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Hybrid materials composed by nanocrystalline ZSM-5 embedded into the MCM-41 mesoporous materials for cracking of vacuum gas oil

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Abstract – This work deals with the synthesis and characterization of hybrid H-MCM-41/ZSM-5 materials. Morphologic properties, such as surface area of the composite is approximately half of the surface area of the conventional MCM-41, and the formation of walls with the double of the density, characterizes the hybrid material, resulting in high stability materials for catalytic application. Aiming to obtain ideal structures of the hybrid material, variations in the synthesis time had been carried out. A compared analysis was performed including XRD, SEM-EDX, TGA and BET measurements. The potential application of hybrid H-MCM-41/ZSM-5 material for the catalytic degradation of heavy oil has been investigated and compared with the H-ZSM-5 catalyst.

Cracking reactions of voluminous molecules over Al-MCM-41 proceeds due to its large pore size and mild acidity. H-ZSM-5 catalyst leads to an end-chain cracking pathway, which has been assigned to its strong acidity and small pore size [1]. Nanocrystalline ZSM-5 has shown a high catalytic activity in polimer cracking due to the presence of high external surface area. Porous materials combine the properties of both zeolites and ordered mesoporous aluminosilicates [1-2]. In this point of view, this work deals with the synthesis, characterization and catalytic test of hybrid MCM-41/ZSM-5 for cracking of vacuum gas oil (VGO).

The acid form of H-MCM-41/ZSM-5 was synthesized hydrothermally in a Teflon-lined stainless steel autoclave according Huang et al. [3]. In order to obtain ideal structures of the hybrid material, variations in the synthesis time had been carried out. The obtained materials were characterized by XRD, SEM-EDX, TGA, and N_2 adsorption (BET), where a clear change in the structural features can be observed (fig.1). The ZSM-5 zeolite was obtained commercially, as ammonia form, by Sentex Industrial Ltda. In order to determine the density of acid sites, n-butylamine adsorption and TGA desorption was used. Results showed that densities of the acid sites was 2,21 mmol.g^{-1} for hybrid H-MCM-41/ZSM-5 and 0,59 mmol.g^{-1} for H-ZSM-5.

Hybrid catalyst was evaluated for cracking of VGO and compared with the H-ZSM-5 catalyst. TG analysis was carried out in Mettler equipment, TGA/SDTA851 model, using nitrogen as a gas carrier flowing at 25 mL.min^{-1}. The catalyst/VGO mixture, relative proportions of 1:8, were heated from room temperature up to 900ºC, at a heating rate of 5, 10 and 20ºC min^{-1} (fig. 2(a)). The Vyazovkin model-free kinetic was used to evaluate the kinetics parameters of the process cracking of vacuum gas oil pure and in the presence of the H-MCM-41/ZSM-5 and H-ZSM-5 catalysts. Activation energy curves for VGO conversion were calculated (fig. 2(b)). Activation energy was around 60 kJ.mol^{-1} for hybrid catalyst, 95 kJ.mol^{-1} for H-ZSM-5 and 130 kJ.mol^{-1} for thermal reaction. It can be concluded that the hybrid catalyst leads to a lower activation energy, and presents a significant potential for catalytic processing of vacuum gas oil degradation due to the combination of acidic sites of H-ZSM-5 and accessibility with the large pores of MCM-41 structure, resulting in a high efficient catalyst.

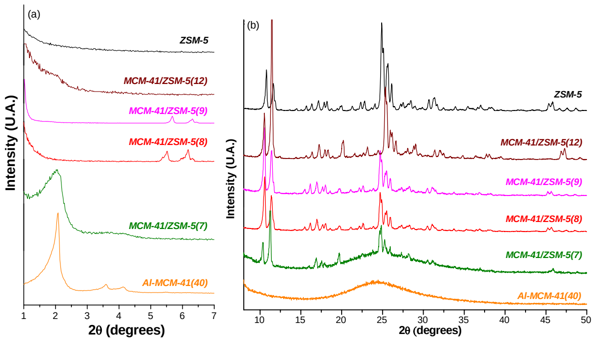

Figure 1: Low-angle (a) and wide-angles (b) XRD spectra of calcined samples.

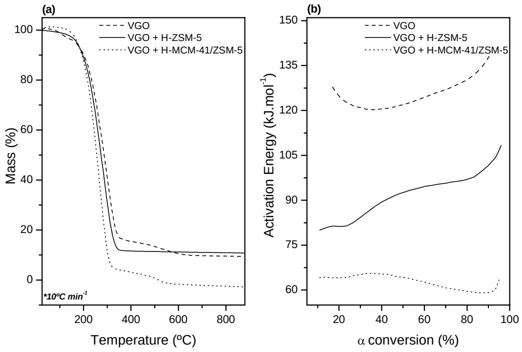

Figure 2: (a) TG/DTG and (b) Activation energy curves for thermal and catalytic cracking of VGO.

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