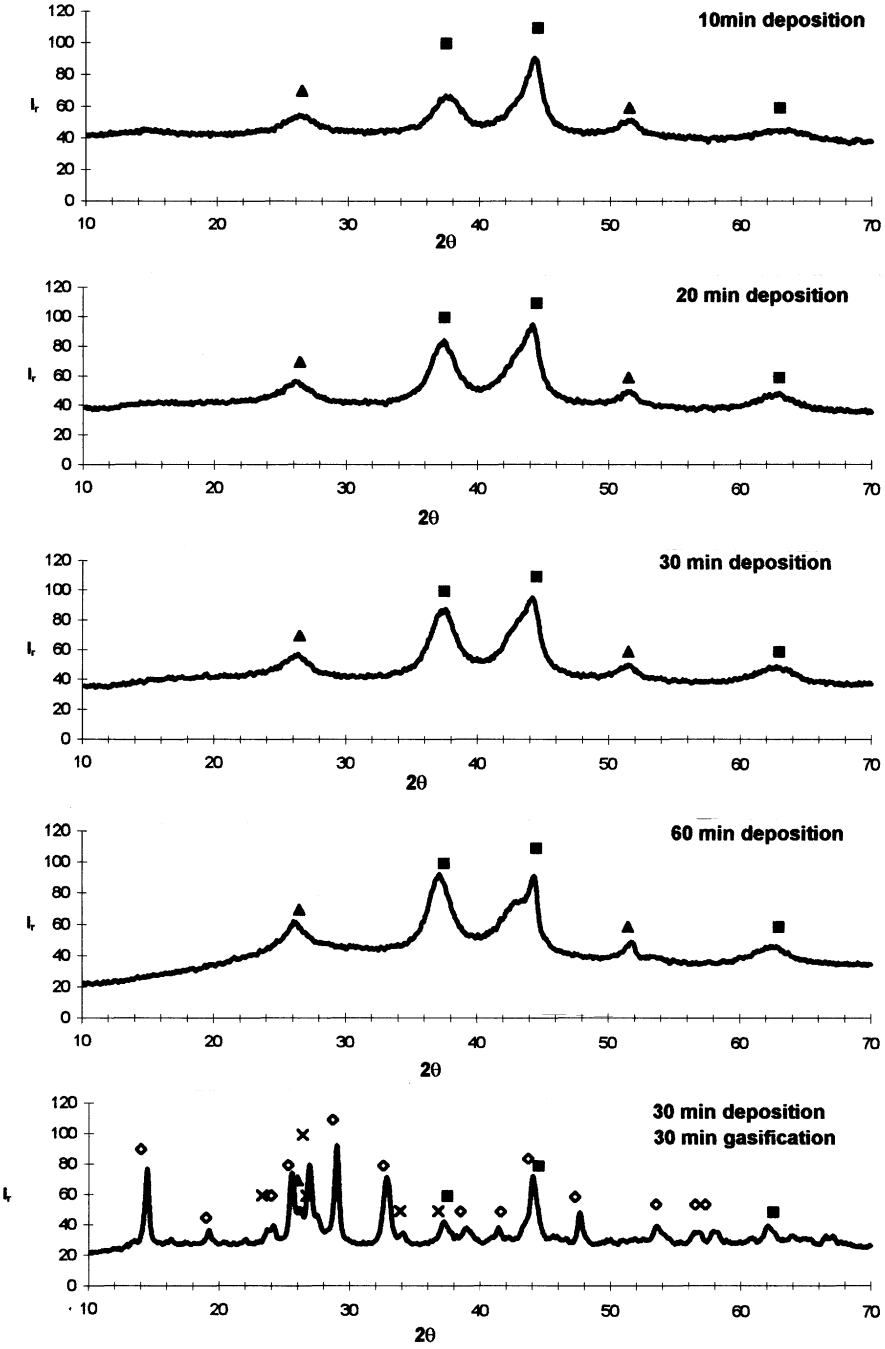

FIG. 4. XRD diffractograms (at room temperature) of the coked catalysts at different deposition times and after the gasification process ($NiMoO_4$ α-phase, ◇; $NiMoO_4$ β-phase, ×; MoO_3, ▲; NiO, ■).

oxydehydrogenation reaction shows greater stabilization of the β-phase and a certain segregation into NiO and MoO_3.

Two catalyst samples with previous coke deposition–gasification treatments were studied by XRD after 30 h of oxydehydrogenation of butane. The first sample was pretreated with 30 min of coke deposition and 30 min of coke gasification; the second one, had two similar cycles of coke deposition–gasification before the reaction. The maximum temperature reached in both cases was around 600°C, decreasing quickly to about 550–560°C. As has been mentioned above, the coke gasification is not complete after these processes. The X-ray spectra of both samples (Fig. 5) after 30 h of dehydrogenation reaction exhibit principally β-phase and the proportion of this phase is higher in the sample with two cycles of coke deposition–gasification. It is noteworthy that these X-ray experiments were performed

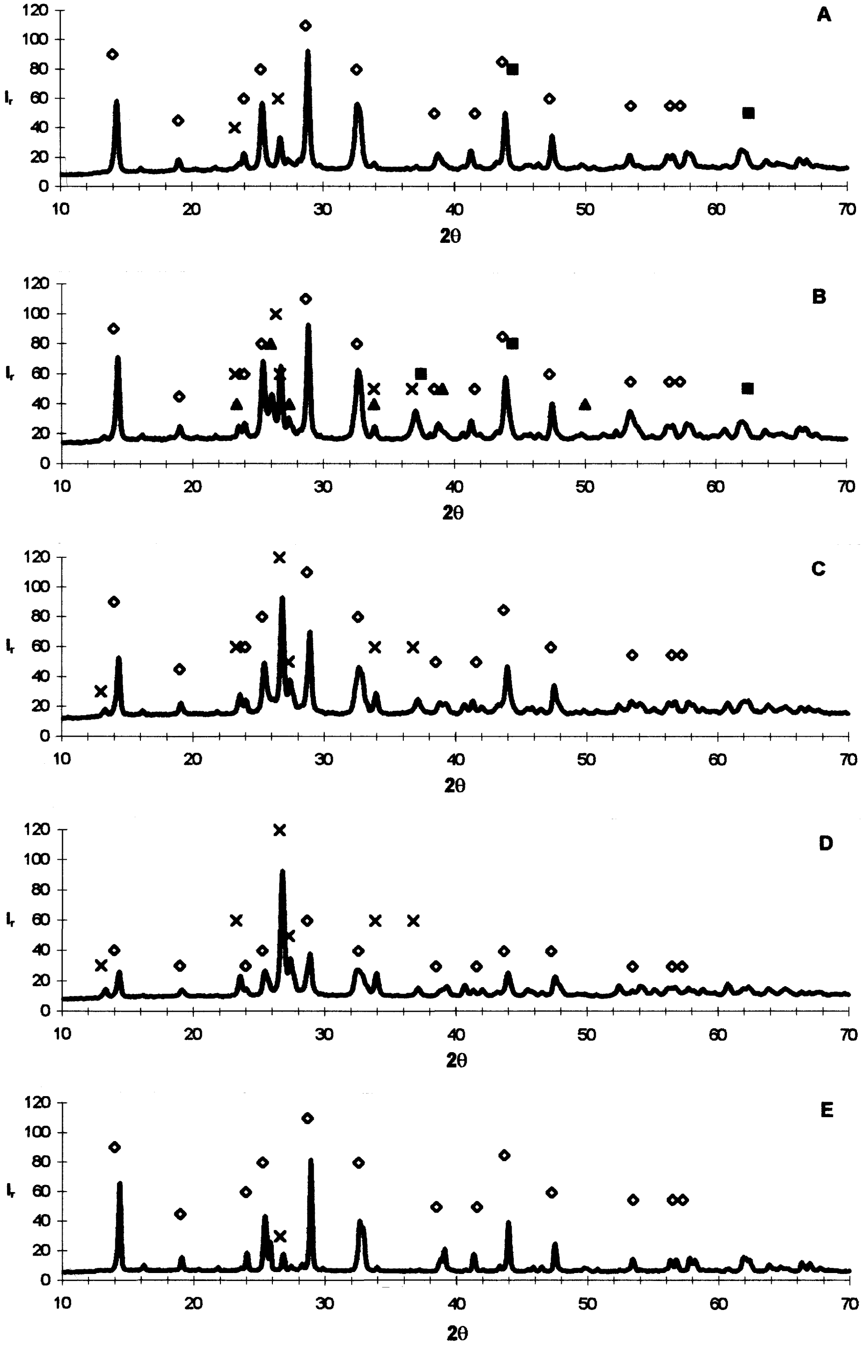

FIG. 5. XRD diffractograms (at room temperature) of catalysts used for butane dehydrogenation [570°C, 0.4 g of catalyst and $Q_T = 12$ liter/h (5% butane, 10% O_2, 85% He)]: (A) after 30 h reaction; (B) after 50 h reaction; (C) with pretreatment and 30 h reaction; (D) with two cycles of pretreatment and 30 h of reaction; (E) with two cycles of pretreatment and 30 h of reaction and total elimination of coke. Symbols as in Fig. 4.

at room temperature some weeks after the dehydrogenation reaction, and consequently the observed transition from α- to β-phase seems to be irreversible or extremely slow in samples with coke deposition–gasification pretreatment. The stabilization of the β-phase at room temperature is very important because it is well known that this phase is more selective for dehydrogenation products (18–20), but it is unstable at low temperatures. An investigation has been carried out with this objective using organic precursors (20). Therefore the role of the carbonaceous materials in these processes seems to be an interesting investigation field.

The experimental conditions for the α–β transition have been studied by Mazzochia *et al.* (18–20). According to these authors the β-phase is already present at 595°C, but more severe experimental conditions are required to obtain a full α–β transformation (usually 15 min at 710°C). For example, after 2h at 625°C the fraction of α transformed into β is only around 25%, and the transition rate decreases strongly at lower temperatures (19). Consequently, in our case, the increment of temperature occurring during the coke gasification is not sufficiently severe and extensive to lead to the α–β transition.

As was stated, after coke deposition and gasification, coke elimination is not complete and the catalyst shows a typical α-structure with a portion of segregated NiO and MoO_3, and an important amount of β-phase (Fig. 4). In these conditions, the transition to β-phase and its stabilization is favored by the oxydehydrogenation reaction. In fact, it is practically complete after 30 h of reaction (Fig. 5) for the catalyst with two pretreatment cycles. It is known (18, 21) that the presence of NiO stabilizes the β-phase at room temperature and that the use of organic precursors (20) leads to lower temperature of crystallization and beta phase stabilization.

In order to elucidate the role of the coke in β-phase stabilization, the used catalyst with greater proportion of this phase (two pretreatment cycles and 30 h of reaction), was heated at 800°C in air flow for 1 h to eliminate completely the coke. After this process, the XRD spectrum at room temperature did not show β-phase, evidencing that the transition to α-phase is almost complete (Fig. 5) in spite of the strong thermal treatment undergone.

FTIR Analysis

The α-phase of $NiMoO_4$ is characterized by bands at 608, 934, and 958 cm^{-1} (10, 19). When the β-phase is present by stabilization, the spectrum shows an absorption band at 950 cm^{-1}, but two characteristic new bands at 800 and 880 cm^{-1} are also observed as consequence of the change in the coordination number of Mo from 6 to 4 (19, 22).

Our fresh and used catalysts were also characterized by FTIR (Fig. 6). The α-$NiMoO_4$ catalyst exhibits a well defined octahedral structure (curve I). No important changes were observed in the FTIR spectrum of the catalyst used 50 h for dehydrogenation of butane (curve II). However, the catalyst used 30 h in the same experimental conditions, but pretreated with two cycles of coke deposition–gasification evidences the stabilization of the beta phase by well defined bands at 800 and 880 cm^{-1} (curve III).

The important role of the coke in β-phase stabilization was also confirmed by FTIR. After the total elimination of coke (curve IV), the characteristic bands of the β-phase disappear, which confirms that the $\beta \rightarrow \alpha$ transition is complete. These results are in agreement with the XRD data.

BET Surface Areas

In order to evaluate the effects of coke deposition–gasification treatments on the porous texture of the catalyst, the BET surface areas of fresh, coked, regenerated, and used catalysts were measured; the results are presented in Table 2. The coked catalyst (30 min of coke deposition) shows a larger BET surface area than the fresh $NiMoO_4$.

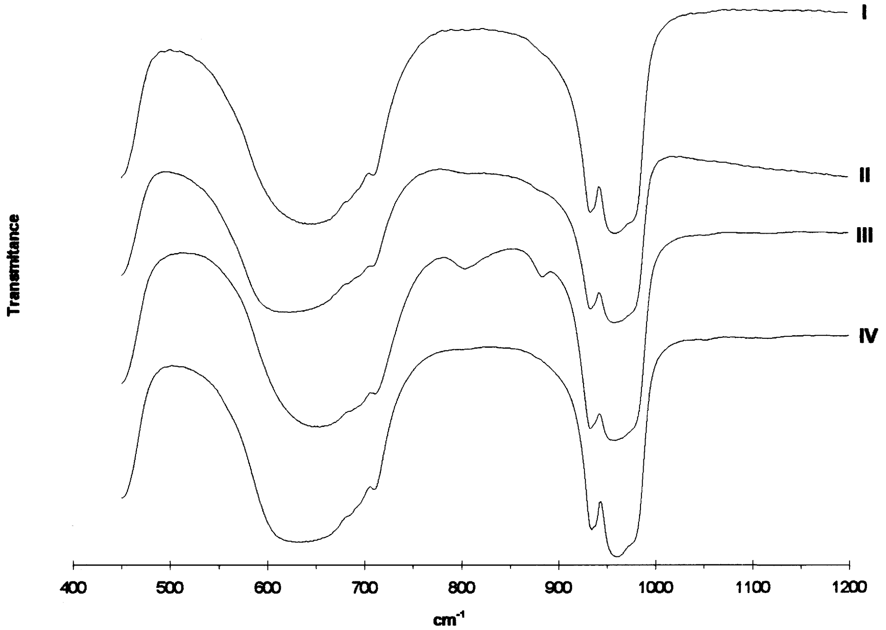

FIG. 6. FTIR spectra of fresh and used catalyst: (I) fresh catalyst; (II) after 50 h reaction (operating conditions as in Fig. 5); (III) with two cycles of pretreatment and 30 h of reaction; (IV) with two cycles of pretreatment and 30 h of reaction and total elimination of coke.

TABLE 2

BET Surface Areas of Fresh and Coked Catalysts

Sample	S_{BET} (m^2/g)
$NiMoO_4$	44.1
$NiMoO_4$ + 30 min coke deposition	53.4
$NiMoO_4$ + 30 min coke deposition + 30 min coke gasification	28.8
$NiMoO_4$ + 1 cycle coke deposition–gasification + 30 h reaction	27.9
$NiMoO_4$ + 2 cycles coke deposition–gasification + 30 h reaction	27.6

However, after regeneration (30 min of coke deposition and 30 min of gasification) this parameter strongly decreases but remains practically unaffected after reaction. When coke was completely eliminated (by heating at 800°C in air flow for 1 h), although only α-$NiMoO_4$ was found at room temperature, the BET surface area becomes 6.7 m^2/g due to the very drastic thermal treatment. The larger BET surface area of the coked catalyst can be attributed to the contribution of coke. When coke is partially removed, the catalyst becomes a mixture of α- and β-phases of $NiMoO_4$, NiO, and MoO_3.

Catalytic Tests

The stability of the $NiMoO_4$ activity in the oxidative dehydrogenation of *n*-butane was tested for 50 h. Other authors (23) have studied the catalytic behavior of the $NiMoO_4$–MoO_3 system in the conversion of 1-butene to maleic anhydride for about 200 h. They have not recorded changes after reaching the steady state. In our case (Fig. 7), a good stability in conversion was observed with our experimental conditions. The product distribution also exhibits stability (Fig. 7). Both carbon oxides (CO and CO_2) show selectivities around 40%. The butadiene selectivity seems to increase slightly with values between 10 and 15%. The butenes selectivities are practically constant around 5% for 1-butene and 3% for both 2-butenes.

After this experiment the used catalyst was analyzed by TG in air flow and the loss of weight percentage observed was less than 1% (Table 1).

During coke deposition experiments, it was observed that the products distribution differed from the one recorded for the test carried out in the presence of O_2. Both CO and CO_2 were always observed mainly at the beginning of the reaction. No formation of butadiene was observed in any case, and besides dehydrogenation products (1-butene and 2-butenes) variable amounts of isobutane, H_2, CH_4, and C_2H_4 were noticed due to isomerization and cracking reactions.

In order to evaluate the effect of coke deposition and subsequent gasification on catalytic behavior, tests were carried out after this pretreatment under identical experimental conditions. As was mentioned above, the coke is not totally eliminated after the regeneration process, consequently the CO_x recorded can be formed partially from coke combustion along with butane reaction. However, the carbon unbalance was always less than 3% and therefore the CO_x formation from coke will be negligible with respect to the one resulting from butane.

Experiment 1. After 30 min of coke deposition (Q_{He} = 5.7 liter/h and Q_{but} = 0.6 liter/h) and 30 min of coke gasification (Q_{He} = 5.7 liter/h and Q_{air} = 5.7 liter/h) the

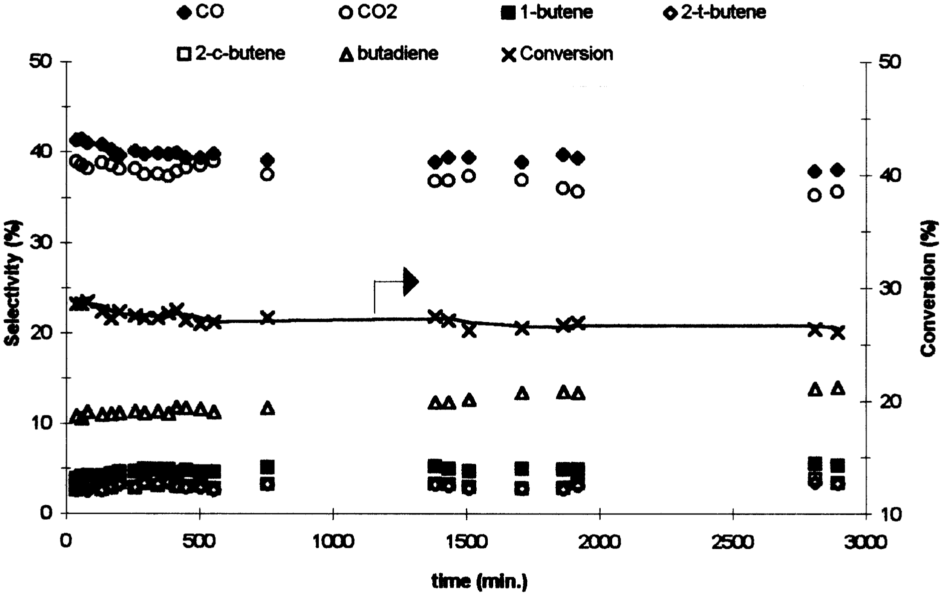

FIG. 7. Conversion and product distribution without pretreatment (operating conditions as in Fig. 5).

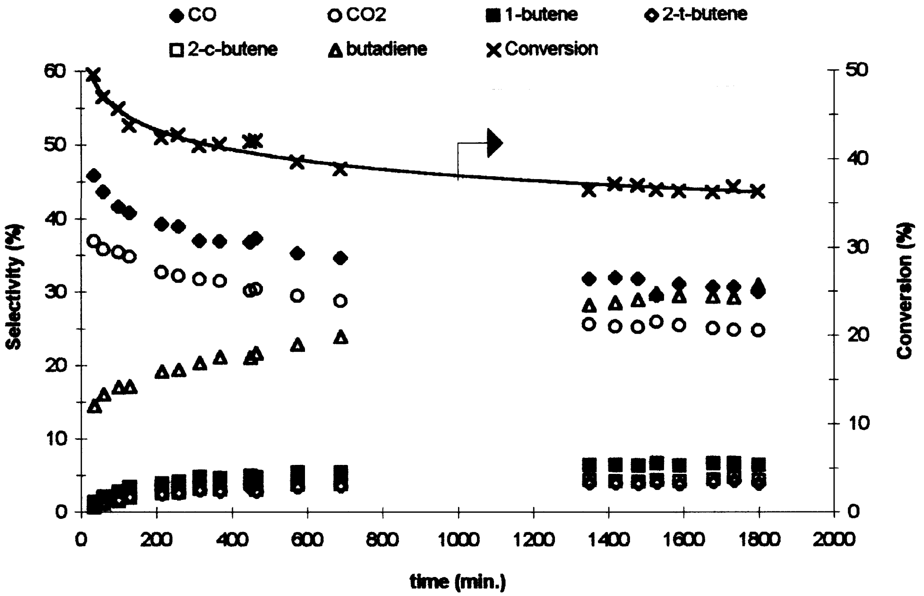

FIG. 8. Conversion and product distribution after one cycle of coke deposition–gasification (operating conditions as in Fig. 5).

oxidative dehydrogenation of butane was performed for 30 h under the same experimental conditions, as those used previously to test the catalyst activity (catalyst charge = 0.4 g). The results are presented in Fig. 8. The catalyst pretreatment led, after stabilization, to a conversion about 40% higher than without pretreatment. Simultaneously, the selectivity to butadiene increased along the 30 h of reaction, becoming more than twice higher than without pretreatment.

Experiment 2. In this experiment the amount of catalyst changed to 0.3 g keeping all the other experimental conditions of the previous experiment namely using the same coke deposition-gasification pretreatment. The results are presented in Fig. 9. Conversion is higher than without pretreatment, although the amount of catalyst is 25% lower. The selectivity to dehydrogenation products increased more than that in the Experiment 1. In particular, the selectivity to butadiene had a strong increase

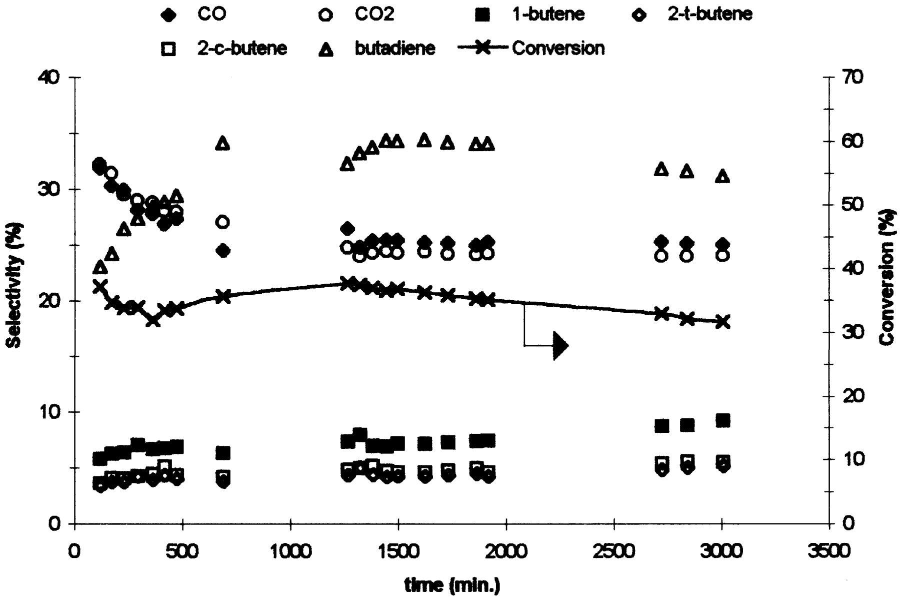

FIG. 9. Conversion and product distribution after one cycle of coke deposition–gasification varying the contact time (with the same operating conditions as in Fig. 5, but using 0.3 g of catalyst).

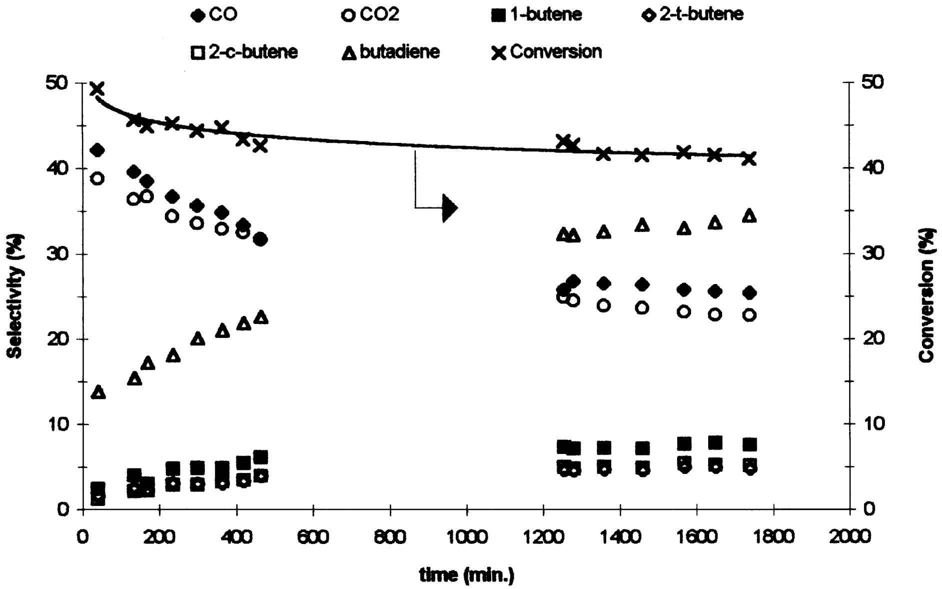

FIG. 10. Conversion and product distribution after two cycles of coke deposition–gasification (operating conditions as in Fig. 5).

specially during the first 8 h of the reaction run, reaching values around 35%. Afterward, butadiene becomes the main product.

Experiment 3. The catalytic behavior was also tested after two cycles of coke deposition–gasification carried out under the same conditions as Experiment 1. The results are shown in Fig. 10. The same conversion level of the previous experiments (around 45%) was observed. However, in this experiment, the selectivity of C_4's dehydrogenation products is even higher, butadiene becoming clearly the main product, with a selectivity of 35%. After this experiment the used catalyst was analyzed by TG in air flow, and a loss of weight of 2.2% was recorded (Table 1).

Experiment 4. In order to evaluate the role of coke in the catalytic bed, the fresh $NiMoO_4$ was intimately mixed with 0.04 g of a demineralized (HCl, HF pretreatment) and pyrolized (840°C in N_2 flow) Spanish lignite. The analysis of this char (wt%, dry basis) was C, 80.2; H, 1.5; N, 1.0; S, 2.6; O (by difference) 14.7. The catalytic results are showed in Fig. 11. A behavior similar to that for experiments with coke deposition was observed, and selectivity to butadiene increased up to 35%.

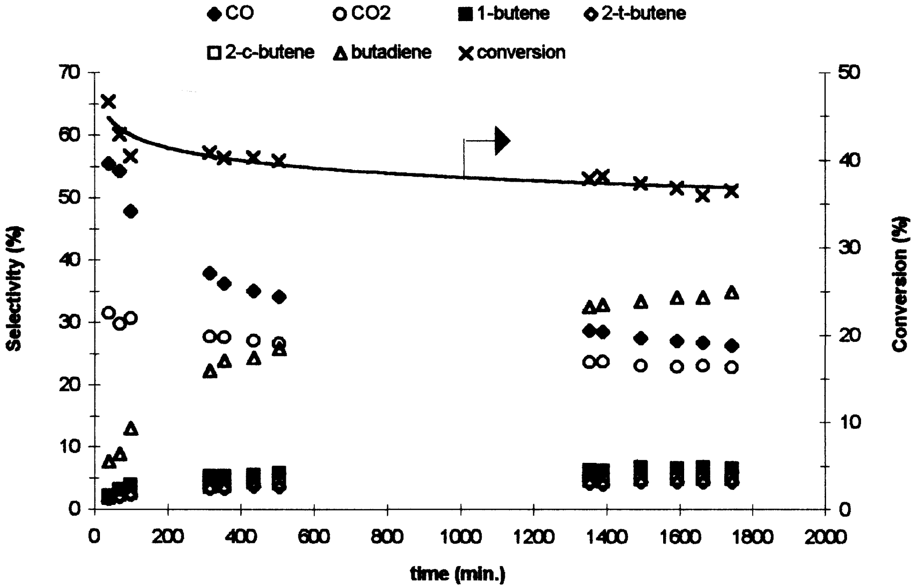

FIG. 11. Conversion and product distribution obtained adding to $NiMoO_4$ 10 wt% of a char (operating conditions as in Fig. 5).

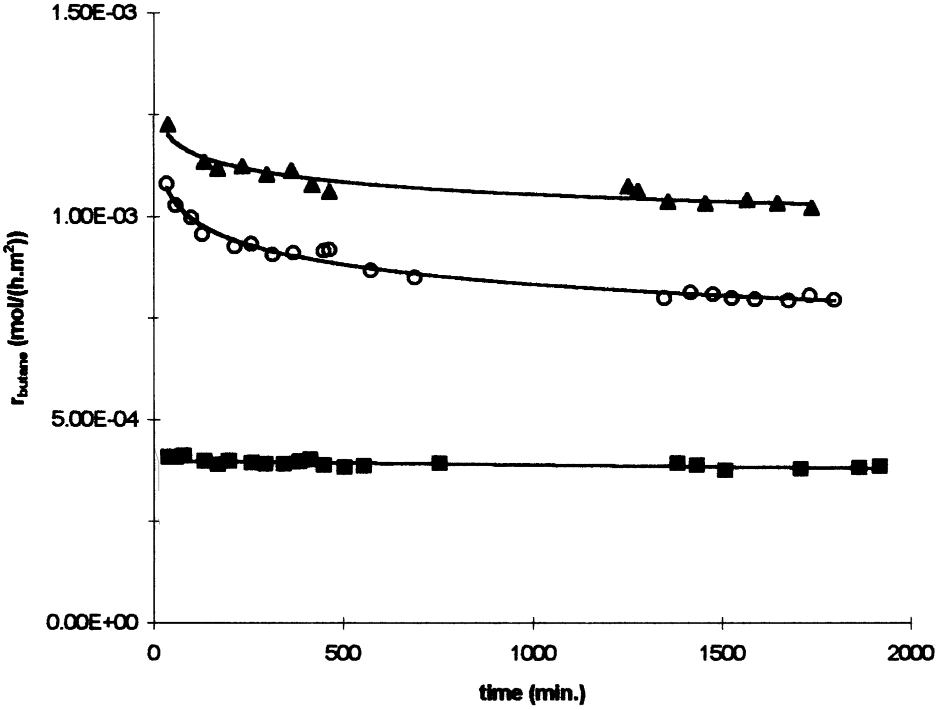

FIG. 12. Normalized butane reaction rates for catalysts without pretreatment (■); with one cycle of pretreatment (○); with two cycles of pretreatment (▲) (operating conditions as in Fig. 5).

Activity of the catalysts with and without pretreatment are compared on a surface area basis in Fig. 12. The rate of butane conversion for the untreated $NiMoO_4$, which is 3.9×10^{-4} mol/(h · m^2), increased 2.0–2.8 times for the catalyst with one cycle of pretreatment and 2.6–3.1 times if two cycles of coke deposition–gasification pretreatment were used. It is noteworthy that the increase in normalized activity is so high that it surpasses the effect of decreasing surface area.

It is clear that in all the experiments with coke deposition–gasification pretreatments, the catalyst is not deactivated by coke, but activity increases significantly with respect to the experiment without pretreatment. Besides the conversion increase, the selectivity to dehydrogenation products also increases, principally due to the enhanced formation of butadiene (the selectivity of 1-butene and both 2-butene isomers is always around 5%). However, while both the activity and the selectivities are practically constant during 50 h in the experiment without pretreatment, when pretreatment is applied the selectivities (specially of butadiene) increased along the time on stream in parallel with decreases of both carbon oxides' selectivities. These results could be related with the structural changes occurring during the dehydrogenation process and induced by the pretreatments, as has been evidenced by FTIR and XRD (β-phase formation and stabilization).

However, it is well known (10, 19) that the β-phase is more selective, but less active for alkanes conversion. Consequently, besides the increase of selectivity induced by the β-phase, the coke that remains after the gasification processes must have also another very important role. As has been evidenced by adding a char to the catalyst, the presence of carbonaceous material in the catalytic bed enhances conversion and butadiene selectivity. Therefore, the combination of both effects (β-phase stabilization and coke presence) leads to a more effective and selective catalyst than the original one. Coke deposition, instead of deactivating the catalyst is, under our used experimental conditions, a good process for catalyst activation.

CONCLUSIONS

Coke deposition on α-$NiMoO_4$ catalyst, under the experimental conditions used in this work, takes place mainly during the first 10–15 min. The increase in deposition time leads to the formation of two types of coke with different reactivities in air. This process causes segregation of $NiMoO_4$ into NiO and MoO_3. The gasification treatment performed (30 min) is not sufficient to eliminate completely the deposited coke (it remains 7.2%). After this process, the catalyst recovers its structure (α-phase), but NiO and MoO_3 still remain, and a significant amount of the unstable β-phase is observed at room temperature.

The β-phase in the presence of coke is stable at room temperature. The transformation into α-phase is irreversible or extremely slow. An α-phase catalyst undergoing coke deposition–gasification pretreatment shows after 30 h of butane dehydrogenation mainly β-phase, and the proportion of this phase is larger if the catalyst undergoes two cycles of coke deposition–gasification. The role of coke in this stabilization was demonstrated by eliminating completely the coke from this catalyst. After this process, the catalyst shows again the typical α-structure; i.e., without coke, the transition from β-to α-phase is again reversible.

The catalytic results evidence that coke formed by deposition–gasification pretreatments, instead of leading to catalyst deactivation, enhances the activity and selectivity of the $NiMoO_4$ in the dehydrogenation of butane. The conversion increases from 27% with fresh catalyst to values higher than 38%. Simultaneously, the selectivity to dehydrogenation products increases, mainly due to the large formation of butadiene. The catalytic activity of the carbonaceous materials was confirmed by adding to the fresh catalyst 10% of a char.

The role of coke seems to be very important for the stabilization of the β-phase and for catalytic activity. The combination of both effects leads to a more active and selective catalyst for the dehydrogenation of butane.

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