Structure and Performance of New TiO_2 and TiO_2-Al_2O_3 Materials as V traps in FCC

Iván Alonso Santos-López[1], Brent E. Handy[1]*, María Guadalupe Cárdenas-Galindo[1], Ma. Rosario Morales-Armenta[1], Roberto García de León[2]
[1]*CIEP/Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. Manuel Nava #6, Zona Universitaria, San Luis Potosí, SLP 78210 (México)*
[2]*Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas #152, Col. San Bartolo Atepehuacán, Delg. Gustavo Madero, México, DF 07730 (México).*
*handy@uaslp.mx

Introduction

Metal levels on equilibrium fluidized cracking catalysts (FCC) have been increasing throughout the years. The catalytic performance of the ultra stable Y zeolite used as catalyst in the fluid catalytic cracking (FCC) process is seriously affected by metal contaminants, such as vanadium or nickel, appearing in crude oil as organic complexes. These organic species, mostly porphyrins, are deposited on the catalytic surface and V oxide compounds are formed. The so called V traps used in a diluted form in the catalyst inventory separate particulate phase can scavenge and immobilize vanadium species thus preventing major catalyst deactivation. It has been shown that boehmite which is commonly used as a matrix active component in FCC catalyst has a passivating effect on vanadium. The use of the anatase phase of titania as the active phase of vanadium traps has also been reported. Similar to the materials used as V trapping agents, both alumina and anatase have basic properties. Moreover, anatase, alumina basicity has been observed to increase upon reduction under hydrogen [1].

Titanium dioxide (TiO_2) is an exceptional material of which both nanoscale tubes and wires have been claimed to have been synthesized, having many important applications in areas such as environmental purification, photocatalysts, gas sensors, and high efficiency solar cell. Research on TiO_2 includes nanoparticles thin film, and mesoporous TiO_2 [2]. Among the different chemical methods available for titania nanotubes (NT) fabrication, a method introduced by Kasuga et al, received much attention for producing thin-walled nanotubes [3].

In previous work with TiO_2-Al_2O_3 traps we found good performance through use of a grafting procedure to obtain highly-dispersed titania on alumina. In this work, we report on further studies with Ti-grafted traps and also on the structure and performance of NT-based traps.

Materials and Methods

TiO_2-Al_2O_3 Synthesis. Three mixed oxide traps were prepared as follows. Alumina (denoted AS, 340 m^2/g) was prepared by a sol-gel process [5]. A portion of this gel, calcined form, was grafted with Ti(IV) isopropoxide(TG1AS). Another mixed oxide (TG1AC) was prepared by Ti grafting onto a commercial alumina (Degussa, 100 m^2/g).

NT Synthesis. The precursor used for nanotube production was a commercial TiO_2 (P25, Degussa AG). A first production of NT were synthesized according to [4]. Typically, 2 g of P25 was added to 100 mL of 10 M NaOH, and the mixture was refluxed for 60 h at 118 °C. In a second preparation, the fresh reaction mixture was treated in a Teflon-lined autoclave at 120°C for 60 h. Material characterization employed the following techniques: X-ray diffraction, transmission electron microscopy, N_2 adsorption at 77 K. Standard MAT protocol was used to evaluate trap performance (ASTM D-3907-87).

Results and Discussion

Textural studies of a NT synthesized by method (a.) are shown in Fig. 1. TEM confirms the morphology of 6 nm diameter fibers, formed from titania sheets. Physisorption data and analysis give a surface area of 300 m^2/g from entirely mesoporous structure, and the diffractogram indicates poorly crystalline anatase. This and similar NT's are being tested as V trap additives using the protocols as with the existing TiO_2-Al_2O_3 preparations.

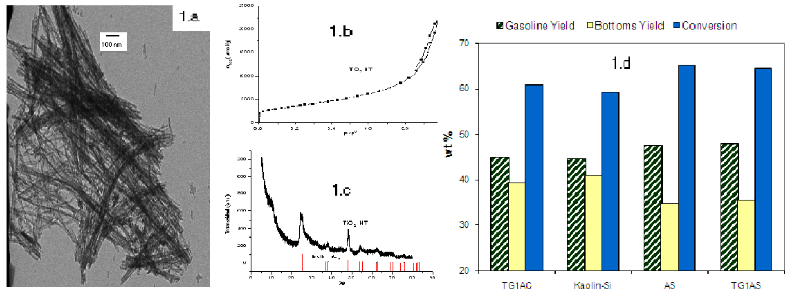

Figure 1. Textural analysis of TiO_2 nanotubes and MAT results.

Trap performance for several preparations is also shown in Fig. 1, the Kaolin-silica serving as a trap-free reference. The highest conversions are registered with AS and TG1AS, perhaps a result of their superior vanadium trapping efficiency. Slightly higher gasoline and bottoms yields were obtained with TG1AS, however dry gas and coke yields (not shown)were lower. Factors such as accessible surface area and Ti content are involved here. The TG1AC has Ti grafted onto a lower area alumina, and shows performance similar to the trap-free reference.

Significance

V trap additives are an essential ingredient for maintaining FCC performance in the face of increased bottoms processing. The grafting technique serves to enhance trap performance. Also, new trap additives based on NT materials present advantages that may lead to better performing traps.

References

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