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Reducibility, heats of re-oxidation, and structure of vanadia supported on TiO_2 and TiO_2–Al_2O_3 supports used as vanadium traps in FCC

Silvia Martínez [a], Rosario Morales [a], Maria Guadalupe Cárdenas-Galindo [a], A. Gabriel Rodríguez [b], Francisco Pedraza [c], Brent E. Handy [a,*]

[a] CIEP/Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. Manuel Nava #6, Zona Universitaria, CP 78210 San Luis Potosí, SLP Mexico, Mexico
[b] Instituto de Investigaciones en Comunicaciones y Opticas, Universidad Autónoma de San Luis Potosí, Av. Karakorum #1470, CP 78216 San Luis Potosí, SLP Mexico, Mexico
[c] Instituto Mexicano del Petróleo, Eje Centrale Lázaro Cárdenas #152, Col. San Bartolo Atepehuacán, Delg. Gustavo I. Madero, México DF 07730, Mexico

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Abstract

V/TiO_2 and V/TiO_2–Al_2O_3 (1:1 w/w basis) supports were characterized by TPR, Raman spectroscopy, and heats of re-oxidation of samples pre-reduced in CO at 770 K with a heat-flow calorimeter. Supports were pure anatase or rutile dispersed with hydrated aluminas (boehmite, gibbsite, bayerite) subsequently calcined at 870 K. Raman spectroscopy of fully oxidized, air-exposed samples show the presence of polymeric polyvanadate species, but not of isolated monomeric species. Sample loadings were 4 wt.% and show different reduction and structural features. During TPR, vanadia reduced to V(III) and V(IV) in V/rutile and V/anatase, respectively, and multiple reduction peaks were observed due to crystalline V_2O_5 and amorphous vanadia. In V/TiO_2–Al_2O_3 samples, vanadium coverages were 6–8 μmol V m^{-2} yielding well-dispersed, amorphous vanadia. Trends observed during TPR were: addition of bayerite phase to anatase or rutile increases H_2 consumption by 100%, implying formation of V(III) and V(II), respectively. However, with addition of boehmite or gibbsite to either titania phase, vanadia reduces only to V(IV). Oxygen doses at 473 K of pre-reduced samples titrated about one-third of total vanadia content. Re-oxidation heat values range from 400 to 500 kJ mol^{-1} O_2 and represent oxygen–vanadium ion bond strengths within the dispersed vanadia. The heat values are higher than expected for re-oxidation of a bulk phase, and are indicative of the degree of stabilization provided by the support.

Keywords: Calorimetry; TPR; Vanadia; Titania; Alumina; Titania–alumina

1. Introduction

Vanadium is a common metal contaminant of heavy distillation residues that poisons the catalytically important zeolite component of the FCC catalyst by entering its micropores and accelerating the dealumination and destruction of the faujasite structure. The poisoning mechanism involves the reaction of vanadium oxidic species with high temperature steam during the regeneration stage during FCC, forming vanadic acid that attacks the aluminum and silicon sites within the faujasite framework [1]. Traditionally, transition metal levels in the equlibrium 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 sulfur 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

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[*] Corresponding author. Tel.: +52 444 826 2440; fax: +52 444 826 2372.
E-mail address: handy@uaslp.mx (B.E. Handy).

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rely principally on the Maya crude oil deposits for its energy needs in the coming decades. The Maya crude feedstock [2] unfortunately contains among the highest contents of sulfur and metals content of any feedstock available. The principal strategy of preventing vanadium poisoning of the FCC catalyst, as noted in the recent patent literature [3], 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. The immobilization of vanadium may be due to the formation of stoichiometric or non-stoichiometric mixed metal oxide phases or solid solutions, whose exact composition may depend on a number of factors, such as metal concentrations, support synthesis, thermal pre-treatments, the presence of stabilizing anions. The objective of this work was to probe the redox properties of vanadia supported on several V-traps prepared from titania and titania–alumina, and hopefully gain more insight into the V-support interaction operative on these materials.

2. Experimental

2.1. Sample preparation

The titania supports used were either pure anatase (A) phase (Sachtleben Chemie, 100 $m^2 g^{-1}$) or a pure rutile (R) phase, prepared by a precipitation method reported previously [4]. Mixed titania–alumina supports were prepared by mechanically dispersing equal amounts (weight basis) of pure titania (A or R) with one of three commercial, hydrated aluminas (Engelland Intercat) of the phases boehmite, gibbsite, and bayerite, identified here as C, G, and B, respectively. Prior to mixing with the titania component, a portion (20%) of the alumina component was peptized to impart mechanical resistance to the resulting particles. The peptization procedure employed was similar to that described by Magee and Mitchell [5], dispersing the 20% alumina portion in 1 N HNO_3. The remaining 80% portion was mechanically mixed with the titania component and then gradually added to the peptidized solution, after which the temperature was raised to 343 K and held under constant agitation until the water evaporated completely. The sample was further dried at 373 K for 4 h and calcined by heating at 4 K min^{-1} to 870 K over an additional 4-h period. Powder X-ray diffraction analysis of all calcined samples show that in all samples the alumina component formed γ-alumina crystallites, and that the crystal structure of the starting titania component was retained. The BET surface areas of the mixed oxides ranged from 92 to 116 $m^2 g^{-1}$. Vanadium-impregnated samples of ca. 3 wt.% loading were prepared by the incipient wetness method, using a solution of ammonium metavanadate–oxalic acid (1:2 ratio). The samples were dried for 5 h at 423 K and then calcined at 770–813 K for 4 h. Vanadium content and surface area data are summarized in Table 1.

2.2. Characterization

Temperature-programmed reduction experiments were conducted using a 4 mm i.d. quartz reactor tube, with exit stream connected to a Chrompak MicroGC capable of analyzing gas concentrations within intervals of 30 s. Sample size was 0.1 g in each case, and each run was performed at a heating rate of 10 K min^{-1} in 5% H_2/Ar flowed at 100 $cm^3 min^{-1}$. Prior to TPR, samples were pre-oxidized in pure oxygen at 100 $cm^3 min^{-1}$ for 30 min at 870 K and cooled under oxygen flow to room temperature, after which the gas was switched to the reducing gas. Heats of re-oxidation of pre-reduced samples were obtained using a homemade Tian–Calvet calorimeter system similar to that described elsewhere [6]. In brief, this instrument consisted of four components: (i) a calorimeter unit, consisting of two custom-designed heat-flux transducers (ITI Co., Del Mar, CA, USA) within a stainless steel heat sink capable of being heated and maintained to 473 K; (ii) stainless steel dosing section equipped with two capacitance manometers (MKS Instruments, Billerica, MA, USA) for measuring dosing and equilibration pressures; (iii) oil diffusion pump system backed by mechanic pump and capable of maintaining the system at 10^{-4} Pa under dynamic pumping; (iv) high purity dosing and treatment gas storage system consisting of 5-l spheres with glass high vacuum stopcocks. Helium, hydrogen, and carbon monoxide were purified by flowing through copper turnings trap heated to 548 K followed by activated 5 A MS trap maintained at 196 K. Quartz sample cells (20 mm o.d., 20 mm height) were loaded with ca. 0.5 g finely ground sample powder. The sample was pre-reduced by heating under vacuum (10^{-3} Pa) to 770 K and then exposing the sample to several 0.67 kPa doses of hydrogen or carbon monoxide, evacuating the cell after 5 min of exposure to each dose, and then exposing the sample to one 33 kPa dose for 30 min, after which the sample was evacuated, allowed to cool, and inserted in the calorimeter unit to stabilize at 473 K. Heats of re-oxidation were performed at 473 K with small doses (0.2–1 kPa) of oxygen, introduced in succession, until the heat response was too small to measure. Equilibration times between doses were 30–45 min. Heat-flow signals were amplified and recorded by computer using data-acquisition software (LABVIEW) and quantified by previous calibration with a powdered sample of known heat yield. Gas consumption for each dose was determined as the difference between initial and final amounts of gas present in dosing section (20 cm^3) and cell headspace (25 cm^3), the latter of which was determined at the end of each run using helium. Differential heat plots were formed by dividing the specific heat yield per dose by the amount of gas consumed in each dose. Laser Raman spectroscopy was performed using a Jobin–Yvon T6400 spectrometer equipped with a triple-pass monochromator, CCD detector, and a laser excitation wavelength of 514.5 nm. The illumination area was 10 μm, and spectra were collected with three scans over a 60 s period at a resolution of 0.5 cm^{-1}.