Fuel Processing Technology 153 (2016) 50–57

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Catalytic cracking additives based on mesoporous MCM-41 for sulfur removal

Eduard A. Karakhanov [a,*], Aleksandr P. Glotov [a], Aina G. Nikiforova [a], Anna V. Vutolkina [a], Andrei O. Ivanov [b], Sergei V. Kardashev [a], Anton L. Maksimov [a,b], Sergei V. Lysenko [a]

[a] Lomonosov Moscow State University, Chemistry Department, GSP-1, 1-3 Leninskiye Gory, Moscow 119991, Russia
[b] Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky pr. 29, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form 2 June 2016
Accepted 24 July 2016
Available online 7 August 2016

Keywords:
Sulfur reduction
FCC
Catalytic cracking
Mesoporous materials
Vacuum gas oil

ABSTRACT

Materials based on mesoporous MCM-41/γ-Al_2O_3 silicon oxide with the supported compounds of La, W, and Ni and with W, Co, Mo, Zn, Ni, and La supported on γ-Al_2O_3 were synthesized and studied as additives to FCC catalysts. The samples were characterized by BET, TEM, and NH_3-TPD methods, IR spectroscopy, and XRD analysis. The catalytic tests of the above additives in mixtures with a commercial cracking catalyst were performed in a MAT laboratory system. It was established that the addition of 10 wt% La/MCM-41/γ-Al_2O_3 to the catalyst made it possible to decrease the sulfur content of the liquid products of the cracking of vacuum gas oil to 40%.

1. Introduction

Fluid catalytic cracking (FCC) is a large-scale oil refining process and its products occupy a key place in the manufacture of commercial grade fuels [1]. In recent years, motor fuels are subject to strict ecological requirements in terms of sulfur content. Thus, in a number of cases, catalytically cracked gasoline accounts for 50% of the total gasoline pool of a refinery [2]. However, in some countries, to 90% gasoline contains sulfur compounds in the final product; therefore, gasoline from catalytic cracking units is subjected to hydrofining. A decrease in the octane number because of the hydrogenation of olefins and aromatics is a disadvantage of the hydrofining of a gasoline fraction [3]. Other deep desulfurization techniques are under research, including adsorptive desulfurization [4,5], oxidation desulfurization [6], biodesulfurization [7], extractive desulfurization with ionic liquids [8]. The use of these methods in industry is still quite limited. Therefore, desulfurization in the process of catalytic cracking is an important task for the production of high-quality motor fuels. Desulfurization before hydrofining can be performed with the use of several methods: it is possible to take a gasoline fraction with a lower final boiling point, to use low sulfur raw materials, to vary reactor and regenerator temperatures and a circulation ratio, and to add sulfur reduction additives [9]. The development of desulfurizing agent additives to commercial microspherical cracking catalysts containing zeolites is in progress [9,10]. The decrease of the concentration of sulfur compounds in the liquid products makes it possible to carry out the subsequent hydrofining of a gasoline fraction under milder conditions.

Various additives to FCC catalysts were described [9,11], including the compounds of Ni, Zn, Ag, Cd, Pb, Bi, B, Al, In, Sn, Hg, Mo, W, La [9,12], Cu, Zn, Ga, V, Co, Fe [9,13], Ti, Zr, and Mg [9] supported onto different oxides. The most commonly used catalyst support is γ-alumina. On the other hand, in accordance with published data, zeolites containing metal compounds in their structure were used as an active matrix. Additives based on metal aluminosilicates were patented [14]. An aluminosilicate of offretite topology with Zn is such an additive, 10 wt% of which in a mixture with a commercial cracking catalyst exhibited a good effectiveness in decreasing the concentration of thiophene sulfur [15].

In the middle 1990s, new materials – structured mesoporous oxides with pore sizes from 20 to 500 Å – were synthesized [16]. Depending on synthesis conditions, it is possible to regulate their pore size, specific surface area, specific pore volume, acidity, etc. [17]. The M41S family of silica and aluminosilicates was firstly introduced by the Mobil group [16], which includes hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 phases. The preparation of MCM-41 material involves ionic surfactants, exemplified by cetyltrimethyl ammonium bromide (CTMAB), as structure directing agent [18,19]. The materials of the MCM-41 type have very high surface area and extra-large pores (2–10 nm pore size) [16]. Thus, the materials of MCM-41 type open up interesting perspectives for catalytic cracking of vacuum gas oil (VGO) [20,21].

* Corresponding author.
E-mail address: kar@petrol.chem.msu.ru (E.A. Karakhanov).

http://dx.doi.org/10.1016/j.fuproc.2016.07.023
0378-3820/

Nomenclature

BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CTMAB	cetyltrimethylammonium bromide
e-cat	equilibrium microspherical zeolite-containing cracking catalyst
FCC	fluid catalytic cracking
HCO	heavy cycle oil
HY	zeolite type Y (Zeolyst CBV 600) in H-form
IR	infrared
LCO	light cycle oil
MAS NMR	magic-angle spinning nuclear magnetic resonance
MAT	micro activity testing
NH_3-TPD	temperature-programmed desorption of ammonia
TEM	transmission electron microscopy
TEOS	tetraethylorthosilicate
VGO	vacuum gas oil
XRD	X-ray diffraction

Gao X.-H. reported that mesoporous MCM-41 co-promoted REUSY FCC catalyst has been positive to improve the selectivity's for gasoline, diesel and propylene and negative to coke formation [22]. Such conversion and selectivity differences were caused by diffusional transport and pre-cracking in the mesoporous promoter of the catalyst. Thus, changes in matrix may also lead in catalytic cracking to differences in both activity and selectivity. Da Jian-Wen et al. reported that the MCM-41 added FCC catalyst is positively capable to crack heavy oil feedstock, in which the yields of the diesel and lighter oil increased 1.85 and 3.47%, respectively and coke yield decreased 0.29%, while the sulfur concentration decreased to 6% in gasoline and to 7.5% in diesel [23].

Transition metal halides CuCl and $PdCl_2$ supported on MCM-41 or SBA-15 were used for desulfurization of commercial fuel [4,24]. Metallic nickel nanoparticles supported on mesoporous silica KIT-6 and SBA-15 were described in [25]. La/MCM-41material exhibited highest feature of thiophenic sulfur removal from diesel due to the interaction of HO-La(OSiAl) with sulfur in thiophene and its derivatives [5].

The aim of this work was to test a modified mesoporous silicon oxides of the MCM-41 type as a desulfurizing agent component to be added to commercial cracking catalysts. We demonstrated that additive based on La-MCM-41 synthesized in the presence boehmite can be used for decrease sulfur in FCC products.

2. Materials and methods

2.1. Materials

VGO was used as a feedstock in the experiments, Table 1 summarizes its characteristics.

An equilibrium microspherical zeolite-containing cracking catalyst (e-cat) was used (Table 2).

Commercially available zeolite Y (Zeolyst CBV 600) in the hydrogen form (HY) with the ratio Si/Al = 5.2 was used.

Table 1
Properties of the feedstock.

Sulfur content (wt%)	Density at 20 °C (g/cm^3)	Conradson carbon residue (wt%)	Distillation (°C)			
			Initial boiling point	10%	50%	Final boiling point
1.93	0.910	0.16	333	380	437	535

2.2. Additive preparation procedure

The MCM-41/γ-Al_2O_3 support was obtained in accordance with modified procedures described previously [5,26]. For this purpose, a weighed portion of pseudoboehmite was mixed with distilled water, and an aqueous solution of CTMAB was added to the resulting mixture at a temperature of 35 °C; the contents were stirred for 1 h. Then, tetraethyl orthosilicate (TEOS) and an aqueous solution of ammonia were added drop by drop to the obtained mixture to pH 11. The resulting gel was allowed to stand overnight. The gel had the following composition: $5SiO_2$:2,1Al_2O_3:CTMAB: 462H_2O. The sample was dried and calcined at 650 °C in a flow of air for 4 h. The resulting sample had the following composition: MCM-41/Al_2O_3 (58:42, by weight).

The additives of La/MCM-41/γ-Al_2O_3, W/MCM-41/γ-Al_2O_3, and Ni/MCM-41/γ-Al_2O_3 were prepared by the impregnation of MCM-41/γ-Al_2O_3 with the aqueous solutions of lanthanum nitrate, ammonium paratungstate, and nickel nitrate for supporting 5 wt% metal. The additives based on γ-Al_2O_3 were obtained by the impregnation of pseudoboehmite with the calculated quantities of the aqueous solutions of metal salts for supporting 10 wt% metal onto the carrier. The samples were dried in air for 8 h and in a drying oven at 110 °C for 12 h and then calcined in a flow of air at 650 °C for 4 h. The following salts were used as parent compounds: ammonium paratungstate, cobalt nitrate, ammonium paramolybdate, zinc nitrate, nickel nitrate, and lanthanum nitrate.

2.3. Steaming procedure

The thermal steam stabilization of La/MCM-41/γ-Al_2O_3, MCM-41 and zeolite HY was performed at a temperature of 600 °C in an atmosphere of 100% water vapor for 2, 4, and 8 h. The unit for the hydrothermal deactivation experiments consists of a stainless steel fixed bed reactor heated by a 3-zone furnace. The capacity of the reactor for the steaming procedure is 20 g catalyst/additive. Temperature control is achieved by the means of an internal thermocouple in the catalyst bed. Steaming can be terminated after a desired period of time.

2.4. Characterization

The isotherms of nitrogen adsorption/desorption at 77 K were measured with the aid of a Micromeritics Gemini VII 2390t instrument. Before the measurements, the samples were outgassed at a temperature of 350 °C for 6 h. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method in a range of the relative pressures $P/P_0 = 0.04–0.20$. The pore volume and pore size distribution were determined from the adsorption branches of the isotherms based on the Barrett–Joyner–Halenda (BJH) model. The specific pore volume was determined based on the amount of adsorbed nitrogen at the relative pressure $P/P_0 = 0.99$.

Transmission electron microscopy (TEM) analysis was carried out with the aid of a LEO 912 ABOMEGA microscope.

X-ray diffraction (XRD) data were obtained at room temperature on a Bruker D2 PHASER powder diffractometer in the θ–θ geometry with X-ray generation at 30 kV and 10 mA using a copper anode (λ(CuKα) = 1.5418 Å). Diffraction patterns were recorded with sample rotation in the horizontal plane in the angle interval of 2θ of 1.5(1.5) to 70(6)° in 0.05(0.01) steps, slit widths of 0.1 mm at the tube outlet and 1.15 mm in front of the detector, and a recording time per step of 3 s. The diffraction patterns were processed using the Bruker software package diffrac.EVA. Identification of phases was carried out on the basis of ICDD.

The infrared (IR) spectra were measured on a Nicolet IR200 Fourier transform spectrometer in a range of 400–4000 cm^{-1}. The samples were formed as pellets with potassium bromide (2 wt%).

The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out at a heating rate of 8 K/min and a final temperature of 800 °C.