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Deactivation by coking and poisoning of spinel-type Ni catalysts

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Abstract

The effect of the addition of structure-modifying agents such as ZnO on the processes of coke formation and sulphur poisoning of NiO/Al_2O_3 catalyst during ethyne hydrogenation has been studied. With or without the presence of modifiers, the addition of H_2S to the feed gives rise to a strong increment in the rate of catalyst coking. However, pretreating the catalyst with H_2S has a different effect when ZnO is added to the catalyst. In a NiO/Al_2O_3 catalyst, sulphur preferentially deactivates metallic sites which are very active for coke formation. However, when ZnO is present in the catalyst structure, the addition of sulphur gives rise to a lower hydrogenation yield, and a greater rate of coke formation with respect to the fresh catalyst. Pretreating the catalyst with H_2S also changes the coke morphology.

Keywords: Spinel-type Ni catalysts; Ethyne hydrogenation; Sulphur poisoning; Coking

1. Introduction

Catalyst coking is perhaps the most intensely studied catalyst deactivation process. Coke deposition usually occurs as an undesired side reaction, leading to the coverage of the active sites responsible for the reaction, with the associated loss of catalytic activity. If coke build-up rises beyond a certain limit, pore blockage takes place, which removes active sites from contact with the reactant stream at a greater rate than direct site coverage. In extreme cases, interparticle coke growth may increase the pressure drop in fixed bed reactors and ultimately block the passage of fluid [1,2].

Coke formation usually occurs by degradation of reactants and/or products, and therefore it is difficult to avoid in practice. Thus, after a certain time on stream it is generally necessary to regenerate the coked catalysts, by means of combustion with a diluted oxygen stream, or by gasification treatments involving steam, CO_2 or H_2 [3,4]. Alternatively, the operating conditions can be modified to diminish coke formation (e.g., lowering temperature, adding steam to the feedstream), or the catalyst can be specifically designed either to give lower coking rates or to be less sensitive to coke formation. In fact, one of the main reasons to use noble metal catalysts in industrial hydrogenation processes (rather than their cheaper counterparts such as Ni or Cu) is related not only to the higher activity and selectivity but also to the lower coking rates of the former.

In addition to coking, catalyst poisoning often contributes to the overall catalyst deactivation. This is frequently the case when working in industrial reactors where, unlike laboratory studies, the reactants

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often contain a significant amount of impurities. Even if a relatively high-purity feedstock is used, it must be taken into account that the presence of impurities (e.g., H_2S, thiophene) at levels of a few parts per million is often sufficient to cause significant catalyst poisoning. The presence of these compounds on the catalyst surface generally leads to a decreased chemisorption capacity, which in turn decreases the observed activity [5,6]. However, there are abundant examples showing that catalyst poisoning also affects the catalyst selectivity, sometimes to a greater extent than the activity. Dalla Betta et al. [7] found that sulphur addition increased the production of high molecular weight products during CO hydrogenation. Other authors [8–10] showed that the presence of electron-donating compounds (such as nitrogen-containing compounds) or electron-attracting compounds (e.g., sulphur- or chlorine-containing compounds) on the catalyst surface provokes important variations in the selectivity to butenes during butadiene hydrogenation over several metallic catalysts. Ng and Martin [11] found that the addition of H_2S over Ni/SiO_2 catalysts strongly decreases the chemisorption of H_2 and CO. However, the capacity to adsorb unsaturated hydrocarbons such as C_2H_2 or C_6H_6 was much less affected by the level of sulphur content. All of these results indicate that sulphur poisoning is a complex phenomenon with consequences that cannot always be explained by a simple process of suppression of active sites.

There are relatively few works [12–14] dealing with the effect of the simultaneous presence of coke and sulphur on activity and selectivity of the catalyst for the main reaction. Even fewer investigations have studied the competition between coke precursors, sulphur and reactant molecules for the active sites. Among these, Oudar et al. [15] found that H_2S adsorption on Pt catalysts during butadiene hydrogenation was reversible, and could be eliminated by the diolefin, through competitive adsorption on the metallic sites. Rostrup-Nielsen [16] reported that the characteristic activity of Ni to form carbon whiskers was strongly decreased by the action of sulphur-containing compounds, while only a small effect was observed on the steam reforming activity of the catalyst.

In this work, the effect of coking and sulphur poisoning on the performance of Ni-based catalysts in ethyne hydrogenation has been studied. This process is interesting not only as a model reaction, but also because of the need to eliminate ethyne from the ethene streams obtained by naphtha cracking. This is required for the catalytic production of polyethene, in which ethyne acts as a poison [17]. While the use of Pd catalysts for the selective hydrogenation of ethyne is customary, there is also interest in the development of alternative catalysts based on Ni, Cu or Co, or at least in the modification of the traditional Pd catalyst with these metals [18,19].

It is well known that the hydrogenation of highly unsaturated hydrocarbons (such as acetylenic or diolefinic compounds) is a structure-insensitive process [20–24]. This is due to the fact that the reaction does not take place on the free metal surface, but on a chemisorbed layer of CH_x species. However, other simultaneous processes such as hydrocarbon adsorption/desorption [8], coke formation [25–27], or sulphur poisoning [28], are structure-sensitive reactions taking place on bare active sites. This gives a scenario in which the presence of poison molecules in the feedstream of hydrogenation reactors may strongly modify the coking behaviour of the catalyst and the adsorption/desorption characteristics of the catalytic surface, leading to significant changes in the observed yield and selectivity.

In previous works [29–31], it has been shown that the addition of structural promoters such as Zn, Cr or Ti to Ni/Al_2O_3 catalysts can significantly modify the coking tendency of the original catalyst, with a strong reduction in the observed coking rates. In this work, the effect of H_2S poisoning on the activity, selectivity and coking behaviour of $NiAl_2O_4$ and $(NiO)ZnAl_2O_4$ catalysts during ethyne hydrogenation has been studied.

2. Experimental

The $NiAl_2O_4$ (termed Ni–Al), and $(NiO)ZnAl_2O_4$ (termed Ni–Zn–Al) catalysts, were prepared by coprecipitation at a constant temperature (60°C), and pH (7.2±0.2). The precipitation was carried out under low relative oversaturation, by simultaneous dropwise addition of a 1 M (total cation concentration) solution containing $Ni(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$, in the appropriate molar proportions (1:2:0 for the $NiAl_2O_4$ catalyst and 1:2:1 for the $(NiO)ZnAl_2O_4$ catalyst, respectively), and a 1 M solution of Na_2CO_3, over a stirred tank containing initially deionized water. The precipitate was washed with deionized water, dried at 70°C for 12 h, and then calcined at 500°C under a N_2 atmosphere for 14 h. The resulting solid was crushed and sieved to a size between 125 and 400 μm. In previous works [31], it has been shown that this method leads to a high degree of homogeneity in the solids obtained, which have an inverse non-stoichiometric spinel structure.

BET surface areas were determined by N_2 adsorption using a Micromeritics Pulse Chemisorb 2700. The temperature-programmed-reduction (TPR) system was described in a previous work [32]. The samples were reduced using 6% of H_2 in N_2, under a linear temperature ramp of 10°C/min up to a maximum temperature of 900°C. The sample size used was 200 mg, and the gas flow rate 106 ml/min. The catalyst surface was examined using a JEOL JSM 6400 scanning electron microscope. This allowed an assessment of the morphology of the catalyst surface and of the coke deposits.

X-ray photoelectron spectroscopy (XPS) studies were carried out at room temperature on a Fisons Escalab 200R spectrometer using MgK_α radiation. The samples were pretreated in a quartz tubular reactor with controlled conditions of atmosphere and temperature, analogous to those used in the kinetic experiments. After reduction, the sample was transferred to the analysis chamber under an inert atmosphere, and turbopumped to a residual pressure of about 4×10^{-10} Torr. The adventitious C 1s line at a binding energy of 284.6 eV was used as an internal standard.

In some of the experiments, the catalyst was subjected to a pretreatment with H_2S in a quartz, 8 mm i.d., flow reactor with automatic controls of flow and temperature. The usual catalyst sample size was 125 mg. Before introducing H_2S, the catalyst was reduced in situ, using a 50% H_2/N_2 mixture, with a total flow rate of 600 ml/min, following a temperature ramp of 10°C/min to a maximum temperature of 500°C, at which temperature the sample was maintained for 2.5 h. The catalyst temperature was brought down to 175°C under N_2, and a 94% H_2/6% N_2 stream containing 15 ppm of H_2S was then contacted with the catalyst for 30 or 90 min. This concentration was achieved by mixing a certified mixture containing 246.1 ppm of H_2S with a N_2 stream, until the desired sulphur level was reached.

After the sulphur treatment, the catalyst was cooled in N_2 and transferred to a thermobalance (CI Electronics) equipped with on-line GC analysis, where the reaction of ethyne hydrogenation was carried out. This allowed simultaneous gathering of coke weight and activity data during reaction. Before the start of the reaction, any possible oxidative passivation of the catalyst surface was eliminated by treating the catalyst with a 50% N_2/H_2 mixture using a temperature ramp (10°C/min), to 350°C, and keeping at this temperature for 90 min. After this, the catalyst was cooled down to the reaction temperature (175°C), and the reaction was started using a $N_2/H_2/C_2H_2$ ratio of 40:45:15, with a total flow rate of 700 ml/min. In a few experiments, the effect of an oxidation treatment on the poisoned catalyst was investigated. In this case, instead of the usual reduction treatment prior to reaction, the catalyst was treated with 10% O_2 in N_2 at 500°C for 1 h, followed by reduction with a 50%N_2/H_2 mixture at 500°C for 2.5 h.

Finally, some experiments were also carried out in which catalyst poisoning occurred simultaneously to the main reaction. These were performed in the same reaction system used for the catalyst pretreatment with H_2S, and with the same H_2S concentration, although in this case the reacting mixture contained 6% N_2, 92% H_2 and 2% C_2H_2, with a total flow rate of 1350 ml/min.

Selectivities are defined as the ratio of the number of moles of carbon in a given product to the total number of moles of carbon in the gas phase products. The yield to a given product species is calculated as the ratio of the number of moles of carbon of this species to twice the number of moles of ethyne in the reactor feed.

3. Results

Fig. 1A shows the results of the evolution with time of the total yield to gas products (methane+ethane+ethene) and of the ethene selectivity for experiments carried out in the fixed bed reactor. The open symbols in the figure correspond to experiments carried out without addition of H_2S, i.e., sulphur-free feed on a fresh catalyst, while the full symbols correspond to an experiment in which 15 ppm of H_2S are

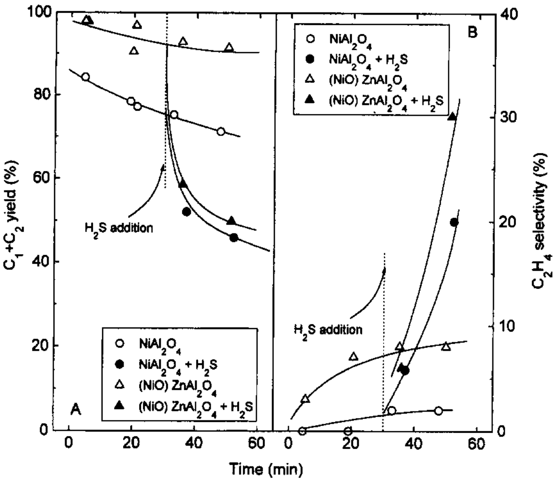

Fig. 1. Evolution of the total gas yield (C_1+C_2) (A) and of the C_2H_4 selectivity (B) with and without simultaneous addition of H_2S in the feed.

introduced after 30 min on stream. In the sulphur-free experiment there is a gradual loss of activity with time (catalyst coking), simultaneous to an increase in the selectivity to C_2H_4 (Fig. 1B). It is worth noting that the rather low selectivity to ethene is due to the high H_2/C_2H_2 ratio (46:1), used to minimize coke formation.

The introduction of H_2S during reaction gives rise to an important decrease in the gas yield as well as a higher selectivity to ethene. In fact, upon the introduction of H_2S in the feed, the yield to ethene increases between two (Ni–Zn–Al) and five (Ni–Al) times, as shown in Table 1. The table also shows that very substantial coke loadings are reached when H_2S is added, in spite of the high proportion of H_2 in the feed. With or without sulphur present in the feed, the Ni–Zn–Al catalyst always presents a higher yield to hydrogenation products (ethane+ethene), and a higher ethene/ethane ratio. However, it should be noticed that, after the introduction of H_2S, the relative decrease of the total hydrogenation yield is higher for the Ni–Zn–Al catalyst.

Table 1
Coke content and ethene yield for the $NiAl_2O_4$ and $(NiO)ZnAl_2O_4$ catalysts with or without simultaneous addition of H_2S to the feed (refer to Fig. 1), after 50 min of reaction

Treatment	Cc (mg/mg cat)	C_2H_4 yield (%)
$NiAl_2O_4$		
Absence of H_2S	0.08	1.7
H_2S introduced in the feed	0.165	9.2
$(NiO)ZnAl_2O_4$		
Absence of H_2S	0.061	7.3
H_2S introduced in the feed	0.176	15.5

In the experiments with simultaneous catalyst poisoning, the addition of H_2S starts after 30 min of reaction time.

While the experiments in Fig. 1 showed the behaviour of a catalyst with simultaneous coking and poisoning in the above described fixed bed reactor, Figs. 2–6 present results obtained in experiments carried out in a thermobalance, without sulphur present in the feed, using both sulphur-free and prepoisoned catalysts. It may be noticed that the conversion obtained in the thermobalance is considerably lower than in the fixed bed reactor, due to the different range of space times employed in both systems. In Fig. 2 the evolution of the total yield to gases (which would be equivalent to the total conversion if coke formation was neglected) is represented after sulphur treatments of different duration. It can be seen that the fresh Ni–Al catalyst presents a rapid initial deactivation, followed by a partial recovery of the catalytic activity to a yield level of 7.5% after 3 h on stream. On the other hand, the Ni–Zn–Al catalyst shows a slower, monotonic deactivation, with a gas yield still over 10% after 3 h. The effect of the prepoisoning treatment is rather

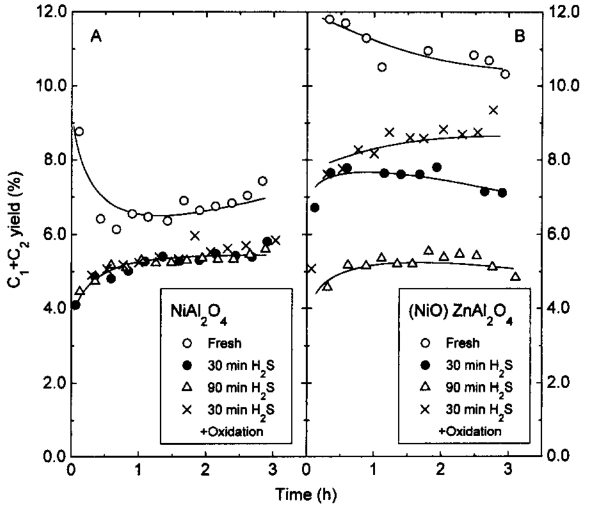

Fig. 2. Evolution of the total gas yield (C_1+C_2) for catalysts subjected to different degrees of sulphur poisoning: (A) $NiAl_2O_4$ catalyst; (B) $(NiO)ZnAl_2O_4$ catalyst.

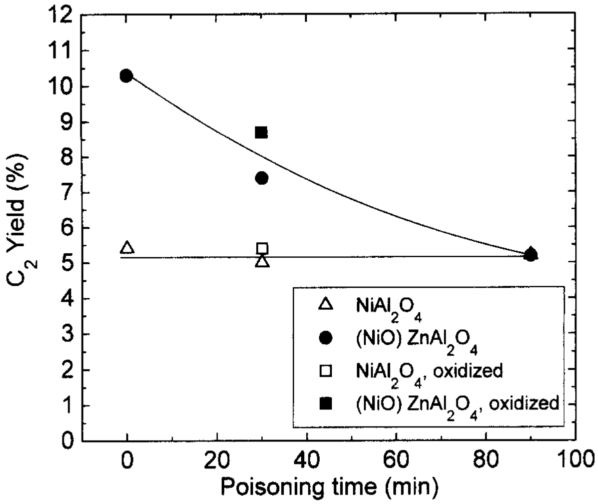

Fig. 3. C_2 yield versus poisoning time for the two catalysts studied.

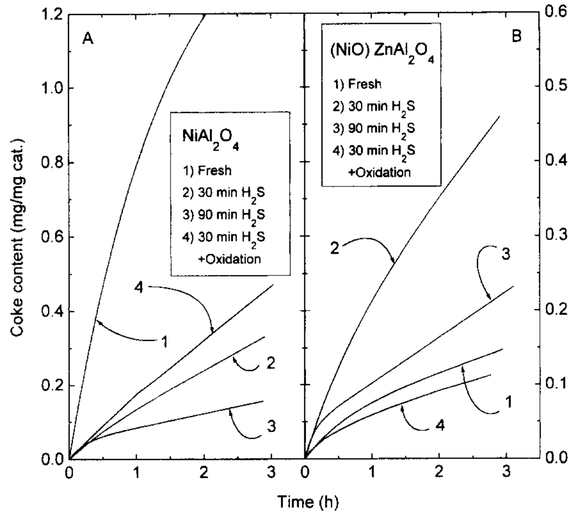

Fig. 4. Coke loading on the catalyst versus time, for catalysts subjected to different degrees of sulphur poisoning: (A) $NiAl_2O_4$ catalyst; (B) $(NiO)ZnAl_2O_4$ catalyst.

different for both catalysts: The gas yield obtained with the Ni–Al catalyst decreases after being treated with H_2S for 30 min, and then does not show any further decline for longer periods of exposure. In the Ni–Zn–Al catalyst, however, the decrease observed after the 30 min pretreatment in H_2S is much stronger than in the Ni–Al catalyst, and there is a further drop when the pretreatment duration is increased to 90 min.

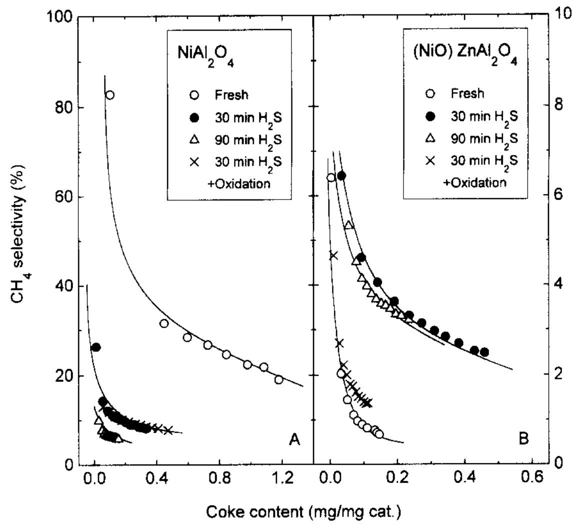

Fig. 5. CH_4 selectivity versus coke content, for catalysts subjected to different degrees of sulphur poisoning: (A) $NiAl_2O_4$ catalyst; (B) $(NiO)ZnAl_2O_4$ catalyst.

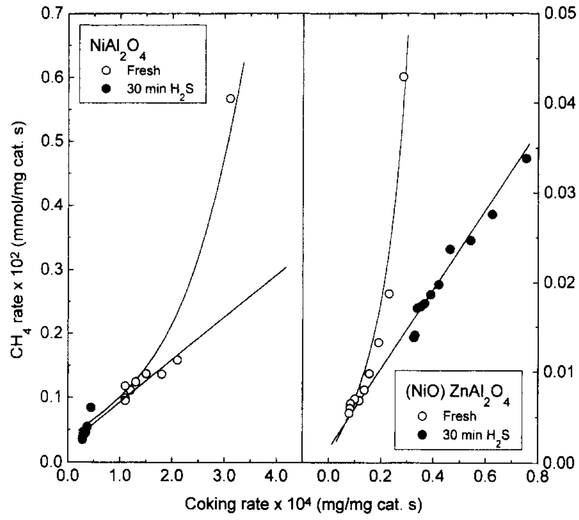

Fig. 6. Rate of methane formation versus rate of coking for fresh catalyst and after 30 min of exposure to H_2S: (Left) $NiAl_2O_4$ catalyst; (Right) $(NiO)ZnAl_2O_4$ catalyst.

After being treated 90 min in H_2S the activity level was similar in both catalysts. Also, in both catalysts, the effect of oxidation at 500°C after poisoning for 30 min is small, albeit more noticeable in the Ni–Zn–Al catalyst.

In Fig. 3, the average yield towards C_2 products (C_2H_4+C_2H_6), obtained in the experiments of Fig. 2, is represented as a function of the poisoning time. It can be seen that the total C_2 yield was little affected in the case of the Ni–Al catalyst, although the C_2 product distribution changes considerably, as will be shown later. Conversely, an important (50%) reduction can be observed for the Ni–Zn–Al catalyst as the pretreatment time increases, with a final level (corresponding to a 90 min poisoning period) approximately coincident with that of the Ni–Al catalyst.

The experimental data on the evolution of the coke content for both catalysts are given in Fig. 4. Again, important qualitative and quantitative differences are observed (note the different scales in both parts of the figure). Thus, the Ni–Al catalyst initially forms coke at a much faster rate than the Ni–Zn–Al catalyst, and the pretreatments with H_2S strongly reduce the coking rate, with a much higher decrease for the first 30 min pretreatment. On the other hand, the Ni–Zn–Al catalyst shows a more complex behaviour. The initial pretreatment increases the coking rate with respect to that of the fresh catalyst. However, a further exposure (90 min) to H_2S lowers the coking rate to values similar to those of the Ni–Al catalyst after the same pretreatment. Finally, oxidation and reduction at 500°C causes the coking rate of the Ni–Al catalyst to increase, while in the Ni–Zn–Al catalyst it decreases to values similar to those of the fresh catalyst.

The evolution of the selectivity to methane as a function of coke concentration is shown in Fig. 5. A similar behaviour would have been obtained representing methane selectivity versus time, although coke concentration is a more meaningful variable since methane production can be considered as a byproduct of coke formation in some cases [32]. It can be seen that the effect of the poisoning pretreatment on the methane production is analogous to that observed for coke formation: The initial (sulphur-free catalyst) methane selectivities are much higher for the Ni–Al catalyst (note again the different scale in Fig. 5A and B) and they decrease as the catalyst is poisoned, while a reverse trend is observed for the Ni–Zn–Al catalyst, with an increase of the selectivity to methane after poisoning for 30 min. It should also be noticed that when the coking rate is the highest, i.e., at the start of the reaction (Fig. 4), the rate of methane formation is also the highest, and both rates decrease in parallel. This similar behaviour suggests that methane formation is related to coke formation also in the catalytic system studied in this work. However, it is interesting to examine the results presented in Fig. 6, where the rates of coke formation and of methane formation (hydrogenolysis) are represented for fresh and poisoned Ni–Al and Ni–Zn–Al catalysts. An approximately linear relationship can be observed that includes data from both poisoned and fresh catalysts, in which the ratio of the rate of methane formation to the rate of coke formation is roughly constant. The exception to this trend are the initial data points of the fresh catalysts where this ratio is much higher than in the rest of the experiment. This could be indicative of the existence of a different type of coke or of a different coke formation mechanism in the initial stages of the reaction. This initial type of coke or of coking mechanism would disappear for the poisoned catalyst, as indicated by the data in Fig. 6.

In Fig. 7, the ethene selectivity (the desired product) is also represented as a function of the coke content of the catalyst. It can be observed that coking has a beneficial effect on the C_2H_4 selectivity, which increases strongly with coke content for both Ni–Al and Ni–Zn–Al catalysts, whether fresh or poisoned.

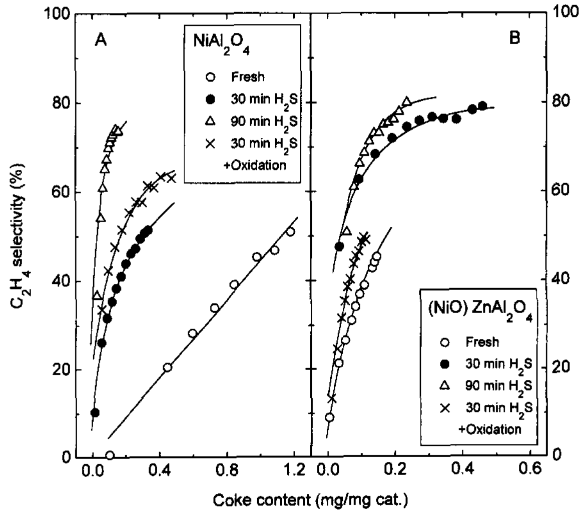

Fig. 7. C_2H_4 selectivity versus coke content, for catalysts subjected to different degrees of sulphur poisoning: (A) $NiAl_2O_4$ catalyst; (B) $(NiO)ZnAl_2O_4$ catalyst.

However, it should be noticed that the H_2S pretreatment is also beneficial, and thus the amount of coke at which a certain selectivity level is attained decreases as poisoning time increases. Therefore, either the coke or the sulphur present on the catalyst surface or both are responsible for this increase of selectivity. Also, the Ni–Zn–Al catalyst gives the same level of selectivity as the Ni–Al catalyst at lower coke levels, indicating that the addition of ZnO has a positive effect on the overall catalytic performance. Finally, the effect of the oxidation treatment follows similar trends to those already discussed for coking and methane formation.

Regarding catalyst characterization, BET surface areas were similar, 235 and 210 m^2/g for the Ni–Al and the Ni–Zn–Al catalysts, respectively. The temperature programmed reduction results (not shown) revealed a similar reducibility of the Ni^{2+} species present in both catalysts, with a single peak around 890 K. Nevertheless, the Ni–Al catalyst presents a higher concentration of reducible species, which explains its relatively high overall activity. However, as we have seen in Figs. 2, 4, 5, a significant part of this activity is directed towards methane and coke formation, while the Ni–Zn–Al catalyst is more selective and gives higher yields of the main reaction products.

Electron microscopy studies indicated that coke formation also proceeds differently on both catalysts studied. Fig. 8 shows an example of the SEM results obtained for the Ni–Zn–Al catalyst. It can be seen that the coking of the fresh Ni–Zn–Al catalyst proceeds with considerable whisker formation (Fig. 8A), while these were mostly absent from the sulphur-passivated catalyst which was covered by an amorphous type of coke (Fig. 8B). Conversely, whisker formation could not be observed in SEM micrographs of the Ni–Al catalyst, irrespective of whether it was used fresh (Fig. 8C) or poisoned (not shown).

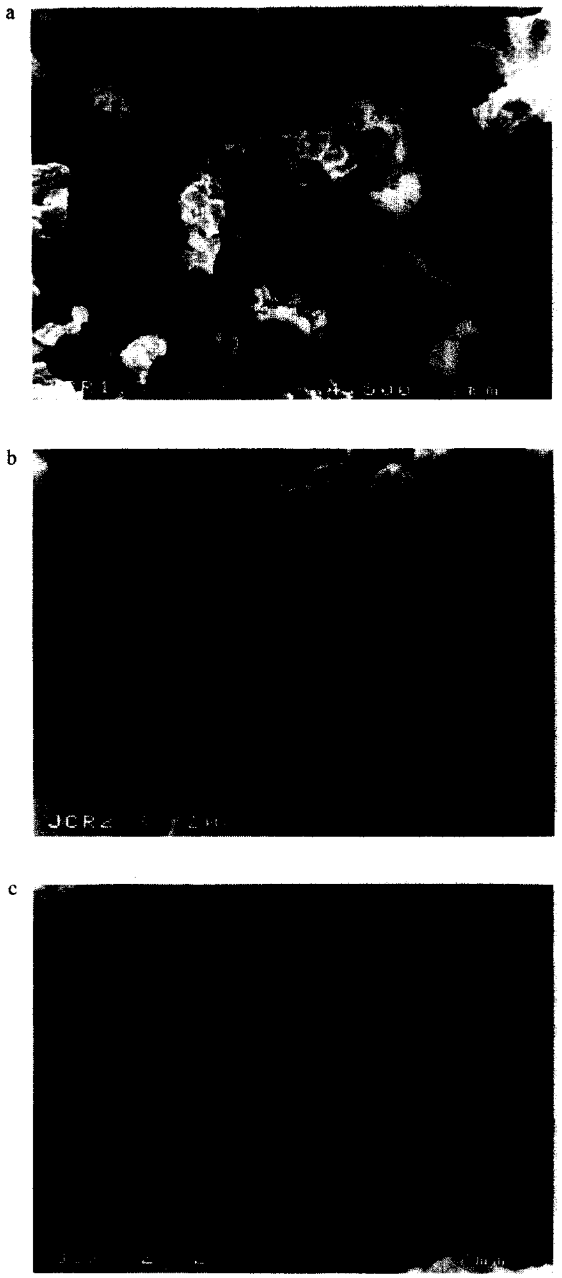

Fig. 8. SEM micrographs of coked catalysts with different degrees of sulphur poisoning: (A) Fresh $(NiO)ZnAl_2O_4$ catalyst; (B) poisoned $(NiO)ZnAl_2O_4$ catalyst; (C) fresh $NiAl_2O_4$ catalyst.

XPS analysis was used to determine the percentage of reduction of surface Ni (i.e., atomic ratio of Ni^0 on surface/total Ni on surface), using similar conditions to those employed in the reaction experiments. Reduction percentages of 45% and 35% were obtained, respectively, for the Ni–Zn–Al and Ni–Al catalysts. After passivation in sulphur for 90 min (Fig. 9A,B), the percentage of sulphided Ni (i.e., sulphided Ni on surface/total Ni on surface) was higher for the Ni–Zn–Al catalyst (15% versus 10% for the Ni–Zn–Al and Ni–Al catalysts, respectively), as shown in Fig. 9 by the band at 854 eV, assigned to Ni_3S_2 [33]. Combining the percentages of sulphided and reduced Ni, one

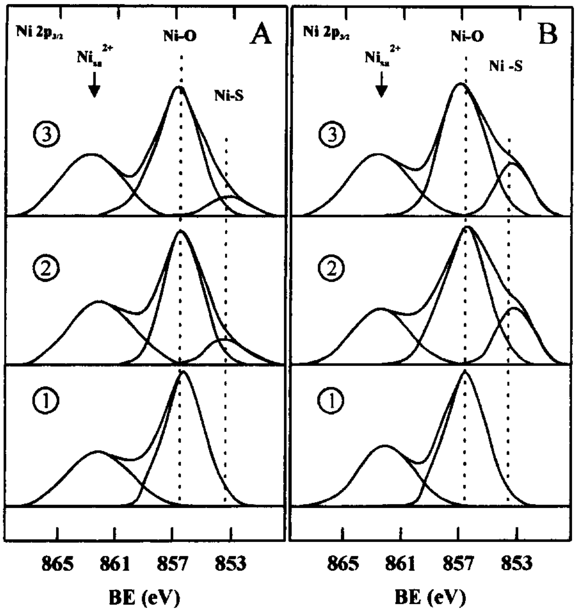

Fig. 9. XPS analysis of fresh and poisoned catalysts. (A) $NiAl_2O_4$; (B) $(NiO)ZnAl_2O_4$: (1) Fresh catalysts; (2) after treatment in 15 ppm H_2S for 90 min; (3) same as (2) plus oxidation at 500°C for 1 h.

could arrive at similar figures (29% and 33%) for the fraction of metallic Ni that is likely to be sulphided after a 90 min treatment. It is also worth noticing that the oxidation treatment was not able to remove sulphur from the catalyst surface, as shown in Fig. 9. Supplementary XPS data (not shown), indicated that Zn in the Ni–Zn–Al catalyst was not sulphided under any of the treatments carried out.

4. Discussion

4.1. Experiments with simultaneous reaction and poisoning of the catalyst

As shown above, the introduction of H_2S during reaction gives rise to a fast increase in the coking rate and ethene selectivity, together with a decrease in the total gas yield. Since the introduction of H_2S takes place after 30 min on stream, the metallic surface is already partly covered by hydrogen and C_2H_x species, which are a result of the adsorption and partial degradation of ethyne. The formation of this layer of partly dehydrogenated species plays an important role in ethene production from ethyne [24]. The C_2H_x species remain strongly attached to the metallic surface during the course of reaction, and their hydrogenation rate is low compared to ethyne hydrogenation. The latter may take place over the clean metal surface to give either methane or ethane, or over the layer of C_2H_x species, to give ethene [24].

Given the conditions used in the reaction experiments before the introduction of H_2S (92% of hydrogen in the reactor feed), it seems reasonable to consider that the surface is preferentially covered by hydrogen (note the high selectivity to ethane in Table 1). The introduction of H_2S modifies the selectivity by displacing part of the hydrogen adsorbed onto metallic sites, which decreases the extent of the reactions taking place on these, as indicated by the rapid decrease of the C_1+C_2 yield in Fig. 1. On the other hand, the selectivity to ethene increases, which was expected since this reaction takes place over the C_2H_x layer. The conversion of ethyne was around 100% in the experiments shown in Figs. 1 and 2, even after the introduction of H_2S. The decrease in the C_1+C_2 yield in the presence of H_2S takes place along with an increase in ethyne oligomerization, giving a faster coking and heavier reaction products [7]. In this work, however, only coke is reported, since gas products heavier than C_2 were not analysed.

4.2. Experiments with catalysts poisoning previous to reaction

4.2.1. Behaviour of sulphur-free catalysts

It has been shown above that the Ni–Zn–Al catalyst has a higher hydrogenation activity, and a lower tendency to coke and methane formation compared to the Ni–Al catalyst. It has been established [20–24] that the presence of a carbonaceous residue on the catalyst surface has an important influence on the activity and selectivity of reactions such as ethyne hydrogenation. In this work, the results obtained indicate that, as coking proceeds, a parallel increase in the selectivity to ethene is observed. Again, this can be explained by considering that CH_4 and C_2H_6 are formed on bare metallic sites, while C_2H_4 is formed over the C_2H_x layer. Thus, as the surface is covered by carbonaceous species, the relative contribution of the reactions giving C_2H_4 increases, which results in a higher selectivity.

When the hydrogenation of unsaturated hydrocarbons takes place on a chemisorbed hydrocarbon layer rather than on the clean metal surface, there is a basis to consider the process as a structure-insensitive reaction. However, recent results indicate that the nature of the predominant surface species and the strength of adsorption of reactant molecules often depend not only on the operating conditions but also on the metal faces exposed. Thus, Pradier and Berthier [34] found that the highest activity for butadiene hydrogenation corresponded to a Pt(1 1 0) face, then Pt(1 0 0) and finally Pt(1 1 1). Also, Boitiaux et al. [8] found that the irreversible adsorption of highly unsaturated molecules such as butadiene or butyne depends on the degree of dispersion and hence on the particle size.

It seems clear that the interaction between the active metal and the support may influence the strength of adsorption of ethyne via modification of the physical configuration of the metal particles and their electron density fields. In this work, in the Ni–Zn–Al catalyst there is NiO dispersed over a non-stoichiometric $ZnAl_2O_4$ spinel support, with a well defined structure [30], while the crystalline structure of the $NiAl_2O_4$ is less defined, and NiO, $NiAl_2O_4$ and Al_2O_3 coexist on the catalyst [30,35]. This is the result of the lower tendency of Ni to form spinel-type structures, compared to Zn [36]. In this type of oxides ($NiO–Al_2O_3$), the presence of $NiAl_2O_4$ inside or on the surface of the NiO particles often plays a significant role in the thermal stability and resistance to sintering shown by this type of catalysts [36], and could also explain the tendency of the Ni–Al catalyst to form coke and methane: The presence of $NiAl_2O_4$ species, which are not substantially reduced under the conditions used to activate the catalyst (up to 500°C), would give rise to an irregular geometry of the metallic particles, with a very high concentration of active sites for the rupture of C–C bonds [27]. The consequence of the different activity of the metal in both catalysts is that, for a given amount of coke deposited, the selectivity to ethene is considerably lower in the Ni–Al catalyst, as shown in Fig. 7. The dominant process in this catalyst seems to be C–C cleavage, leading to coke and methane, while it could be speculated that in the Ni–Zn–Al catalyst a lower strength of the metal–ethyne bond gives a higher selectivity to hydrogenation products.

Electron micrographs (Fig. 8) showed only amorphous carbon in the Ni–Al catalyst, while in the fresh Ni–Zn–Al catalyst both amporphous and filamentous carbon were present. Thus, in the Ni–Zn–Al catalyst the carbon formed in the first stages of reaction diffuses through the metal and is able to detach the Ni crystallite from the support. This does not take place with the Ni–Al catalyst, probably due to the more intense metal–support interaction [35], which leads to a preferential encapsulation of the metal crystallites rather than to whisker formation [37]. A preferential encapsulation would certainly be a contributing factor for the fast initial deactivation of this catalyst.

4.2.2. *Behaviour of poisoned catalysts*

It has been shown that pretreating the catalyst with 15 ppm of H_2S in H_2 for 30 or 90 min strongly influences the activity of the catalyst for the main and coking reactions (Figs. 2–4). In the Ni–Al catalyst the presence of H_2S rapidly deactivates a large proportion of the sites responsible for coke and methane formation, with only a small effect on the hydrogenation activity. On the contrary, in the Ni–Zn–Al catalyst, the initially low methane and coke formation rates are increased as a result of sulphur poisoning, which partly offsets the improvement in catalyst performance resulting from the introduction of Zn.

The XPS results indicate that the degree of sulphiding of metallic Ni is around 30% in both catalysts, i.e., most of the active surface (approx. 70%) is still available for reaction. From Figs. 3–5, it appears that the Ni–Al catalyst has been selectively poisoned, with a preferential attack on the active sites (kinks, steps, corners, etc.), responsible for structure-sensitive reactions, such as hydrogenolysis (methane formation) and coking, while hydrogenation sites seem to be less affected. However, in the Ni–Zn–Al catalyst, with a lower concentration of active sites for demanding reactions (as indicated by its low initial activity for coking and methane production), a mild (30 min) poisoning treatment mainly deactivates the dominant kind of sites, i.e., hydrogenation sites.

The strong increase observed in the coking and methane formation rates on the Ni–Zn–Al catalyst after a 30 min exposure to H_2S can be explained by the presence of electron-attracting compounds (H_2S) on the catalyst surface. It is well documented

[8–10,13,38] that this may enhance side reactions (such as coke formation), due to an effect of charge transfer to sulphur, which increases the strength of adsorption of ethyne molecules, thus favouring their degradation towards coke [24]. Obviously, this also takes place on the Ni–Al catalyst, although in this case the dominant process is initially the deactivation of active sites for demanding reactions, as discussed above. An increase in the poisoning time to 90 min leads to a further decrease on the catalytic activity for both the main and coking reactions and this effect overcomes the activation of coking in the Ni–Zn–Al catalyst via charge transfer. As a result of these competing processes (increase of the coking rate due to charge transfer and decrease due to deactivation), a maximum was observed in the coking rate of the Ni–Zn–Al catalyst for a 30 min poisoning time. It should be noted that when the exposure to H_2S is extended to 90 min the coking rates are similar on the Ni–Zn–Al and Ni–Al catalysts.

Finally, subjecting the catalyst to an oxidation treatment at 500°C after poisoning for 30 min leads to very different results for both catalysts. From the kinetic results alone, it would seem that the oxidation treatment was able to remove sulphur from the surface of the Ni–Zn–Al catalyst, since after oxidation its behaviour regarding the coking rate and the selectivity to the different reaction products was similar to that of the fresh catalyst. This does not take place on the Ni–Al catalyst, where the behaviour of the catalyst after a 30 min poisoning period was approximately the same, with or without oxidation treatment. On the other hand, XPS analysis (Fig. 9), clearly showed that the amount of sulphided metal before and after the oxidation treatment was substantially the same, thus indicating that sulphur was not eliminated from the catalyst surface. An alternative explanation to the fact that after the oxidation treatment the coking rate of the Ni–Zn–Al catalyst goes down to approximately the same level as in the fresh catalyst would be that the oxidation treatment effectively destroys the charge transfer effect between Ni and sulphur, which in the above discussion was deemed responsible for the observed increase in the coking rate. This could be the result of the segregation of Ni_3S_2 and NiO during oxidation at 500°C. After the ensuing reduction, the resulting Ni^0 phase would have little or no interaction with Ni_3S_2.

5. Conclusions

Highly active sites on the surface of the Ni–Al catalyst are responsible for the substantial rates of coking and methane formation observed on the fresh catalyst. H_2S effectively deactivates these sites, thus improving the catalytic performance. On the other hand, the presence of ZnO in the fresh catalyst is also beneficial, giving rise to a more selective catalyst with reduced rates of coking and methane formation. Poisoning in this catalyst also increases the selectivity to ethene, by reducing the rate of ethane formation. However, unlike the Ni–Al catalyst, the presence of sulphur increases the rates of methane and coke formation. The presence of H_2S in the feedstream also eliminates the formation of carbon whiskers on this catalyst. As a result of the comparison between the two catalysts studied, it can be concluded that the metal–support interaction, which can be modified by promoters such as ZnO, has a strong effect upon the sensitivity of the catalyst towards deactivation by coking and poisoning.

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