Fuel Processing Technology 180 (2018) 56–66

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

The influence of hydrothermal crystallization temperature on a novel FDU-12 mesoporous composite assembled by ZSM-5 nanoclusters and its hydrodesulfurization performance for DBT and FCC diesel

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ABSTRACT

A novel FDU-12 composite assembled by the ZSM-5 nanoclusters, which contained the primary and secondary building units of ZSM-5 zeolites, was synthesized successfully by in-situ assembly crystallization method. The influence of hydrothermal crystallization temperature on the properties of FDU-12 materials was studied comprehensively. The as-synthesized materials and catalysts, named as ZF-T and NiMo/ZF-T, were characterized by various methods, including XRD, nitrogen physisorption, pyridine-FTIR, H_2-TPR, HRTEM and XPS characterization. The characterization results showed that NiMo/ZF-T series catalysts exhibited the satisfactory pore properties, more moderate metal-support interaction, preferable dispersion and sulfidation degree of Mo species than those of the commercial NiMo/Al_2O_3, which led to better hydrotreating performance than those of NiMo/Al_2O_3 (except NiMo/ZF-140 °C). Moreover, when the hydrothermal crystallization temperature was 110 °C, the obtained NiMo/ZF-110 °C catalyst achieved the best HDS and HDN efficiencies of 98.6% and 99.5%, respectively, which could be mainly ascribed to the synergistic effects of the largest specific surface area, the best dispersion and the highest sulfidation degree of Mo species as well as its appropriate acidic properties and moderate metal-support interaction.

1. Introduction

In 2015, it was conservatively estimated that 9 million people were premature to death due to the environmental pollution, which accounts for 16% of global deaths. And it was three times more than the total number of AIDS, pneumonia and malaria deaths. The economic losses caused by pollution reached up to 4.6 trillion dollars, which covered 6.2% of global GDP [1]. Thus, the environmental problems considered as the "Man-made disaster" became huge hurdles to human beings. However, the development of economic would inevitably consume a lot of energy resources, such as petroleum resources. More and more strict regulations have been made to limit the harmful substances in fuel i.e., sulfur, aromatics all over the world. Furthermore, some European countries issued a decree on fuel-powered cars, which indicated that the traditional fuel-powered cars would not be sold in the future. In this situation, the clean fuel-powered vehicles would be a good option to reduce the vehicle exhaust pollution. And the improvement of ultra-clean fuel would still be the most effective method to meet the actual challenges.

In China, diesel has a wider range of applications and the consumption of diesel keeps higher level than gasoline in large vehicles, ships, generators and other heavy machinery, which benefits from its splendid properties of good power performance, long life, high safety and less pollution. FCC process covers 30% diesel, which embraces lots of impurities (i.e. sulfides and nitrides) and contributes 80% of the sulfur to the final product. Meanwhile, hydrodesulfurization (HDS) is one of the most widely profitable processes to remove toxic compounds. The highest refractory compounds in diesel fraction are macromolecule sulfur-containing compounds, such as dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT), all of which have multiple aromatic rings. These macromolecule sulfur-containing compounds request large pore size of the catalyst to preferably eliminate the macromolecule diffusion resistance and realize the effective desulfurization. Considering the limitations of the commercial alumina, such as small pore diameter, unconcentrated pore diameter distribution and low surface area, the mesoporous materials with extensive mesochannels, concentrated pore diameter distribution and large surface area are the ideal candidates to meet the diffusion and reaction demands. Currently, the mesoporous materials including MCM-41, MCM-48 [2,3], SBA-15 [4], FDU-12 [5], KIT-5 [6] and others have been designed and applied in the processes of hydrodesulfurization. However, pure silica-based mesoporous materials exhibit typical characteristics of weak acidity and amorphous pore wall, which results in less active sites and poor hydrothermal stability. In order to compensate the poor hydrothermal

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https://doi.org/10.1016/j.fuproc.2018.08.010
Received 24 April 2018; Received in revised form 4 August 2018; Accepted 15 August 2018

stability of mesoporous materials, some researches [7–9] used structure-directing agents to synthesize ordered mesoporous materials constructed by primary and secondary structure building units of microporous zeolites, which obtained excellent hydrothermal stability and catalytic activity. Simultaneously, the good hierarchical porous structure and appropriate acidity of the as-synthesized samples making them of great potentiality for application of hydrodesulfurization [10–15]. Pinnavaia et al. [10] synthesized the mesoporous material MSU-S with hexagonal closed-packed structure using the crystal seeds of Y zeolites and hexadecyl trimethyl ammonium bromide (CTAB) by self-assembly method. And the as-synthesized MSU-S materials exhibited a better thermostability than the "ultra-stable" silica-based mesoporous MCM-41 materials as well as a better performance of catalytic cracking than that of Al-MCM-41 catalyst. Xiao et al. [14] used the triblock copolymer and directing agents of Beta zeolite to synthesize mesoporous material MAS-7, which possessed high hydrothermal stability, strong acidity and preferable catalytic performance. The as-synthesized MAS-7 catalyst displayed good catalytic cracking performance for both isopropylbenzene and 1,3,5-triisopropylbenzene comparing with the microporous HZSM-5 materials and the mesoporous Al-SBA-15 materials. The results indicated that the mesoporous MAS-7 materials, fabricated by the primary and secondary building units of microporous zeolite, combined the advantages of microporous and mesoporous materials with appropriate acidity and large pore channel.

As for the removal of sulfur-containing macromolecule compounds, the materials mentioned above also revealed a more satisfactory catalytic performance [16–20] than that of alumina, where the excellent texture properties, such as big pore diameter and large specific surface area, made a great contribution to the activity of the catalysts. Li et al. [16] synthesized the mesoporous material FDU-12 with primary and secondary building units of microporous Beta zeolite and it showed a superior HDS performance for diesel. The authors ascribed high HDS efficiency to the excellent structural properties and moderate acidity of mesoporous Beta-FDU-12 materials. Zhang et al. [18] used the precursors of microporous Beta zeolite and Pluronic P123 triblock copolymer (EO_{20}–PO_{70}–EO_{20}) to assemble meso-microporous composite material Beta-KIT-6 with cubic Ia3d mesoporous structure. The HDS results indicated that NiMo/Beta-KIT-6 catalyst revealed the best conversion of dibenzothiophene, which was better than that of the industrial catalyst NiMo/Al_2O_3. The higher activity of NiMo/Beta-KIT-6 catalyst than that of the pure silica supported catalyst was attributed to the large uniform pore size, pore volume, and surface area, combing with more and stronger acidic sites. Apparently, the in-situ assembly strategy is an alternative method to synthesize the mesoporous materials constructed by the primary and secondary building units of zeolites.

Meanwhile, in the synthesis process of molecular sieves, hydrothermal crystallization temperature played a very important role to significantly influence the polymerization of the silicate ions and self-generated pressure in the crystallization tank, then resulted in the change of the pore structure construction and acid property of molecular sieve. Aiexandridis et al. [21] and Zhou et al. [22] pointed out that the hydrodynamic radius of Piuronic micelles (F108 and F68) mainly remained the same with the increase of temperature. But the aggregation level of micelles increased significantly with the enhancement of temperature, while the polydispersity of micelles decreased and the micelles tended to keep a relatively uniform size. Wang et al. [23] investigated the synergistic effect of crystallization temperature and NaF on MCM-48. The results exhibited that the crystallization temperature was a very critical factor for the improvement of the hydrothermal stability of MCM-48. Enhancing the crystallization temperature was beneficial to accelerate the synthesization and improved the order degree of MCM-48, which would further modify the stability of MCM-48. Hence, hydrothermal crystallization temperature played an important role on the properties of catalysts, while it was barely to find the relevant researches.

In this research, the mesoporous material FDU-12 was successfully synthesized (named with ZF) by self-assembly method under the presence of preformed aluminosilicate nanoclusters of ZSM-5 and triblock copolymers $EO_{106}PO_{70}EO_{106}$ (F127) micella. Then, a series of ZF composites were synthesized under different hydrothermal crystallization temperatures. The as-synthesized ZF composites supported Ni and Mo catalysts were prepared through a two-step incipient wetness impregnation procedures. The characterization of the materials and catalysts were characterized by various techniques, including ICP, XRD, nitrogen physisorption, TEM, pyridine-FTIR, H_2-TPR and XPS. The HDS performances of the corresponding catalysts were evaluated in a micro reactor unit with DBT and Hohhot FCC diesel, where the conventional NiMo/γ-Al_2O_3 catalyst was taken as a reference. Finally, the influence of different hydrothermal crystallization temperatures on the physicochemical properties of catalysts was systematically discussed to address the structure-activity relationship.

2. Experimental

2.1. Synthesis of materials

The ZSM-5 nanoclusters were synthesized by in-situ crystallization method. First, the mixture of 0.6 g sodium hydroxide (NaOH) and 5.3 g tetra-propyl ammonium bromide (TPABr) were dissolved in 8 g deionized water. Then added 10 g colloidal silica (40 wt%) in above solution while stirring. Another solution was the mixture of 1.0 g sodium aluminate ($NaAlO_2$), 0.287 g NaOH and 10 g deionized water, which was dropwise added in the above solution. And the mixture was stirring for 4 h at ambient temperature. Afterwards, the homogeneous solution was transferred into a teflon-lined autoclave and crystallized at 170 °C for 21 h to obtain ZSM-5 nanoclusters precursor. The ZSM-5 zeolite with full crystallinity was synthesized by same procedures, while crystallized for 48 h. Consequently, the ZSM-5 zeolite and its nanoclusters precursor were obtained with the molar ratio of Al_2O_3:SiO_2:TPABr:NaOH:H_2O = 1:30:14.7:17:2000.

ZSM-FDU-12 materials were successfully synthesized via a nano-assembling method by mixing 2.0 g triblock copolymers $EO_{106}PO_{70}EO_{106}$ (F127), 5 g KCl and 2.0 g TMB in 120 ml 2 M hydrochloric acid (HCl) solution. The above solution was stirring for 24 h at 20 °C. Then, 2.0 g tetraethylorthosilicate (TEOS) and 7.0 g ZSM-5 aluminosilicate nanoclusters was dropwise added in above solution and stirred for another 24 h. Afterwards, the mixture solution was transferred into a teflon-lined autoclave and crystallized at different temperatures of 80 °C, 100 °C, 110 °C, 120 °C and 140 °C for 24 h to obtain the composite materials named with ZF-T (T = 80 °C, 100 °C, 110 °C, 120 °C and 140 °C). Finally, the as-synthesized samples of ZF-T materials were eventually completed after filtering, washing, drying and calcinating at 550 °C for 6 h.

2.2. Preparation of catalysts

The as-synthesized ZSM-FDU-12 materials needed to be treated by ion exchange for further process. The specific steps were as follows: The mixture of 1 g ZSM-FDU-12 materials and 3 g ammonium chloride (NH_4Cl) were dissolved in 30 g deionized water, stirred for 2 h at 80 °C and then filtered, washed, dried and calcinated at 550 °C for 3 h. Another ion exchange followed the same procedures as above steps.

The hydrodesulfurization catalysts were prepared by two-steps incipient-wetness impregnation with the active components of Ni and Mo salts. First, the $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ aqueous solution was dropwise added in the as-synthesized materials while stirring. And followed by drying and calcining at 550 °C for 6 h. Then Ni was supported by the same procedures using $Ni(NO_3)_2\cdot6H_2O$. The amounts of NiO and MoO_3 are 3.5 wt% and 10 wt%, respectively. The as-synthesized catalysts were named as NiMo/ZF-T, where T represented the hydrothermal crystallization temperature of 80 °C, 100 °C, 110 °C, 120 °C and 140 °C.