TiO_2-Al_2O_3 FCC Traps: Characterization and V Mobility Testing

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Introduction

Vanadium contaminants in heavy distillation residues are responsible for the accelerated destruction of the faujasite structure in FCC catalysts. Traditionally, transition metal levels in the equilibrium FCC catalyst have been kept tolerable by removing resids from the gasoil feedstock, yet in the interest of increasing gasoline yields per barrel of crude, and as low sulphur crude stocks are becoming depleted, it has become necessary to include increasing amounts of resid in the FCC feed. This issue is of particular importance to Mexico, which will rely principally on Maya and other crude feedstocks that contain amongst the highest contents of sulfur and metals content of any feedstock available [1].

The principal strategy of preventing vanadium poisoning of the FCC catalyst is to retard or prevent vanadium species from entering the zeolite pores by adding a refractory ingredient, typically a spinel phase or basic oxide, that can bind strongly with the vanadium, yet not be catalytically active to adversely affect the product composition. Vanadium trap additives based on titania have been patented before [2], although details of the trapping mechanism are not well known. This work summarizes characterization work to-date on several TiO_2-Al_2O_3 trap candidates and their ability to capture vanadium under laboratory conditions with IMP catalyst FCC-51.

Materials and Methods

Several TiO_2-Al_2O_3 trap materials were prepared using the following constituents: pure anatase (A) (Sachtleben Chemie 100 m^2/g); pure rutile (R) prepared by a precipitation method [3]; hydrated aluminas (Engelland Intercat) of the phases boehmite (C), gibbsite (G), and bayerite (B). Mixed titania-alumina supports of 1:1 weight ratio were prepared by mechanically dispersing equal amounts of one of the pure titania phases (A or R) with one of three commercial alumina phases [4]. Another support was prepared by grafting, using titanium isopropoxide dissolved in toluene on Al_2O_3 (Degussa 100 m^2/g) (labeled TgAl). Vanadium was impregnated to 3-4 wt% by the incipient wetness method, using a solution of ammonium metavanadato-oxalic acid (1:2).

Previous characterization work [4] was supplemented with studies to evaluate V / TiO_2-Al_2O_3 acidity, using IR and microcalorimetry, as well as olefin / CO_2 selectivity with the oxidative dehydrogenation of n-butane (ODH). Work is in progress to evaluate trap efficiency, by encapsulating trap material in a clay matrix and using dual-particle catalyst-trap mixtures in a fluidized bed steaming experiments [5].

Results and Discussion

Results from infrared spectroscopy and ammonia adsorption calorimetry show clearly that vanadia supported on the TiO_2-Al_2O_3 traps is acidic, either from the vanadia or from the inherent properties of the traps. Pyridine adsorption shows that the acidity is of the Lewis type in all traps except for the alumina prepared by Ti grafting, which has some Brønsted acidity. IR studies of the first overtone of V=O groups in the Ti grafted trap (TgAl) also showed evidence hinting at a stronger V-support interaction than in some of the other trap candidates. Ammonia calorimetry showed initial heats of adsorption as high as 200 kJ/mol (V / AB, V / AG, V / RB, V / RG) and 175 kJ/mol in V / AC and V / RC. In V / A and V / R, however, NH_3 heats and coverage levels were significantly lower, with initial heat values of 80-120 kJ/mol. In general, there was a greater density of 90-125 kJ/mol sites in rutile-alumina traps vs. anatase-alumina traps.

Activity/selectivity studies of V-impregnated trap materials for the ODH reaction demonstrate the acidic character of V / TiO_2-Al_2O_3, in that selectivity to CO_2 is 50%, as expected for this reaction under the reaction conditions used (450°C, HC / O_2 = 1.8, conv. = 15-20%). For instance, in V catalysts of basic character, total oxidation selectivity is considerably lower [6]. Butadiene selectivity was highest (52%) in the case of V / A, whereas on V / RC and V / AC the selectivities were 32 and 37%, respectively. Lower butadiene selectivities imply less accessibility of oxygen for oxidation reactions. The re-oxidation heats for V / RC and V / A were found [4] to be lower than in the other samples, supporting this notion. The higher total oxidation selectivity in V / RC could be attributed to the stronger acidity available in this sample vs. in V / A. Trap efficiency experiments, still in progress, will compare results with the acidic, basic, and redox properties of these trap materials.

Significance

An attempt is being made to correlate acid, basic, and redox properties to V trap efficiency in TiO_2-Al_2O_3 traps, due to the different regenerating conditions existing in the FCC unit, and the interrelationship between trap efficiency and vanadium-trap interaction.

References

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