Effects of iron doping on manganese oxide octahedral molecular sieves used as $DeSO_x$ catalysts

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Introduction

The fluid catalytic cracking (FCC) is an important step of petroleum refining and the main source of pollutant gases such as SO_x. More restrictive laws are often approved in order to control its emissions. The efficiency of a FCC DeSOx catalyst is determined by its capacity to absorb the SO_x at high temperatures (700 – 730 °C), oxidize it to a sulfate form and, finally, reduce it to H_2S in a reducing atmosphere at lower temperatures (520 – 600 °C) [1,2]. Manganese oxide octahedral molecular sieves (OMS-2), known as cryptomelane, consist of MnO_6 octahedra which are linked at vertices and edges. It has properties that are useful for catalysis, for instance: mixed valency, porosity and acidity, due to the presence of Lewis sites [3]. In this paper, we present the advantages of the iron doped OMS-2 compared to pure OMS-2, that were tested in similar conditions to FCC process.

Results and Discussion

The catalysts were synthesized by the reflux method [3] at five Fe/Mn molar ratios: 0, 1/100, 1/50, 1/25 and 1/10. They were characterized by X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and scanning electronic microscopy (SEM). All the results were in agreement with literature. The $DeSO_x$ experiments were carried out in a Netzsch thermogravimetric analyzer (TG) that simulated the FCC conditions; the patterns for each catalyst are summarized in Figure 1. The experimental conditions comprehend four regions described as follows [2]: **Region I,** heating from 50 °C to 725 °C, under He flow, which comprehends the weight loss from water and oxygen release [2], about 12 wt%. for all catalysts. In **Region II**, the atmosphere was changed to a mixture of 0.5% SO_2/2.0% O_2 and He, at isothermal of 725 °C for 30 minutes. In spite of the use of oxides with different iron contents, the weight gain was approximately 30 wt% for each catalyst. At this step, potassium and manganese sulfates are formed. In **Region III**, which consists of the reduction step, the temperature was decreased to 575 °C under a He flow and the atmosphere was changed to a mixture of 15% H_2/He. In this step, however, the weight loss varied according to the increase of iron contents. Pure OMS-2 had 3.1 wt%. weight loss whereas the catalyst with higher iron content (1/10) had 18.1 wt% . Besides that, the rate of the process increases with the iron content, as evidenced by the slope of the curve (Figure 1). This could be explained by the fact that iron is a redox-active metal and improved the sulfate reduction [2]. Afterwards, the temperature, under the same flow, was increased to 900 ºC to remove the remaining sulfate.

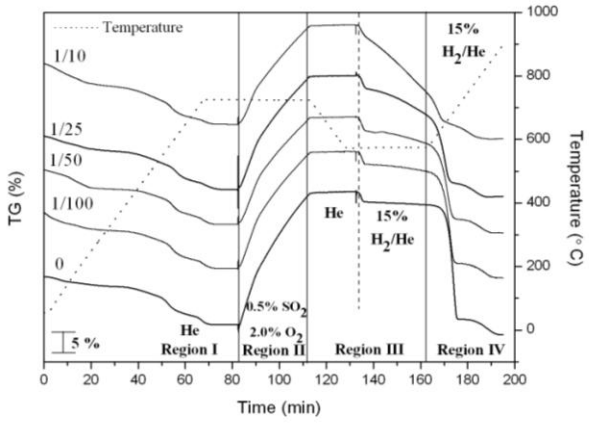

Figure 1. $DeSO_x$ patterns of all catalysts.

Conclusions

The presence of iron in the structure of cryptomelane improved the reduction step, as the amount of iron doped in OMS-2 increases, the weight loss in this region also increases. These results demonstrate the applicability of the studied material as FCC DeSOx catalyst.

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