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Research article

Kinetic modeling of deep hydrodesulfurization of dibenzothiophenes on NiMo/alumina catalysts modified by phosphorus

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A B S T R A C T

A series of NiMo/alumina catalysts modified with phosphorus was prepared and evaluated in a trickle-bed high-pressure flow micro-reactor. The kinetics of deep hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) was investigated based on conversion and products distribution data. The estimated parameters obtained were statistically significant, suggesting an accurate representation of the system. Phosphorus addition led to a two-fold increase in the formation of direct desulfurization over hydrogenation products for the HDS of DBT. On the other hand, the HDS of DMDBT increased mainly due to an increase in the hydrogenation route, leading to high yields of hydrogenated products. The observed phenomena were described well by the estimated parameters and may be related to an increase in metal dispersion, formation of more active sites and enhancement in Brønsted acidity in the catalyst upon phosphorus addition.

1. Introduction

The production of clean fuels, as required by increasingly restrictive environmental legislation, represents a significant challenge for the refining industry, especially considering the ultra-low S contents (below 10 mg kg^{-1}) specified for diesel [1,2]. The most efficient way to achieve these goals is by deep hydrodesulfurization (HDS) of most refractory sulfur-containing compounds, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) [3–5]. The HDS of these compounds requires more severe operating conditions such as high temperatures and pressures [6].

Conventional industrial HDS catalysts are usually composed by MoS_2 promoted by atoms of Co or Ni [7–9]. Promoters such as phosphorus have been used to improve catalytic performance, and several studies have been reported about its effects on HDS [10–14]. Ali et al. [12] reported an increase of about 50% in the HDS rates upon addition of 1 wt% of P_2O_5 to $CoMo/Al_2O_3$ catalysts attributed to an increase in Mo dispersion. On the other hand, Ferdous et al. [13] did not observe an enhancement in the catalytic activity of DBT HDS using $NiMo/Al_2O_3$ catalysts. Zhou et al. [14] reported that the addition of phosphorus to NiMo catalysts weakened the interaction between the metals and the support, forming a more active phase, which led to an increase in the HDS of DBT.

It is usually accepted that HDS reactions occur through two main pathways: direct desulfurization (DDS), with the cleavage of C—S bond, or hydrogenation (HYD), which involves the formation of partially hydrogenated intermediates which further react to cyclohexylbenzene and bicyclohexyls [15,16]. It is well established that DBT reacts preferentially through DDS route whereas DMDBT HDS occurs predominantly via HYD route [17,18].

The knowledge of the reaction kinetics is a crucial component in the project and simulation of industrial reactors. However, the development of kinetic models of hydrotreatment reactions of oil streams may be incredibly complicated. A large quantity of different sulfur compounds that can be found in those streams, as well as the interference of aromatic and organo-nitrogen molecules which compete for the same active sites, contribute to the system's complexity.

HDS kinetic modeling has been extensively studied in the past years, with different kinetic models and approaches being reported in the literature [19–23], which can be classified into three categories. The first one deals with the kinetic study based on elemental analysis of real oil feed streams. The second one is the use of power law models applied to model compounds or macroscopic properties of real feeds. The last category deals with the evaluation of kinetic and adsorptive parameters, using Langmuir-Hinshelwood (L-H) type kinetics [24–27]. In general, the L-H model requires the determination of several

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parameters, such as adsorption constants, which might be difficult to obtain [28]. The power law model, however, is more widely adopted for its simplicity. It involves the lumping of parameters but is still able to provide relevant information on the kinetics of HDS reactions [29,30].

Kinetic models that are developed considering experimental errors and statistical significance are not usually available, let alone in hydrotreatment reactions using a wide range of operating conditions in a trickle-bed continuous reactor, which is closer to the industrial reality. Nevertheless, it is not common to associate the changes in kinetic parameters to the catalyst physicochemical properties or even its composition. Furthermore, to the best of our knowledge, rigorous kinetic modeling of HDS reactions that investigated the effects of phosphorus content over $NiMo/Al_2O_3$ catalysts is missing from the hydrodesulfurization literature. These gaps motivated us to investigate the influence of phosphorus loading on $NiMo/Al_2O_3$ catalysts on the kinetics of two HDS model compounds, DBT and DMDBT. We used original experimental data from a continuous reactor adopting a wide range of operating conditions. Power law kinetic models were examined, considering the experimental errors in the estimation of kinetic parameters. The parameters were evaluated and validated by their phenomenological and statistical significance.

2. Experimental section

2.1. Catalyst preparation

A series of $NiMoP/Al_2O_3$ catalysts containing 15 wt% of MoO_3 and Ni/(Ni + Mo) atomic ratio of 0.3 were prepared by incipient wetness impregnation method using three phosphorus concentrations (0, 1 and 2 wt%). The catalysts were labeled as NiMoPx, where x is the phosphorus concentration. The detailed synthesis procedure and catalyst characterization can be found elsewhere [31].

2.2. Reaction system

HDS of DBT (Sigma-Aldrich, 97%) or DMDBT (Sigma-Aldrich, 97%) were carried out in a trickle-bed reactor (Microactivity-Reference Reactor of PID Eng & Tech), operated in downflow mode under different conditions. A typical procedure was as follows: about 1.0 g of the catalyst in oxide form (60–100 mesh) was placed into the reactor middle zone diluted with silicon carbide. Before the activity test, the catalyst was sulfided in situ with a solution of 4 wt% CS_2 in n-hexane ($0.1\ mL\ min^{-1}$) from room temperature to 350 °C ($2.5\ °C\ min^{-1}$) under 3.1 MPa of hydrogen (flow rate: $400\ N\ mL\ min^{-1}$) during 2 h. The feedstock was composed of DBT or DMDBT (1000 ppmw of S) in n-hexadecane (Sigma Aldrich, 99%). Reaction samples were periodically collected and analyzed by a gas chromatograph (Agilent 6890) coupled with a flame ionization detector (FID) and a capillary column (DB-1, J&W). Additionally, reaction products were identified by GC–mass spectrometry (Agilent 5975 MS/7820A GC). Steady-state was reached after 5 h of reaction, considering a variation less than 0.2% in reactant conversion. Mass balance was always better than 95% for the HDS of DBT and 90% for the HDS of 4,6-DMDBT. Table 1 presents the experimental conditions used to evaluate the HDS activity.

Table 1
Experimental conditions.

Conditions	Range	Reference[a]
Pressure (bar)	31–51	31 (41)
Temperature (°C)	185–300	230 (250)
WHSV (h^{-1})	4–10	4 (6)

[a] Numbers not in parenthesis refer to DBT and the ones in parenthesis refer to DMDBT.

The absence of mass transfer limitations was verified by the Weisz–Prater and Mears criteria (see Section S2 for details).

2.3. Kinetic modeling

In parameters estimation, it was assumed that experimental errors followed a normal distribution, experiments were conducted independently of each other, dependent and independent variables were not correlated, and that independent variables errors were negligible. Thus, considering these hypotheses, a weighted least-squares objective function was obtained and minimized [32,33].

The parameters were estimated through a hybrid numerical routine combining a heuristic optimization method (particle swarm) with a deterministic method (Gauss-Newton) for the minimization of the weighted least-squares objective function [34]. The differential balance equations were numerically integrated using Dassl routine [35]. The experimental errors of the species concentrations were estimated from replicates obtained in the middle of the range of operational conditions, calculating, then, an average relative variance that was extrapolated for the other experimental conditions. The confidence interval of each parameter was obtained for a confidence level of 95%.

The following assumptions were considered while constructing the reaction rate equations: (i) the disappearance of reactants follows irreversible first-order kinetics; (ii) the hydrogen is fed in excess, so its concentration is constant along the reactor; and (iii) isothermal conditions are assumed along the reactor. The hydrogen concentration in the liquid phase was determined in HYSYS by a flash calculation considering vapor-liquid equilibria using the Soave-Redlich-Kwong equation of state.

The rate constant was modeled by a reparametrized Arrhenius equation to reduce parametric correlation.

$$k_j = \exp\left(-a_j + b_j\left(1 - \frac{T_R}{T}\right)\right) \tag{1}$$

where a_j and b_j are adjustable parameters related to the apparent activation energy (E_j) and the frequency factor (k_{0j}), T is the reaction temperature in K, and T_R is a reference temperature (the mean temperature in the range evaluated).

$$E_j = RT_Rb_j \tag{2}$$

$$k_{0j} = \exp(b_j - a_j) \tag{3}$$

where R is the ideal gas constant.

3. Results and discussion

3.1. HDS of DBT and DMDBT

Fig. 1 shows the product yields over a broad range of sulfur compounds conversions for the catalysts. It was observed that HDS of DBT proceeded predominantly via DDS pathway whereas DMDBT reacted mostly via HYD. These trends are in line with previous reports [17,22,36].

For both reactions, the presence of partially hydrogenated sulfur compounds such as tetrahydrodibenzothiophene (THDBT), as reported in the literature [37,38], was not observed probably due to the high pressure used in the current work. Moreover, DDS and HYD routes can be considered as parallel for both reactions since there is no significant conversion of biphenyl (BP) or 3,3′-dimethylbiphenyl (3,3′-DMBP) into the corresponding hydrogenated compounds, cyclohexylbenzene (CHB) or methylcyclohexyltoluene (MCHT), respectively. At high conversions of DMDBT, MCHT is converted to the fully hydrogenated molecule dimethylbicyclohexane (DMBCH) for the catalysts containing phosphorus. We also observed isomerization products of MCHT and DMBCH in the chromatograms. However, it was not possible to distinguish between them. Therefore, for quantification purposes, all the isomers

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