Self-assembly mesoporous silica on clay nanotubes as a component of sulfur removal additives to cracking catalysts

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Production of ultra-low sulfur content gasoline and diesel is a major trend of refinery nowadays. Up to 40 % sulfur of total gasoline pool volume can be traced from FCC (Fluid Catalytic Cracking) unit. To decrease sulfur content in gasoline fraction, sulfur removal additives to FCC catalysts can be used [1]. Commercial additives consist of alumina based support with Zn-Mg and form spinels. The main disadvantages of these additives are decrease of FCC gasoline fraction yields and high coke formation [1, 2].

Earlier we reported highly efficient sulfur removal additives based on ordered mesoporous silica oxides [2, 3]. But commercial application of these materials is limited due to their low steaming and mechanical stabilities. To improve these properties we suggested reinforcing mesoporous structure by halloysite nanotubes – natural aluminosilicate clay with silica outside and alumina inside surfaces which can be selectively modified for different core-shell structures formation [4].

Material MCM-41/halloysite (50/50 wt %) was synthesized using sol-gel method resulted in self-assembly of ordered mesoporous silica MCM-41 type on halloysite nanotubes. Dried and calcined carrier was impregnated by aqueous solutions of $La(NO_3)_3$, $Mg(NO_3)_3$ and $Zn(NO_3)_3$ to deposit 5 % wt of metals on MCM-41/halloysite. According to low-temperature nitrogen adsorption/desorption data resulted samples are mesoporous materials with pore diameter of 2.5 nm and BET surface area about 616 m^2/g. It is also confirmed by TEM (pore diameter around 2.4 nm). TEM microphotographs confirm mesoporous structure of the samples with pore diameter around 2.4 nm. XRD reveals peaks at small angles (2-6 °) indicating mesoporous silica oxide phase MCM-41 type formation. Additives were blended with commercial equilibrium zeolite-containing FCC catalyst (e-cat) with mass ratio of 1/10 and tested on MAT-unit with a fixed bed reactor at 500 °C and VHSV of 15.6 h^{-1}. Vacuum gas oil with sulfur content of 1.93 wt % was used as a feed. Liquid products were analyzed on a gas chromatograph “Chromos GC-1000”. The concentration of sulfur in liquid products was determined by XRF analysis.

Synthesized MCM-41/halloysite composite is thermally stable up to 1100 °C and has a good steaming resistance. All additives with e-cat are active in sulfur removal from liquid products of vacuum gas oil cracking (sulfur decreasing – 15-25 %) compared to e-cat without additives. It should be noted that highly active La/MCM-41/halloysite provides the best sulfur removal (25 %) with only 1 wt % gasoline loss with light cycle oil increasing. In the case of magnesium and zinc based additives sulfur removal was lower with gasoline yield increasing by 1-2 wt % compared to e-cat.

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References

[1] T. Myrstad, H. Engan, B. Seljestokken, E. Rytter, Appl. Catal. A: Gen. 187, *1999*, 207-212.

[2] A. Glotov, N. Levshakov, A. Vutolkina, S. Lysenko, E. Karakhanov, V. Vinokurov. Catal. Today. *2019*, *in press, doi.org/10.1016/j.cattod.2018.10.009.*

[3] E.A. Karakhanov, A.P. Glotov, A.G. Nikiforova, A.V. Vutolkina, A.O. Ivanov, S.V. Kardashev, A.L. Maksimov, S.V. Lysenko, Fuel Process. Technol. 153, *2016*, 50-57.

[4] Y.M. Lvov, D.G. Shchukin, H. Mohwald, R.R. Price. ACS Nano, 2 (5), *2008*, 814-820.