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# Ring opening of 1,2,3,4-tetrahydroquinoline and decahydroquinoline on $MoS_2/\gamma$ -Al\_2O\_3 and Ni-MoS\_2/\gamma-Al\_2O\_3

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# ABSTRACT

The hydrodenitrogenation of decahydroquinoline (DHQ) and quinoline on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> proceeds via two routes. The first one proceeds via DHQ  $\rightarrow$  propylcyclohexylamine  $\rightarrow$  propylcyclohexene  $\rightarrow$  propylcyclohexane, and the ring opening in DHQ is the rate-limiting step. The second route proceeds via 1,2,3,4-tetrahydroquinoline (14THQ)  $\rightarrow$  o-propylaniline  $\rightarrow$  propylcyclohexylamine and propylbenzene with the ring opening of 14THQ and the hydrogenation of o-propylaniline being the rate determining steps (the intrinsic rate of C(sp<sup>3</sup>)–N bond cleavage being slower in 14THQ than in DHQ). The active sites for the ring opening via Hofmann elimination are acidic –SH groups and basic S<sup>2–</sup> ions. The parallel conversion of dibenzothiophene (DBT) via direct desulfurization provides increasing concentrations of S<sup>2–</sup> ions and –SH groups. Nickel facilitates the adsorption of H<sub>2</sub>S and H<sub>2</sub> and the mobility of hydrogen. Thus, the presence of DBT and Ni accelerates the rate of the C(sp<sup>3</sup>)–N bond cleavage. H<sub>2</sub>S as sulfur source enhances the ring-opening steps in a minor extent than DBT. The presence of –SH groups and the effect of Ni on them were probed by TPR, TPD and IR-spectroscopy of adsorbed 2,6-dimethylpyridine.

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# 1. Introduction

The increasing demand for transportation fuels and the rigorous specifications for sulfur content and for allowed emissions of sulfur and nitrogen oxides have led to a high interest in the catalytic removal of heteroatoms from oil feedstocks [1]. In order to remove nitrogen, hydrodenitrogenation (HDN) is conducted with alumina-supported MoS<sub>2</sub> catalysts promoted with Ni or Co. While the HDN of anilines and aliphatic amines is facile, the more abundant heterocyclic aromatic compounds containing five-member pyrrolic or six-member pyridinic rings are difficult to convert [2].

The bicyclic quinoline is a good model compound to study HDN, because its hydroconversion provides detailed insight into the elementary steps of HDN reactions [3–8]. The saturation of the benzoic ring prior to  $C(sp^3)$ –N bond cleavage is mandatory, because the high energy of the  $C(sp^2)$ –N bond in the aromatic ring prevents its cleavage [9]. The hydrogenation steps are reversible and exothermic. Thus, the equilibrium concentration of the saturated products decreases with temperature [10]. In contrast, the ring opening via  $C(sp^3)$ –N bond cleavage is irreversible under typical HDN reaction conditions.

Understanding the mechanistic differences in the C(sp<sup>3</sup>)–N bond cleavage of the intermediates is challenging because the nitrogen-

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containing hydrogenated intermediates adsorb strongly and compete with quinoline for the adsorption sites. Therefore, we have decided to solely address the initial steps, that is, the HDN of quinoline (Q) and decahydroquinoline (DHQ). This approach offers the possibility to evaluate the initial hydrogenation/dehydrogenation steps followed by the  $C(sp^3)$ -N bond cleavage in 1,2,3,4-tetrahydroquinoline (14THQ) and DHQ leading to o-propylaniline (OPA) and propylcyclohexylamine (PCHA), respectively.

The ring-opening steps of bicyclic molecules, for example, 14THQ and DHQ, has received less attention than DDN and hydrogenation steps. However, the efficiency of the overall quinoline HDN process depends to a large extent on the ability of the catalyst to cleave the  $C(sp^3)$ –N bond prior to the complete removal of nitrogen. The individual rates are strongly influenced by the presence of sulfur-containing compounds and by the promotion of MoS<sub>2</sub> with cations such as Ni. In the current work, we explore, therefore, the effect of Ni as promoter for MoS<sub>2</sub> and the impact of sulfur-containing compounds on the HDN of Q and DHQ.

# 2. Experimental

# 2.1. Catalyst synthesis and characterization

# 2.1.1. Catalyst synthesis and physicochemical properties

The Mo and NiMo oxide catalyst precursors were prepared by consecutive incipient wetness impregnation on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support



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(BET specific surface area of 237 m<sup>2</sup>/g) using aqueous solutions of ammonium heptamolybdate, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, and nickel nitrate, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. After each impregnation, the oxide catalysts were dried overnight at 120 °C and calcined at 500 °C for 4 h (1 °C/min) in flow of synthetic air. Hereafter, the oxidic precursors are referred as Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, whereas the corresponding sulfide catalysts are denoted as MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Detailed characterization of the catalysts has been reported somewhere else [11]; therefore, only experimental procedures of characterization techniques not reported in Ref. [11] are described here.

# 2.1.2. Temperature-programmed reduction and desorption

Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) were used to analyze sites potentially active in  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni– $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, via reduction of the sulfide phase and desorption of adsorbed species. The experiments were carried out in a quartz reactor and the evolved gases were detected by a mass spectrometer (Balzers QME 200). Prior to the experiments, oxidic catalyst precursors (0.1 g) were activated in situ for 2 h in 10% H<sub>2</sub>S in H<sub>2</sub> at 400 °C (5 °C/min). In the case of TPR experiments, cooling to room temperature in the presence of the sulfiding agent was followed by flushing of the reactor with high purity He for 1 h to remove H<sub>2</sub>S. The catalysts were then heated in 20% H<sub>2</sub> in He to 1000 °C with 5 °C/min. For TPD studies, after sulfidation and flushing the reactor with He at room temperature, the temperature was increased to 920 °C with heating rate of 5 °C/min.

#### 2.1.3. IR spectrum of adsorbed 2,6-dimethylpyridine

The IR spectra of adsorbed 2,6-dimethylpyridine (DMP) were acquired in a Nicolet 6700 FT-IR spectrometer equipped with a flow cell. Samples of the catalysts (6–7 mg) were pressed into self-supporting circular wafers of 1 cm diameter. The materials were sulfided in situ in a flow of H<sub>2</sub>S (10 vol.%) in H<sub>2</sub> at 400 °C for 2 h. Subsequently, the cell was evacuated for 1 h at 400 °C. DMP was equilibrated at 1 mbar, followed by evacuation for 15 min. Finally, H<sub>2</sub>S was admitted to the cell until reaching 1 mbar. Spectra were recorded before and after the adsorption of H<sub>2</sub>S. All reported spectra were normalized to the wafer mass and the background spectrum was subtracted. The differences in the intensities were quantitatively determined using the OMNIC program.

#### 2.2. Kinetic measurements

The kinetic studies were carried out in a continuous flow trickle bed reactor system. A stainless steel, glass lined coated reactor was loaded with 0.05 g of oxide catalyst precursor for each run. Gas and liquid feeds were introduced into the reactor via high pressure mass flow meters (Bronkhorst) and a HPLC pump (Shimadzu LC-20AD), respectively. After separation of the liquid and the gas effluent phase, the liquid was collected via 16 port sampling valve every 1.5 h. The liquid samples were analyzed off-line by gas chromatography with a HP 6890 GC equipped with a flame ionization detector (FID) and an Agilent DB-17 capillary column.

Prior to the experiments, the catalysts were activated in situ in 10% H<sub>2</sub>S in H<sub>2</sub> flow at 400 °C and 1.8 MPa for 8 h. HDN reactions were performed at 370 °C and a total pressure of 5.0 MPa. The steady state was reached after 16 h time on stream. The HDN was investigated as a space time dependent experiment. Space time was defined as  $m_{cat}/F_N$ , where  $m_{cat}$  is the amount of the oxide catalyst precursor and  $F_N$  is the molar flow of nitrogen-containing compound [(h)·(g of catalyst)/(mol of N-containing compound)]. The reactions were performed in excess of hydrogen keeping the ratio of liquid and gas flow constant to ensure constant partial pressures (the H<sub>2</sub> to hydrocarbon ratio was 330 N dm<sup>3</sup>/dm<sup>3</sup>). The

catalyst powder ( $250-500 \,\mu$ m) was evenly dispersed in SiO<sub>2</sub> ( $<250 \,\mu$ m). The absence of artifacts, for example, bypassing, and incomplete wetting was verified by performing experiments using different amounts of catalyst and flow rates (see Supporting information).

The initial concentration of quinoline (Aldrich, 98%) or DHQ (Aldrich, mixture of cis and trans, 97%) was set to 1000 ppm wt. N (equivalent to 14.6 kPa) in a mixture of 5% hexadecane (Merck, 99%) in tetradecane (Alfa Aesar, 99+%) as a solvent. For studying the effect of sulfur-containing compound on the HDN reaction, dibenzothiophene (DBT) (Aldrich, 99%) or dimethyl disulfide (DMDS) was added at the concentration of 500 ppm wt. S (equivalent to 3.2 or 1.6 kPa of DBT or DMDS). The conversion toward nitrogen-free products was referred as the HDN conversion and it was calculated as shown in equation (i), where  $c_{[Nx]o}$  is the initial concentration of the studied compound x (quinoline or decahydroquinoline);  $c_{[Nx]}$  is the concentration of the studied compound x at the measured space time; and  $c_{[N]}$  is the concentration of all nitrogen-containing products at the measured space time.

HDN conversion 
$$= \frac{c_{[Nx]_O} - c_{[Nx]} - c_{[N]}}{c_{[Nx]_O}} 100$$
 (i)

The conversions of the lumped compounds (Q + 14THQ) and (DHQ + 58THQ) were analyzed instead of the pure reactants (58THQ stands for 5,6,7,8-tetrahydroquinoline). The conversion of the so grouped compounds was defined as shown in equations (ii) and (iii), where  $c_{[Q]o}$  and  $c_{[DHQ]o}$  are the initial concentrations of quinoline or decahydroquinoline;  $c_{[Q]}$ ,  $c_{[14THQ]}$ ,  $c_{[DHQ]}$ , and  $c_{[58THQ]}$  are the concentration of Q, 14THQ, DHQ and 58THQ, respectively.

$$(Q + 14THQ) \text{ conversion} = \frac{c_{[Q]_0} - c_{[Q]} - c_{[14THQ]}}{c_{[Q]_0}} 100$$
(ii)

$$(DHQ + 58THQ) \text{ conversion} = \frac{c_{[DHQ]_0} - c_{[DHQ]} - c_{[58THQ]}}{c_{[DHQ]_0}} 100$$
 (iii)

#### 3. Results

# 3.1. Catalyst characterization

# 3.1.1. Physicochemical properties

Relevant characteristics of the catalysts studied in this work were reported in Ref. [11]. The metal concentration was 8.6 wt.% Mo in the unpromoted and 8.6 wt.% Mo and 3.6 wt.% Ni in the promoted oxidic catalyst precursor leading to molar fractions of 0.4 for Ni and 0.6 for Mo. The surface areas were 220 and 206  $m^2/g$  for  $MoS_2/\gamma$ - $Al_2O_3$  and Ni- $MoS_2/\gamma$ - $Al_2O_3$ , respectively, whereas the average pore diameter was 8.5 nm in both materials. The surface density of Mo in Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 2.5 atoms/ nm<sup>2</sup>, which is below the monolayer concentration of 4.6 atoms/ nm<sup>2</sup> determined on alumina [12]. Ni-aluminates or Ni-molybdates were not detected in the oxide precursors, likely due to the low concentration of Ni. Therefore, only bands ascribed to MoS<sub>2</sub> were observed in the Raman spectra after sulfidation. This sulfide phase was present with high dispersion as proved by the absence of any agglomerated crystalline Mo- or Ni-containing species (XRD) and the low stacking degree of the MoS<sub>2</sub> particles (TEM).

The total NO uptake on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni– $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 130 and 160 µmol/g<sub>cat</sub>, respectively. That is, the addition of 3.6 wt.% of Ni enhanced the concentration of the coordinatively unsaturated sites (CUS) by approximately 25%, which is less than the molar concentration of Ni added. It is not straightforward to derive a specific concentration of CUS for the sulfide phase because NO may adsorb on metal cations of the MoS<sub>2</sub> phase as mononitrosyl or dinitrosyl species depending on the adsorption location [13]. However, the lack of specificity of the NO adsorption (indicated by the disparity between the concentrations of NO adsorbed and Ni added) allows us to assume that both, Ni and Mo cations, are exposed in the promoted catalysts. This assumption is in line with IR and STM studies that show that the promoter atoms do not deposit on all MoS<sub>2</sub> edges with the same preference [13,14].

# 3.1.2. Temperature-programmed desorption (TPD) and reduction (TPR)

The TPD profiles of H<sub>2</sub>S and H<sub>2</sub> recorded in parallel during the experiment are shown in Fig. 1.  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed continuous H<sub>2</sub> and H<sub>2</sub>S desorption from about 100 and 50 °C, respectively, to above 900 °C. The H<sub>2</sub> desorption profile of both catalysts can be divided in four regions, Fig. 1. The first region, below 280 °C, exhibits a shoulder (Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) or a peak (MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) at 250 °C. This desorption is assigned to the recombination of -SH groups according to reaction (1), where surface species are preceded by (\*-) [15]. In the second region, between 280 °C and 420 °C, the H<sub>2</sub> desorption shows a maximum at 340 °C associated with the heterolytic recombination of hydrogen with hydride character and -SH groups, as shown in reaction (2), where (\*) represents a vacancy (CUS) [16]. Note that (1) and (2), are the reverse reactions for the homolytic and heterolytic dissociation of H<sub>2</sub> on MoS<sub>2</sub> [17]. The broad desorption signal in the 420-600 °C range forming the third region with maximum at 450 °C is attributed to the recombination of two hydride ions according to reaction (3). Finally, above 600 °C, H<sub>2</sub> desorbs continuously with a low rate due to the condensation of -SH groups from different slabs [18].

$$^{*}-\mathrm{SH}^{-}+^{*}-\mathrm{SH}^{-}\rightleftharpoons\mathrm{H}_{2}+2^{*}-\mathrm{S}^{-}$$

$$\tag{1}$$

$$^{*}-H^{-} + ^{*}-SH^{-} \rightleftharpoons H_{2} + ^{*}-S^{2-} + ^{*}$$
 (2)

$$^{*}-H^{-} + ^{*}-H^{-} \rightarrow 2^{*} + H_{2} + 2e^{-}$$
 (3)

The H<sub>2</sub>S temperature-programmed desorption from  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni– $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> can also be divided into four regions, Fig. 1. The first desorption region, below 280 °C, is attributed to the release of physisorbed H<sub>2</sub>S (maxima at 110 °C) [18] and to the recombination of –SH groups as shown in reaction (4). The functional groups involved in the desorption of H<sub>2</sub> and H<sub>2</sub>S in reactions (1) and (4) are identical, and the reactions might occur in parallel and on the same sites [19]. Note also that below 280 °C, the H<sub>2</sub>S desorption from Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is higher than from MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, whereas the desorption of H<sub>2</sub> is higher for the latter than for the former also suggesting competitive desorption of H<sub>2</sub> and H<sub>2</sub>S. The region between 280 and 400 °C, characterized by a local maximum in the H<sub>2</sub>S release profile (with shoulders at 320 °C for MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and 300 °C for Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), can be associated with the recombination of –SH groups and hydride ions according to reaction (5) [15]. The third region, 400–600 °C, characterized by H<sub>2</sub>S desorption with a maximum at 450–480 °C corresponds also to reaction (5) occurring after the transfer of mobile hydrogen to the edges from the basal planes [20]. The continuously decreasing H<sub>2</sub>S release above 600 °C is attributed to catalyst sintering.

$$^{*}-SH^{-} + ^{*}-SH^{-} \rightleftharpoons H_{2}S + ^{*}-S^{2-} + ^{*}$$

$$\tag{4}$$

$$^{*}-H^{-} + ^{*}-SH^{-} \rightleftharpoons H_{2}S + 2^{*} + 2e^{-}$$
<sup>(5)</sup>

The TPR of  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was monitored following the H<sub>2</sub>S signal, as shown in Fig. 2. The reduction of Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> is more facile than that of the unpromoted catalyst, as the H<sub>2</sub>S evolution maxima are shifted to lower temperatures. This confirms that Ni increases the rate of vacancy formation in the same way as it increases the concentration of vacancies at equilibrium coverage [21–23]. For  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the H<sub>2</sub>S release at low temperature (onset at 70 °C) forming a shoulder at 100 °C is attributed to physisorbed H<sub>2</sub>S. This signal is probably overshadowed by the more intense main reduction peak in the TPR profile of Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The most intense H<sub>2</sub>S-release signals, with maxima at 176 and 204 °C for Ni-MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, and MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, respectively, are attributed to the elimination of weakly bound -SH groups [24]. We propose that the H<sub>2</sub>S release at low temperature proceeds via the reverse reaction (1) (hydrogen activation) and subsequent reaction (4), in analogy to the assignment of the low temperature H<sub>2</sub>-release signal in the TPD profiles. This assignment is supported by recent studies of the reduction of the MoS<sub>2</sub> phase [25-27]. The reduction region between 280 and 400 °C is associated with more strongly bound S<sup>2-</sup> ions [28]. The H<sub>2</sub> activation via the reverse reaction (2) and subsequent reaction (5) are proposed to occur in this temperature range. A shoulder in the TPR pattern is found with  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 290 °C, which is not



Fig. 1. Temperature-programmed decomposition in flowing He leading to evolution of H<sub>2</sub> and H<sub>2</sub>S from MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and Ni-MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.



Fig. 2. H<sub>2</sub>S mass spectrometer signal followed during the temperature-programmed reduction of MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and Ni-MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.

observed with Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> probably because Ni accelerates the elimination of H<sub>2</sub>S leading to a single peak. Above 450 °C, it can be assumed that H<sub>2</sub> is dissociated at the edges, transfers to different sites in the slabs and reacts with less reactive sulfur. Also this process is promoted by nickel given that the maximum shifts from 525 °C to 480 °C with MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. The continuous H<sub>2</sub>S release above 600 °C is associated with sintering, whereas the final slight increase in the H<sub>2</sub>S evolution above 900 °C is related to the elimination of sulfur from the basal planes required for the full reduction [28].

## 3.1.3. IR of adsorbed 2,6-dimethylpyridine

Fig. 3 shows the IR spectra of DMP adsorbed on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> before and after adsorption of H<sub>2</sub>S. All the bands labeled in Fig. 3 correspond to adsorbed DMP species. The peaks for Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are less intense than those for MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> due to the higher opacity of the Ni-containing material. The bands at 1650 and 1625 cm<sup>-1</sup> are assigned to the ring vibrations ( $v_{8a}$  and  $v_{8b}$  modes) of protonated DMP indicating Brønsted acid sites. The bands at 1618, 1602, and 1580 cm<sup>-1</sup> are attributed to DMP species interacting with Lewis acid sites, weakly adsorbed DMP, and these both kinds of interaction, respectively [29,30].

For both catalysts, the intensity of the signals at 1650 and 1625 cm<sup>-1</sup> (DMP adsorbed on Brønsted sites) increased after the adsorption of H<sub>2</sub>S. In parallel, the intensity of the signals between 1618 and 1580 cm<sup>-1</sup> (DMP weakly adsorbed on Lewis acid sites) decreased. The bands between 1650 and 1625 cm<sup>-1</sup> increased after the adsorption of H<sub>2</sub>S by 35% and 45% for MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. The intensity decrease in the bands



Fig. 3. IR spectra of 2,6-dimethylpyridine adsorbed on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> before (dashed lines) and after (continuous lines) exposure to H<sub>2</sub>S.

in the 1618–1580 cm<sup>-1</sup> region upon co-adsorbing H<sub>2</sub>S was 18% for  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 25% for Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The ratio between the increase and decrease in absorbance for both cases is almost the same, that is, 1.9 (MoS<sub>2</sub> $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and 1.8 (Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). These observations imply that after adsorbing H<sub>2</sub>S a notable concentration of Lewis acid sites convert to Brønsted acid sites and that Ni promotes this transformation. It is likely that –SH groups are formed via inverse reaction (4) in which H<sub>2</sub>S adsorbs on vacancies leading to –SH groups.

# 3.2. Hydrodenitrogenation of decahydroquinoline (DHQ)

# 3.2.1. HDN reaction network

Thermodynamic equilibrium between quinoline and 14THQ was rapidly established, whereas the thermodynamic equilibrium between DHQ and 58THQ was reached at space times above 100 h g<sub>cat</sub>/mol (see the Supporting information). Thus, the concentrations of quinoline and 14THQ as well as DHQ and 58THQ were lumped together. The product yield as a function of (DHQ + 58THQ) conversion in the absence and presence of DBT is shown in Fig. 4. The dehydrogenated products detected were 14THO and guinoline. Products formed from ring-opening reactions were OPA and PCHA and the final nitrogen-free products under all conditions were propylbenzene (PB), PCH, and PCHE in form of three equilibrated isomers, that is, 1-propylcyclohexene, 3-propylcyclohexene, and propylidene cyclohexane. 14THQ (produced by the dehydrogenation of the benzoic ring in DHQ) and PCHA (product of the ringopening reaction via  $C(sp^3)$ -N bond cleavage) were the primary products. PCHA and OPA were detected in very low concentrations (<3%) (see Figs. 4B and C). Among the nitrogen-free products, the only aromatic end product PB, Fig. 4D, was formed with the lowest yield compared to PCHE and PCH, Fig. 4E and F.

The HDN of DHQ and quinoline on  $MoS_2/\gamma-Al_2O_3$  and  $Ni-MoS_2-\gamma-Al_2O_3$  proceeds as schematically outlined in Fig. 5. Starting from DHQ, the dehydrogenation of the nitrogen-containing ring leads to the fast formation of 58THQ, reaching thermodynamic equilibrium, whereas the dehydrogenation of the carbocyclic ring leads to the formation of 14THQ, which is equilibrated with quinoline. In parallel, the HDN of DHQ proceeds via the sequence DHQ  $\rightarrow$  PCHA (via ring opening)  $\rightarrow$  PCHE (via denitrogenation)  $\rightarrow$  PCH (via hydrogenation). This reaction network is commented in detail in the following.

With respect to the conversion of DBT (Fig. 6A), Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was more active for hydrodesulfurization (HDS) than MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, for example, at space time of 100 h g<sub>cat</sub>/mol, the DBT conversion was 12% with MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 95% with Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The product distribution is shown in Fig. 6B and C. Low concentrations of phenylcyclohexane (PhCH) were detected over the whole space time, < 2% on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and <8% on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, indicating that the main route for DBT conversion was the direct desulfurization (DDS) to biphenyl (BPh).



**Fig. 4.** Yield of (quinoline + 1,2,3,4-tetrahydroquinoline) (A), propylcyclohexylamine (B), o-propylaniline (C), propylbenzene (D), propylcyclohexene (E), and propylcyclohexane (F) as a function of (DHQ + 58THQ) conversion on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bullet$ ,  $\blacksquare$ ) and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\square$ ). The experiments were carried out in the absence ( $\bullet$ ,  $\bigcirc$ ) and presence of DBT ( $\blacksquare$ ,  $\square$ ).



Fig. 5. HDN reaction network of quinoline (Q), where the abbreviations are defined as follows: 14THQ – 1,2,3,4-tetrahydroquinoline; PCHA – propylcyclohexylamine; 58THQ – 5,6,7,8-tetrahydroquinoline; PB – propylbenzene; DHQ – decahydroquinoline; PCHE – propylcyclohexene; OPA – o-propylaniline; PCH – propylcyclohexane.

# 3.2.2. Effect of Ni and dibenzothiophene

The total conversion of (DHQ + 58THQ) and the HDN conversion are shown in Fig. 7A and B, respectively. Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was more active than MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence and presence of DBT. The promoting effect of Ni was more pronounced, when the reaction was carried out in the presence of DBT, whereas the activity of MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is hardly influenced by the S-containing molecule. The beneficial effect of the presence of sulfur-containing compounds in the C–N bond cleavage has been reported [31–35], focusing, however, on Co(Ni)–MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and making it so difficult to interpret the combined impact.

The yields of individual products are shown in Fig. 8. The rate of DHQ dehydrogenation to 14THQ was three times higher with

Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than with MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence and presence of DBT, Fig. 8 A. DBT enhanced the dehydrogenation rate of DHQ to 14THQ by 25% on both catalysts. The rates of PCHA and OPA formation via C(sp<sup>3</sup>)–N bond cleavage of DHQ and 14THQ were very low, as seen in Figs. 8B and C. The bond cleavage of DHQ was promoted by DBT on both catalysts, but the effect was much more pronounced with Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It also appears that at space times above 100 h g<sub>cat</sub>/mol, PCHA was converted to OPA. The rates to nitrogen-free products PB, PCHE, and PCH were also higher with Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than with MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as seen in Fig. 8D–F. DBT inhibited the rate of PB formation by 50% with MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The rate of PCHE formation was promoted by DBT with both



**Fig. 6.** DBT conversion (A) and yield of PhCH (B) and BPh (C) in the parallel reaction with the HDN of DHQ ( $\blacklozenge$ ,  $\diamondsuit$ ) or quinoline ( $\blacktriangle$ ,  $\bigtriangleup$ ), carried out on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\diamondsuit$ ,  $\blacktriangle$ ) and Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\diamondsuit$ ,  $\bigtriangleup$ ).

catalysts. The rate of PCH formation was not affected by DBT with  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, while it was promoted with  $Ni-MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The higher yield of PB with  $Ni-MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> than with  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> is attributed to the dehydrogenation of PCHE, because Ni (and Co) suppress the formation of PB by OPA hydrogenolysis [11,14,36].

Fig. 8 shows clearly that DBT promotes the rate of PCHA, and PCHE, formation on both catalysts in the HDN of DHQ. As DBT does not influence the hydrogenation of OPA and further  $C(sp^3)$ –N bond cleavage on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [11], the increase in PCHE formation in the presence of DBT is concluded to be caused by the acceleration of the DHQ ring opening. The rate of PCHA formation (detected only in very low concentrations) is lower than that of the further conversion to PCHE, see Fig. 8B and E. Hence, the C(sp<sup>3</sup>)–N bond cleavage in the primary amine (PCHA) is fast and the rate of the C(sp<sup>3</sup>)–N bond cleavage in DHQ has to be the rate-limiting step in agreement with Ref. [37].

#### 3.3. Hydrodenitrogenation of quinoline

#### 3.3.1. HDN reaction network

The product yields in the absence and presence of DBT as a function of the quinoline conversion are shown in Figs. 9 and 10 for  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ni– $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The products detected are those observed in the HDN of DHQ, that is, THQ, OPA, PB, PCHA, PCHE, and PCH. Thermodynamic equilibrium between quinoline and 14THQ is rapidly reached (see the Supporting information). Thus, in the further discussion, the two equilibrated compounds



**Fig. 7.** (DHQ + 58THQ) conversion (A) and HDN conversion (B) as a function of space time on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bullet$ ,  $\blacksquare$ ) and Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\Box$ ). The experiments were carried out in the absence ( $\bullet$ ,  $\bigcirc$ ) and presence of DBT ( $\blacksquare$ ,  $\Box$ ).

are considered as educts and the (Q + 14THQ) conversion is presented in the following instead of quinoline conversion alone.

DHQ, 58THQ, and OPA are identified as primary products, because they show a positive slope at zero (Q + 14THQ) conversions. DHQ and 58THQ formed by the hydrogenation of the benzoic ring in 14THQ and quinoline, respectively, exhibited similar yields, for example, about 10%, at 30% of (Q + 14THQ) conversion, Figs. 9A and 9B. OPA, formed from the ring opening of 14THQ, shows a maximum yield of about 8%, indicating rapid further conversion, Fig. 9C. The other ring-opening intermediate, PCHA, was either not present or its concentration did not exceed 1%, Fig. 9D. The lower concentration of OPA than DHQ over the whole space time indicated that the ring opening of 14THQ via C(sp<sup>3</sup>)–N bond cleavage had a lower reaction rate compared to the parallel hydrogenation of the benzoic ring to form DHQ [38]. PB, the only aromatic nitrogen-free end product, had the lowest yield compared to the other N-free products, PCHE, and PCH (see Fig. 10).

It is important to note that the low concentration of OPA cannot be attributed to the fast transformation to PCHA, as long as quinoline, 14THQ, 58THQ and DHQ are present, because their strong adsorption would limit the access of OPA to the active surface [36,38]. Having established that further 14THQ conversion to OPA is slow, the main pathway for the nitrogen removal from quinoline has to proceed mainly via DHQ intermediate and subsequent ring opening and denitrogenation [39,40].

During the HDN of quinoline, the conversion of DBT was also monitored with both catalysts (see Fig. 6). The Ni-containing catalyst had the highest HDS activity. The main route for DBT conversion was the DDS, given the low concentration of PhCH formed, and the high yield of BPh with both catalysts.

### 3.3.2. Effect of Ni and sulfur-containing compounds

The HDN of quinoline was performed on  $MoS_2/\gamma$ - $Al_2O_3$  and Ni- $MoS_2/\gamma$ - $Al_2O_3$  in the presence of dibenzothiophene (DBT) or dimethyl disulfide (DMDS) in the feed to investigate the effect of the sulfur source on the HDN mechanism. DMDS is expected to decompose quickly to  $H_2S$ , and therefore in the following, we discuss the effect of  $H_2S$  on the HDN. The total conversion of quinoline and 14THQ and the HDN conversion are shown in Fig. 11. The rate



**Fig. 8.** Yield of quinoline + 1,2,3,4-tetrahydroquinoline (A), propylcyclohexylamine (B), o-propylaniline (C), propylbenzene (D), propylcyclohexene (E), and propylcyclohexane (F) as a function of space time in DHQ HDN carried out on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bullet$ ,  $\blacksquare$ ) and Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\circ$ ,  $\Box$ ). The experiments were carried out in the absence ( $\bullet$ ,  $\bigcirc$ ) and presence of DBT ( $\blacksquare$ ,  $\Box$ ).



**Fig. 9.** Yield of decahydroquinoline (A), 5,6,7,8-tetrahydroquinoline (B), o-propylaniline (C), and propylcyclohexylamine (D) as a function of (Q + 14THQ) conversion on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bullet$ ,  $\blacksquare$ ) and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\square$ ). The experiments were carried out in the absence ( $\bullet$ ,  $\bigcirc$ ) and presence of DBT ( $\blacksquare$ ,  $\square$ ).

of nitrogen removal was at first negligible and only at space time above 100 h·g<sub>cat</sub>/mol the rate increased. Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was more active than MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, in the absence and presence of DBT or H<sub>2</sub>S. The promoting effect of Ni was more pronounced when the reaction was carried out in the presence of DBT or H<sub>2</sub>S. In contrast, the presence of sulfur did not influence the conversion of quinoline, when the reaction was carried out with MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. On Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the nature of the sulfur source did not alter the (Q + 14THQ) conversion but the HDN conversion was lower in the presence of H<sub>2</sub>S than in the presence of DBT. This suggests that the nature of the sulfur compound markedly influences the rate to N-free products.

The yields of the products as a function of space time are presented in Figs. 12 and 13. The yields of the bicyclic intermediates DHQ and 58THQ, as well as the yields of PCHA, on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and those of OPA and PCHA on Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> were insensitive



**Fig. 10.** Yield of propylbenzene (A), propylcyclohexene (B), and propylcyclohexane (C) as a function of (Q + 14THQ) conversion on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\blacksquare$ ) and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\Box$ ). The experiments were carried out in the absence ( $\bigcirc$ ,  $\bigcirc$ ) and presence of DBT ( $\blacksquare$ ,  $\Box$ ).

to the nature of the sulfur-containing compound. The initial hydrogenation rate of the benzoic ring in quinoline (leading to 58THQ) was higher on Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, two times in the absence of sulfur and three times in the presence of DBT or H<sub>2</sub>S. Note that the yield of 58THQ was higher with H<sub>2</sub>S than with



**Fig. 11.** (Q + 14THQ) conversion (A) and HDN conversion (B) as a function of space time on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\oplus$ ,  $\blacksquare$ ,  $\blacktriangle$ ) and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\square$ ,  $\triangle$ ). The experiments were carried out in the absence of sulfur-containing compounds, ( $\oplus$ ,  $\bigcirc$ ), and adding DBT ( $\blacksquare$ ,  $\square$ ) or DMDS ( $\blacktriangle$ ,  $\triangle$ ) to the feed.

DBT on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at space time above 100 h·g<sub>cat</sub>/mol. The initial hydrogenation rate (<100 h·g<sub>cat</sub>/mol) of the benzoic ring in 14THQ, producing DHQ, was three times higher on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence and the presence of sulfur. DBT or H<sub>2</sub>S only promoted further DHQ conversion with Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the DHQ yield peaked at 15% at around 210 h·g<sub>cat</sub>/mol. The initial rate of ring opening in 14THQ via the C(sp<sup>3</sup>)–N bond cleavage (leading to OPA) was twice higher on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the presence of DBT (Fig. 12C). However, the difference is small in the presence of H<sub>2</sub>S. Interestingly, on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the yield of OPA increases in the presence of h<sub>2</sub>S compared to the presence of DBT. The inspection of the yields of nitrogen-free products showed that this high OPA yield with H<sub>2</sub>S was due to the inhibition of the



**Fig. 12.** Yield of decahydroquinoline (A), 5,6,7,8-tetrahydroquinoline (B), o-propylaniline (C), and propylcyclohexylamine (D) as a function of space time in quinoline HDN carried out on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bullet$ ,  $\blacksquare$ ,  $\blacktriangle$ ) and Ni– $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\square$ ,  $\bigtriangleup$ ). The experiments were carried out in the absence of sulfur-containing compounds, ( $\bullet$ ,  $\bigcirc$ ), and adding DBT ( $\blacksquare$ ,  $\square$ ) or DMDS ( $\blacktriangle$ ,  $\bigtriangleup$ ) to the feed.



**Fig. 13.** Yield of propylbenzene (A), propylcyclohexene (B), and propylcyclohexane (C) as a function of space time in quinoline HDN carried out on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\blacksquare$ ,  $\blacktriangle$ ) and Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\bigcirc$ ,  $\square$ ,  $\bigtriangleup$ ). The experiments were carried out in the absence of sulfur-containing compounds, ( $\bigcirc$ ,  $\bigcirc$ ), and adding DBT ( $\blacksquare$ ,  $\square$ ) or DMDS ( $\blacktriangle$ ,  $\bigtriangleup$ ) to the feed.

denitrogenation of OPA to PB, because the yield of PCH and PCHE were unaffected, whereas the yield of PB decreased on replacing DBT by  $H_2S$ . The acceleration of the ring-opening step is discarded because the (Q + 14THQ) conversion is also unaffected by the nature of the sulfur compound.

PCHA, the product of the C(sp<sup>3</sup>)–N bond cleavage in DHQ, was observed only when the reaction was carried out on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the presence of sulfur. Especially in the presence of DBT, the formation rate of PCHE and PCH was higher with the Ni-promoted catalyst (see Fig. 13). It should be emphasized that the rate of formation of these products was enhanced by the presence of sulfur only on the promoted catalyst.

On Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the lower yields of the final denitrogenated products in the presence of H<sub>2</sub>S than in the presence of DBT allowed concluding that the high yield of 58THQ observed on the promoted catalyst in the presence of H<sub>2</sub>S was mainly caused by the slowing down of the route: 58THQ  $\rightarrow$  DHQ  $\rightarrow$  PCHA  $\rightarrow$  P-CHE  $\rightarrow$  PCH + PB. Given that the steps 58THQ  $\rightarrow$  DHQ and PCHA  $\rightarrow$  PCHE are fast, it is likely that the presence of H<sub>2</sub>S enhances the ring opening (DHQ  $\rightarrow$  PCHA) to a lower extent than DBT.

# 4. Discussion

# 4.1. Probing -SH groups by TPD, TPR, and IR-spectroscopy

Surface –SH groups on MoS<sub>2</sub> are the key functional groups for the catalytic chemistry discussed in this paper. In principle, several

possibilities exist, how these groups can be formed on  $MoS_2$  slabs [15,17,41–43]. Theoretical and experimental studies, for example, indicate that molecular hydrogen is able to dissociate on  $(S-S)^{2-}$  dimers leading to the formation of –SH groups (reverse reaction (1)). Acid–base pairs formed by CUS and  $S^{2-}$  ions can heterolytically dissociate H<sub>2</sub> to form a hydride and a –SH group (reverse reaction (2)). Alternatively, also H<sub>2</sub>S can dissociate leading to two –SH groups on such an ion pair (reverse reaction (4)). The –SH groups act not only as hydrogen supply for hydrogenation or hydrogenolysis, but also as adsorption sites [17].

The direct observation of –SH groups with IR-spectroscopy has been already reported [44]. However, the interpretation of the spectra of sulfide catalysts in the pertinent region is still under debate due to the large width of the bands. Therefore, the –SH groups have been probed using basic compounds that adsorb on Brønsted acid sites [45,46]. In this work, we applied the protocol reported by Petit et al. [46] to verify the effect of H<sub>2</sub>S and Ni on the formation of –SH groups. The appearance of protonated DMP demonstrates the existence of Brønsted acid sites identified as –SH groups. Evidence of this assignment is that the concentration of the sites is increased after adsorption of H<sub>2</sub>S. The presence of Ni increases the concentration of protonated DMP species, likely due to increasing concentration of H<sub>2</sub>S being dissociatively adsorbed as –SH groups.

We also rely in the present study on TPD and TPR results to further characterize the labile –SH groups. TPD indicates that the sulfided catalysts release molecularly adsorbed  $H_2S$  and also  $H_2S$  from the recombination of –SH groups and hydrogen. The differences between the TPD profiles of both catalysts are subtle, but significant. The intensity of the  $H_2S$  and  $H_2$  desorption signals below 250 °C (see Fig. 1) suggests that in the Ni-promoted catalyst  $H_2S$  desorption is preferred over the recombination of hydrogen in the –SH groups. This indicates that Ni weakens the metal–sulfur bond strength, in agreement with Refs. [22,47,48]. Further effects of Ni cannot be discussed on the basis of TPD, because the  $H_2$  and  $H_2S$  desorption peaks are very similar.

The shift in the main TPR H<sub>2</sub>S desorption peak to lower temperatures (Fig. 2) indicates weakening of the metal-sulfur bond facilitating H<sub>2</sub>S elimination in excess of H<sub>2</sub> by Ni promotion. It should be also noted that the fraction of H<sub>2</sub>S desorbing in the low temperature region is more intense for the Ni-promoted catalyst. Thus, it is reasonable to associate the presence of nickel in Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with more efficient hydrogen activation than with  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> [41]. H<sub>2</sub>S desorption at temperatures above 450 °C due to the elimination of low reactive sulfur is easier with Ni–MoS<sub>2</sub>/ $\gamma$ - $Al_2O_3$  than with  $MoS_2/\gamma$ - $Al_2O_3$ . This observation is well in line with the more facile availability of hydrogen induced by the presence of nickel. Consequently, we postulate that Ni not only weakens the metal-sulfur bond, but also increases the H<sub>2</sub> activation and mobility. As a consequence of the enhanced activation and hydrogen mobility, the electron-rich sites near the edges are expected to contain higher concentrations of hydrogen.

Fig. 14 summarizes the process described in reactions (1, 2, 4 and 5) as a conclusion of the TPD-TPR analysis. It is reasonable to assert that after sulfidation, all configurations are possible (A-E, in Fig. 14). In the H<sub>2</sub> atmosphere of the TPR experiments, the continuous H<sub>2</sub> incorporation to the surface and H<sub>2</sub>S removal would lead to the high concentrations of CUS depicted in configuration E. In contrast, in the TPD experiments, the surface has only low concentrations of hydrogen available and the elimination of sulfur is limited in consequence. Thus, configurations A, C, and E are expected after complete H<sub>2</sub> removal.

# 4.2. Kinetic analysis

Kinetic modeling considering the strong adsorption of N-containing intermediates and different kinds of adsorption sites has been developed by Satterfield et al. [39,49], Jian and Prins [37,50,51] and more recently by Massoth et al. [52,53]. We have adopted a simplified reaction network that allows analyzing all critical reaction steps of the HDN of quinoline via calculation of pseudo first-order reaction constants. For this purpose, the reaction network of Fig. 5 was reduced to that presented in Fig. 15. Several assumptions have been made in order to obtain the reaction network in Fig. 15, all of them were justified by experimental observations or preliminary data fitting. For instance, quinoline and 14THQ as well as 58THQ and DHQ reach equilibrium composition (see the Supporting information). Therefore, they were

lumped together for the purpose of kinetic modeling. The concentrations of PCHA and PCHE were also grouped in view of the very low concentrations of PCHA found in all experiments and its very fast conversion to PCHE [11]. We acknowledge that lumping PCHA and PCHE as a single pseudo-component is not the most convenient simplification for the analysis of the kinetics results because PCHA contains nitrogen and PCHE is the denitrogenated product. However, the very low concentration of PCHA makes it difficult to calculate a reliable rate constant for its denitrogenation.

The assumption of first reaction order in all steps does not contradict the well-known fact that the hydrogenated products of



Fig. 14. Scheme of H<sub>2</sub> and H<sub>2</sub>S adsorption-desorption as concluded from the analysis of the TPD-TPR experiments.



**Fig. 15.** Simplified HDN reaction network of quinoline (Q) and DHQ, where the abbreviations are defined as follows: 14THQ – 1,2,3,4-tetrahydroquinoline; PCHA – propylcyclohexylamine; 58THQ – 5,6,7,8-tetrahydroquinoline; PB – propylbenzene; DHQ – decahydroquinoline; PCHE – propylcyclohexene; OPA – o-propylaniline; PCH – propylcyclohexane.

#### Table 1

Pseudo first-order reaction rate constants of the simplified reaction network of the HDN of quinoline and DHQ (Fig. 15). The reactions were carried out on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence (x) and presence of 3.4 kPa DBT ( $\sqrt{}$ ).

Catalyst	DBT	Rate cons	Rate constants ( $\times 10^{-5}$ mol/h g <sub>cat</sub> )								
		$k_1$	$k_2$	$k_2'$	$k_3$	$k_4$	$k_5$	k <sub>6</sub>	$k_6'$	<i>k</i> <sub>7</sub>	
$MoS_2/\gamma$ - $Al_2O_3$	x	2.71	1.32	0.51	4.40	0.33	0.72	1.09	0.22	0	
	√	2.03	0.51	0.42	4.01	0.32	1.03	1.06	0.22	0	
Ni-MoS <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	x	1.61	0.40	0.42	12.0	0.33	1.60	3.27	0.64	1.48	
	√	1.40	0.62	0.51	15.0	0.64	3.33	4.96	0.94	1.03	

quinoline (e.g., 14THQ, 58THQ, DHQ) adsorb strongly on the active phase, as the bond strength and the concentration of bicyclic compounds vary within acceptable limits. The pseudo first order is further favored by the excess of hydrogen and the low concentration of monocyclic products. As the comparison of experimental with fitted data shows (see Supporting information), this assumption holds true in a wide range of quinoline and DHQ conversion. The calculation of the reaction rate constants is described in the Supporting information, whereas the values are summarized in Table 1. The conversion rate of (Q+14THQ) is higher than that of (DHQ + 58THQ), that is,  $(k_4 + k_6) > (k_5 + k'_6)$  in all cases, leading us to the conclusion that the pair Q-14THQ is intrinsically more reactive than DHQ – 58THQ. A closer look to the values of  $k_4$ ,  $k_5$ , and  $k_6$  shows that the hydrogenation step  $(k_6)$  is the fastest. Thus, the higher reactivity of (Q + 14THQ) than (DHQ + 58THQ) is mainly due to the fast hydrogenation of the former pair. The values of  $k_6$ are higher than those of  $k'_6$  by a factor of 5, which is in line with Refs. [39,51] concluding that the hydrogenation steps  $Q \rightarrow 58THQ$ and  $14THQ \rightarrow DHQ$  are much faster than the respective reverse dehydrogenation reactions.

Ni has the same positive effect on  $k_6$  and  $k'_6$ , which are accelerated by a factor of 3 in the absence of DBT and 4.5 in the presence of DBT. This suggests that Ni accelerates the hydrogenation and dehydrogenation of adsorbed reactants as it has been observed for the HDN of other model compounds [54,55]. These (de)hydrogenation steps are further enhanced by the presence of DBT on Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $k_6$  and  $k'_6$  increase 1.5 times). Interestingly, the presence of DBT in the reaction carried out on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> does not affect this (de)hydrogenation step. Therefore, we conclude that a synergetic effect exists between Ni and DBT in the step requiring hydrogen transfer between the reactant molecules and the catalyst.

Previous experiments showed that the concentration of exposed cations increases proportionally to the loading of Ni [11]. However, it is difficult to associate the increased concentration of these sites with the improvement of the (de)hydrogenation routes because of the positive effect of DBT (as the HDS of DBT has to block the CUS). The synergy of DBT and Ni observed for the (de)hydrogenation step allows also rejecting the hypothesis of creating new Ni-containing adsorption sites, because the competitive adsorption of DBT would decrease the activity instead of enhancing it [21]. In consequence, the (de)hydrogenation of adsorbed bicyclic molecules is facilitated by the presence of Ni and sulfur, but not in the form of active sites containing exposed cations, for example, Ni or Mo CUS.

The ring-opening step is faster for DHQ than for 14THQ in all experiments ( $k_5 > k_4$ ) increasing the difference up to a factor of five. This has to be related to the lower intrinsic reactivity of 14THQ than that of DHQ. The ring opening of 14THQ ( $k_4$ ) is not affected to a large extent by the Ni addition or the presence of DBT alone; however, on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and in the presence of DBT,  $k_4$  increases by a factor of 2. The ring opening in DHQ ( $k_5$ ) is also enhanced by the addition of nickel and the presence of DBT. Therefore, as it was concluded for the (de)hydrogenation steps, it seems that the sites active for the ring-opening steps do not contain CUS or Ni although they are favored by Ni and sulfur produced from DBT.

The positive effect of DBT on the (de)hydrogenation and ringopening reactions indicates that fully sulfided phases are required for the both elementary steps. The conclusion that Ni enhances the activity of the active sites without being part of such a site opens the possibility of (de)hydrogenation and ring opening occurring at the same active sites. Nevertheless, we are inclined to suggest that different kinds of active sites are involved in (de)hydrogenation and ring opening, because the quantitative impact of Ni and DBT on  $k_4$  and  $k_5$  is not the same as it is for  $k_6$  and  $k'_6$ . The nature

of the interaction between reactants and active sites is concluded to be different for both reactions. Whereas the adsorption of aromatic compounds has to occur through electron donation from the reactant to a surface site with a Lewis acid character, the ring opening requires the protonation of nitrogen in the molecule, that is, a Brønsted acid site (vide infra). Other authors agree in the existence of different active sites for (de)hydrogenation and C-N bond scission [52,56]. We will not attempt to discuss in detail the variation of  $k_1$ ,  $k_2$ , and  $k_3$ , because the adsorption and surface reaction of OPA, PB and PCHA, PCHE, and PCH are strongly influenced by the presence of quinoline, 58THQ, 14THQ, and DHQ [57]. However, it must be pointed out that in order to obtain a satisfactory fit for the variation of the OPA concentration, it was necessary to add a dehydrogenation step from PCHA to OPA in all cases and from (PCHA + PCHE) to PB for the experiments carried out on Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>. These steps were not needed for the fitting of pseudo first-order constants in the HDN of OPA in a previous work [11]. This indicates that the presence of polyaromatic molecules slows down the rate of OPA and PCHA conversion (products of ring opening) and the dehydrogenation reactions become noticeable. The dehydrogenation of PCHE to PB is observable only with Ni-containing catalysts, emphasizing the easier (de)hydrogenation in the presence of Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The values of  $k_6$  are higher than those of  $k_4$ , that is, the hydrogenation of (Q + 14THQ) is faster than the ring opening of 14THQ. On the other hand, the ring opening of DHQ is faster than the dehydrogenation of (58THQ + DHQ) and faster than the ring opening of 14THQ ( $k_5 > k'_6$ ,  $k_5 > k_4$ ). This comparison of the absolute values of the rate constants suggests that the ring opening of 14THQ is one of the slowest steps to complete the nitrogen removal. The hydrogenation of OPA ( $k_2$ ) seems to be also rather slow, probably due to the inhibiting effect of bicyclic compounds [39,49]. Therefore, both steps ring opening of 14THQ and hydrogenation of OPA may determine the overall rate of nitrogen removal in the sequence 14THQ  $\rightarrow$  OPA  $\rightarrow$  PCHA  $\rightarrow$  PCHE. The nitrogen removal seems to be faster through the sequence DHQ  $\rightarrow$  PCHA  $\rightarrow$  PCHE where the determining step is the ring opening of DHQ ( $k_5$ ).

# 4.3. The active sites and mechanism for the ring opening via $C(sp^3)-N$ bond cleavage

It is widely accepted that the active sites for the removal of heteroatoms are coordinatively unsaturated metal cations [23,58], for example, Mo, with an incomplete coordination at the MoS<sub>2</sub> perimeter. The promoter elements, that is, Ni or Co, replace Mo atoms at the edge of MoS<sub>2</sub> slabs leading to the Ni(Co)–Mo–S phase that exhibits much higher hydrotreating activity than the unpromoted MoS<sub>2</sub> [59]. The location of the promoters has been recently confirmed by detailed atomic scale studies [60,61]. Also scanning tunneling microscopy indicates the presence of an electron-rich region on the edge of the sulfide slabs tagged as "brim" site [62,63]. The – SH groups formed via the dissociative adsorption of H<sub>2</sub> or H<sub>2</sub>S are proposed to act as hydrogen providing sites, but adsorb the substrate only weakly. The CUS, in contrast, may act as sorption site of PCHA or OPA.

The dominant reaction mechanism for the  $C(sp^3)$ –N bond cleavage depends on the reaction conditions and the structure of the reacting molecules [64]. A S<sub>N</sub>2 substitution, with the consequent formation of thiols, has been mechanistically proven for the HDN of *n*-hexylamines at relatively low temperatures (270–320 °C) and pressures (3 MPa) as well as with high H<sub>2</sub>S partial pressure (10–100 kPa) [65–70]. In contrast, the Hofmann-type elimination has been considered as the main mechanism in the HDN of cyclohexylamine and aniline-type compounds, carried out at high temperature (350–370 °C) and pressure (3–5 MPa) and with H<sub>2</sub>S partial pressure up to 17.5 kPa [71–74]. The relatively high



**Fig. 16.** (A) The Hofmann elimination type mechanism proposed for the  $C(sp^3)$ –N bond cleavage in the ring opening of DHQ. Illustrative presentation is given for the Brønsted acidic –SH groups, necessary for the adsorption and protonation, and basic S<sup>2–</sup> groups, necessary for the  $\beta$ -H elimination. (B) Generation of the CUS via surface reduction with H<sub>2</sub> and formation of sulfur ions at the edges of the sulfide slabs by DBT conversion.

reaction temperature and pressure (370 °C, 5 MPa) and the low DBT concentrations at which the HDN was carried out in this study as well as the notable absence of thiols allow us to conclude that the ring opening in 14THQ and DHQ follows the Hofmann-type elimination [75].

The Hofmann-type elimination mechanism requires that the leaving nitrogen is quaternized before the  $C(sp^3)$ -N bond is cleaved by the removal of a  $\beta$ -H atom. Thus, a site with an acidic and a basic functionality is required. While the edge of the MoS<sub>2</sub> slabs offers such sites in principal, we use the impact of Ni on the ring-opening reactions in presence and absence of DBT to identify the acid and base sites participating in the Hofmann-type elimination.

The kinetic analysis allowed us concluding that the sites active for the ring-opening step do not contain exposed cations in agreement with early proposals of Satterfield et al. [33,40]. The increase in the ring-opening rate by adding sulfur implies that the active sites are created by the presence of DBT or H<sub>2</sub>S. The much higher rate of  $C(sp^3)$ –N bond cleavage on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the presence of DBT ( $k_4$  and  $k_5$  increase by a factor of 2 and 3.3, respectively) is concluded to be related to the much more efficient sulfur removal on the former catalyst. Thus, we propose that the direct desulfurization of DBT stabilizes the MoS<sub>2</sub> edge by converting the inactive CUS into labile S<sup>2–</sup> ions able to form also SH<sup>–</sup> groups with the sufficient acidity to allow protonation of DHQ and 14THQ by reacting with hydrogen [76]. Thus, Ni induces three positive effects, that is, it increases the concentration of labile sulfur, adjusts its acid-base properties by increasing the sulfur electron density (and, hence, the basicity of the  $S^{2-}$  ions), and facilitates the dissociation of  $H_2$  increasing so the concentration of -SH groups. The overall mechanism for the Hofmann-type C-N bond cleavage is shown in Fig. 16. The fully sulfided edge of the slabs reacts with hydrogen to form -SH groups or CUS. The proton of the -SH group can adsorb DHQ via protonation of the nitrogen atom. Then, the  $\beta$ -hydrogen abstraction by the  $S^{2-}$  ion starts the concerted E2 mechanism leading to the  $C(sp^3)$ -N bond cleavage and the desorption of a molecule with a primary amine group. DBT enhances in this model the concentration of labile  $S^{2-}$  ions.

We attribute the lower rate of ring opening in 14THQ than in DHQ to the presence of the aromatic ring. The interaction of the free electron pair of the nitrogen in 14THQ with the benzoic ring increases the stability of the molecule. Alternatively, the recent work of Temel et al. [77], showing the adsorption of pyridine on the "brim" sites suggests that the delocalized  $\pi$ -character of 14THQ would result in a much stronger adsorption on brim sites and a concomitant low reactivity.

# 4.4. On the active sites for (de)hydrogenation steps

It has been observed that the hydrogenation and dehydrogenation of PCHE was promoted by Ni, as it increases the PCHE conversion by increasing both  $k_3$  and  $k_7$  (Table 1). The hydrogenation and dehydrogenation of the lumped bicyclic compounds ( $k_6$ ,  $k_6'$ ) is also accelerated by the addition of Ni. The values of  $k_3$ ,  $k_6$ , and  $k_6'$  increase by a factor of 3, while  $k_7$  becomes significant with the Ni promotion. DBT, on the other hand, does not affect the rate of these steps on the unpromoted  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, while on Ni-MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the presence of DBT increases further  $k_6$ ,  $k'_6$ , and  $k_3$ . Due to this synergistic effect of DBT and Ni, it is inferred that the sites active for those (de)hydrogenation steps do not contain exposed metal cation (expected to be blocked by sulfur). Therefore, it is likely that such sites are the sites with a metal-like edge state, "brim" sites, at the rim of the MoS<sub>2</sub> clusters [78]. While the sites do not exhibit vacancies, they may play a key role in hydrogenation and C-heteroatom bond cleavage reactions [76]. The beneficial effect of Ni is associated with the more facile dissociative adsorption of hydrogen leading to a higher concentration of -SH groups. Furthermore. Ni would increase the electron density at the brim sites, leading to an enhanced mobility of surface hydrogen, increasing so the rate of (de)hydrogenation. The presence of sulfur-containing molecules, acting as electron pair donors, increases the electron density and the concentration of labile  $S^{2-}/SH^{-}$ . This conclusion agrees well with the previous study of OPA HDN, suggesting that the electron-rich zone participates in the sorption of the substrates during hydrogenation [11].

#### 4.5. On the effect of S-containing compounds

The effect of sulfur-containing compounds in the HDN activity of MoS<sub>2</sub>-based catalysts has been extensively studied because HDN occurs in parallel to hydrodesulfurization for real feedstocks. The majority of the studies have used H<sub>2</sub>S, CS<sub>2</sub>, or DMDS (the latter two expected to decompose readily to H<sub>2</sub>S) [38]. The common observation is that H<sub>2</sub>S increases the rate of C–S cleavage decreasing the hydrogenation rate. However, the effect of sulfur may be complex and depend on many parameters [54]. For instance, few studies using DBT as sulfur source have reported that the selectivity to hydrogenation is enhanced [79]. In a previous study, it was found that the presence of DBT strongly increases the rate of hydrogenation of OPA on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [11].

In the present study, DBT was selected as the main sulfur source and it was observed that both the C-N bond cleavage in the ring-opening step and hydrogenation are accelerated only in the presence of Ni. DBT inhibits the denitrogenation of OPA on MoS<sub>2</sub>/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The HDN of quinoline performed with the presence of DMDS in the feed shows that H<sub>2</sub>S (ex-DMDS) has similar effects with significant differences. That is, H<sub>2</sub>S has stronger inhibition effect on the denitrogenation of OPA (on  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and weaker beneficial effect on the ring opening of DHQ (on Ni–MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) than DBT. The inhibiting effect is easily ascribed to the competitive adsorption of the sulfur compound of the Mo-associated CUS that are postulated as the active centers for the denitrogenation of OPA. In this context, DBT (and the products of HDS) may adsorb on several kinds of adsorption sites via donation from the sulfur of the aromatic ring. In contrast, H<sub>2</sub>S adsorbs preferentially on CUS. Furthermore, when DBT is introduced in the reactor, the concentration of H<sub>2</sub>S is significant only at relevant DBT conversions. The net result is a more effective blocking of CUS when DMDS is added to the feed (leading high concentrations of H<sub>2</sub>S) than in the presence of DBT. At present, we attribute the better enhancing effect of DBT than H<sub>2</sub>S on the rate of ring opening of DHQ on Ni- $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> to the aromatic character of DBT and the HDS products. The electron donor properties of these aromatic compounds would increase the electron density of the brim sites and the basicity of sulfur ions. This argument was already used to rationalize the enhancing effect of DBT in the hydrogenation of OPA [11].

# 5. Conclusions

The study of guinoline and decahydroguinoline HDN allows establishing the ring-opening reactions as one of the crucial steps in the overall HDN mechanism. The two main routes examined, that is, DHQ  $\rightarrow$  PCHA  $\rightarrow$  PCHE  $\rightarrow$  PCH and Q  $\rightarrow$  14THQ  $\rightarrow$  OPA  $\rightarrow$  P-CHA and PB, exhibited different rate-limiting steps. In the first route, the rate-limiting step is the ring opening in DHQ via  $C(sp^3)$ -N bond cleavage, while in the latter route, the rate-limiting step is the ring opening of 14THQ and the hydrogenation of OPA (being the intrinsic rate lower for 14THQ than for DHQ). The ring-opening step occurs via a Hofmann-type mechanism on a dual functional site, which comprises of -SH groups with mildly acidic character on the edges of the sulfide slabs (formed with  $S^{2-}$  by reacting with hydrogen) and the corresponding basic  $S^{2-}$  ions. DHQ and 14THQ adsorption involves the interaction of the -NHfragment with -SH groups. It is suggested that DBT stabilizes the sulfide surface converting the CUS (inactive for the ring opening) into labile  $S^{2-}$  ions active for the formation of the –SH groups. H<sub>2</sub>S as sulfur compound has stronger inhibiting and weaker promoter effect on the denitrogenation of OPA and ring opening of DHQ, respectively, than DBT. The TPR, TPD, and IR characterization allow us inferring that nickel as a promoter facilitates H<sub>2</sub> dissociation, increases the concentration of labile S<sup>2-</sup> ions, and provides more of the active -SH groups. Nickel also increases the electron density of sulfide anions, increasing so the basicity of the S<sup>2-</sup> ions facilitating the  $\beta$ -H removal.

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# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.08.003.

#### References

- C. Brannigan, E. Glenn, F. Twisse, A. Griffin, N. Hill, EU Fuel Quality Monitoring – 2007 Summary Report, 2009.
- [2] T.C. Ho, Catal. Rev. Sci. Eng. 30 (1988) 117.
- [3] S.H. Yang, C.N. Satterfield, J. Catal. 81 (1983) 168.
- [4] H.A. Rangwala, I.G. Dalla Lana, F.D. Otto, H. Yeniova, K. Al-Nuaimi, Energ. Fuel 4 (1990) 599.
- [5] S. Eijsbouts, C. Sudhakar, V.H.J. de Beer, R. Prins, J. Catal. 127 (1991) 605.
- [6] S. Eijsbouts, V.H.J. de Beer, R. Prins, J. Catal. 127 (1991) 619.
- [7] R. Prins, M. Jian, M. Flechsenhar, Polyhedron 16 (1997) 3235.
- [8] R.Z. Lee, M. Zhang, F.T.T. Ng, Top. Catal. 37 (2006) 121.
- [9] J. Ancheyta, J.G. Speight, Hydroprocessing of Heavy Oils and Residua, Taylor & Francis, 2007.
- [10] J.F. Cocchetto, C.N. Satterfield, Ind. Eng. Chem. Process Des. Dev. 20 (1981) 49.
- [11] A. Hrabar, J. Hein, O.Y. Gutiérrez, J.A. Lercher, J. Catal. 281 (2011) 325.
- [12] I.E. Wachs, Catal. Today 27 (1996) 437.
- [13] N.Y. Topsøe, A. Tuxen, B. Hinnemann, J.V. Lauritsen, K.G. Knudsen, F. Besenbacher, Henrik Topsøe, J. Catal. 279 (2011) 337.
- [14] M.J. van Gestel, C. Dujardin, F. Maugé, J. Catal. 202 (2001) 78.
- [15] J. Polz, H. Zeilinger, B. Müller, J. Catal. 120 (1989) 22.
- [16] G.B. McGarvey, S. Kasztelan, J. Catal. 148 (1994) 149.
- [17] M. Breysse, E. Furimsky, S. Kasztelan, M. Lacroix, G. Pérot, Catal. Rev. 44 (2002) 651.
- [18] L.P. Nielsen, S.V. Christensen, H. Topsøe, B.S. Clausen, Catal. Lett. 67 (2000) 81.
- [19] C. Thomas, L. Vivier, J.L. Lemberton, S. Kasztelan, G. Pérot, J. Catal. 167 (1997) 1.
- [20] X.S. Li, Q. Xin, X.X. Guo, P. Grange, B. Delmon, J. Catal. 137 (1992) 385.
- [21] F. Besenbacher, M. Brorson, B.S. Clausen, S. Helveg, B. Hinnemann, J. Kibsgaard,
- J.V. Lauritsen, P.G. Moses, J.K. Nørskov, H. Topsøe, Catal. Today 130 (2008) 86.
   L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, Sulphur bonding in transition metal sulphides and MoS2 based structures, in: T. Weber, R. Prins, R.A. van

Santen (Eds.), Transition Metal Sulphides – Chemistry and Catalysis, Kluwer Academic Publishers.

- [23] M. Sun, J. Adjaye, A.E. Nelson, Appl. Catal. A 263 (2004) 131.
- [24] S. Kasztelan, H. Toulhoat, J. Grimblot, J.P. Bonnelle, Appl. Catal. 13 (1984) 127.
   [25] P. Afanasiev, H. Jobic, C. Lorentz, P. Leverd, N. Mastubayashi, L. Piccolo, M. Vrinat, J. Phys. Chem. C 113 (2009) 4139.
- [26] P. Afanasiev, J. Catal. 269 (2010) 269.
- [27] N. Dinter, M. Rusanen, P. Raybaud, S. Kasztelan, P. da Silva, H. Toulhoat, J. Catal. 267 (2009) 67.
- [28] F. Labruyere, M. Lacroix, D. Schweich, M. Breysse, J. Catal. 167 (1997) 464.
- [29] C. Lahousse, A. Aboulayt, F. Maugé, J. Bachelier, J.C. Lavalley, J. Mol. Catal. 84 (1993) 283.
- [30] L. Oliviero, A. Vimont, J.C. Lavalley, F. Romero, M. Gaillard, F. Maugé, Phys. Chem. Chem. Phys. 7 (2005) 1861.
- [31] S. Brunet, G. Pérot, React. Kinet. Catal. Lett. 29 (1985) 15.
- [32] L. Vivier, V. Dominguez, G. Pérot, J. Mol. Catal. 67 (1991) 267.
- [33] S.H. Yang, C. Satterfield, J. Catal. 81 (1983) 168.
- [34] C.N. Satterfield, M. Modell, J.F. Mayer, AIChE J. 21 (1975) 1100.
- [35] A. Bunch, L. Zhang, G. Karakas, U.S. Ozkan, Appl. Catal. A 190 (2000) 51.
- [36] M. Jian, R. Prins, Catal. Lett. 50 (1998) 9.
- [37] M. Jian, R. Prins, Ind. Eng. Chem. Res. 37 (1998) 834.
- [38] G. Pérot, Catal. Today 10 (1991) 447.
- [39] C.N. Satterfield, S.H. Yang, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 11.
- [40] S.H. Yang, C.N. Satterfield, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 20.
- [41] A.B. Anderson, Z.Y. Al-Saigh, W.K. Hall, J. Phys. Chem. 92 (1988) 803.
- [42] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, J. Catal. 190 (2000) 128.
- [43] M. Sun, A.E. Nelson, J. Adjaye, Catal. Today 105 (2005) 36.
- [44] N.Y. Topsøe, H. Topsøe, J. Catal. 139 (1993) 641.
- [45] A. Travert, F. Maugé, Stud. Surf. Sci. Catal. 127 (1999) 269.
- [46] C. Petit, F. Maugé, J.C. Lavalley, Stud. Surf. Sci. Catal. 106 (1997) 157.
- [47] L.S. Byskov, B. Hammer, J.K. Nørskov, B.S. Clausen, H. Topsøe, Catal. Lett. 47 (1997) 177.
- [48] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, J. Catal. 187 (1999) 109.
- [49] C.N. Satterfield, J.F. Cocchetto, Ind. Eng. Chem. Process Des. Dev. 20 (1981) 53.
- [50] M. Jian, R. Prins, Stud. Surf. Sci. Catal. 101 (1996) 87.
- [51] M. Jian, R. Prins, Stud. Surf. Sci. Catal. 113 (1998) 111.
- [52] F.E. Massoth, S.C. Kim, Ind. Eng. Chem. Res. 42 (2003) 1011.

- [53] S.C. Kim, J. Simons, F.E. Massoth, J. Catal. 212 (2002) 201.
- [54] X.L. Zhang, U.S. Ozkan, Stud. Surf. Sci. Catal. 106 (1997) 69.
   [55] L. Zhang, U.S. Ozkan, Stud. Surf. Sci. Catal. 101 (1996) 1223.
- 55] L. Zhang, U.S. OZKan, Stud. Sun. Sci. Catal. 101 (
- [56] M. Jian, R. Prins, J. Catal. 179 (1998) 18.
- [57] N. Gnofam, L. Viviver, S. Brunet, J.L. Lemberton, G. Pérot, Catal. Lett. 2 (1989) 81.
- [58] C. Moreau, J. Joffre, C. Saenz, P. Geneste, J. Catal. 122 (1990) 448.
- [59] N.-Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 386.
- [60] J.V. Lauritsen, J. Kibsgaard, G.H. Olesen, P.G. Moses, B. Hinnemann, S. Helveg, J.K. Nørskov, B.S. Clausen, H. Topsøe, E. Lægsgaard, F. Besenbacher, J. Catal. 249 (2007) 220.
- [61] F.L. Deepak, R. Esparza, B. Borges, X. Lopez, M.J. Yacaman, ACS Catal. 1 (2011) 537.
- [62] H. Topsøe, Appl. Catal. A 322 (2007) 8.
- [63] J. Kibsgaard, A. Tuxen, K.G. Knudsen, M. Brorson, H. Topsøe, E. Laegsgaard, J.V. Lauritsen, F. Besenbacher, J. Catal. 272 (2010) 195.
- [64] M. Cattenot, J.L. Portefaix, J. Afonso, M. Breysse, M. Lacroix, G. Pérot, J. Catal. 173 (1998) 366.
- [65] F. Rota, R. Prins, Top. Catal. 11 (12) (2000) 327.
- [66] L. Qu, R. Prins, Appl. Catal. A 250 (2003) 105.
- [67] Y. Zhao, P. Kukula, R. Prins, J. Catal. 221 (2004) 441.
- [68] Y. Zhao, R. Prins, J. Catal. 229 (2005) 213.
- [69] R. Prins, Y. Zhao, N. Sivasankar, P. Kukula, J. Catal. 234 (2005) 509.
- [70] R. Prins, M. Egorova, A. Röthlisberger, Y. Zhao, N. Sivasankar, P. Kukula, Catal. Today 111 (2006) 84.
- [71] M. Sun, R. Prins, J. Catal. 201 (2001) 138.
- [72] L. Qu, R. Prins, J. Catal. 210 (2002) 183.
- [73] P. Clark, X. Wang, P. Deck, S.T. Oyama, J. Catal. 210 (2002) 116.
- [74] L. Qu, M. Flechsenhar, R. Prins, J. Catal. 217 (2003) 284.
- [75] J.L. Portefaix, M. Cattenot, M. Guerriche, M. Breysse, Catal. Lett. 9 (1991) 127.
   [76] J.V. Lauritsen, M. Nyberg, J.K. Nørskov, B.S. Clausen, H. Topsøe, E. Laegsgaard, F.
- Besenbacher, J. Catal. 224 (2004) 94. [77] B. Temel, A.K. Tuxen, J. Kibsgaard, N. Topsøe, B. Hinnemann, K.G. Knudsen, H.
- Topsøe, J.V. Lauritsen, F. Besenbacher, J. Catal. 271 (2010) 280.
- [78] J.V. Lauritsen, M.V. Bollinger, E. Lægsgaard, K.W. Jacobsen, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 221 (2004) 510.
- [79] M.S. Rana, R. Navarro, J. Leglise, Catal. Today 98 (2004) 67.