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Kinetics of thiophene hydrodesulfurization over a supported Mo–Co–Ni catalyst

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ABSTRACT

In this study, the kinetics of thiophene (TH) hydrodesulfurization (HDS) over the Mo–Co–Ni-supported catalyst was investigated. Trimetallic catalyst was synthesized by pore volume impregnation and the metal loadings were 11.5 wt % Mo, 2 wt % Co, and 2 wt % Ni. A large surface area of 243 m^2/g and a relatively large pore volume of 0.34 cm^3/g for the fresh Mo–Co–Ni-supported catalyst indicate a good accessibility to the catalytic centers for the HDS reaction. The acid strength distribution of the fresh and spent catalysts, as well as for the support, was determined by thermal desorption of diethylamine (DEA) with increase in temperature from 20 to 600 °C. The weak acid centers are obtained within a temperature range between 160 and 300 °C, followed by medium acid sites up to 440 °C. The strong acid centers are revealed above 440 °C. We found a higher content of weak acid centers for fresh and spent catalysts as well as alumina as compared to medium and strong acid sites. The catalyst stability in terms of conversion as a function of time on stream in a fixed bed flow reactor was examined and almost no loss in the catalyst activity was observed. Consequently, this fact demonstrated superior activity of the Mo–Co–Ni-based catalyst for TH HDS. The activity tests by varying the temperature from 200 to 275 °C and pressure from 30 to 60 bar with various space velocities of 1–4 h^{-1} were investigated. A Langmuir–Hinshelwood model was used to analyze the kinetic data and to derive activation energy and adsorption parameters for TH HDS. The effect of temperature, pressure, and liquid hourly space velocity on the TH HDS activity was studied.

1. Introduction

Hydrodesulfurization (HDS) has received much attention in recent years due to environmental and clean-fuel legislation [1]. This process aims to remove the sulfur-containing molecules that are present in the petroleum fractions. The sulfur-based compounds are hydrodesulfurized through various reaction routes, such as the direct desulfurization and the hydrogenation (HYD) followed by desulfurization. The high reactivity molecules, such as thiophene (TH) and benzothiophene, are mainly hydrodesulfurized via direct desulfurization [2]. The catalytic HYD of sulfur-containing molecules to hydrocarbons and hydrogen sulfide (H_2S) has been intensively studied in the past decades [3,4]. The choice of the catalyst depends mainly on the required HDS conversion and the characteristics of the processed feedstock. The metal sulfide catalyst, in particular sulfided form of molybdenum-based catalysts, has been used as HDS catalysts for many years

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Nomenclature

A (in Arrhenius equation)	pre-exponential factor
ARE	average relative error
B	butadiene
BET	Brunauer–Emmett–Teller
DEA	diethylamine
E_{HDS}	hydrodesulfurization activation energy, J/mol
F_S	molar flow rate of solvent (n-hexane), mol/s
F_{TH}	molar flow rate of thiophene, mol/s
F_{TH0}	molar flow rate of thiophene at the inlet of the reactor, mol/s
HDS	hydrodesulfurization
H_2	hydrogen
H_2S	hydrogen sulfide
K_{TH}	adsorption constant of thiophene, bar^{-1}
K_{H_2}	adsorption constant of hydrogen, bar^{-1}
K_{H_2S}	adsorption constant of hydrogen sulfide, bar^{-1}
K_i	adsorption constant of component i, bar^{-1}
k	reaction rate constant, mol/min kg
LHSV	liquid hourly space velocity, h^{-1}
m_{cat}	catalyst weight, g
p_{TH}	partial pressure of thiophene, bar
p_{H_2}	partial pressure of hydrogen, bar
p_{H_2S}	partial pressure of hydrogen sulfide, bar
r	reaction rate, mol/min kg
R	gas constant
R^2	coefficient of determination
S	solvent, e.g., hexane
SEE	objective function
T	temperature
TH	thiophene
x_{TH}	thiophene conversion
Δ	sulfur vacancies
ΔH_i	adsorption enthalpy of component i
θ	adsorption sites

[5,6]. The typical HDS catalysts containing nickel and/or cobalt as a promoter were deposited on the high surface area carriers such as γ-Al_2O_3 and SiO_2–Al_2O_3 [7,8].

Supported cobalt–molybdenum (namely, CoMo) and nickel–molybdenum (NiMo) were comprehensively studied lately. CoMo can be considered as a promising catalyst for lighter fractions, whereas NiMo can be regarded as more active toward heavier fractions or deep HDS, being less sensitive to amines than the Mo and CoMo catalysts [9,10]. A comparative study of both catalysts was done [11]. Our study confirmed the dependency of the catalyst activity on feed.

Many different supports have been tested and many combinations were investigated. However, the typical support for commercial hydrotreating catalysts remains γ-Al_2O_3. The important features of alumina include their good mechanical and textural properties and their ability to provide high dispersion of the active metals [12,13]. The support material enhances the catalytic properties, whereas the surface orientation of alumina affects the catalytic functionality, such as activity toward HDS [14,15].

The effect of promoters on catalytic activity in the hydrotreating reactions has been widely investigated. The role of the promoter is to enhance the catalyst activity toward the increasing of the conversion and improving the reactivity of the compounds that are difficult to be removed. The usual promoters for HDS reaction are Ni and Co, whereas tungsten was also found to be active for hydrotreating [1,16].

The increasing demand to lower the sulfur levels in fuels leads to the motivation for the improvement of the current hydrotreating catalysts and the development of new materials. The additives and stabilizers (e.g., phosphorus and boron) may either change the HDS chemistry or improve the promoter atom distribution. During the last decade, phosphorus addition became the favored option as a stabilizer during the synthesis of hydrotreating catalysts. The effect of phosphorus addition on NiMo- and CoMo-supported materials was studied and some interesting findings were revealed. The increased catalytic activity is attributed to the dispersion of the active compound and increased Brønsted acidity [17,18]. The presence of phosphorus can decrease the coke formation, hence increasing the HDS activity [19,20]. The boron addition on NiMo/γ-Al_2O_3 was reported to increase the catalyst acidity and to improve the hydrocracking activity [21,22].

The continuous requirements for cleaner fuels indicate a better design and the formulation of new catalysts as well as the development of new active phases or supports. An option is to modify alumina support with different oxides. The metal oxides such as TiO_2, ZrO_2, and SiO_2 are used for this purpose, having an important contribution for the HDS reaction [23–25]. Carbon as a support material was the subject of many studies and its positive role in HDS activity was detected [26–28]. Mesoporous materials like MCM-41 *(Mobil Composition of Matter No. 41)* are estimated to develop a better activity for deep HDS [29,30], whereas the zeolite materials (e.g., type Y, X) were found to have a significant effect on the HDS activity [31–33].

Promising efforts have been directed toward the TH HDS activity over trimetallic Co–Mo–Ni–supported catalysts. Few studies investigate trimetallic Co–Mo–Ni catalysts supported on Al_2O_3 and TiO_2–Al_2O_3 [34,35]. The comparative study with the commercial Co–Mo–Ni/Al_2O_3 shows the superior HDS activity for homemade catalysts [34]. Low titania loading in the support composition enhances the HDS activity, being considered as promising supports for Mo-based catalysts in TH HDS and deep HDS processes [34].

Because of the lack of studies of TH HDS over trimetallic Mo–Co–Ni-supported catalysts, the objective of the present work was to investigate the activity of the Mo–Co–Ni/γ-Al_2O_3 catalyst for TH HDS. Kinetics is also studied and the obtained results are compared with the experimental data.

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