JOURNAL OF CATALYSIS **143**, 187–200 (1993)

The Deactivation of Nickel Catalysts in the Hydrogenation of Acetonitrile

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Received September 24, 1992; revised March 15, 1993

Nickel catalysts tend to deactivate in the hydrogenation of acetonitrile. Using temperature-programmed techniques, combined with a number of different analytical procedures, including mass spectrometry, it was established that the formation of surface nickel carbides was the major cause of the loss of activity with time on stream. The presence of partly dehydrogenated species was a second factor causing the loss of activity. Even in the presence of hydrogen adsorbed nitrile molecules were partly dehydrogenated during the process. The resulting species were strongly adsorbed on the nickel surface and blocked some of the active sites for hydrogenation. Treatment of the deactivated catalyst with hydrogen at an elevated temperature (>200°C) restored both the catalytic activity and the selectivity of the catalyst. The influence of the hydrogen partial pressure on the rate of deactivation was assessed by performing the hydrogenation at several different molar hydrogen-to-acetonitrile (H/C) ratios. It was found that the performance of the catalyst could be maintained when a large excess of hydrogen was present in the feed. Under the experimental conditions, a H/C ratio higher than about 25 was required to maintain productivity. © 1993 Academic Press, Inc.

INTRODUCTION

In oil refining and petrochemical processes, catalyst deactivation through the lay-down of carbonaceous residues is a major problem. The activity declines with process time at a rate that depends on the prevailing conditions. The loss of catalytic activity may proceed gradually or very rapidly. In the steam reforming and methanation reactions, supported nickel catalysts can deactivate rapidly due to coke formation (*1*). Especially at low steam or hydrogen concentrations and at high temperatures, the buildup of carbon is fast.

Based on the reactivity of deposited carbon with hydrogen, McCarty and Wise (*2*) distinguished several distinct carbon species in a carburized nickel-on-alumina catalyst. Using temperature-programmed surface reaction (TPSR) and electron microscopy, they identified the different carbon structures as chemisorbed carbon, nickel carbide, and filamentous and encapsulating carbon (3). Because all reactants containing carbon are potential coke precursors, carbon is usually deposited to some extent onto catalysts used in the processing of organic feeds. Especially organic reactants containing an aromatic nucleus have a high tendency for coke formation, but also acetylenes, olefins, and paraffins are known to be liable to deposit carbon onto catalysts (*4, 5*). The rate of carbon accumulation is a balance between the rate of carbon deposition and the rate of carbon removal. The operating conditions and the nature of the catalyst influence the net carbon accumulation on the surface of the catalyst. To minimize carbon formation, all factors affecting the rates of deposition and removal have to be controlled carefully. The removal of carbonaceous deposits can be achieved by reactions with several carbon gasifying agents, such as steam, hydrogen, or oxygen. The extent of carbon removal is largely de-

0021-9517/93 $5.00

termined by its reactivity and its nature, as well as by the regenerating conditions (*4*, *6*).

Anderson and Clark (*7*) studying the reactions of aliphatic amines over vapor-deposited metal films of Pt, Pd, Ni, Co, and W, showed that the adsorbed amines decomposed, which resulted in the incorporation of carbon into the surface of the catalyst. With a vanadium metal film the formation of nitrides was also observed. In another study by Baiker *et al.* (*8*) similar results were obtained. Using the disproportionation of methyl- and dimethylamine as test reactions, these authors observed three different deactivation processes, namely, the formation of metal nitride, of metal carbide, and of carbonaceous deposits. The presence of (a small amount of) hydrogen prevented nitride formation and inhibited both the formation of carbides and the buildup of carbon deposits.

In this study the deactivation of supported nickel catalysts in the gas-phase hydrogenation of acetonitrile has been investigated. The investigation is part of a larger research program on nitrile hydrogenations with metal-based catalysts. For a review on nitrile hydrogenation, the reader is referred to the article by Volf and Pasek (*9*). Since the supported nickel catalysts appeared to lose activity to a considerable extent, a study was conducted to reveal the origin of the activity loss. To that end several experimental techniques were adapted, including TPSR and *in situ* deactivation experiments in a microflow apparatus. It is demonstrated that the extent to which deactivation occurs can be reduced substantially by performing the hydrogenation under appropriate operating conditions.

EXPERIMENTAL

Preparation of the Catalysts

A 25 wt% nickel-on-silica catalyst was prepared by means of a homogeneous precipitation method as described by van Dillen *et al.* (*10*). The decomposition of urea was used to raise the pH of a nickel salt solution, containing suspended silica, homogeneously. Above about 70°C, urea hydrolyzes; the decomposition generates hydroxyl ions homogeneously throughout the solution. The liberated hydroxyl ions precipitate the nickel ions exclusively onto the surface of the support material in the form of nickel hydrosilicate (*11*). After the precipitation was completed, the green precursor was filtered, washed thoroughly with hot (80°C) bidistilled water, and air-dried overnight at 120°C.

Samples of the precursor were diluted to obtain a 5-wt% Ni-loaded catalyst. To achieve this the dried precursor was powdered in a mortar and diluted with Aerosil 200 in a precursor-to-silica ratio of 1/4. The diluted precursor was pressed at 1000 kg/cm^2, crushed, and finally sieved. The diluted nickel-on-silica catalyst is encoded S25U-d. A sieve fraction of 0.50 to 0.85 mm was used in all experiments.

Characterization

Prior to any characterization, the dried precursor was previously reduced at 450°C for 10 h in flowing hydrogen (75 ml/min). Using thermogravimetric analysis, it was determined that after this reduction procedure the nickel was 90% reduced.

The specific surface area was measured by nitrogen adsorption at -196°C using the BET-method. Prior to adsorption, the sample was outgassed at 125°C for 3 h. The surface area of the reduced catalyst was 245 m^2/g.

The nickel surface area was determined by static hydrogen adsorption at room temperature. After reduction, adsorbed hydrogen was removed by evacuation at 450°C for 30 min. After the reduced sample was cooled to room temperature under vacuum, the hydrogen pressure was increased in steps to approximately 80 Torr. The monolayer coverage was determined using back-extrapolation of the data points to zero pressure. Dissociative adsorption was assumed with an adsorption stoichiometry of one H atom per surface Ni atom. A value of 6.33×10^{-20} m^2 was used for the area of one nickel atom (*12*). The specific nickel surface area of the 25-wt% Ni-on-silica catalyst was 110 m^2/g Ni.

Gas-Phase Hydrogenation of Acetonitrile

The deactivation of catalyst S25U-d in the gas-phase hydrogenation of acetonitrile to primary, secondary, and tertiary amines was studied in an atmospheric continuous-flow reactor with gas chromatographic detection (*13*). Sampling of reactant and product gases was performed with pneumatically controlled six-way valves, and gas samples were analyzed by GLC using a Perkin–Elmer 8500 gas chromatograph equipped with a flame ionization detector. Prior to the experiments, the precursor was dried at 125°C for 30 min in flowing hydrogen (75 ml/min). The gas mixture was passed downflow through the catalyst bed (diameter 10 mm), which consisted initially of 0.25 g of the precursor. The temperature was measured just below the catalyst bed with a chromel–alumel thermocouple. The reactor temperature was raised at a rate of 2°C/min to 450°C and kept at this temperature for 10 h. After the reduced catalyst had been cooled to room temperature, the gas composition was switched to a variable mixture of N_2 and H_2 of a total flow rate of 75 ml/min. The gas composition could be varied between 100 vol% hydrogen and 100 vol% nitrogen.

After reduction the gas flow was saturated with acetonitrile (Merck, p.a.) by passing it through a saturator thermostated at −4°C by means of a cooled circulator (Tamson TLC-3), resulting in a concentration of 2.5 vol% acetonitrile in the gas stream (*14*).

In the deactivation experiments, the reactor temperature was raised from room temperature to 125°C at a rate of 10°C/min. When this temperature was attained, the catalytic performance was monitored as a function of process time.

To study the effect of temperature on the reaction, the reactor temperature was raised from room temperature to 40°C (where catalytic activity develops) and the temperature of the catalyst bed was stabilized for 25 min. Then, the bed temperature was raised in steps of 5 to 140°C with a 25-min stabilization time between two measurements. The same procedure was followed with decreasing bed temperatures. Data points were collected every 25 min. A typical run consisted of the analysis of a product sample ($\text{acetonitrile}_{\text{out}}$) and of a reference sample withdrawn from the reactant gas entering the reactor ($\text{acetonitrile}_{\text{ent}}$).

The conversion is defined as

$$\text{Conversion (\%)} = \left(1 - \frac{\text{acetonitrile}_{\text{out}}}{\text{acetonitrile}_{\text{ent}}}\right) \times 100.$$

Product selectivities have been calculated from peak areas corrected for different response factors in the flame ionization detector and normalized to moles of product. Since the carbon balance was always near 100%, the selectivity for product *i* is defined as

$$\text{Selectivity}^i\text{(mol\%)} = \frac{\text{Corrected area}^i}{\text{Summed area of all peaks}} \times 100.$$

In Table 1 the general test conditions adopted in the kinetic measurements are summarized.

Preliminary experiments ruled out the existence of transport limitations. To this end, the usual experimental checks were performed (*15*). The sieve fractions 0.212–0.50 and 0.50–0.85 mm produced identical conversion patterns, indicating the absence of intraparticle transport limitations. Variation of the bed depth and gas flow rate at constant space-velocity also resulted in similar conversion patterns. Interparticle heat and mass transfer limitations were therefore absent also.

Temperature-Programmed Surface Reactions

Three different sets of experiments were performed, differing mainly in the analytical

TABLE 1

General Test Conditions for the Hydrogenation of Acetonitrile

Catalyst weight	0.25 g
Grain size	0.50–0.85 mm
Gas flow rate	75 ml/min
Feed (variable)	x vol% nitrogen (97.5-x) vol% hydrogen 2.5 vol% acetonitrile (fixed)
H/C ratio	Variable: 0–39
Total pressure	1 bar
Deactivation temperature	125°C
Temperature range for Conversion measurements	40–140°C
Analysis	Gas chromatography Column: Tenax TA (packed) Detector: FID (carrier N_2)

procedure. In the first TPSR experiment, 0.15 g of the diluted precursor S25U-d was dried at 125°C for 30 min in flowing hydrogen (75 ml/min). After drying, the reactor temperature was raised to 550°C at a heating rate of 2°C/min and the reduction was allowed to proceed at this temperature for 16 h. This somewhat high reduction temperature was adopted to avoid interference of nickel reduction in subsequent experiments. The reduced catalyst was cooled in the hydrogen flow to room temperature, and a mixture containing 65 vol% N_2, 32.5 vol% H_2, and 2.5 vol% acetonitrile was fed to the reactor at a rate of 75 ml/min. The temperature of the catalyst bed was increased from room temperature to 125°C at a rate of 10°C/min, and kept at 125°C for 10 h, during which time the deactivation of the catalyst proceeded. After the catalyst had been deactivated at 125°C, it was cooled to room temperature in the acetonitrile-containing gas flow. The reactor was closed, disconnected, transported to the TPSR apparatus, and connected. Extreme care was taken to prevent exposure of the reduced catalyst to air. Argon was passed through the catalyst bed and the reactor was flushed for 30 min at room temperature. During the measurement, the gas composition downstream of the reactor was monitored continuously with a quadrupole mass spectrometer (Balzers, model QMG 420) equipped with a secondary electron multiplier. A portion of the effluent gas stream was admitted into the vacuum system of the mass spectrometer through an adjustable atmospheric leak valve. Selected fragments of mass-to-charge ratios of 2, 12, 13, 14, 15, 16, 17, 18, 28, 30, 41, 45, 73, and 101 were simultaneously analyzed every 6 s. Two sequential measurements were performed on the thus pretreated catalyst sample.

In the first measurement, the catalyst was heated in argon from room temperature to 300°C at a rate of 5°C/min. Then the sample was cooled in argon to room temperature, and a switch was made from argon to 10 vol% H_2 in argon. In the second measurement, the temperature was raised to 325°C also at a linear rate of 5°C/min. Relative peak intensities are plotted as a function of temperature for both measurements in Figs. 4 and 5, respectively.

In the second TPSR experiment, 0.15 g of the diluted S25U-d precursor was reduced and deactivated analogously to the procedure described above. After the catalyst had been deactivated at 125°C, however, the catalyst was cooled to 100°C, the acetonitrile and hydrogen feed were shut off, and the reactor was flushed with nitrogen for 30 min. Then, the catalyst was cooled to room temperature in flowing nitrogen. The reactor was closed, disconnected, transported to the TPSR apparatus, and connected. Again precautions were taken to prevent exposure to air. Before the TPSR experiment was started, the bypass of the reactor was flushed for 30 min with a 10 vol% H_2 in argon mixture to prevent oxidation. The gas mixture was then directed through the catalyst bed, and the temperature was raised from room temperature to 650°C at a linear rate of 3°C/min. A thermal conductivity detector monitored the change in the hydrogen concentration continuously. Before entering the detector, the reactor effluent was passed through a cold trap (solid carbon dioxide/acetone). The resulting hydrogen consumption profile is plotted in Fig. 6 as a function of the temperature of the catalyst.

The third TPSR experiment was performed *in situ* in the microflow apparatus. After the S25U-d precursor had been reduced and deactivated according to the procedure described for the first and second experiment, the catalyst was cooled to 100°C and purged for 30 min with nitrogen. Then the catalyst was cooled to room temperature in flowing nitrogen. The gas composition was switched to 10 vol% hydrogen in nitrogen, and the reactor temperature was raised at a rate of 3°C/min to 300°C. Every 5 min a gas sample was taken and analyzed using the gas chromatograph. Figures 7, 8, and 9 show the results.

RESULTS AND DISCUSSION

The Deactivation of Nickel Catalysts in the Hydrogenation of Acetonitrile

Deactivation of the nickel-on-silica catalysts was observed during measurements of the conversion of acetonitrile as a function of the temperature. A typical plot of the acetonitrile conversion versus the temperature of catalyst S25U-d is shown in the left-hand part of Fig. 1, labeled "fresh catalyst." At increasing temperatures (as indicated by the arrow pointing up), the conversion was always higher than that at decreasing temperatures (arrow pointing down) due to the loss of hydrogenation activity.

To inspect the deactivation more closely, the conversion was measured isothermally at 125°C for several hours. As can be concluded from the left-hand curve labeled "fresh catalyst" in Fig. 2, the catalyst lost a substantial part of its activity during the first 15 h of isothermal operation.

It was possible to regenerate the deactivated catalyst. Treatment of the deactivated catalyst with 10 vol% H_2 in N_2 at 250°C for 2 h, after the catalyst had been operative for various periods of time, fully restored its initial performance. Both the activity and the selectivity were restored to their initial values. Figures 2 and 3 show the results. Several consecutive deactivation/regeneration cycles were performed, and after each regeneration both the decline of the activity and the course of the selectivity followed the same pattern. It can be seen in Fig. 3 that the selectivity toward the primary amine increases with time on stream. Therefore it seems that with a progressive deactivation there is a decrease in the extent to which the condensation reactions, leading to the formation of secondary and tertiary amines (9), proceed.

Quite the opposite was found when the deactivated catalyst was treated in pure nitrogen at 250°C for 2 h. As can be seen from the lower curve in Fig. 1, the catalytic activity decreased drastically after this treatment. It is therefore obvious that the presence of hydrogen is essential for the regeneration of the deactivated catalyst. The almost fully deactivated catalyst that resulted from the treatment in nitrogen at 250°C could, however, be regenerated completely through a subsequent hydrogen treatment at 250°C for 2 h.

From these results it may be concluded that during operation some species that blocks part of the active hydrogenation sites is deposited onto the surface of the catalyst and thus lowers the catalytic activity. This species can be removed from the surface at

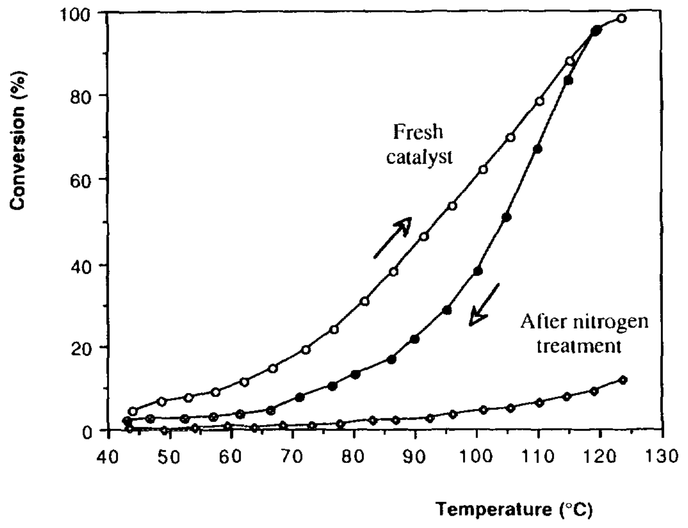

FIG. 1. Conversion of acetonitrile as a function of temperature for catalyst S25U-d. Upper curve: fresh catalyst. Arrow pointing up indicates rising temperature, arrow pointing down decreasing temperature. Lower curve: the same sample after nitrogen treatment at 250°C for 2 h. Gas composition: 65 vol% N_2, 32.5 vol% H_2, and 2.5 vol% acetonitrile.

elevated temperatures in a hydrogen-containing gas flow. In the absence of hydrogen and at elevated temperatures, on the other hand, decomposition of the adsorbed species occurs, resulting in a further, more extensive contamination of the surface. An almost completely deactivated catalyst then results. This hypothesis was checked experimentally using temperature-programmed surface reactions. To this end, a sample of a deactivated catalyst S25U-d was heated in an argon flow, while the chemical compo-

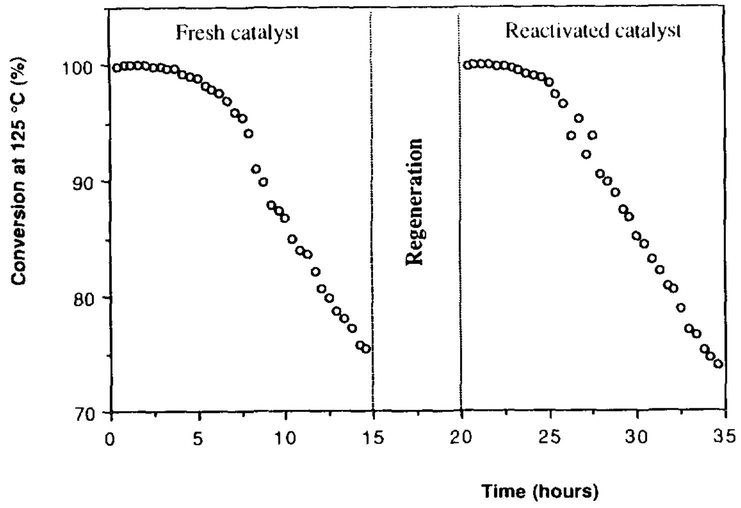

FIG. 2. Conversion of acetonitrile at 125°C as a function of time for catalyst S25U-d, before and after regeneration in 10 vol% H_2/N_2 at 250°C for 2 h. Gas composition: 65 vol% N_2, 32.5 vol% H_2, and 2.5 vol% acetonitrile.

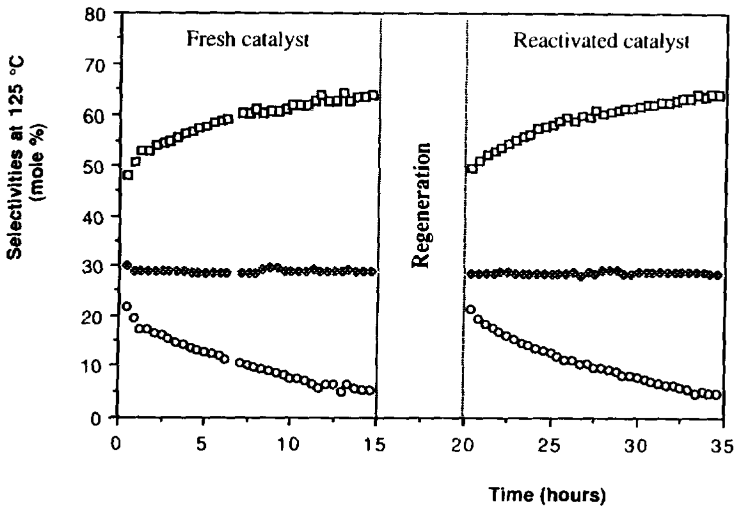

FIG. 3. Selectivity at 125°C as a function of time for catalyst S25U-d, before and after regeneration in 10 vol% H_2/N_2 at 250°C for 2 h. Gas composition: 65 vol% N_2, 32.5 vol% H_2, and 2.5 vol% acetonitrile. (□) MEA, monoethylamine; (◆) DEA, diethylamine; and (○) TEA, triethylamine.

sition of the reactor effluent was monitored continuously using a mass spectrometer. The results from this experiment are shown in Fig. 4, where relative peak intensities are plotted as a function of temperature.

Desorption of undissociated acetonitrile (mass 41) started at about 75°C and attained a significant rate above 135°C. When a temperature of 180°C was reached, several other species emerged in the effluent gas. A maximum intensity was reached for all monitored masses at temperatures near 210°C. As can be seen, a large amount of mass 2 (hydrogen) was evolved at this tem-

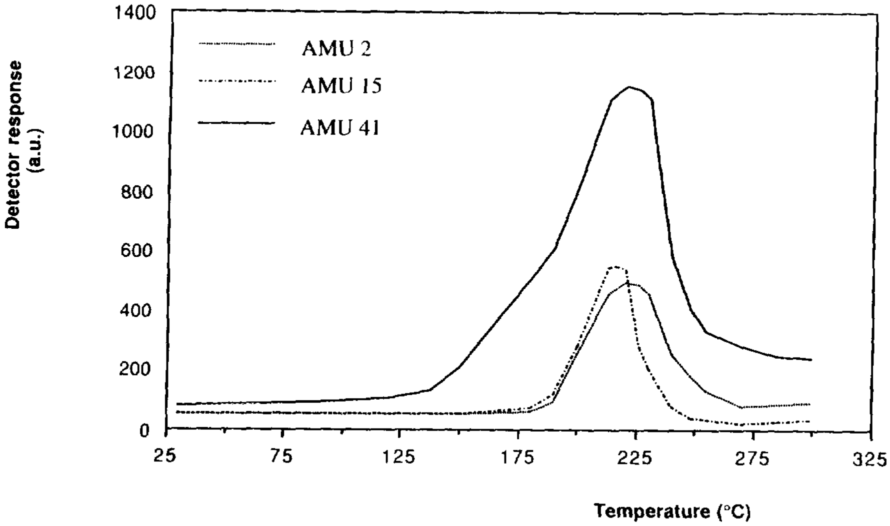

FIG. 4. Mass spectrometric analysis of the effluent gas stream during a TPSR measurement in argon with catalyst S25U-d, deactivated in the hydrogenation of acetonitrile at 125°C for 10 h. The curve marked "AMU 15" is representative for masses 12–17.

perature. Also, masses 12, 13, 14, 15, 16, and 17 were detected, undoubtedly methane and ammonia resulting from decomposition of adsorbed acetonitrile. Minor amounts of masses 28 and 30 were detected, both of which can be ascribed to either ethane or amine fragments. Since molecular ion masses 45 (ethylamine), 73 (diethylamine), and 101 (triethylamine) were not detected in the effluent gas, it is concluded that adsorbed amines were absent. It is highly probable that the decomposition product responsible for the mass fragments 28 and 30 is ethane. However, the possibility that the mass-28 peak is a sum of several compounds present in the effluent gas stream (nitrogen, ethylene, and ethane) cannot be excluded.

Summarizing, the desorption of acetonitrile starts at about 75°C and still adsorbed nitrile molecules/fragments are being cracked in argon or in another inert gas above 180°C. Small decomposition products, such as methane, ethane (nitrogen or possibly ethylene), hydrogen, and ammonia, are then evolved. The decomposition must result in a contamination of the catalyst with carbon and possibly nitrogen, because the hydrogen content of acetonitrile is not sufficient to hydrogenate all carbon and nitrogen atoms within the molecule. The deposition of carbon was verified experimentally in the following measurement.

After treatment in the argon flow, the catalyst was cooled in argon to room temperature and the gas flow was switched to a 10 vol% hydrogen in argon mixture. While the catalyst temperature was raised, again desorbing molecules were detected using the mass spectrometer. Only methane fragments 12, 13, 14, 15, and 16 were detected. Mass fragment 17 (NH_3) was absent. The mass 15 amu fragment (CH_3^+) was used to measure the methane concentration.

Figure 5 shows the intensity profile of methane as a function of the temperature. Two maxima are present. The first maximum is positioned at a peak temperature of 80°C, the other one at a peak temperature of 200°C. These peak temperatures are in good agreement with the TPSR maxima found by McCarty and Wise (*2*) for carburized nickel-on-alumina. These authors identified the low-temperature carbon as α'-carbon, a very reactive chemisorbed carbon species. At 200 ± 20°C McCarty and Wise identified a carbon phase they designated as α-carbon, which, by electron microscope analysis, was identified as (surface) nickel carbide. The same phase was detected by Kock *et al.* in a partially carbided nickel-on-silica catalyst (*16*). The latter authors also observed in a similar TPSR experiment a peak positioned near 220°C. Many other publications dealing with the deactivation of nickel catalysts in methanation reactions report the formation of a carbide phase that is hydrogenated at about 200°C (*17–21*). Bartholomew *et al.* (*22*) quantitatively regenerated their carburized nickel methanation catalysts through a mild treatment in oxygen diluted with nitrogen at 300–350°C. Oxygen can also gasify deposited carbon. In reactions of amines over nickel films, Anderson and Clark (*7*) also reported on the formation of carbonaceous deposits. They, however, did not inspect the regeneration behavior of their carburized metal films.

The decomposition of acetonitrile in argon at elevated temperatures thus leaves two different carbon species at the nickel surface that both can be removed by hydrogen treatment above 200°C. This explains why the almost completely deactivated catalyst that resulted from treatment in nitrogen at 250°C could be fully regenerated by a subsequent hydrogen treatment at an elevated temperature.

The question that arises now is whether these two carbon species are also present when the deactivated catalyst is not treated first with an inert gas at an elevated temperature. Two further TPSR experiments were performed to answer this question. In the first of these the deactivated catalyst was heated in a 10 vol% H_2 in argon flow, while the hydrogen concentration was monitored using a thermal conductivity detector. Figure 6 shows the resulting hydrogen con-

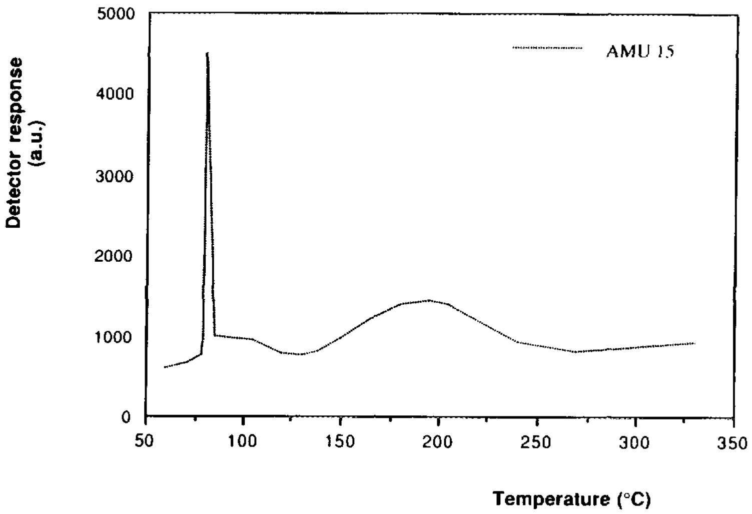

FIG. 5. Mass spectrometric analysis of the effluent gas stream during a TPSR measurement in 10% H_2/argon with catalyst S25U-d after a previous TPSR measurement in 100% argon, as represented in Fig. 4.

sumption profile. Again two peak maxima can be discerned at approximately the same temperatures as those with the TPSR measurement described previously, although representing different processes.

In the next TPSR experiment the same procedure was followed, but now every 5 min a sample was taken from the effluent gas stream and analyzed using GLC. The resulting detector signal is plotted in Fig. 7. The gas chromatogram (Fig. 7) thus consists of several consecutive analyses, plotted in the same figure. The resemblance between Figs. 6 and 7 is striking even though a com-

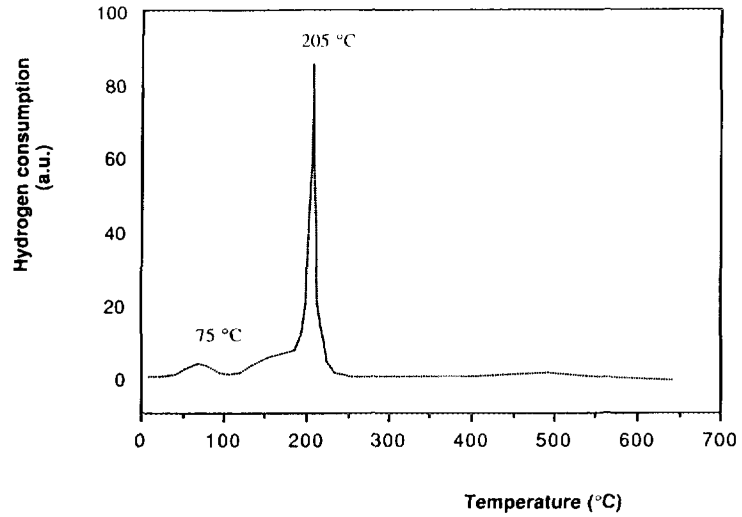

FIG. 6. Analysis of the effluent gas stream with a thermal conductivity detector during a TPSR measurement in 10% H_2/argon with catalyst S25U-d, deactivated in the hydrogenation of acetonitrile at 125°C for 10 h. The dotted line indicates the hydrogen consumption.

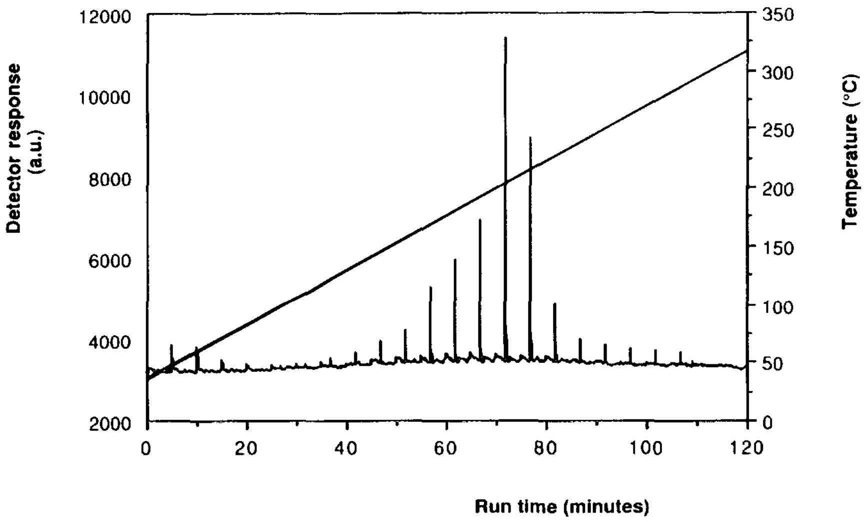

FIG. 7. Gas chromatographic analysis of the effluent gas stream during a TPSR measurement in 10% H_2/nitrogen with catalyst S25U-d, deactivated in the hydrogenation of acetonitrile at 125°C for 10 h. The straight line indicates the temperature.

pletely different analysis procedure was followed. Products were identified from their retention times: methane eluted every ($1.9+5x$) min, ethane every ($1.95+5x$) min, ethylamine every ($3.5+5x$) min, and acetonitrile every ($5.0+5x$) min, with x ranging from 0 to 23. Using a flame ionization detector, ammonia could not be detected. Zooming in on the baseline provides interesting information. In the magnifications shown in Figs. 8 and 9, "a" stands for acetonitrile, "m" for methane, and "e" for ethylamine. The following is observed.

At low temperatures, below 100°C, the only product desorbing from the catalyst was acetonitrile. When the temperature was raised, methane was evolved above about 100°C, its concentration reaching a maximum value near 190°C. Above 170°C acetonitrile and ethylamine also were detected in the effluent gas stream, although they were present in a much smaller amount than methane. The arrows in Fig. 9 indicate peaks arising from ethane, which, judging from the peak area, was present in a very small amount. When the temperature was raised to over approximately 250°C, no more products were detected with the gas chromatograph. Combining the results from both TPSR experiments, it can be concluded that the hydrogen consumption peak at low temperatures originates from desorbing acetonitrile. The presence of hydrogen is needed to remove this species (Fig. 6), since a desorption maximum was not observed in 100% argon, as was shown in Fig. 4. Moreover, before the TPSR profiles in Figs. 6 and 7 were measured, the reactor was purged with nitrogen at 100°C for 30 min. Consequently, it may be assumed that this treatment removed all acetonitrile that would otherwise desorb below this temperature. An obvious explanation is that this species is an adsorbed, hydrogen-deficient acetonitrile fragment with its C–C–N skeleton still intact. The high-temperature peaks near 200°C in Figs. 6 and 7 are caused by a combination of several reactions taking place. First, there is still a very strongly bound, hydrogen-deficient acetonitrile species present on the surface that is hydrogenated only at this relatively high temperature. Hydrogenation produces acetonitrile that can either desorb or remain adsorbed, producing ethylamine on further hydrogenation. The small-scale rupture of the carbon-to-

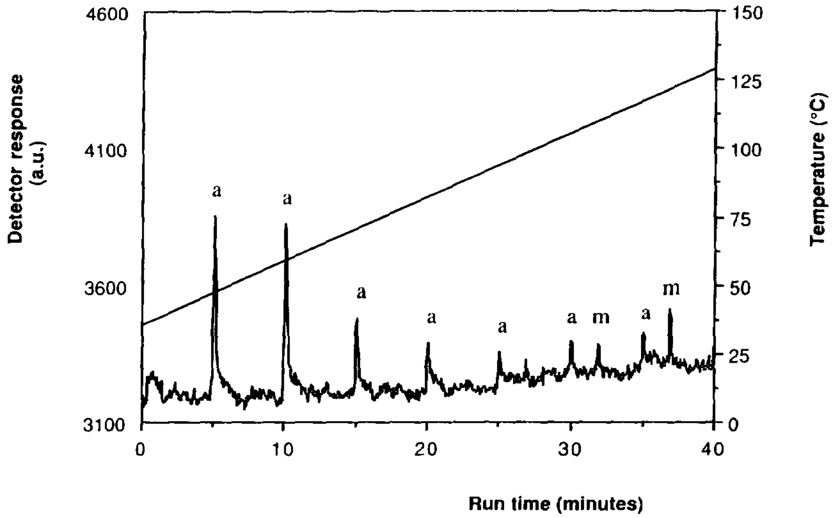

FIG. 8. Magnification of the run time interval of 0–40 min of Fig. 7. In the plot "a" is acetonitrile and "m" is methane.

nitrogen bond in ethylamine leads to a very small amount of ethane (and undoubtedly ammonia which, however, could not be detected using the FID). In the absence of hydrogen the adsorbed nitrile is partially cracked, which resulted in the evolution of methane, ethane, hydrogen, and ammonia. In addition, extensive carbon lay-down results from this treatment. Besides acetonitrile, there is also a carbonaceous phase present on the deactivated surface which, because of the position of its peak hydrogenation temperature, we designate α-carbon by analogy with McCarty and Wise (*2*, *3*). This α-carbon is hydrogenated at a significant rate above 180°C, producing methane exclusively.

Deactivation of nickel catalysts in the gas-

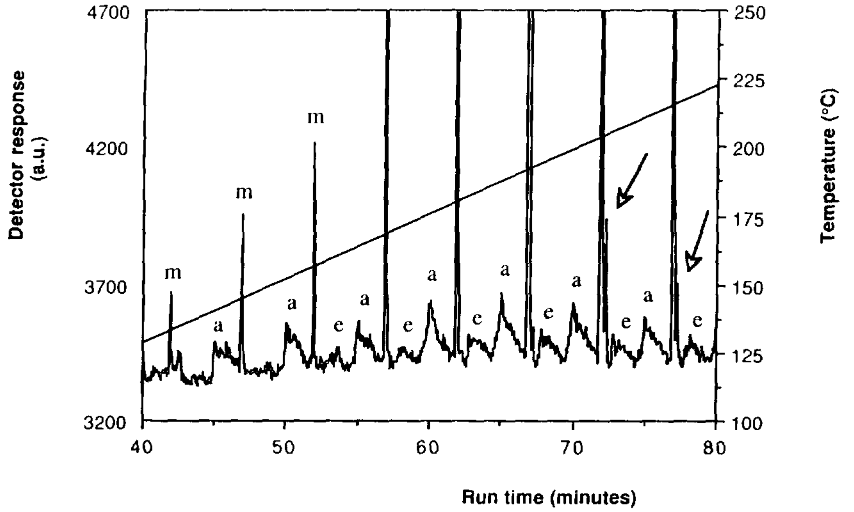

FIG. 9. Magnification of the run-time interval of 40–80 min of Fig. 7. In the plot "a" is acetonitrile, "m" is methane, and "e" is ethylamine. The arrows point to peaks due to ethane.

phase hydrogenation of acetonitrile can now be fully understood. There are two processes involved. First, decomposition of reactants or products (or both) takes place during the process, contaminating the nickel surface with a carbonaceous residue, which according to our TPSR results combined with the literature (*2, 3*) is a surface nickel carbide. Second, the nitrile adsorbs on specific nickel surface sites so strongly that at the maximum process temperature adopted in this study, 125°C, this species cannot be hydrogenated completely. This partly dehydrogenated acetonitrile species resides on the surface even under hydrogenation conditions. Quenching the steady-state condition of the nickel surface by shutting off the hydrogen and acetonitrile feed simultaneously leaves the dehydrogenated species present on the surface. As a result, part of the surface is covered with this strongly bound, dehydrogenated species, covering hydrogenation sites and thus lowering the activity. A speculative assumption is that this hydrogen-deficient nitrile species is the precursor state for adsorbed carbon.

Hydrogen treatment at elevated temperatures restores the catalytic performance since both the carbonaceous deposit and the strongly bound acetonitrile species are removed, providing a fresh catalytically active nickel surface.

Influence of the Hydrogen Partial Pressure on the Rate of Deactivation

Experiments were carried out to investigate the influence of the hydrogen partial pressure on the deactivation rate of catalyst S25U-d. To this end, the catalytic performance was measured as a function of time isothermally at 125°C at various hydrogen concentrations. All experiments were executed at atmospheric pressure and a fixed acetonitrile concentration of 2.5 vol%.

Because the hydrogen concentration in the reaction mixture was always well above 5 vol% (i.e., the stoichiometric amount needed to hydrogenate acetonitrile completely), the molar hydrogen-to-acetonitrile ratio (the H/C ratio) exceeded the value 2 in all experiments. Consequently, excess hydrogen was always present. In Fig. 10, the activity, expressed as the conversion of acetonitrile, is plotted as a function of the time on stream for various hydrogen partial pressures, ranging from 0.1 to 0.5 bar. Several consecutive deactivation runs were performed on a sample of catalyst S25U-d. Between each two runs the catalyst was reactivated in 10 vol% H_2 in nitrogen at 250°C for 2 h. Previous experiments have shown that this treatment fully restores the catalytic performance. As can be deduced from Fig. 10, the hydrogen partial pressure has a significant influence on the rate of deactivation. Raising the hydrogen concentration in the gas mixture or, expressed as the H/CH_3CN ratio, increasing the H/C ratio slows down the rate of deactivation. When the conversion remaining after a fixed period of time, in this case 10 h, for several hydrogen concentrations is extracted from the measurements and is plotted as function of the H/C ratio, Fig. 11 is obtained. Figure 11 shows that if the hydrogen partial pressure is above 0.5 bar or, more relevantly, if the H/C ratio is higher than about 20, deactivation is not observed within the time span of these experiments.

Because the rate of deactivation by carbon deposition is a balance between the rates of formation and removal of carbon, it follows that at a higher hydrogen partial pressure either the carbonization reaction is slowed down or even prevented completely or the coke gasification reaction is accelerated. Presumably the drop in the rate of carbon deposition and the increase in the rate of carbon gasification proceed simultaneously. The reaction of deposited carbon with hydrogen to methane is more rapid at higher hydrogen pressures. When hydrogen competes with acetonitrile for nickel sites on which decomposition of acetonitrile can proceed, a higher hydrogen partial pressure will diminish adsorption of acetonitrile on the dissociation sites. An increase in the hydrogen partial pressure causing reduction

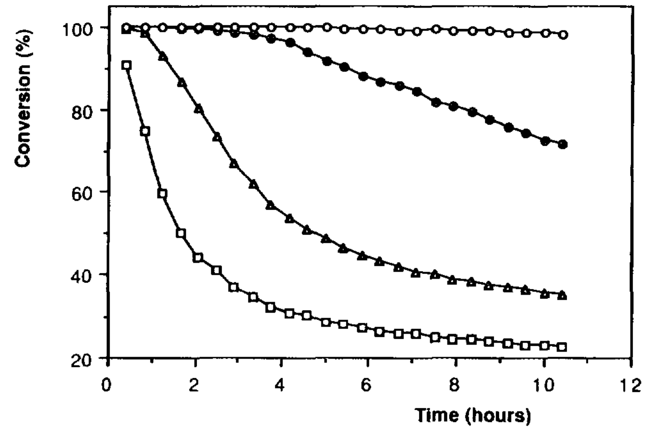

FIG. 10. The rate of deactivation of catalyst S25U-d in the hydrogenation of acetonitrile at 125°C. The different curves were measured at the following hydrogen concentrations: (□) 13.0 vol%, (△) 19.5 vol%, (●) 32.5 vol%, and (○) 52.0 vol%. The concentration of acetonitrile was fixed at 2.5 vol% with the balance nitrogen.

of carbon deposition during methanation over nickel catalysts was reported earlier in the literature (*6*). Increasing the H_2/CO ratio minimizes the buildup of carbon on the catalyst.

In their report on the disproportionation of amines over nickel catalysts, Baiker *et al.* (*8*) mentioned the formation of carbonaceous deposits during operation. They demonstrated that the presence of hydrogen could reduce the extent of carbon buildup, which is in agreement with the results presented here.

An increased hydrogen partial pressure, however, did *not* change the selectivities. The selectivities toward ethyl-, diethyl-, and triethylamine were exactly the same at the various hydrogen partial pressures. Neither the temperature dependence of the selectivities nor the course of the selectivities as a

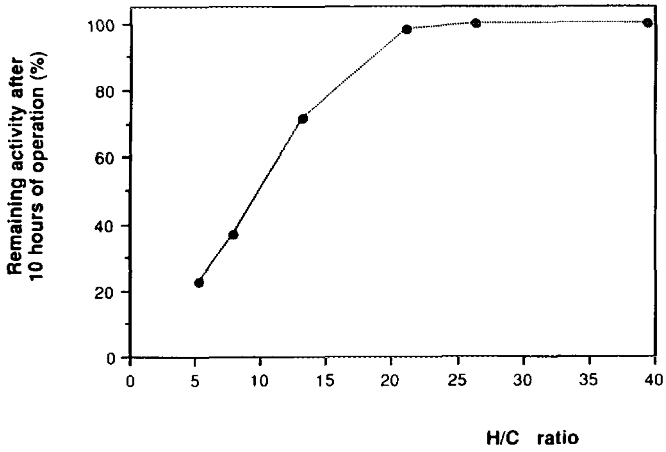

FIG. 11. The activity of catalyst S25U-d remaining after 10 h of isothermal operation at 125°C in feeds of different hydrogen concentrations (Fig. 10) as a function of the molar hydrogen-to-hydrocarbon ratio.

function of the time on stream in the isothermal experiments changed. It thus seems that the activity of the catalyst does not influence the selectivity of the process. The lack of an effect of the hydrogen partial pressure on the selectivity has to be attributed to the fact that the active sites responsible for the occurrence of the condensation reactions leading to the formation of secondary and tertiary amines are not located on the nickel surface. Experimental evidence that supports this hypothesis will be given in a following paper.

CONCLUSIONS

Nickel catalysts tend to deactivate in the gas-phase hydrogenation of acetonitrile. Especially when the molar hydrogen-to-acetonitrile ratio is low, the deactivation is fast. The nature of the deactivation was established using temperature-programmed surface reactions. From these experiments it was concluded that two species are responsible for the loss of activity. During operation a very strongly adsorbed, partly dehydrogenated, acetonitrile species is deposited on the catalytic surface and cannot be hydrogenated completely unless a large excess of hydrogen is used. This partly decomposed species covers active sites and thus lowers the activity. Deposited carbon is the second species causing the loss of catalytic activity. The gradual lay-down of a surface nickel carbide during operation additionally leads to blocking of hydrogenation sites. Both (inactive) species can be removed by treatment with hydrogen at elevated temperatures, resulting in a clean nickel surface.

Treating the partially deactivated catalyst in an inert gas at an elevated temperature causes a further, even more severe, deactivation of the catalyst. The resulting, fully deactivated catalyst can also be regenerated above 200°C in a hydrogen-containing environment. Deactivation can be at least partially inhibited by using a large excess of hydrogen during operation. Under our experimental conditions, a H/C ratio of 20–25 or higher was required.

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