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Hydrogenation of naphthalene on NiMo- and Ni/Al_2O_3 catalysts: Pre-treatment and deactivation

Ana Cristina Alves Monteiro-Gezork [*], Astrid Effendi, John Mike Winterbottom

Department of Chemical Engineering, School of Engineering, The University of Birmingham, Birmingham B15 2TT, United Kingdom

Abstract

Nickel (Ni) and nickel molybdate (NiMo) supported on alumina (Al_2O_3) catalysts, both in a presulphided and prereduced forms, were investigated for the hydrogenation (HYD) of naphthalene. The deactivation of the catalysts with time on stream and sulphur (S) content in feed was studied and a detailed characterization of the catalysts was performed. The catalytic activity of the presulphided NiMo/Al_2O_3 catalyst was found to be 2.5 times higher than the prereduced form, at the same HYD conditions. Testing the commercial prereduced Ni catalyst, it was observed that, although the catalyst aged quite quickly, it gave a higher turnover frequency at a temperature that was significantly lower than the one needed for the presulphided NiMo/Al_2O_3 catalyst. The presulphided Ni/Al_2O_3 catalyst showed a low activity towards naphthalene HYD, for the same experimental conditions applied to the prereduced form. The presulphided form of this catalyst was not the active site for this HYD. The Ni catalyst should be used in a sulphur free environment in order to fully make use its hydrodearomatisation (HDA) properties, whereas the NiMo/Al_2O_3 catalyst exhibited a higher HYD activity in the presulphided form.

Keywords: Naphthalene hydrogenation; Hydrodearomatisation; Hydrotreating; Catalyst pretreatment; Catalyst deactivation; NiMo/Al_2O_3; Ni/Al_2O_3

1. Introduction

HYD of aromatics is an essential process stage in the oil refining, which produces environmentally friendly fuels. A high aromatic content is associated with poor fuel quality, giving a low cetane number in diesel fuel and a high smoke point in jet fuel [1–3] making it important to reduce the aromatics content in liquid fuels [4]. During the hydrotreating process, the HYD of the aromatic rings prior to sulphur removal is considered essential to alleviate the steric hindrance of substituted dibenzothiophenes, which are regarded as most unreactive towards hydrodesulphurisation (HDS), and therefore facilitate HDS reaction [5,6]. Moreover, nitrogen removal from polycyclic aromatics does not take place until ring saturation has occurred. There is also evidence that particulate emissions in diesel exhaust gases correlate with the aromatic content of the fuel [3]. Because of the health hazards associated with these emissions [7], tighter environmental regulations have been introduced to limit the aromatic content of the fuel. The importance of HDA is therefore increasing together with tightening legislation of fuel quality and exhaust emissions, leading to new catalyst and process development.

Aromatic HYD in industrial feedstocks may be carried out over supported metal or metal sulphided catalysts. For hydrotreating of feedstocks that contain appreciable concentrations of sulphur and nitrogen, sulphided NiMo, NiW (nickel tungsten) or CoMo (cobalt molybdenum) on gamma alumina (γ-Al_2O_3) catalysts are generally used, whereas supported Ni or noble metal catalysts have been used for sulphur- and nitrogen-free feedstocks, i.e., relatively clean pretreated feedstocks. As a result, poisoning by asphaltenes, metals or fouling is minimized or does not occur. Consequently, chemical poisoning by coke and sulphur are the most relevant deactivation mechanisms for hydrotreating catalysts.

In hydrotreating, the deactivation of catalysts is fast when the catalyst is first brought on line and subsequent deactivation is slower. A review by Absi-Halabi and Stanislaus [8] shows that an initial deactivation is usually caused by coke deposition, which appears to reach a pseudo steady-state (in terms of activity) rather rapidly. Continued deactivation over a longer period of time is then caused by metal deposits and the final

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[*] Corresponding author. Present address: Stühlinger Straße 17, 79106 Freiburg, Germany.

E-mail address: acm848@yahoo.com (A.C.A. Monteiro-Gezork).

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Nomenclature

DMDS	dimethyldisulphide
HDA	hydrodearomatisation
HDS	hydrodesulphurisation
HYD	hydrogenation
$r_{w,\mathrm{N}}^{\mathrm{obs}}$	observed naphthalene reaction rate per mass of active phase of catalyst ($\mathrm{mol_N\,kg_{NiMo}}^{-1}\,\mathrm{s}^{-1}$, $\mathrm{mol_N\,kg_{Ni}}^{-1}\,\mathrm{s}^{-1}$)
Rc	correlation coefficient
S	sulphur
T	temperature
TPO	temperature programmed oxidation
TPR	temperature programmed reduction
TPS	temperature programmed sulphidation
XRD	X-ray diffraction
$\mathcal{P}$	poisoning factor

Subscripts and superscripts

cat	catalyst
L	liquid (bulk)
N	naphthalene
obs	observed

total loss in activity is attributed to pore constriction and ultimate pore blocking. Initial catalyst deactivation is a major issue in the refining industry [9] and the replacement of the deactivated catalyst is an economically demanding and time consuming procedure.

It is usually assumed that hydrogen sulphide (or sulphur content), H_2S, has an inhibiting effect on the HYD activity of hydrotreating catalysts [10,11]. However, many studies can be found in the literature on the effect of H_2S partial pressure in hydrotreating reactions and the conclusions differ widely. These studies have shown that the effect of H_2S partial pressure is complex with reports of promotional [12–14], inhibiting [13,15–17] or absence of effect [13,18] depending on the reaction, the reactant and the experimental conditions considered.

In the present work, commercial NiMo and Ni supported on trilobe Al_2O_3 catalysts have been investigated for the HYD of naphthalene in both prereduced and presulphided forms. In view of the interest in getting a better knowledge of the HYD properties of these catalysts, the resistance of the catalysts to high sulphur content of feed was tested and the deactivation of the catalysts due to coke deposition was also addressed. In order to elucidate the catalyst deactivation, a temperature programmed oxidation (TPO) of fresh and spent presulphided and prereduced NiMo and Ni/Al_2O_3 catalysts, was performed. This technique also allowed the qualitative and quantitative determination of sulphur present in the catalyst. The NiMo catalyst, both in the presulphided and prereduced forms, was also characterized by means of a temperature programmed reduction (TPR) and sulphidation (TPS) analysis. TPR and TPS analysis of the Ni/Al_2O_3 have been carried out by Hoffer et al. [19]. Moreover, an X-ray diffraction (XRD) analysis of the catalysts, in both presulphided and prereduced forms, was also carried out. The objective of the characterization carried out in the present study was to obtain a general insight into the chemical nature of the active phase and crystallinity of the catalysts, after the two pretreatments, in order to explain their activity towards naphthalene HYD.

2. Experimental

2.1. Apparatus

The kinetic study was carried out in a Carberry reactor, a three-phase spinning catalyst basket autoclave reactor, operated as a dead-end mode. The reactor was automated and controlled to ensure reliable and reproducible experiments. For the monitor and control of the operation parameters, LabVIEW software was installed. A more detailed description of the apparatus can be found elsewhere [20].

2.2. Catalysts and materials

Commercial Al_2O_3 trilobe support based catalysts namely NiMo/Al_2O_3 (26 wt.% MoO_3, 5 wt.% NiO, 4 wt.% P_2O_5, Grace Davison) and Ni/Al_2O_3 (15 wt.% Ni, HTC 400 RP, Johnson and Matthey) with a particle size of 2.5×10^{-3} $\mathrm{m_{cat}}$ were used. As a feed, naphthalene (99%, Aldrich) was dissolved in *n*-hexadecane (99%, Avocado) to the required concentration and *n*-octadecane (99%, Aldrich) was used as an internal standard. With the presulphided Ni based catalysts, dimethyldisulphide, DMDS, (99%, Acros) was added to the reaction mixture, providing a source of sulphur that was essential to stabilize the catalyst maintaining it in the sulphided form. Liquid products were analysed using a gas chromatograph (Ai Cambridge GC, model GC94M) equipped with a capillary column (CP-Wax 52CB FS 25 × 0.25(1.2), Chrompack). The nitrogen (oxygen free), argon (Ar), air, hydrogen (H_2) and helium (>99.995%) cylinder gases were supplied by BOC Gases.

2.3. Pretreatment of the catalysts and activation

2.3.1. Sulphidation of the NiMo and Ni/Al_2O_3 catalysts

The NiMo and Ni/Al_2O_3 catalysts were presulphided in the same way in the Carberry reactor. Initially, the catalysts were dried *in situ* at 573.15 K in a 250 ml min^{-1} nitrogen stream for 2 h to remove traces of moisture. A stirring rate of 8.3 s^{-1} was used. The reactor was cooled to room temperature. Then DMDS in *n*-hexadecane (10% of the weight of the catalyst, BP-private communication) was charged into the reactor. The temperature was increased to 493.15 K and held for 1 h at this temperature with a hydrogen pressure of 20×10^5 Pa. Subsequently, the temperature was increased slowly to 573.15 K at 20 K h^{-1} and held isothermally for 1 h. The catalyst was cooled down in hydrogen. The reactor was depressurised, the excess of DMDS was drained and finally the reactor was flushed for a considerable period of time with nitrogen.

2.3.2. Prereduction of the NiMo/Al_2O_3 catalyst

The reduction of NiMo/Al_2O_3 catalyst was done in the sulphur contaminated Carberry reactor. A stirring rate of 8.3 s^{-1} was used. The temperature program for the reduction was the same as the one used for the sulphidation. The catalyst was reduced in a 100 ml min^{-1} stream of pure hydrogen.

2.3.3. Prereduction of the Ni/Al_2O_3 catalyst

The deactivation of the Ni/Al_2O_3 catalyst by sulphur and coke deposition was also studied in the sulphur contaminated Carberry reactor. For the prereduction of the Ni/Al_2O_3 catalyst the pretreatment was performed *in situ* using a hydrogen flow of 100 ml min^{-1}. The catalyst temperature in the reactor was increased to 393.15 K and held isothermally at this value for 1 h, subsequently it was increased to 503.15 K and held for 2 h. A stirring rate of 8.3 s^{-1} was used throughout the activation. The catalyst was cooled down in hydrogen to room temperature.

2.4. Catalytic activity experiments

The activity of NiMo and Ni/Al_2O_3 catalysts, both in the presulphided and prereduced forms, towards naphthalene HYD was studied at 15×10^5 Pa and 325 $mol_N\ m_L^{-3}$ and at 573.15 and 373.15 K, respectively. The catalysts were tested for their resistance to sulphur and coke deposition. From the catalytic activity measurements of both pre-treated catalysts, an initial reaction rate was determined by calculating the hydrogen consumption during the initial stage of the reaction, i.e., when no significant amount of tetralin formation was observed (naphthalene conversion $< 10\%$).

2.5. Catalyst characterization

A brief description of the characterization methods used is given below. A more detailed description of the above characterization methods is given elsewhere [20]. To establish homogeneous sampling for all experiments and to avoid mass- and heat-transfer limitations in the temperature-programmed reactions, the catalyst extrudates were crushed and sieved and the particle size fraction between 39 and 150 mm was employed. Prior to the temperature-programmed reactions, the catalyst samples were washed with hexane for half an hour and dried in oven at 333.15 K. They were then dried *in situ* at 423.15 K for 1 h in Ar.

2.5.1. Temperature programmed reduction

The TPR analysis of the oxidic NiMo/Al_2O_3 catalyst (80 mg) and Ni/Al_2O_3 (200 mg) was performed in a quartz reactor. The catalyst sample and reactor were placed in a furnace and heated up. For the NiMo catalyst, the temperature was increased from room temperature to 493.15 K, at a rate of 3 K min^{-1} and held for 1 h. The temperature was again increased up to 573.15 K at a heating rate of 3 K min^{-1} and held again for 1 h followed by a ramp rate of 20 K min^{-1}. The experiment was stopped at around 2008 K. For the Ni/Al_2O_3 catalyst, a heating rate of 10 K min^{-1} was applied. Ten percent of hydrogen in Ar with a total flow rate of 100 ml min^{-1} was used as a reducing agent. The catalyst sample was cooled to room temperature. The reactant and product gases were monitored using a mass spectrometer.

2.5.2. Temperature programmed sulphidation

To mimic the sulphidation of the oxidic NiMo and Ni/Al_2O_3 catalyst in the Carberry reactor, a TPS was performed using the same equipment described above. A sample of approximately 50 mg of NiMo and 186 mg of Ni/Al_2O_3 catalyst was used for these experiments. The catalyst was heated to 493.15 K at a temperature rate of 3 K min^{-1} and held for 1 h. The temperature was again increased to 573.15 K at the same rate and held again for 1 h. As a sulphiding agent, 50 ml of 1% H_2S in hydrogen was used. The catalyst sample was cooled to room temperature.

2.5.3. Temperature programmed oxidation

The same equipment used for the TPR experiments was used for the TPO experiments. Approximately 50–180 mg of the presulphided and prereduced NiMo catalyst and 180–200 mg of presulphided and prereduced Ni/Al_2O_3 catalyst was used for these experiments. After cooling down to room temperature, the sample was flushed with air for 30 min and the experiment started. A heating rate of 10 K min^{-1} was applied and as an oxidising agent, air in Ar (resulting in 7% of oxygen in the gases) with a total flow rate of 50 ml min^{-1} was used. Carbon dioxide (CO_2) and sulphur dioxide (SO_2) signals were monitored using mass spectrometry and detected for temperatures ranging from 323.15 to 1123.15 K.

2.5.4. X-ray diffraction

The XRD analysis was performed using a Siemens D5000 diffractometer. The XRD analysis was carried out in the scanning angle (2θ) range of 25–70°.

3. Results and discussion

3.1. Presulphided versus prereduced NiMo/Al_2O_3

3.1.1. Effect of sulphur and time on stream

The presulphided form. The same batch of NiMo/Al_2O_3 presulphided catalyst was used to test both its resistance to sulphur and coke deposition. A standard experiment, carried out at 15×10^5 Pa hydrogen partial pressure and 573.15 K, was performed repeatedly between experiments to ensure experimental reproducibility and to ensure that no catalyst deactivation occurred.

The resistance of the presulphided NiMo/Al_2O_3 catalyst to high sulphur content of feed was tested (0-3741 ppm S in *n*-hexadecane) at 573.15 K and 15×10^5 Pa hydrogen partial pressure. Fig. 1 shows the HYD activity of the catalyst represented by the percentage of naphthalene disappearance under various concentrations of sulphur. As the results show, the naphthalene converted was relatively constant for less than 1122 ppm S in the feed. When the sulphur content was increased above this value, the conversion decreased significantly. The

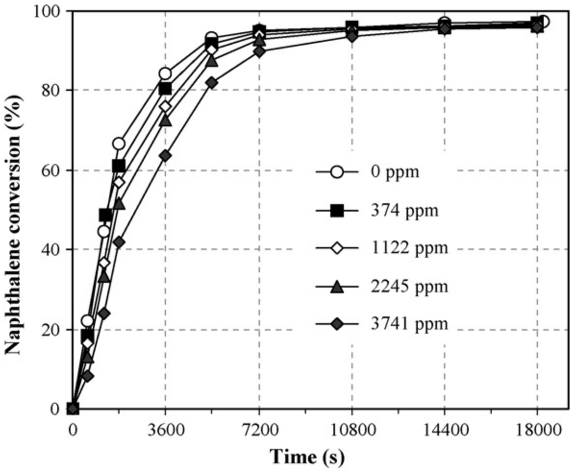

Fig. 1. Naphthalene conversion as a function of sulphur content in the feed at 573.15 K, $PH_2 = 15 \times 10^5$ Pa, 325 $mol_N\ m_L^{-3}$, 27.6 $kg_{NiMo}\ m_L^{-3}$ and 12.5 s^{-1} over the presulphided NiMo/Al_2O_3 catalyst.

catalytic activity trend is in agreement with the calculated initial rate of HYD of naphthalene presented in Fig. 2. The rate observed was close to 8×10^{-3} $mol_N\ kg_{NiMo}^{-1}\ s^{-1}$ for sulphur content <1122 ppm, then decreased to approximately 5×10^{-3} $mol_N\ kg_{NiMo}^{-1}\ s^{-1}$ during the HYD of naphthalene poisoned with 3741 ppm S. As an outcome, two domains of sulphur content could be distinguished. In the low sulphur content in the feed solution, the rate of naphthalene HYD was maximum, stable and independent of the sulphur content. In the higher sulphur content domain, sulphur had an inhibiting effect on the rate of HYD of naphthalene. A log–log plot of the initial rate of HYD of naphthalene versus sulphur content shows clear evidence of the two domains aforementioned (see Fig. 3). The reaction order relative to sulphur content (or H_2S content) has also been determined for each domain. At low ($S \leq 1122$ ppm) sulphur content, a zero order of reaction relative to sulphur content was found. At higher sulphur contents ($1122 \leq S \leq 3741$ ppm), sulphur content has an inhibiting effect translated in a slightly negative order of reaction, −0.31. This is in good agreement with available literature data on a supported NiMo catalyst [21,22]. However, it has been reported in the literature that at very high H_2S partial pressures, H_2S has no more effect on the rate of HYD [21–23]. This third domain was not observed in the present study, probably because the range of sulphur content in feed was not extremely large.

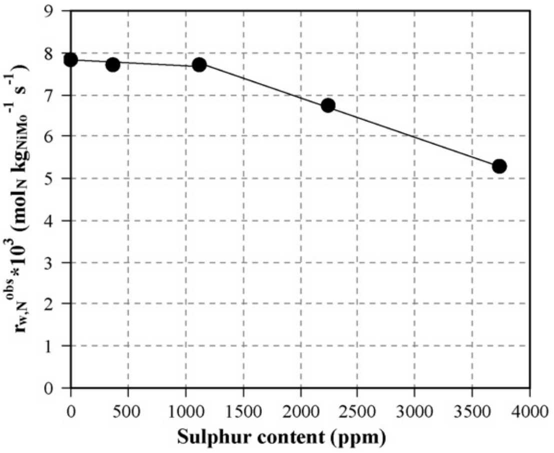

Fig. 2. Initial reaction rate as a function of sulphur content for naphthalene HYD over the presulphided NiMo/Al_2O_3 catalyst. Reaction conditions: 573.15 K, 15×10^5 Pa, 325 $mol_N\ m_L^{-3}$, 27.6 $kg_{NiMo}\ m_L^{-3}$ and 12.5 s^{-1}. *Note*: First point corresponds to a contamination by sulphur.

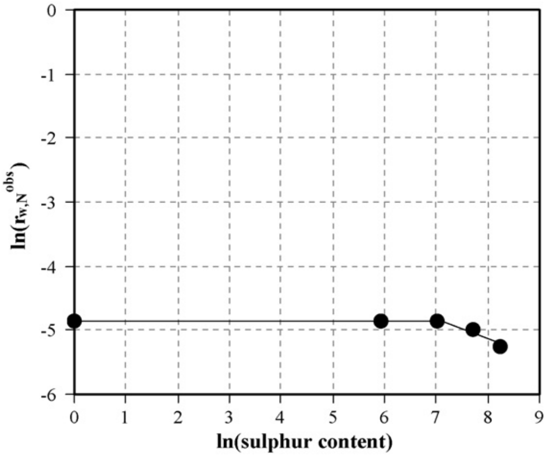

Fig. 3. Log–log plot of the initial rate of naphthalene HYD in $mol_N\ kg_{NiMo}^{-1}\ s^{-1}$ vs. sulphur content in the feed in ppm. *Note*: First point corresponds to a contamination by sulphur.

After experiencing the HYD of naphthalene using 3741 ppm S in the feed, the presulphided NiMo was flushed with nitrogen and tested for the standard naphthalene HYD experiment at 573.15 K, $PH_2 = 15 \times 10^5$ Pa and 325 $mol_N\ m_L^{-3}$ in *n*-hexadecane. The results showed that the initial naphthalene conversion was obtained and no significant deactivation, either by sulphur or coke deposition, of the NiMo/Al_2O_3 catalyst was observed under this condition. It seems that poisoning by sulphur might be reversible as the catalyst activity was recovered. This is also an indication that the effect of sulphur on the rate of naphthalene HYD is probably more kinetic rather than being due to structural modifications of the active phase.

A few experiments without any sulphur were carried out at the beginning of this study and it was found that, although the catalyst deactivated with very high sulphur content in the feed, a certain amount of sulphur (≤1122 ppm) present in each experiment was essential to stabilize the catalyst by maintaining it in the sulphided form [24].

The prereduced form. The prereduced NiMo/Al_2O_3 catalyst, similarly to the presulphided form, was tested for its stability and resistance to coke and sulphur at 573.15 K and 15×10^5 Pa hydrogen partial pressure. The same batch of prereduced NiMo/Al_2O_3 catalyst was tested repeatedly for naphthalene HYD using fresh feeds at 573.15 K and 15×10^5 Pa. After running each experiment for 6 h, it was observed that the naphthalene conversion, at a certain reaction time, decreased as the prereduced NiMo catalyst aged. This decrease in the conversion might indicate a deactivation of the catalyst due to coke deposition. Although the Carberry reactor was contaminated by sulphur that could not be removed, deactivation by sulphur was neglected, as sulphur was not desorbed during the TPO analysis of the spent reduced catalyst. Moreover, the initial HYD rate

Table 1
Initial HYD rate of naphthalene over the same batch of prereduced NiMo/Al_2O_3 catalyst and poisoning factor, at 573.15 K, $PH_2 = 15 \times 10^5$ Pa, 325 mol_N m_L^{-3} and 27.6 kg_{NiMo} m_L^{-3}

Experiment	Time on stream (s)	$r_{w,N}^{obs}$ (mol_N kg_{NiMo}^{-1} s^{-1})	$\mathcal{P}$
1	0	2.72×10^{-3}	1
2	21,000 (≈6 h)	1.31×10^{-3}	0.48
3	42,000 (≈12 h)	9.53×10^{-4}	0.35

decreased from 2.72×10^{-3} mol_N kg_{NiMo}^{-1} s^{-1} to 9.53×10^{-4} mol_N kg_{NiMo}^{-1} s^{-1} during nearly 12 h on stream, which was in agreement with the decrease of the naphthalene conversion. The poisoning factor ($\mathcal{P}$) of the catalyst at a certain time on stream, defined as the ratio between the observed reaction rate under poisoning conditions and the observed rate with unpoisoned catalyst and the initial reaction rate of naphthalene HYD, is presented in Table 1. The rate of deactivation of the catalyst decreased with increased time on stream. Nevertheless, a linear plot of $\mathcal{P}$ versus time on stream, with a correlation coefficient, Rc, of 0.89, allowed the determination of an overall rate of deactivation during the 12 h on stream. A value of 1.55×10^{-5} s^{-1} for the deactivation rate, which corresponded to a decrease of activity of nearly three fold during 12 h of use, was found.

The prereduced NiMo/Al_2O_3 catalyst was tested for its resistance to high sulphur feed content, namely 1122 and 2245 ppm of sulphur in *n*-hexadecane, at 573.15 K and 15×10^5 Pa hydrogen partial pressure. A fresh batch of prereduced catalyst was used in each experiment in order to eliminate the effect of loss of activity due to catalyst aging. The results are presented in Table 2. It was observed that naphthalene conversion decreased as the sulphur content in the feed increased. The initial reaction rate decreased 10% as the sulphur content in the feed increased from 0 to 1122 ppm and decreased nearly 30% as the sulphur was increased further to 2245 ppm. These results correspond to a rate of deactivation with sulphur content (Rc for the linear plot = 0.980) of 1.17×10^{-4} ppm S^{-1} in the range of conditions studied.

The catalytic activity of the prereduced form of the NiMo/Al_2O_3 catalyst was tested and compared to the one of the presulphided form. Fig. 4 shows the naphthalene conversion and initial reaction rate of the presulphided and prereduced NiMo/Al_2O_3 for the HYD of naphthalene at 573.15 K and 15×10^5 Pa. At the same reaction condition a lower conversion was obtained with the prereduced NiMo/Al_2O_3, during 5 h of reaction time. Moreover, the initial reaction rates calculated were 6.84×10^{-3} and 2.72×10^{-3} mol_N kg_{NiMo} m_L^{-3} for the presulphided and prereduced NiMo/Al_2O_3 catalysts, respectively. A lower initial naphthalene HYD rate was given by the prereduced catalyst for the same operating conditions. Although the activity of prereduced NiMo catalyst is much lower than the presulphided one this is still quite surprising. The Ni surface area of the reduced catalyst was evaluated from hydrogen–chemisorption at 1×10^5 Pa. The chemisorption results showed a value of 0.3×10^3 m_{Ni}^2 kg_{cat}^{-1} for the Ni surface area. This is a quite small value that nevertheless showed some activity for the HYD of naphthalene.

Table 2
Initial HYD rate of naphthalene over fresh prereduced NiMo/Al_2O_3 catalyst and poisoning factor, for different sulphur contents in feed at 573.15 K, $PH_2 = 15 \times 10^5$ Pa, 325 mol_N m_L^{-3} and 27.6 kg_{NiMo} m_L^{-3}

Sulphur content (ppm)	$r_{w,N}^{obs}$ (mol_N kg_{NiMo}^{-1} s^{-1})	$\mathcal{P}$
≈0[a]	2.72×10^{-3}	1
1122	2.45×10^{-3}	0.90
2245	2.00×10^{-3}	0.74

[a] Carberry reactor was contaminated with sulphur that could not be removed.

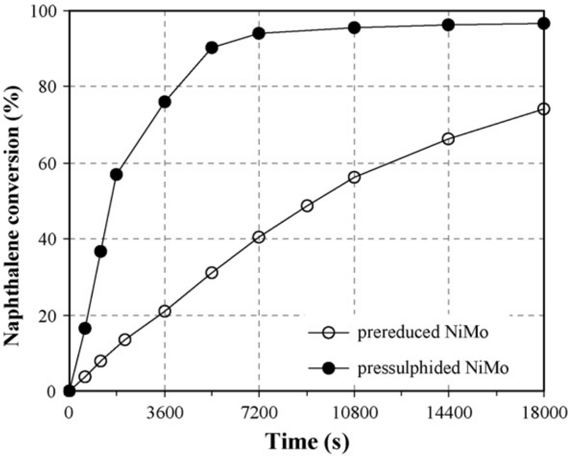

Fig. 4. Naphthalene conversion for the presulphided and prereduced NiMo/Al_2O_3 catalyst at 573.15 K, 15×10^5 Pa, 325 mol_N m_L^{-3} and 27.6 kg_{NiMo} m_L^{-3}.

From the aforementioned results, it can be concluded that the presulphided NiMo/Al_2O_3 catalyst was a more stable and more resistant catalyst to sulphur than the equivalent prereduced form. In addition, the presulphided form exhibited a much higher activity towards naphthalene HYD than the prereduced one. These observations reinforce the fact that the catalytic active sites for naphthalene HYD in both catalysts are different and dependent on the pretreatment of the catalyst.

3.1.2. Characterization of the NiMo/Al_2O_3

Temperature programmed sulphidation. The TPS profile of the oxidic form of NiMo/Al_2O_3 catalyst as received from the manufacturer, is collected in Fig. 5. The hydrogen and H_2S consumption or production curves were normalized to 100 mg of the catalyst. The figure shows a H_2S consumption during the isothermal stage at room temperature (region I). Just after the start of the temperature program, slightly above room temperature and below 400.15 K (region II), a reasonable H_2S consumption was again observed without a simultaneous hydrogen production. In the temperature region from 400.15 and 493.15 K (held for 1 h), a small amount of H_2S was produced accompanied with hydrogen consumption (region III). While temperature was increased further from 493.15 to 573.15 K and held isothermally at 573.15 K for 1 h (region IV), a major H_2S consumption simultaneous with a hydrogen production could be seen. A similar profile was found by Hoffer et al. [19] for a Ni/Al_2O_3 catalyst with different pretreatments.

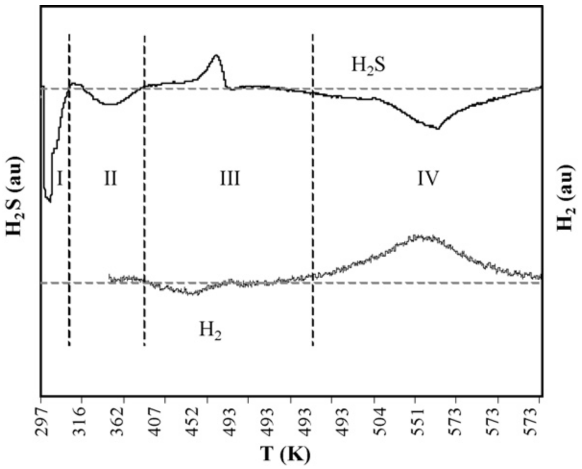

Fig. 5. TPS profile of the NiMo/Al$_2$O$_3$ catalyst (upper curve is the mass spectrometer signal which represents the H$_2$S consumption/production; lower curve is the mass spectrometer signal representing the H$_2$ consumption/production). The profile is normalized to 100 mg of catalyst sample.

In this work, as supported by the results of these authors, the H$_2$S consumption during the isothermal sulphidation of the catalyst at room temperature can be explained part as a consequence of the sulphidation of Ni and Mo surface oxide and part can be attributed to adsorption by the alumina. The reasonable H$_2$S consumption observed in region II indicate that the Mo oxide was sulphided in this region, as supported by the results of Qian et al. [25]. In addition, the major sulphidation of the NiMo/Al$_2$O$_3$ observed in region IV can be attributed to the sulphidation of the Ni oxide.

Temperature programmed reduction. The TPR profile for the oxidic form of NiMo/Al$_2$O$_3$ catalyst is illustrated in Fig. 6. The catalyst showed a slight, but not quantifiable, hydrogen consumption as the temperature was increased up to 573.15 K and held for 1 h. Immediately after increasing the temperature ramp rate to 20 K/min, the hydrogen consumption/water production increased significantly and a two-peak pattern, with maxima around 793.15 and a 1273.15 K, could be observed. This pattern has been reported previously [26–30]. Similarly to these works, for the present study, the low-temperature peak can be assigned to Mo and Ni reduction and the high-temperature one is possibly associated mainly with Ni or Ni aluminates reduction since at this very high temperature (1273 K) Mo loss likely occurred.

Temperature programmed oxidation. Figs. 7 and 8 show the mass spectrometer signals of SO$_2$ and CO$_2$ desorbed, respectively, from the NiMo/Al$_2$O$_3$ catalysts (spent prereduced and presulphided and fresh presulphided). Fig. 7 indicates that the fresh presulphided NiMo/Al$_2$O$_3$ catalyst exhibited various species easily sulphided from 373.15 to 773.15 K. The main SO$_2$ production occurred in a well-defined peak with a maximum at 540.15–590.15 K. An additional and reasonable production of SO$_2$, peaking at 723.15 K, could also be observed. Metal active species were composed of approximately 80% readily sulphided sites below 623.15 K, 15% at 723.15 K and also some traces above 873.15 K. The same type of trend, as the one reported here, is observed in the open literature [31–33]. There is a general agreement that the low temperature peak is originated from the oxidation of deposited sulphur and of metal sulphides. It is believed that the second peak corresponds to sulphur that is ‘‘fixed’’ on the catalyst and is, in fact, present as sulphate (aluminium sulphate). The fresh presulphided NiMo/Al$_2$O$_3$ showed a considerable higher intensity of SO$_2$ signal compared to that of the spent presulphided catalyst and desorbed at similar temperature, ranging from 373.15 to 773.15 K. Table 3 summarizes the quantitative data from the TPO experiments. Both fresh and spent catalysts exhibited relatively high sulphur contents. In the open literature the sulphur to Mo ratio is reported to be between 1 and 2 depending if the molybdena is incompletely (mild sulphiding conditions) or completely sulphided to MoS$_2$ (more severe sulphiding conditions) [34]. In this work, much more sulphur was present in the catalyst than the one required by

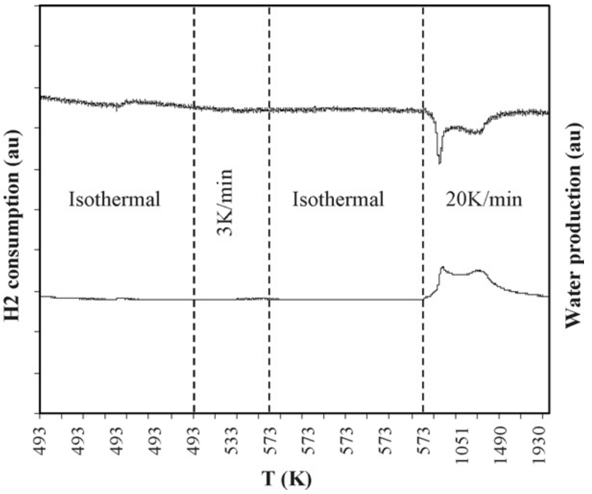

Fig. 6. TPR profile of the NiMo/Al$_2$O$_3$ catalyst (upper curve is the mass spectrometer signal which represents the H$_2$ consumption; lower curve is the mass spectrometer signal representing the water production). The profile is normalized to 100 mg of catalyst sample.

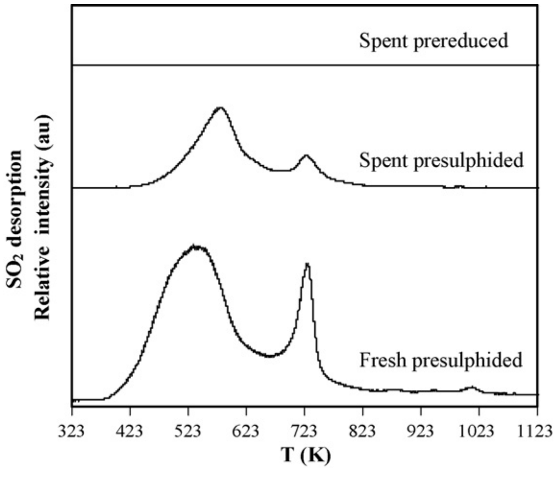

Fig. 7. SO$_2$ desorption as a function of temperature for fresh, spent presulphided and prereduced NiMo/Al$_2$O$_3$. The profiles are normalized to 100 mg of catalyst sample.

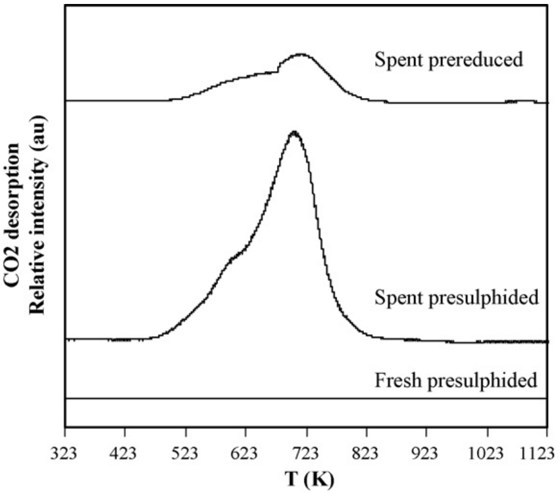

Fig. 8. CO_2 desorption as a function of temperature for fresh, spent presulphided and prereduced NiMo/Al_2O_3. The profiles are normalized to 100 mg of catalyst sample.

stoichiometry, as Table 3 shows. This high sulphur content (S/NiMo > 2) analysed for the fresh and spent catalysts is in agreement with the findings from Hagenbach et al. [35] for unsupported MoS_2 and MoS_2-Co_9S_8 catalysts, de Beer et al. [36] for a CoO-MoO_3/γAl_2O_3 catalyst and Vissers et al. [37] for CoMo/carbon catalysts. The nature of this excess of sulphur is not completely clear. According to Massoth [34] this may be due to adsorbed H_2S and not sulphide sulphur. H_2S is strongly adsorbed on the sulphided catalyst and Massoth [38] showed that at least 1 h purging at temperature was needed to remove it. For the present work, a 30 min purge with air at room temperature may have not been enough to remove much of the adsorbed H_2S. The high sulphur values reported in the present work may not accurately reflect the stoichiometric sulphide content on the catalyst. The catalyst may have needed to be well purged and completely freed from physically adsorbed H_2S prior to sulphur determination in order to obtain true stoichiometric values. On the other hand, this high sulphur content can also be attributed, apart from the formation of MoS_2 and Ni-sulphided species, to the occurrence of S-polymers on the catalyst [37,39] and to the conversion of Al_2O_3 to a form of surface sulphide [40]. The sulphur-to-NiMo ratio decreased three times as the catalyst aged during the experimental work. It should be noted that the catalyst named as fresh presulphided catalyst was sulphided prior to the TPO experiment with a mixture of pure H_2S and hydrogen, while the spent presulphided was sulphided with the S-generating compound DMDS and this could have been one of the reasons for such a considerable difference in sulphur content for the two catalysts. The spent prereduced NiMo/Al_2O_3 showed no SO_2 desorption (refer to Fig. 7).

Table 3
Amount of sulphur and CO_2 present in the fresh and spent presulphided and prereduced NiMo/Al_2O_3 catalyst and the corresponding sulphur-to-NiMo ratios (mol/mol) obtained from the quantitative TPO

	Total SO_2 area	S (mol)	S/NiMo (mol/mol)	Total CO_2 area
Fresh sulphided	1.67×10^{-7}	1.62×10^{-3}	11.60	–
Spent sulphided	5.29×10^{-8}	5.13×10^{-4}	3.68	7.88×10^{-8}
Spent prereduced				3.16×10^{-8}

The values presented were normalized to 100 mg of catalyst sample.

In Fig. 8, the desorbed CO_2 from 473.15 to 823.15 K was assigned to a carbon species formation on the spent catalyst samples. The CO_2 signal had its maximum at around 720.15 K and a shoulder was observed at 600.15 K. Both spent catalysts showed similar carbon species oxidised at almost the same temperature. The prereduced catalyst had a much smaller (2.5 times) intensity of CO_2 desorption than the presulphided catalyst. This can be explained by the fact that the presulphided catalyst was on stream at least 20 times more than the prereduced one. In addition, Yoshimura and Furimsky [32] observed that a smaller amount of coke was deposited on the sulphidic CoMo/Al_2O_3 catalyst compared with that deposited on the oxidic catalyst under the same hydrotreating conditions. The fresh oxidic NiMo catalyst had a BET surface area, determined by nitrogen physisorption, of 203 $m^2\,g_{cat}^{-1}$ and this one decreased to 190 $m^2\,g_{cat}^{-1}$ in the case of the spent prereduced catalyst. This result supports the conclusion of coke deposition in the catalyst.

Comparing both SO_2 and CO_2 formation curves (Figs. 7 and 8), it appears that a substantial portion of sulphur can be removed at temperatures where carbon removal is relatively low. This is in agreement with large driving forces for the conversion of Mo and Ni sulphides to their oxides and SO_2 compared with that for the conversion of carbon to CO_2 [32]. The presence of carbonaceous deposits seems to have little effect on the conversion of Mo and Co sulphides to their oxides as indicated by similar trends in SO_2 formation for the fresh and spent presulphided catalysts. Despite the coke deposition and the decrease of sulphided species as the presulphided NiMo/Al_2O_3 catalyst aged, the catalyst maintained its activity towards naphthalene HYD throughout all the experimental work. This carbon on the surface was then excluded as a contributor to the catalyst deactivation.

X-ray diffraction. The XRD spectra for the oxidic (curve (a)), prereduced (curve (b)) and presulphided NiMo/Al_2O_3 (curve (c)) catalysts, is presented in Fig. 9. Two peaks at around 46° and 67° were observed for all catalysts. These two peaks were assigned to the Al_2O_3 phase. For the oxidic catalyst, the XRD spectra could be associated to Ni hydroxide, MoO_3 and NiO phases but no reasonable match was found. The absence of a matching diffraction line, however, is not proof that the phase in question is not present in the catalyst [34]. A clear difference can be found by comparing the XRD curves for the oxidic and the presulphided forms. Two other peaks, at 33° and 59°, were observed for the presulphided catalyst. These were eventually related to the formation of one or more crystalline sulphided phases and are probably responsible for the activity of the presulphided catalyst. A search through the XRD database (JCPDS) showed that these could be related to several possible crystalline phases, such as MoS_2, Ni_3S_2, NiS and $NiMo_2S_4$, but again, no perfect match could be found and therefore no clear

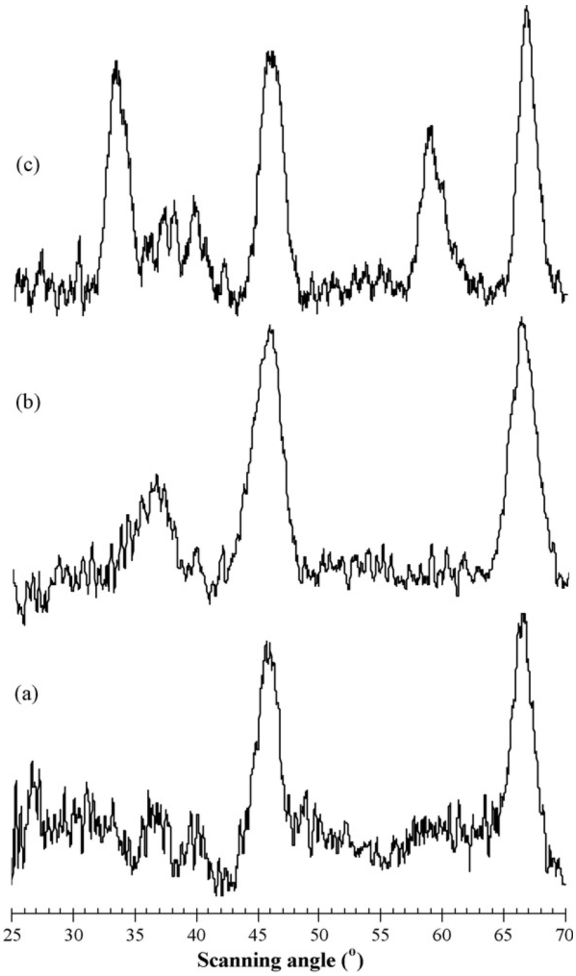

Fig. 9. X-ray diffraction analysis on (a) fresh oxidic NiMo/Al_2O_3 catalyst and after two different pretreatments: (b) prereduced and (c) presulphided (the curves are not normalized). *Note*: curves (a) and (b) were smoothed.

conclusion could be drawn. Contrary to what was observed for the presulphided catalyst, the XRD spectra of the prereduced catalyst matched quite well the one of the $NiAl_2O_4$ phase. From these results, it can be concluded that the oxidic, presulphided and prereduced catalysts exhibited different crystalline phases and these were responsible for the different activities of the catalysts towards HDA.

From the characterization results it can be most plausibly inferred that in the presulphided catalyst part of the sulphur was chemically bonded to Mo and Ni. This results most probably in the formation of MoS_2 and/or Ni_3S_2, NiS and $NiMo_2S_4$. Other sulphur species, the formation of which during the sulphiding process cannot be excluded, are aluminium sulphide (Slager T.L. and Amberg C.H., 1972), H_2S adsorbed on aluminium hydroxyl and even polymeric sulphur, for instance S_2^{2-} and S_3^{2-} [39].

3.2. *Presulphided versus prereduced Ni/Al_2O_3 catalyst*

3.2.1. *Effect of sulphur and time on stream*

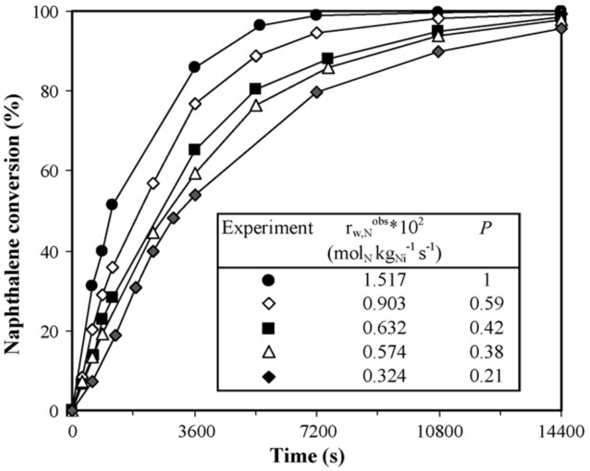

Fig. 10. Naphthalene conversion and initial reaction rate tested repeatedly over the same batch of prereduced Ni/Al_2O_3 catalyst (373.15 K, 15×10^5 Pa, 325 $mol_N\ m_L^{-3}$, 12.2 $kg_{Ni}\ m_L^{-3}$ and 20.8 s^{-1}).

The prereduced form. The prereduced Ni/Al_2O_3 catalyst was tested repeatedly for naphthalene HYD using the same batch of catalyst and fresh feeds. The results are depicted in Fig. 10. Naphthalene conversion was found to decrease as the Ni/Al_2O_3 catalyst aged. The calculated initial reaction rate decreased from 1.52×10^{-2} to 0.32×10^{-2} $mol_N\ kg_{Ni}^{-1}\ s^{-1}$ during the use of the catalyst for 16 h, which was in agreement with the decrease of the conversion of naphthalene. This decrease indicates a Ni/Al_2O_3 catalyst deactivation. A linear plot of $\mathcal{P}$ versus time on stream (Rc of 0.890), allowed the determination of an overall rate of deactivation during the 16 h on stream. A value of 1.24×10^{-5} s^{-1} for the deactivation rate was found. The activity of the catalyst decreased nearly five fold in the range of conditions studied.

The resistance of the prereduced Ni/Al_2O_3 catalyst to sulphur was tested for 0–2245 ppm of sulphur in *n*-hexadecane, at 373.15 K and 15×10^5 Pa hydrogen partial pressure. Fig. 11 illustrates the initial HYD rate of naphthalene and poisoning factor as a function of sulphur content in the feed, using fresh batches of catalyst. As the results show, the initial reaction rate decreased markedly as the sulphur increased to 374 ppm. As the

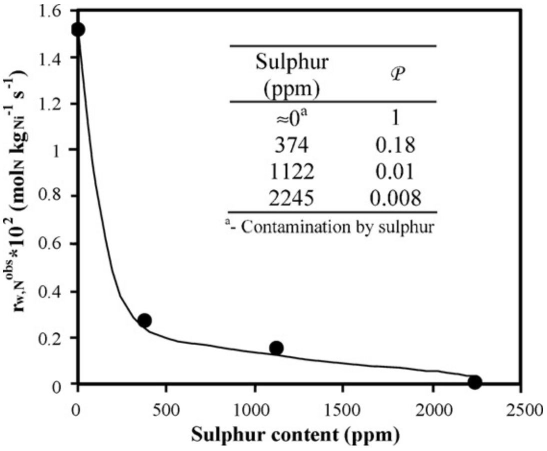

Fig. 11. Initial HYD rate of naphthalene as a function of sulphur content over the prereduced Ni/Al_2O_3 catalyst. Reaction conditions: 373.15 K, $PH_2 = 15 \times 10^5$ Pa, 325 $mol_N\ m_L^{-3}$, 12.2 $kg_{Ni}\ m_L^{-3}$ and 20.8 s^{-1}.

sulphur content in feed increased further to 2245 ppm S, the initial rate decreased to a value close to zero. The initial reaction rate followed a -0.32 order towards sulphur content for sulphur contents in the range of $S \leq 1122$ ppm. Under more severe sulphur conditions, $S \geq 1122$ ppm, the order decreased further. After experiencing the HYD of naphthalene using 2245 ppm S in the feed, the prereduced Ni/Al_2O_3 catalyst was washed with fresh *n*-hexadecane, flushed with nitrogen and tested for naphthalene HYD at the same experimental conditions but in the absence of sulphur. The catalyst activity towards naphthalene HYD could not be restored indicating that poison by sulphur of the Ni catalyst was irreversible. Similarly, an irreversible Ni catalyst deactivation due to sulphur presence in the feed has been reported by Poels et al. [41]. It was concluded that the deactivation of the catalyst by sulphur proceeded through the formation of a surface sulphided (sulphur adsorbed on the surface), which blocked the active surface.

The presulphided form. Nevertheless the aforementioned results of irreversible deactivation by sulphur of the prereduced form of the Ni/Al_2O_3 catalyst, the catalyst was presulphided using the same procedure as the one used for the $NiMo/Al_2O_3$ catalyst. The presulphided catalyst was tested for the HYD of naphthalene at 373.15 K and 15×10^5 Pa H_2 partial pressure during 4 h. No sulphur was added to the feed. The maximum naphthalene conversion achieved during this reaction period was very low and close to 15%, hence, indicating that the presulphided form of this catalyst was not the active site for this HYD as Ni was poisoned by sulphur during the presulphiding process. This is also an indication that the effect of sulphur on the HYD rate of naphthalene over the Ni catalyst is probably due to structural modifications of the active phase of the catalyst rather than being kinetic.

From the results it can be concluded that the Ni/Al_2O_3 catalyst is easily poisoned by sulphur. The prereduced form of this catalyst showed a significant activity towards naphthalene HYD whereas the presulphided one showed practically no activity. Therefore, the Ni/Al_2O_3 should be used in a sulphur free environment in order to fully make use its HDA properties.

3.2.2. Characterization of the Ni/Al_2O_3

A detailed description of the TPS and TPR profiles of the Ni/Al_2O_3 catalyst, used in this work, is given by Hoffer et al. [19].

Temperature programmed oxidation. Figs. 12 and 13 show the temperature programmed oxidation profiles of this catalyst. The mass spectrometer signal of SO_2 (Fig. 12) shows a strong SO_2 desorption obtained from the spent presulphided Ni/Al_2O_3 catalyst. The desorption initiated at 523.15 K and the major peak was observed in the range of 523.15–923.15 K. Some sulphided species were found to desorbed above 973.15 K resulting in an unresolved peak at around this temperature. These sulphided species showed only a low activity towards naphthalene HYD. Table 4 summarizes the quantitative data from the TPO experiments normalized to 100 mg of catalyst. The sulphur to Ni molar ratios is also presented. The spent presulphided Ni/Al_2O_3 catalysts exhibited a very low sulphur-to-Ni molar ratio compared to the values reported in the open literature. A sulphur-to-Ni ratio varying between 0.70 and 0.81, which indicated that Ni_3S_2 phase was formed, has been reported by Hoffer et al. [19]. The value obtained in the present work is less than half of the latter values. The Ni/S ratio at zero activity was found to be 3. Consequently, the phase calculated would be approximately Ni_3S, which is not as stable as the Ni_3S_2 phase. The Ni/Al_2O_3 sulphiding procedure and reactor used in the present work is in many ways different from the one used by Hoffer et al. and Janssens et al. [19,42] and this could result in the differences observed. Poels et al. [41] studied the deactivation of the fixed-bed Ni/Al_2O_3 HYD catalyst by sulphur and obtained a similar result as the one found in the present work. These authors proposed that instead of a bulk Ni_3S phase formation, about two NiS surface layers would be formed, or less probably, multilayers of sulphur would be formed at the surface. Some traces of SO_2 contaminant were observed from the prereduced catalyst as soon as there was contact with air at ambient temperature. A chemical deactivation of this catalyst by sulphur poisoning could not be

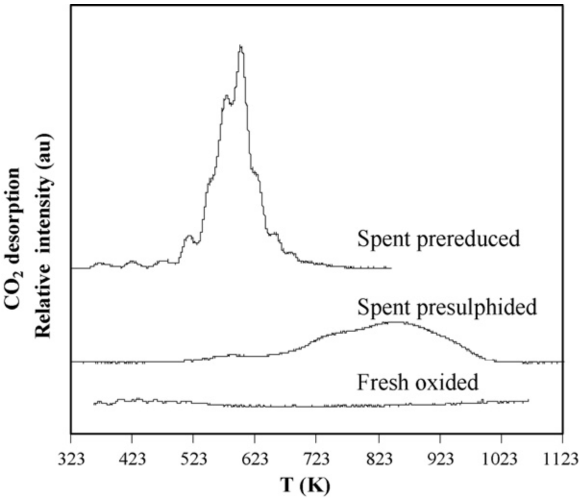

Fig. 13. CO_2 desorption as a function of temperature for spent presulphided and prereduced Ni/Al_2O_3. The profiles are normalized to 100 mg of catalyst sample.

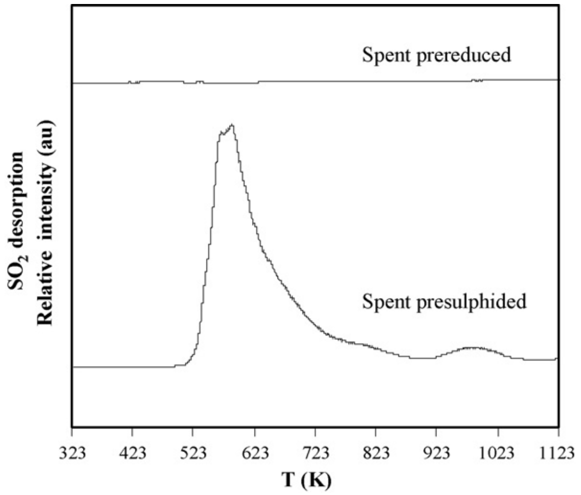

Fig. 12. SO_2 desorption as a function of temperature for spent presulphided and prereduced Ni/Al_2O_3. The profiles are normalized to 100 mg of catalyst sample.

Table 4
Amount of sulphur and CO_2 present in the spent prereduced and presulphided Ni/Al_2O_3 catalyst and the corresponding sulphur-to-Ni ratios (mol/mol) obtained from the quantitative TPO

	Total SO_2 area	S (mol)	S/Ni (mol/mol)	Total CO_2 area
Spent presulphided	8.68×10^{-9}	8.42×10^{-5}	0.32	1.20×10^{-7}
Spent prereduced	–	–	–	1.41×10^{-7}

Values presented were normalized to 100 mg of catalyst sample.

established as the contaminant sulphur might have been physically adsorbed.

The mass spectrometer signal of CO_2 (Fig. 13) shows the desorbed CO_2 from the fresh oxide and spent presulphided and prereduced Ni/Al_2O_3 catalyst. A significant carbon dioxide signal was detected from both spent forms of the catalyst, thus carbon formation occurred during the naphthalene HYD. The spent prereduced catalyst pattern indicated carbon species readily oxidised from 473.15 to 698 K, composing of various species and mainly dominated by species oxidised at 523.15–673.15 K. Carbon species from the spent presulphided catalyst were desorbed at higher temperatures compared to those of the prereduced catalyst. Nevertheless, the prereduced and presulphided forms were found to have the same intensity of CO_2 desorption (see Table 4). The presulphided catalyst was exposed to more severe temperature conditions than the prereduced form and this could explain the higher temperature of desorbed carbon (573.15 against 373.15 K, respectively). Moreover, both forms were on stream during roughly the same time. According to these latter observations and considering the fact that carbon deposition is more severe under more severe temperature conditions, it can be deduced that the sulphided catalyst was more resistant to carbon deposition than the prereduced one.

X-ray diffraction. XRD analysis was carried out in the oxidic, prereduced and presulphided Ni/Al_2O_3 catalyst with the objective to relate the crystallinity of the catalyst to its HYD activity. The XRD spectra obtained is presented in Fig. 14. Similarly to the $NiMo/Al_2O_3$ catalyst, it was difficult to find a perfect match from the XRD database for the crystalline phases observed and therefore, qualitative results are presented in this section. The two peaks observed at around 46° and 67° for all the catalysts, were assigned to the Al_2O_3 phase. According to Hoffer et al. [19], one can expect NiO, Ni_2O_3 or $Ni(OH)_2$ phases to be present in the oxidic catalyst. No discernable pattern match was found in this work. As it can be observed from Fig. 14, the diffraction patterns from the oxidic and spent prereduced Ni/Al_2O_3 catalysts are similar. This may be due to the fact that the catalyst was reduced and passivated by the manufacturer prior to supply. A clear difference could be found by comparing the XRD curves for the oxidic and the presulphided forms. Two other peaks, between 50° and 60°, were observed for the presulphided catalyst. These were eventually related to the formation of one or more crystalline sulphided phases and are probably responsible for the low activity of the presulphided catalyst towards naphthalene HYD. A search through the XRD database showed that these could be related to several possible crystalline phases, such as Ni_3S_2 and NiS, however a clear match could not be found and no conclusion could be drawn.

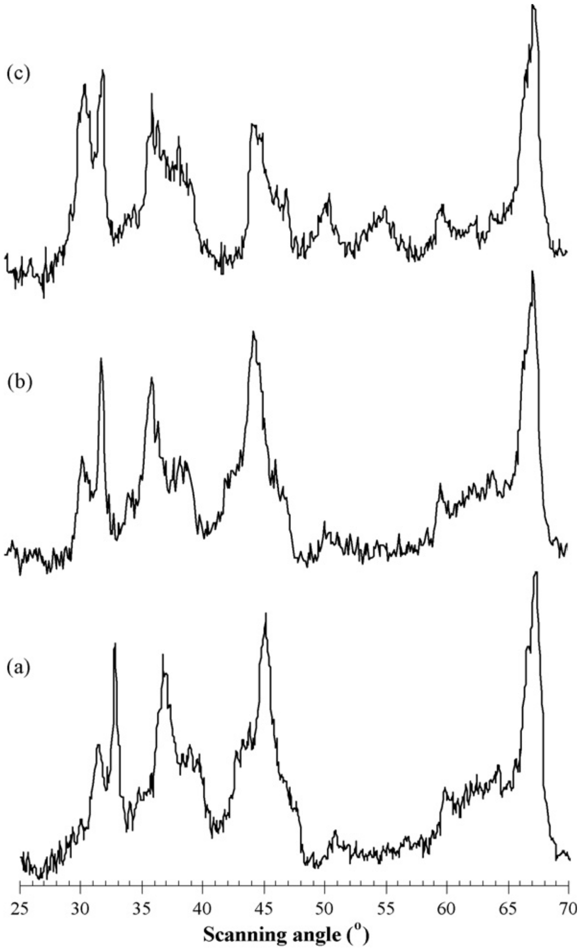

Fig. 14. X-ray diffraction analysis on (a) fresh oxidic Ni/Al_2O_3 catalyst and after two different pretreatments, (b) prereduced and (c) presulphided (the curves are not normalized).

4. Conclusions

The catalytic activity of the presulphided $NiMo/Al_2O_3$ catalyst was found to be 2.5 times higher than the prereduced form, at the same HYD conditions. $NiMo/Al_2O_3$ presulphided catalyst showed a low sensitivity to sulphur up to 1122 ppm. The loss of HYD activity of this catalyst at high sulphur levels was found to be reversible. Its activity was recovered when the source of sulphur was either removed or reduced. On the contrary, the prereduced form was found to deactivate continuously as the sulphur content increased up to 2245 ppm. From the aforementioned results, it can be concluded that the presulphided $NiMo/Al_2O_3$ catalyst was a more stable and more resistant catalyst to sulphur than the equivalent prereduced form. Both spent prereduced and presulphided forms of the $NiMo/Al_2O_3$ catalyst showed carbon species desorbed from 473.15 to 823.15 K. The presence of this carbon had little effect on the activity of the presulphided $NiMo/Al_2O_3$, whereas for the prereduced form it led to a deactivation of the catalyst. From these results, it can be inferred that the presulphided NiMo/Al_2O_3 catalyst was more resistant to coke deposition than the prereduced counterpart. These observations reinforce the fact that the catalytic active sites for naphthalene HYD in both catalysts are different and dependent on the pretreatment of the catalyst.

Testing the commercial prereduced Ni/Al_2O_3 catalyst it was observed that, although the catalyst aged quite quickly, it gave a higher turnover frequency at a temperature that was significantly lower than the one needed for the presulphided NiMo/Al_2O_3 catalyst. The catalytic activity of the prereduced Ni/Al_2O_3 catalyst was found to decrease with increased sulphur content in the feed. It was observed that the catalyst activity towards naphthalene HYD could not be restored after being poisoned by sulphur and therefore, it was concluded that poison by sulphur of the Ni/Al_2O_3 catalyst was irreversible. The presulphided Ni/Al_2O_3 catalyst showed a low activity towards naphthalene HYD, for the same experimental conditions as the prereduced form was tested. The spent presulphided and prereduced Ni/Al_2O_3 catalysts exhibited carbon species formation. The carbon species from the spent presulphided catalyst desorbed at higher temperatures compared to those of the prereduced catalyst. The source of this carbon was not found, but it is believed that it was due to the formation of coke precursor on the surface of the catalyst and this caused a decrease in the catalyst activity with time. The NiMo catalyst exhibited a much lower CO_2 intensity than the Ni catalyst, although the time on stream and temperatures applied were much higher in the case of the NiMo/Al_2O_3. It seems like the promoter Mo decreased the coking rate of Ni catalysts [43]. The presulphided and prereduced forms of the NiMo and Ni/Al_2O_3 catalysts presented different crystalline phases from the oxidic form and these were probably responsible for the observed activity of these catalysts. However, a clear identification of the phases was not possible with the analytical method used.

Acknowledgments

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