Fuel Processing Technology 167 (2017) 684–694

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Activity comparison of Ni-Mo/Al_2O_3 and Ni-Mo/TiO_2 catalysts in hydroprocessing of middle petroleum distillates and their blend with rapeseed oil

Petr Vozka[a,b,*], Diana Orazgaliyeva[a,c], Pavel Šimáček[a], Josef Blažek[a], Gozdem Kilaz[b]

[a] Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology, Prague, Technicka 5, 166 28 Prague, Czech Republic
[b] School of Engineering Technology, Purdue University, West Lafayette, 401 N Grant Street, 47906, IN, USA
[c] CB & I s.r.o., Brno, Czech Republic

ARTICLE INFO

Keywords:
Hydrodesulfurization
Hydrodenitrogenation
Hydrogenation
Catalyst
Hydrodeoxygenation

ABSTRACT

Alumina supports are currently the most widely utilized supports for hydrotreating catalysts, which are used for production of low sulfur diesel fuels. However, the strong metal-support interactions, which may inhibit the desired kinetics of desulfurization, have driven the need to explore novel support systems. This research focuses on one such alternative support system – titania. This study compares the hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation efficiency of sulfide Ni-Mo/Al_2O_3 and Ni-Mo/TiO_2 catalysts in hydrotreating the middle petroleum distillates with and without 20 wt% of rapeseed oil. Hydrotreating experiments were executed in a fixed bed co-current tubular reactor using a commercial Ni-Mo/Al_2O_3 and an in house prepared Ni-Mo/TiO_2 catalyst. The operating parameters were as follows: temperature in the range of 320–360 °C, pressure of 4 and 8 MPa, WHSV of ca 1.0 h^{-1}, and hydrogen to feedstock ratio of ca 240 m^3/m^3. Ni-Mo/Al_2O_3 catalyst showed higher HDS, HDN and hydrogenation activity, mainly at 4 MPa pressure. The Ni-Mo/Al_2O_3 catalyst exhibited greater methanation activity, especially at 8 MPa pressure. The higher efficiency recorded with the Ni-Mo/Al_2O_3 catalyst may be attributed to this catalyst's greater surface, formed by smaller mesopores size range.

1. Introduction

Production of low sulfur fuels is one of the important tasks in the oil industry due to the tightening of environmental legislative regulations. Therefore, emphasis has focused on developing new catalysts with a greater hydrodesulfurization (HDS) activity than those currently utilized. HDS has been the most effective technology for reducing the sulfur content in the fractions used for the production of diesel fuel, especially in the most recent decades [1]. Typically, hydrodesulfurization reactions are catalysed by sulfided Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalysts.

Support is an important component of the HDS catalyst since it plays a vital role in active metal loading and its dispersion. On that note, composition, pore size, and pore structure are some of the support features that can influence the catalytic activity. Due to all these reasons, catalyst support significantly affects HDS efficiency. Hence, the support is a crucial parameter in the development of highly active HDS catalysts [2]. Similarly, it was discovered by other researchers [3–5] that the HDS selectivity is strongly influenced by the support, thus the HDS catalyst support has a lot of future promise for improvement via future potential discoveries [3,6,7].

Almost exclusive use of alumina supports is attributed to its excellent textural and mechanical properties. Alumina support commonly contain phosphorus that improves its properties. Alumina can easily be formed into the desired shape; moreover, it is a highly stable and relatively inexpensive support that contains acidic as well as basic sites [8]. However, metals and alumina exhibit strong interactions that form active surface species, which hinder HDS efficiency [2,8–10]. One example of such interactions was shown in hydrotreating reactions executed on alumina supported molybdenum catalysts. These strong metal-support interactions have revealed the need to discover novel alternatives to alumina [6,8,10].

Titania is a promising substitute to alumina support for HDS catalysts. Previous work showed that TiO_2-supported molybdenum catalysts enabled a higher HDS activity compared to those supported by Al_2O_3 [5,11–13]. This is attributed to the higher number of active Mo sites present on TiO_2 compared to Al_2O_3, SiO_2, and ZrO_2 [7,14]. Similarly, it was reported that the enhanced Mo/TiO_2 catalyst activity enabled a

---

[*] Corresponding author at: KNOY Hall of Technology, 401 N. Grant Street, West Lafayette, Indiana 47907, United States.
E-mail address: pvozka@purdue.edu (P. Vozka).

http://dx.doi.org/10.1016/j.fuproc.2017.08.019
Received 3 April 2017; Received in revised form 5 July 2017; Accepted 14 August 2017

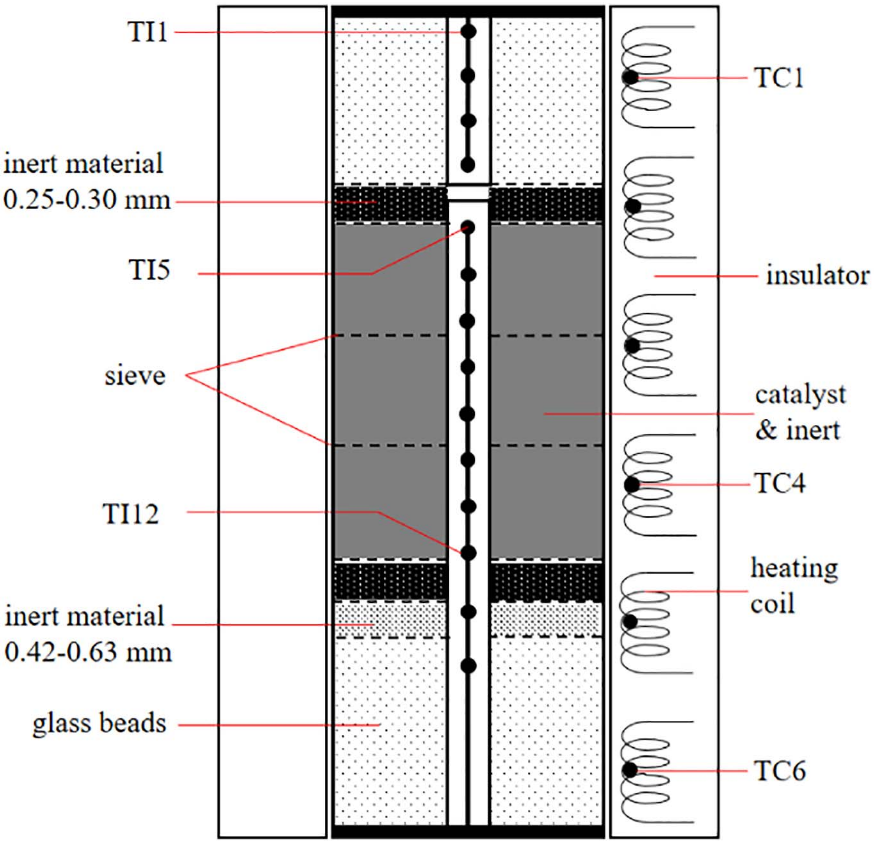

Fig. 1. Schematic diagram of the reactor configuration and catalyst bed distribution.

Table 1
Chromatographic conditions for the analysis of the gaseous products.

Parameters	Description
Analytical column	CP-CARBOBOND FUSED SILICA (50 m × 0.53 mm × 5 µm)
Carrier gas	Helium 5.5, constant pressure of 60 kPa
Oven temperature	Isothermal 30 °C for 5 min, followed by a linear gradient of 30 °C/min to a temperature 180 °C being held isothermally for 40 min
Detector	Channel 1: flame ionization detector (detection of C_1–C_5 hydrocarbons) Channel 2: thermal conductivity detector (detection of permanent gases)

Table 2
Analytical results of feedstocks.

Properties	BF	BF + RO
Sulfur (wt%)	0.30	0.24
Nitrogen (mg/kg)	140	112
CFPP (°C)	− 2	–
Cetane index	50	–
5 vol% recovered at (°C)	237	–
95 vol% recovered at (°C)	362	–
Mono-aromatics (wt%)	17.0	13.6
Di-aromatics (wt%)	9.2	7.4
Tri-aromatics (wt%)	1.1	0.9
Total aromatic hydrocarbons (wt%)	27.3	21.9
Saturated hydrocarbons (wt%)	72.7	58.1
Rapeseed oil (wt%)	0.0	20.0

Table 3
Catalysts composition and amount of active metal component in the reactor.

Catalyst	Content (wt%)					Amount in the reactor (g)	
	NiO	MoO_3	Al_2O_3	TiO_2	P_2O_5	NiO	MoO_3
Ni-Mo/Al_2O_3	5.8	32.4	52.6	–	8.3	5.5	30.5
Ni-Mo/TiO_2	4.6	26.1	–	58.5	7.5	5.3	30.2

Table 4
Pore volume (PV), porosity (P), specific surface area (SSA), and bulk density of the catalysts.

Catalyst	PV, N_2	PV, Hg	P, Hg	BET SSA	t plot SSA	Bulk density
	cm^3/g	cm^3/g	%	m^2/g	m^2/g	g/cm^3
Ni-Mo/Al_2O_3	0.19	0.14	23	85	85	0.99
Ni-Mo/TiO_2	0.15	0.15	25	46	42	1.22

slight increase in the direct desulfurization while significantly enhancing the hydrogenation [3]. Multiple researchers reported that the synergy between the support and the active metal component of the hydrotreating catalyst is much more favourable with titania as opposed to alumina. Molybdenum was observed to disperse on the titania support in a stable configuration that resists segregation and sintering as long as the loading is kept under one monolayer [13,15]. This interaction is more preferable than the multi layered surface species Mo forms with the alumina support since the multi-layer configuration diminishes the hydrotreating efficiency. Nevertheless, TiO_2 alone has not found use as a suitable support for high temperature industrial applications due to a few drawbacks such as low specific surface area, low mechanical strength, and low thermal stability of the active anatase structure [7,10,11,16]. Therefore, it is suggested that support systems that are composed of mixed oxides [7,11], such as TiO_2-Al_2O_3 [17], could possess beneficial features of both oxides, resulting with a higher HDS activity.

Pore size distribution is an important parameter for the HDS activity of catalysts. The optimal catalyst pore size that gives high HDS activity