



Investigation of the nature of V-species on alumina modified by alkali cations: Development of multi-functional DeSO_x catalysts



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ABSTRACT

The location of vanadium species on δ-aluminas modified by lithium, sodium or potassium has been thoroughly investigated by means of several techniques. XRD, TPR and textural analyses showed that vanadium species are preferentially located on group I element or in its close vicinity when compared with the non-modified alumina.

Vanadium species are localized nearby lithium and potassium cations, whilst vanadium species are partially distributed between sodium and alumina support in the sodium-modified alumina. A detailed XPS study was also carried out over potassium-promoted alumina catalysts and confirmed the vanadium distribution nearby potassium.

Experiments of SO_x capture and sulfate reduction to H₂S were performed under realistic Fluid Catalytic Cracking (FCC) conditions with respect to the temperature of the catalyst regeneration (at 725 °C) and during hydrocarbon reactions (around 575 °C).

Among different alkali cation modifiers, alumina modified by potassium exhibited the best performance in the DeSO_x reaction (in terms of mole of absorbed sulfur per mole of group I cation) according to the following ratios: 0.74, 0.34 and 0.24 observed for K, Li and Na, respectively.

Finally, vanadium largely improved the rate of SO₂ oxidation as well as the rate of sulfate reduction to H₂S.

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1. Introduction

Stringent environmental regulations and a growing perception of the need for cleaner industrial processes have motivated several studies on additives or catalysts able to mitigate SO_x emissions [1]. Many of these additives or catalysts used Al₂O₃ or non-stoichiometric magnesium-alumina mixed oxides (MgAl₂O₄·nMgO) as supports [2,3]. The efficiency of these additives or catalysts is defined by their ability for SO_x adsorption under real operating conditions within the fluid catalytic cracking unit (FCC unit). Indeed, a proper DeSO_x catalyst design is warranted to improve the adsorption and oxidation step of SO₂, the trapping of SO₃ as formed sulfated species and subsequently, the desorption and reduction step of the sulfated species. A DeSO_x catalyst should

therefore exhibit a multi-functional behavior in order to improve the aforementioned processes [4–7].

Hydrotalcites are commonly employed as vanadium traps in petrochemistry [8]. The use of those materials aims to combine the basicity of mixed-oxides along with the acidic properties of autogenously formed vanadium species during the FCC process [9,10]. As already reported [10], there is a general interest in taking benefits from the vanadium-trapping properties of some additives, hence to use these vanadium-contaminated materials in the DeSO_x process within the FCC unit. It is well known that vanadium is a contaminant present in most crude oils, particularly in the Brazilian crudes [11,12]. It is usually considered that under the operational conditions of the FCC unit, V⁵⁺ species undergo migration into the zeolite catalyst [13], thus turning out important the understanding of vanadium location, to prevent the deleterious effect of vanadium into the FCC catalysts. Furthermore, it would be desirable (if possible) to simultaneously achieve the following two goals: *to control the vanadium contamination* (by providing a vanadium trap) and *to improve SO_x mitigation* (by the catalyst

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