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Kinetics of thiophene reactive adsorption on Ni/SiO_2 and Ni/ZnO

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Abstract

Kinetics of thiophene reactive adsorption on Ni/SiO_2 and Ni/ZnO was studied by thermal gravimetric analysis at 280–360 °C under 5–40 mbar of thiophene in H_2. In the case of Ni/SiO_2 the interaction proceeds in two steps: a rapid surface reaction is followed by a slower bulk transformation into Ni_3S_2. Maximum Ni conversion depends on reaction conditions and observed conversion profiles can be described by an exponential equation corresponding to a reaction of first order relatively to both sulfidable Ni amount and thiophene. The interaction between Ni/ZnO and thiophene proceeds in a rather different manner. A rapid increase of weight, similar to the first stage observed on Ni/SiO_2, is not followed by bulk Ni sulfidation, but instead by a nucleation-controlled ZnO surface transformation. After formation of the surface ZnS layer, a complete particles sulfidation occurs with kinetics being strongly dependent on the reaction conditions possibly due to comparable rates of different reaction steps.

Keywords: Reactive adsorption; Desulfurization; Thiophene adsorption; Supported Ni

1. Introduction

Removal of sulfur from refinery streams remains one of the most challenging tasks in petroleum industry [1,2]. Although the appearance of new, more active catalyst formulations, enables hydrodesulfurization (HDS) process to produce fuels with a <10–50 ppm S grade, this approach shows a disadvantage of unnecessary hydrogenation of hydrocarbons while removing sulfur species, resulting in an excessive hydrogen cost imposed for refineries. For this reason development of alternatives to classic HDS attracted much interest in recent years [3]. While classical HDS continues to be the only industrially viable technology for diesel hydrotreatment, a panoply of new methods has appeared for gasoline ultra-deep desulfurization with Prime G+ and SCANfining being today the technologies of choice [4]. Although these novel catalytic approaches allow to satisfy the stringent norms on sulfur content (<10–50 ppm S), a loss of octane number is still an intrinsic issue of catalytic hydrodesulfurization processes. That is why development of other methods, based on adsorption or oxidation of sulfur species, continues to attract considerable attention.

One of such novel methods, reactive adsorption, has been implemented in *S-Zorb* desulfurization technology used on industrial scale [5]. In this approach sulfur-containing molecules *react* with a solid adsorbent in the presence of hydrogen [6]. During the reaction the active phase of the adsorbent, consisting of metallic particles supported on ZnO, is transformed into a mixture of sulfides. After complete transformation (saturation) the adsorbent is regenerated in a two-stage process: sulfides are firstly calcined to obtain oxides which are than treated in H_2 in order to reduce the supported metal. The method was demonstrated to possess some valuable features like low hydrogen consumption and absence of side hydrogenation reactions provoking decrease in octane number [7]. Despite these advantages, very little is known about the mechanism of reactive adsorption. It was supposed that ZnO acts as an acceptor for sulfur produced from sulfur-containing molecules on Ni particles which were suggested to be "continuously regenerated" during reaction [6]. Babich and Moulijn proposed a reaction scheme in which thiophene is decomposed on metal surface with following hydrogenation of NiS site and transfer of H_2S to ZnO [1]. However, the key points of the proposed mechanism of reactive adsorption have not yet been understood. It is not clear if sulfur-containing molecules are decomposed by HDS reaction on metallic particles or a novel mechanism operates in this system. Also, we do not know if the reaction is limited by decomposition of sulfur-containing species or by ZnO sulfidation.

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In the present work, we studied reactive adsorption of thiophene in gas phase on a model system Ni/SiO_2 and on an industrially relevant adsorbent Ni/ZnO. Thermal gravimetric analysis was used to characterize the reaction kinetics under varying temperature and thiophene partial pressure. Based on these experimental data, we propose a kinetic description of the interaction and suggest some features of the reaction mechanism for two types of materials.

2. Experimental

$Ni(NO_3)_2{\cdot}6H_2O$ of reactive grade, which was used as Ni precursor, was purchased from Aldrich. Ni/SiO_2 was prepared by homogeneous deposition–precipitation on Aerosil 200 (Degussa, $S_{BET} = 223\ m^2/g$). 4.942 g (0.017 mol) of $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in 190 mL of water and 4 g of Aerosil were suspended in the solution. pH of the mixture was adjusted to 3.5 with HNO_3 and 5.00 g (0.083 mol) of urea was added. The obtained suspension was heated at 90 °C under vigorous stirring for 30 h, the time necessary to obtain a colorless solution. The solid was filtered, thoroughly washed with water and dried in oven overnight at 100 °C. After drying the sample was directly reduced in hydrogen. Firstly, it was heated at 1 °C/min to 230 °C and reduced at this temperature for 1 h. Then the temperature was raised (at 2 °C/min) to 600 °C and maintained for 10 h (such a treatment allows to reduce Ni completely without silicate formation [8]). After reduction the samples were cooled down and passivated in order to avoid a strongly exothermic Ni oxidation upon a direct contact of between reduced Ni and air. The typical procedure described in literature [9] was used. Firstly the sample was purged with a flow consisting of 1 mL/min of air and 100 mL/min of N_2 and then air content was gradually raised before exposure to air.

Ni/ZnO samples were synthesized by co-precipitation of $Zn(NO_3)_2{\cdot}6H_2O$ (reactive grade, Aldrich) and $Ni(NO_3)_2{\cdot}6H_2O$ by sodium carbonate. 6.576 g (0.0221 mol) $Zn(NO_3)_2{\cdot}6H_2O$ and 0.778 g (0.0027 mol) $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in 127 mL of water to obtain 0.2 M solution. Taken quantities correspond to 10 wt% of NiO in NiO/ZnO sample. Co-precipitation was done by dropwise addition of equimolar quantity of 0.5 M solution of Na_2CO_3 under vigorous stirring. Obtained suspension was stirred during 12 h, and then the solid was filtered, thoroughly washed with water and dried in oven overnight at 100 °C. After drying the sample was annealed in air at 400 °C for 4 h (heating rate, 2 °C/min). This was followed by a reduction in hydrogen flow at 400 °C for 5 h. After reduction the samples were cooled down and passivated in the same way as Ni/SiO_2 samples.

X-ray diffraction patterns of the samples were recorded using an INEL CPS120 semicircle counter using Cu Kα monochromatic radiation. Transmission electron microscopy micrographs were obtained on a JEOL JEM 2100 instrument. Ni particles average size in Ni/SiO_2 was obtained from measuring 350–400 particles on different sample areas. The given value is the average weighted by volume:

$$\bar{d} = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3}$$

BET surface areas were measured on a BEL Mini apparatus by N_2 adsorption at 77 K. Chemical analysis of the samples was done by Central Analysis Service (SCA) of the French National Centre for Scientific Research (CNRS).

For thermal gravimetric study of the reaction kinetics a home-made setup was used. The sample was suspended in a silica tube in which a down-up gas flow passed. The sample weight was recorded using a SETARAM B85 balance head which was continuously purged with nitrogen. Before the reaction the solids were reduced in H_2 flow (150 mL/min) during 3 h at 600 °C (Ni/SiO_2) or at 360 °C during 6 h (Ni/ZnO). These conditions are sufficient to reduce completely Ni particles as it follows from TGA (data not shown). After the sample has been reduced, a thiophene/H_2 reaction mixture was brought into the tube. Preliminary experiments were performed in order to determine the operating conditions which would exclude any influence of mass transfer in gas phase and between the powder particles. It was found that a gas flow greater than 130 mL/min should be used and the mass of the sample should not exceed 30 mg. Therefore, the hydrogen flow of 150 mL/min and samples of 20 mg were used systematically throughout this study. The conversion was calculated in the following way:

$$X(t) = \frac{W(t) - W_0}{W(\mathrm{S})_{\max}} \quad \text{for} \quad Ni/SiO_2$$

$$X(t) = \frac{W(t) - W_0}{\Delta W_{\max}} \quad \text{for} \quad Ni/ZnO$$

where $W(t)$ is the sample weight at instant t, W_0 the sample weight after reduction, $W(\mathrm{S})_{\max}$ the maximum amount of sulfur which can react with Ni, and $\Delta W_{\max}$ is the maximum weight change for Ni/ZnO sample. In all cases Ni was supposed to be transformed into Ni_3S_2 and ZnO into ZnS.

3. Results and discussion

3.1. Solids characterization

Composition and textural properties of the solids used in the work are given in Table 1. For Ni/SiO_2 samples we used a nonporous Aerosil silica as support in order to exclude any eventual intrusion of pore diffusion in the overall interaction kinetics. Supported Ni particles have small size and narrow size distribution (3–6 nm) which are typical features of supported material prepared by homogeneous deposition–precipitation [9].

XRD pattern of Ni/ZnO shows presence of NiO despite passivation procedure. To obtain the size of Ni particles (Table 1), the size of NiO was therefore corrected using the ratio

Table 1
Composition and textural properties of the samples used in the work

Sample	S_{BET} (m^2/g)	Ni (wt%)	d_{Ni} (nm)	d_{ZnO} (nm)
Ni/SiO_2	244	17.3	5.2 (TEM)	
Ni/ZnO	32	6.1	5.3[a] (XRD)	14 (XRD)

[a] Calculated from the size of NiO particles using the ratio of molar volumes of Ni and NiO.