

Reactive adsorption of thiophene on Ni/ZnO: kinetic and *in situ* XRD studies

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Introduction

Removal of sulfur-containing molecules from fuels remains one of the major industrial challenges. Using new generation of hydrodesulfurization (HDS) catalysts the sulfur content can be reduced to 10 ppmw as imposed by forthcoming environmental legislation. However, classical HDS seems not to be well adapted for ultimate desulfurization ($S < 10$ ppmw), that's why a number of alternative approaches have recently been proposed [1]. One of the most promising among them is the reactive adsorption in which sulfur-containing molecules are decomposed on a sorbent comprising a metal supported on ZnO [2]. The approach was implemented on industrial scale for gasoline desulfurization (ConocoPhillips's *S-Zorb* process) and was claimed to effectively remove sulfur while retaining the octane number [3].

In our contribution we will describe the mechanism of thiophene reactive adsorption on a model Ni/ZnO adsorbent using the experimental data from thermal gravimetric analysis (TGA), fixed-bed sulfidation and *in situ* time-resolved synchrotron XRD.

Materials and Methods

Model adsorbents NiO/ZnO (12 wt% Ni, $S_{\text{BET}} = 60 \text{ m}^2/\text{g}$) were prepared by coprecipitation from aqueous solution followed by calcination at 400°C. The gas phase tests of thiophene reactive adsorption were done in H_2 under atmospheric pressure with 10–40 mbar of thiophene at 300–375°C. Detailed description of the preparation procedure and setups for TGA and fixed bed sulfidation are given in [4]. The time resolved synchrotron XRD study under reaction conditions was realized on Swiss-Norwegian Beamline at the European Synchrotron Radiation Facility (Grenoble, France).

Results and Discussion

The following points will be presented and discussed in detail in our contribution:

- NiO/ZnO samples can be used in thiophene reactive adsorption without any preliminary reduction in hydrogen: Ni^0 is rapidly formed in thiophene/ H_2 mixture and the sulfidation rate is higher if the sample reacts directly (Fig.1). The decreased reaction rate after preliminary reduction is attributed to formation of NiZn alloy particles detected by XRD.

- During reaction between Ni/ZnO and thiophene in a fixed bed reactor, gaseous products do not contain H_2S until ZnO-ZnS transformation is completed. We conclude therefore that ZnO sulfidation is more rapid than thiophene desulfurization, which appears to be the rate determining step.

- XRD showed that Ni is not sulfided during reaction. The reflections of metallic nickel (fcc structure) are observed in XRD patterns during ZnO sulfidation (Fig.2). However, the corresponding lattice parameter is much bigger than that of pure Ni^0 ($a = 3.70$ versus 3.52 \AA), showing that during reaction the bulk structure of active Ni particles is expanded (presumably due to the presence of dissolved carbon). Surprisingly, Ni_3C is formed after a complete ZnO transformation (Fig.2).

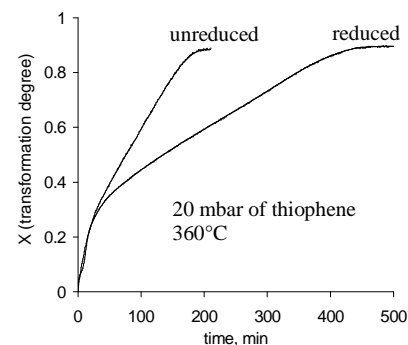


Figure 1 TGA sulfidation profiles of NiO/ZnO samples ($X = 1$ corresponds to formation of $\text{Ni}_3\text{S}_2 + \text{ZnS}$).

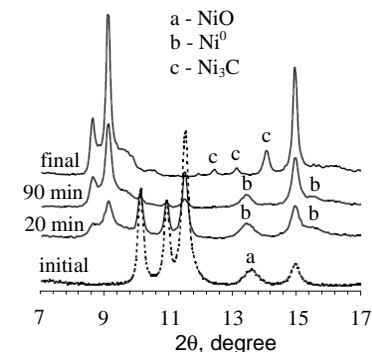


Figure 2 XRD patterns ($\lambda = 0.5 \text{ \AA}$) of NiO/ZnO during reaction with thiophene (20 mbar, 360°C) (All unmarked peaks are those of ZnS or ZnO).

Significance

Two industrially relevant conclusions can be drawn from our work. First, NiO/ZnO adsorbents can be used in oxidized form without any preliminary reduction, which might simplify the process scheme. Second, since the rate determining step of the reactive adsorption is HDS of sulfur-containing molecules, improving the catalytic activity of the sorbents would permit to increase their performance.

References

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