# A Mechanistic Study of Thiophene Hydrodesulfurization by the Parahydrogen-Induced Polarization Technique

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Thiophenic compounds are the least reactive organosulfur compounds in fossil fuels, and thiophene is widely used as a model substrate in studies of industrially important hydrodesulfurization (HDS) processes. It is generally presumed that the HDS process can proceed by two possible pathways, namely hydrogenation or direct desulfurization. In this work, the parahydrogen-induced polarization technique was successfully utilized in a mechanistic study of a hydrodesulfurization reaction

#### Introduction

Sulfur-containing impurities in crude petroleum and its refined products (gasoline, diesel oil) are undesirable because they are able to poison catalysts used in fuel processing and to cause corrosion of apparatus. In addition, sulfur oxides in exhaust gases from sulfur-containing fuels are a major reason for environmental pollution and acid rains. So, in view of stricter legislation regarding the sulfur content of transportation fuels, hydrodesulfurization (HDS) is one of the most important catalytic processes for the removal of sulfur-containing impurities from petroleum fractions.<sup>[1-5]</sup> In a HDS process, C-S bonds undergo hydrogenolysis, which leads to the formation of hydrocarbons and H<sub>2</sub>S. The industrial catalysts, consisting of Co(Ni)-promoted  $MoS_2$  supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, have been developed and optimized for several decades.<sup>[1,2,4,6]</sup> Direct and indirect insights into the structure and activity of these catalysts were gained by experimental<sup>[7-11]</sup> and theoretical<sup>[12,13]</sup> studies. The main sulfur-containing compound in fluidized catalytic cracking gasoline is thiophene, which is also a most suitable model molecule for studying the HDS reaction as a result of its relatively simple structure.<sup>[14]</sup> However, despite the significant number of thiophene HDS investigations, the mechanism of this reaction is still debated.<sup>[15-17]</sup> For instance, both the hydrogenation (HYD) pathway and the direct desulfurization (DDS) pathway,

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by example of a heterogeneous hydrodesulfurization of thiophene over supported catalysts in the presence of parahydrogen. It was demonstrated that the HDS of thiophene on a  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst proceeds preferentially by the hydrogenation pathway to form tetrahydrothiophene, followed by desulfurization. In contrast, if a Pt/TiO<sub>2</sub> catalyst was used, direct desulfurization to 1,3-butadiene and the hydrogenation pathway both contributed to the overall reaction mechanism.



Scheme 1. Possible pathways of thiophene hydrodesulfurization.

as illustrated in Scheme 1, have been proposed for thiophene HDS.<sup>[18]</sup> In the DDS route, the C–S bonds of thiophene are directly broken by hydrogenolysis, with the formation of unsaturated C<sub>4</sub> hydrocarbons,<sup>[19]</sup> whereas in the HYD route, hydrogenation of one or both C=C bonds occurs before the C–S bond scission.<sup>[17]</sup>

The thiophene hydrodesulfurization process involves hydrogen addition, so it is very promising to study the mechanism of this reaction by the parahydrogen-induced polarization (PHIP) technique.<sup>[20,21]</sup> PHIP is based on the pairwise addition of a parahydrogen (p-H<sub>2</sub>) molecule to an unsaturated bond of a substrate molecule followed by <sup>1</sup>H NMR detection of the reaction products. Pairwise addition means that the reaction product molecule incorporates two atoms from one and the same H<sub>2</sub> molecule. If the reaction meets the requirement of pairwise hydrogen addition, the NMR signals of the reaction intermediates and product molecules become significantly enhanced.<sup>[22]</sup> This enhancement of the NMR signals, along with the characteristic antiphase shape of the polarized NMR patterns, makes the PHIP technique a unique tool for mechanistic studies of catalytic reactions and for the indirect identification of reaction pathways.<sup>[23]</sup> The applications of PHIP for mechanis-



tic investigations of homogeneous hydrogenations catalyzed by transition-metal complexes are well established.<sup>[24]</sup> In contrast, for heterogeneous hydrogenations, the observation of PHIP effects was considered impossible for a long time because the accepted Horiuti-Polanyi mechanism for hydrogenation over supported metal catalysts involves dissociative hydrogen adsorption.<sup>[25]</sup> The latter should lead to the loss of spin correlation between the parahydrogen-derived H atoms and, therefore, to an absence of any PHIP effects. However, it was found that, in reality, some fraction of  $H_2$  (about 1–3%) can be added to unsaturated substrates in a pairwise manner, which leads to PHIP effects in the NMR spectra if p-H<sub>2</sub> is used in heterogeneous hydrogenations over supported metals. Recently, the range of catalytic systems suitable for heterogeneous PHIP studies was broadened with the demonstration that ligandcapped metal nanoparticles,<sup>[26]</sup> bulk metals and metal oxides,<sup>[27]</sup> metal-containing zeolites,<sup>[28]</sup> and supported ionicliquid-phase catalysts<sup>[29, 30]</sup> can also produce PHIP effects. Moreover, the PHIP technique was utilized for mechanistic studies of heterogeneous hydrogenation of hydrocarbons such as propene, propyne, 1,3-butadiene, and 1-butyne over supported metal catalysts.<sup>[31]</sup> Recently, the mechanism of heterogeneous hydrogenation of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds was addressed by the PHIP technique.<sup>[32]</sup> The important features of these reaction mechanisms were revealed with the help of <sup>1</sup>H NMR signal enhancement and the characteristic shape of NMR lines.

Herein, the PHIP technique was applied for mechanistic studies of thiophene hydrodesulfurization. The unique capabilities of this method allowed us to establish that thiophene HDS over  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> proceeds mainly by the HYD route, whereas the contribution of the alternative DDS route was found to be more pronounced on Pt/TiO<sub>2</sub>.

#### **Results and Discussion**

As mentioned above, the typical catalyst for thiophene hydrodesulfurization is MoS<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>[1,2,4,6]</sup> To date, there are no reports about the utilization of sulfide catalysts in heterogeneous catalytic processes involving parahydrogen. Therefore, it is not known if the spin correlation between the two hydrogen atoms can be preserved upon hydrogenation on this type of catalyst. With this taken into consideration, commercially available MoS<sub>2</sub> (Sigma–Aldrich) catalyst was used for the hydrogenation of propene gas, which is a standard substrate for heterogeneous PHIP studies.[33-35] Propene hydrogenation was performed at various temperatures (from T = 200to 400 °C with a 50 °C increment) with parahydrogen. PHIP effects were successfully observed for the propane <sup>1</sup>H NMR signals, which implied that H<sub>2</sub> can be added to the propene C=C bond in a pairwise manner with preservation of the parahydrogen spin order over the MoS<sub>2</sub> catalyst (Figure 1).

Notably, this is the first report of PHIP effects in a hydrogenation over a metal sulfide catalyst. The intensities of the hyperpolarized NMR signals were found to increase with an increase in the reaction temperature from 200 to 350 °C; this was accompanied by an increase in propane yield. Successful obser-





**Figure 1.** a) The reaction scheme of propene hydrogenation; b) <sup>1</sup>H NMR spectra acquired during propene hydrogenation with p-H<sub>2</sub> at various temperatures over a commercially available MoS<sub>2</sub> catalyst. All spectra were acquired while the gas was flowing (17 mLs<sup>-1</sup>) with eight signal accumulations and are presented on the same vertical scale.

vation of PHIP effects during heterogeneous hydrogenation of propene over the  $MoS_2$  catalyst gave us an opportunity to use the PHIP technique for the investigation of reactions catalyzed by metal sulfide catalysts.

Next, the supported  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was utilized for thiophene hydrodesulfurization with parahydrogen. Several reaction products were observed including 1-butene, 2-butene, and butane (Figure 2). However, all attempts to observe PHIP effects (polarization) in this reaction by varying the reaction temperature (200–600 °C) and the gas flow rate (0.1–14 mL s<sup>-1</sup>) were unsuccessful. There are two possible explanations for this observation. First, nuclear spin relaxation processes that, without doubt, become operative after the pairwise hydrogen addition, can completely destroy the polarization of the initially polarized products, which would result only in thermally polar-



**Figure 2.** a) The reaction scheme of thiophene hydrodesulfurization; b) <sup>1</sup>H NMR spectrum acquired during thiophene hydrodesulfurization with p-H<sub>2</sub> at T = 600 °C over the MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The spectrum was acquired while the gas was flowing (1.4 mLs<sup>-1</sup>) with 16 signal accumulations.



ized signals that are detected by NMR spectroscopy. Second, whereas the general feasibility to observe PHIP over metal sulfide catalysts was successfully shown above (Figure 1), the hydrogenation of thiophene can occur through a reaction pathway that does not involve pairwise hydrogen addition.

As mentioned in the Introduction, there are two possible pathways of thiophene hydrodesulfurization (Scheme 1). The hydrogenation (HYD) pathway involves thiophene hydrogenation to dihydrothiophenes and tetrahydrothiophene with subsequent hydrodesulfurization to butenes and butane, respectively.<sup>[17,18]</sup> The second pathway, the direct desulfurization (DDS), begins with thiophene hydrodesulfurization to 1,3-butadiene, which is further hydrogenated to butenes and butane. To establish which pathway is involved with our catalytic system, 1,3-butadiene was hydrogenated with p-H<sub>2</sub> over the MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The acquired <sup>1</sup>H NMR spectra clearly show characteristic PHIP patterns for the various reaction products (1-butene, 2-butene, and butane; Figure 3).



**Figure 3.** a) The reaction scheme of 1,3-butadiene hydrogenation; b) and c) <sup>1</sup>H NMR spectra acquired during 1,3-butadiene hydrogenation with p-H<sub>2</sub> at T = 500 °C over the MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (b) while the gas was flowing (4.0 mLs<sup>-1</sup>) and (c) after termination of the gas flow. Both spectra were acquired with 16 signal accumulations and are presented on the same vertical scale.

These results confirm that PHIP effects should be observed for the butenes and butane if thiophene hydrodesulfurization proceeds via the 1,3-butadiene intermediate (DDS pathway). Therefore, we may conclude that 1,3-butadiene is not formed during thiophene hydrodesulfurization over the MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Based on these observations, it can be supposed that the alternative (HYD) pathway is preferentially realized. This is in agreement with the results obtained by Hensen et al. for thiophene hydrodesulfurization over several transition-metal sulfides.<sup>[17]</sup> The absence of PHIP effects in thiophene hydrodesulfurization over MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can then be explained as follows. The first step in the HYD pathway is 1,4-addition of H<sub>2</sub> to thiophene, which leads to 2,5-dihydrothiophene. The next step can be hydrodesulfurization of 2,5-dihydrothiophene to form 2-butene, which can be subsequently further hydrogenated to butane or can isomerize to 1-butene. Alternatively, butane can be formed as a result of 2,5-dihydrothiophene hydrogenation to tetrahydrothiophene and subsequent hydrodesulfurization. For any of these mechanisms, the parahydrogen-derived protons are chemically equivalent in the respective product molecules (2,5-dihydrothiophene, 2-butene, butane). Therefore, the PHIP effects for these compounds should be largely suppressed because of the symmetry of these molecules and chemical equivalence of the p-H<sub>2</sub> nascent protons.<sup>[36,37]</sup>

It is known that supported metal catalysts also catalyze thiophene hydrodesulfurization.<sup>[18]</sup> Previously, it was shown that they can provide PHIP effects in the hydrogenation of such hydrocarbons as propene, propyne, 1,3-butadiene, and 1-butyne.<sup>[31]</sup> Therefore, we examined several supported metal catalysts in thiophene hydrodesulfurization. The Rh/TiO<sub>2</sub> catalyst was found to be completely inactive in the reaction even at temperatures as high as 500 °C. The Pd/TiO<sub>2</sub> catalyst produced some amounts of 2-butene, but no PHIP effects were observed. However, the Pt/TiO<sub>2</sub> catalyst was found to produce polarized lines for all hydrodesulfurization products, namely 1-butene, 2-butene, and especially butane (Figure 4).

This result clearly indicates that the absence of PHIP effects in thiophene hydrodesulfurization over the  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is a result of the peculiarities of the reaction mechanism and not, for instance, because of the relaxation of hyperpolarization during the transfer of reaction products from the reactor to the NMR instrument.<sup>[38]</sup> Thus, in thiophene hydrodesulfurization on Pt/TiO<sub>2</sub>, both possible reaction pathways can be realized, which is in accordance with results of Wang and Iglesia,



**Figure 4.** a) The reaction scheme of thiophene hydrodesulfurization; b) and c) <sup>1</sup>H NMR spectra acquired during thiophene hydrodesulfurization with p-H<sub>2</sub> at T = 500 °C over the Pt/TiO<sub>2</sub> catalyst (c) while the gas was flowing (14 mLs<sup>-1</sup>) and (b) after termination of the gas flow. Both spectra were acquired with 64 signal accumulations and are presented on the same vertical scale.



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who found that thiophene hydrodesulfurization over Pt/SiO<sub>2</sub> proceeds by both pathways with comparable turnover rates.<sup>[18]</sup>

## Conclusion

In this work thiophene hydrodesulfurization was studied by means of the parahydrogen-induced polarization (PHIP) technique. In the case of thiophene hydrodesulfurization over the MoS<sub>2</sub>/y-Al<sub>2</sub>O<sub>3</sub> catalyst, no PHIP effects were observed despite the formation of 1-butene, 2-butene, and butane as reaction products. However, if this catalyst was utilized for 1,3-butadiene hydrogenation, PHIP effects were observed for all reaction products. These results unambiguously show that 1,3-butadiene is not formed during thiophene hydrodesulfurization over  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Therefore, the main reaction pathway in this case should be hydrogenation to dihydro- and tetrahydrothiophenes and their subsequent hydrodesulfurization. On the other hand, in thiophene hydrodesulfurization over the Pt/TiO<sub>2</sub> catalyst, PHIP effects were observed for all reaction products, that is, 1-butene, 2-butene, and butane. This fact suggests that the hydrodesulfurization reaction on Pt/TiO<sub>2</sub> proceeds by both possible pathways (hydrogenation and direct desulfurization) with comparable rates. The obtained results demonstrate the unique capabilities of the PHIP method for mechanistic studies of heterogeneous catalytic hydrodesulfurization reactions.

## **Experimental Section**

The MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation of cylindrical Al<sub>2</sub>O<sub>3</sub> granules (1.5 mm in diameter, BET surface area of 208  $m^2g^{-1}$ , pore volume of 0.68  $cm^3g^{-1}$ , average pore diameter of 13.1 nm; JSC "Promkataliz", Ryazan, Russia) with an aqueous solution containing the required amounts of  $MoO_3$  (grade  $\geq$  99.0%; Vekton, Saint-Petersburg, Russia) and citric acid (grade  $\geq$  99.8%; Vekton, Saint-Petersburg, Russia). The concentration of molybdenum in the solution was 2.8 mol L<sup>-1</sup>; the citric acid/Mo molar ratio was adjusted to 0.7. The granules were dried at T = 110 °C for 4 h and then crushed and sieved to provide 0.14-0.25 mm particles. According to the inductively coupled plasma atomic emission spectroscopy (ICP-AES) data, the Mo/Al<sub>2</sub>O<sub>3</sub> material contained 12.1 wt% of Mo as determined after sample calcination. However, to produce the final catalysts with a highly dispersed MoS<sub>2</sub> phase on the alumina surface, the calcination step of the  $Mo/Al_2O_3$  samples was avoided.  $^{\scriptscriptstyle [39]}$  The catalyst was activated by the standard presulfidation procedure in the gas phase at T = 400 °C with a mixture of gases containing  $H_2S$  (5 vol%) and  $H_2$  (95 vol%).

The elemental analysis of the catalysts was performed with ICP-AES on an Optima 4300 DV instrument (Perkin–Elmer, France); before analysis, the sample was calcined at T=500 °C for 4 h. The sample in the sulfided state was studied with high-resolution transmission electron microscopy (HRTEM) with a JEM-2010 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and resolution of 0.14 nm. The catalyst samples were applied to copper gauze by dispersing an alcoholic suspension of the sample with an ultrasonic disperser. To obtain statistical information, the structural parameters of about 500 particles were measured.

A TEM micrograph depicting the typical surface fragments of the sulfided  $Mo/\gamma\text{-}Al_2O_3$  catalyst is shown in Figure 5. The black thread-



Figure 5. TEM image of the sulfided  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

like fringes visualized by TEM correspond to the layered structure of  $MoS_2$  nanoparticles with different stack heights and lengths evenly distributed on the surface of  $Al_2O_3$ . The average slab length of the sulfide nanoparticles is about 4.5 nm; the mean number of layers is 1.9.

Commercially available hydrogen, thiophene (Sigma–Aldrich,  $\geq$  99%), 1,3-butadiene, and propene were used in the catalytic experiments as received. For PHIP experiments, H<sub>2</sub> gas was enriched with parahydrogen up to 50% by passing it through a spiral tube containing FeO(OH) powder (Sigma–Aldrich) maintained at liquid nitrogen temperature.

For 1,3-butadiene hydrogenation, a substrate/p-H<sub>2</sub> (1:4) mixture was supplied to a 1/4" outside diameter (OD) straight stainless steel tube heated with an electric tube furnace. The  $MoS_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (30 mg) was packed between two pieces of fiberglass tissue in the middle of this steel reactor. The resulting gas mixture was supplied through a 1/16" OD polytetrafluoroethylene capillary to a 10 mm NMR tube located in the NMR spectrometer. For propene hydrogenation, the procedure was generally the same except that a 1:3 substrate/p-H<sub>2</sub> mixture and commercially available MoS<sub>2</sub> catalyst (100 mg; Sigma–Aldrich, 99%) were used. In this case, the catalyst was activated in 18% H<sub>2</sub>/He flow at T=300°C for 4 h and then evacuated at T=500°C for 4 h.

For thiophene hydrogenation, the substrate/p-H<sub>2</sub> mixture ( $\approx$ 1:7.6, according to vapor pressure data) was obtained by bubbling parahydrogen through a two-necked flask containing liquid thiophene. The resulting gas mixture was supplied to the same stainless steel reactor containing either the MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (150 mg) or Pt/TiO<sub>2</sub> (100 mg) catalyst. (In preliminary experiments with supported metal catalysts, Rh/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, or Pt/TiO<sub>2</sub> (30 mg) were used.) The gas mixture was then supplied to the NMR tube located in the NMR spectrometer and maintained at *T*=100 °C to prevent condensation of the reactant and products. The MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was pretreated in the reaction mixture overnight at room temperature before the reaction.

All hydrogenation experiments were performed at atmospheric pressure, with the reaction volume located outside the NMR magnet (an ALTADENA<sup>[40]</sup> experiment). The gas flow rate was measured with an Aalborg rotameter. <sup>1</sup>H NMR spectra were acquired on a 300 MHz Bruker AV 300 NMR spectrometer with a  $\pi/2$  rf pulse in the case of 1,3-butadiene and thiophene hydrogenation and a  $\pi/6$  rf pulse in the case of propene hydrogenation.



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