

# The HDS mechanism: Which “auxiliary” process takes place – sulfur isotopic exchange or replacement – and why is it important to know it?

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## Abstract

In the light of general evaluation of the radioisotopic data obtained during the years of our research two possible ways of sulfur transfer from the catalyst into  $\text{H}_2\text{S}$  in the course of thiophene HDS have been reconsidered. These are (i) sulfur exchange between  $\text{H}_2\text{S}$  formed and the catalyst sulfur and (ii) extrusion of sulfide sulfur into the gas phase by the interaction of the catalyst SH group with  $\text{H}_2$  with the further formation of  $\text{H}_2\text{S}$ . The data of our radioisotopic studies supports the second way, which proceeds within the “forcing out” mechanism. This mechanism assumes either of the two possible schemes of  $\text{H}_2\text{S}$  formation—(a)  $\text{H}_2$  interaction with the catalyst bridge sulfur and (b)  $\text{H}_2$  interaction with the SH group. The radioisotopic studies support the second possibility.

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**Keywords:** Thiophene; SH groups; Radioisotopic study into the HDS mechanism;  $^{35}\text{S}$ ;  $\text{H}_2$  dissociation;  $\text{H}_2\text{S}$  formation; Transition metal sulfides; Catalysis

## 1. Introduction

The mechanism of thiophene HDS was investigated in many publications ([1] and references within, [2–16]). Although various mechanisms of thiophene decomposition over sulfide catalysts have been proposed, the role of sulfide sulfur remains unclear. We studied thiophene HDS using both  $^{35}\text{S}$  [18–23] and  $^3\text{H}$  [17,21,23,24], which allowed us to suggest the “forcing out” mechanism [21,23]. According to it, the sulfur of thiophene “extrudes” the sulfide sulfur from the catalyst surface into the gas phase. The mechanism includes interaction of the gas phase  $\text{H}_2$  with the SH group of the catalyst. The interaction explains a transfer of the radioactivity into the  $\text{H}_2\text{S}$  in the course of thiophene HDS over the catalyst labeled by  $^{35}\text{S}$  (Scheme 1). However, an alternative mechanism could be supposed – radioactivity transfers from the sulfide catalyst into the  $\text{H}_2\text{S}$  molecule due to an isotopic exchange between the labeled catalyst \*SH group and the  $\text{H}_2\text{S}$  formed (path a, Scheme 2). If it were the case, the change in molar radioactivity (MR) would not be related to the catalytic activity in the HDS. To

obtain the answer to the question which of the mechanisms is realized is an aim of the article.

In recent computational studies [25–31] the interaction of the molecular hydrogen with the sulfide bridge sulfur is postulated. But according to the “forcing out” mechanism  $\text{H}_2$  reacts with a catalyst SH group. So, another aim of the paper is to understand which of the alternative mechanisms is true. It is important for correct computing the key elementary steps of thiophene HDS, and, evaluating of the active sites functioning.

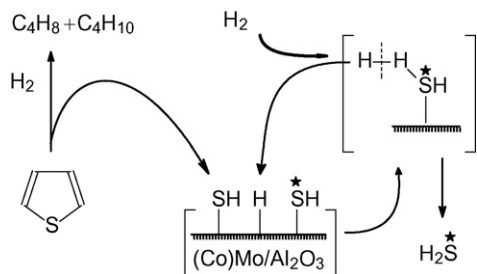
## 2. Experimental

To prepare a sulfide catalyst labeled by  $^{35}\text{S}$  the samples in oxide form were sulfidized in a 21  $\text{cm}^3$  autoclave by using elemental sulfur- ( $^{35}\text{S}$ ) ( $\text{H}_2$ , 6 MPa, 360 °C, catalyst: sulfur ratio = 5:1 wt.). The catalyst samples labeled by  $^3\text{H}$  were prepared by the sulfidation of the oxide form catalyst by non-radioactive sulfur in hydrogen- ( $^3\text{H}$ ) atmosphere.

The sulfidized catalyst containing radioactive sulfur or tritium was loaded in a microreactor of an experimental pulse setup combined with a radiochromatograph. After the catalyst was treated in a He flow, the reactor was fed with hydrogen that also served as a carrier gas for a radiochromatograph and treated by a non-radioactive hydrogen flow to remove all

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Scheme 1. A transfer of the radioactivity into the  $H_2S$  in the course of thiophene HDS over the catalyst labeled by  $^{35}S$  according to the “forcing out” mechanism.

reversibly adsorbed hydrogen from the catalyst. The pulses of unlabeled thiophene or  $H_2S$  of a  $1 \mu l$  and  $0.2 \text{ cm}^3$  volume correspondingly were successively supplied to the catalyst. The signals from the TCD of the gas chromatograph (GC) and from a flow proportional counter of radioactivity, installed outlet of GC, were processed in the *on-line* regime.

Curves of  $H_2S$  MR as a function of the  $H_2S$  produced ( $\text{cm}^3$ ) were calculated, equivalent to the dependence on the amount of reacted thiophene.  $H_2S$  MR values were normalized relatively to the value of the initial MR of sulfide sulfur on the catalyst (%). The dependencies obtained can be approximated by exponential equations of the following type:

$$\alpha = \sum A_i \exp(-\lambda_i x) \quad (1)$$

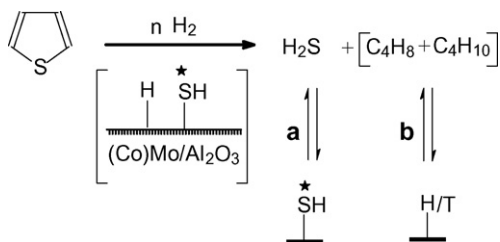
Each item of (1) describes the  $H_2S$  MR changes with an intensity determined by the value of the exponential power  $\lambda_i$ , this intensity being characteristic of active sites (AS) of the given type. Proceeding from Eq. (1), it is possible to estimate the amount of catalyst sulfur  $S_i$  (in mg) that can participate in  $H_2S$  formation (mobile part of sulfur) on the AS of the given type:

$$S_i = \frac{32}{22.4 \times 100} \int_0^\infty A_i \exp(-\lambda_i x) dx \quad (2)$$

Integration of (2) gives

$$S_i = \frac{32}{22.4 \times 100} \frac{A_i}{\lambda_i} \quad (3)$$

If more than one exponent describes the curve, i.e. if several types of active sites take part in the reaction, the total amount of mobile sulfur is estimated by the sum:  $S_{\text{mob}} = \sum S_i$ .



Scheme 2. Possible (a)  $^{32}S \rightleftharpoons ^{35}S$  and (b)  $H \rightleftharpoons T$  isotopic exchange reactions in the course of thiophene HDS.

### 3. Results

#### 3.1. Thiophene HDS over catalyst- $^{35}S$

In the experiments of thiophene HDS on a catalyst sulfided by  $^{35}S$  [17–20] radioactivity was detected only in the  $H_2S$  formed during the reaction but not in non-reacted thiophene, i.e. there was no exchange between sulfide sulfur and thiophene. Experiments in which the sulfidized catalyst was treated in a flow of hydrogen showed that no detectable amounts of  $H_2S$  were formed in the absence of thiophene. Thus, during HDS catalyst sulfur is replaced by sulfur from thiophene. Some of sulfur is “immobile”, i.e. it cannot participate in the formation of  $H_2S$  during the HDS, and some can. The latter can be considered as “mobile”. We have established correlations between catalyst activity in HDS and the amount of mobile sulfur and mobile sulfur reactivity (mobility). A share of mobile sulfur depends on catalyst composition, preparation and pretreatment conditions. Mobile sulfur is not uniform. It can consist of more and less mobile parts (“rapid” and “slow” sulfur). These two parts of mobile sulfur correspond to the two types of the sites that differ in the reactivity of the sulfur during the formation of  $H_2S$  and are named “rapid” and “slow”. We attribute the “rapid” sites to Mo and the “slow” sites to Co or Ni [20,23].

#### 3.2. Isotopic exchange between the catalyst- $^{35}S$ and the gas phase $H_2S$

In the course of the experiment the curve of the MR of the  $H_2S$  depending on the amount of the  $H_2S$  passed over the catalyst labeled by  $^{35}S$  was obtained. The curves obtained in the course of thiophene HDS and  $H_2S$  isotopic exchange (Fig. 1, curves 1 and 2) are close. This may be due to a possible competition between both processes if an essential amount of  $H_2S$  exists in the reaction zone. This is in a good agreement with a well-known observation that  $H_2S$  inhibits the main HDS reaction ([1] and references within, [32]).

#### 3.3. Thiophene HDS over catalyst- $^3H$

To determine the source of hydrogen which takes part in  $H_2S$  formation we studied thiophene HDS on  $CoMo/Al_2O_3$  containing irreversibly adsorbed hydrogen labeled by tritium [17,23]. An initial catalyst sample was sulfided in an atmosphere of radioactive hydrogen. To remove all reversibly adsorbed hydrogen  $^3H$  from the catalyst, the sample was kept for 1 h at  $360^\circ C$  in a flow of  $H_2$  that was non-radioactive. Measurements of gas phase radioactivity showed that already during the first minutes of the  $H_2$  treatment a significant amount of labeled hydrogen left the catalyst. However, some of the tritium remained on the catalyst and did not exchange with gas phase hydrogen, i.e. this tritium was irreversibly adsorbed on the catalyst during sulfidation.

In thiophene HDS experiments on the catalyst labeled by  $^3H$  it was found that a tracer passes from the catalyst to the  $H_2S$  formed. At the same time, next to none radioactivity was found

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