Electronic Supplementary Material (ESI) for Energy & Environmental Science
This journal is © The Royal Society of Chemistry 2011

Novel SOx removal catalysts for the FCC process: Manufacture method, characterization, and pilot-scale testing

Jaime S. Valente and Roberto Quintana-Solorzano*

jsanchez@imp.mx; sanchezvalente@yahoo.com

Electronic Supplementary Information

1. Synthesis procedure

ReSOx-PC: 62.2 g of acetic acid (85 wt.%) are dissolved in 1.92 L of bidistilled H_2O. Then, 376.84 g of MgO (Peñoles, 96.57%) are added and the mixture is stirred at 500 rpm for 1 h (A). Separately, 364.33 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Fermont, 98.5%) as well as 377.69 g of cerium nitrate solution (22.77 wt% Ce) are dissolved in 4.83 L of water. Once the iron nitrate is dissolved, 154.69 g of HiQ-31 boehmite (Engelhard, 99.89%) are added and the resulting mixture is stirred at 500 rpm for 1 h (B). The gel product (B) is mixed with the product (A). Temperature is maintained at 373 K and the mixture is stirred at 500 rpm while it is passed through an in-line high shear mixer for 3 h. The produced slurry is then spray dried with hot air at 673 K and a feed pressure of 120 psi in order to evaporate the aqueous phase. The microsphere particles obtained by spray drying are finally calcined at 1005 K for 4 h.

ReSOx-FC: 62.2 g of acetic acid (85 wt.%) are dissolved in 1.92 L of bidistilled H_2O. Then 383.24 g of MgO are added and stirred at 500 rpm for 1 h (A). 182.16 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Fermont, 98.5%) together with 219.58 g of cerium nitrate solution (22.77 wt.% Ce) are dissolved separately in 4.8 L of water. Once the iron nitrate is dissolved, 197.61 g of HiQ-31 boehmite (Engelhard, 99.89%) are added and the mixture is stirred at 500 rpm for 1 h (B). The gel product (B) is mixed with the product (A). Temperature is maintained at 373 K and the mixture is stirred at 500 rpm while it is passed through an in-line high shear mixer for 3 h. The slurry is subsequently spray dried with hot air at 673 K

This journal is © The Royal Society of Chemistry 2011

and a feed pressure of 120 psi. The spray dried microspheres are finally calcined at 1005 K for 4 h.

2. Characterization techniques

Chemical composition was determined in a Siemens X-Ray Spectrometer SRS 3000.

Surface areas of the calcined samples were obtained from the N2 physisorption isotherms determined at 77 K on a Quantachrome Autosorb-1C equipment. Surface areas were calculated by using BET equation. Prior to N2 adsorption, samples were outgassed at 623 K overnight.

Powder X-Ray Diffraction (XRD) was carried out in a Siemens D-500 diffractometer, equipped with a CuKα radiation source (1.5406 Å), operating at 35 kV and 25 mA, in the 2θ range from 4 to 70°, with a 0.03º step size. The average crystal size was calculated from indicated reflections according to the Debye-Scherrer equation, $L = K\lambda [B(\theta) \cos(\theta)]^{-1}$; where L represents the average crystal size, K the shape factor, λ the radiation wavelength, B(θ) the full width at half maximum (FWHM) and θ the diffraction angle.

Scanning electron microscopy (SEM) was carried out in a Phillips XL 30 environmental SEM. The chemical composition and bidimensional spatial distribution was examined by X-ray Mapping using an Energy-Dispersive X-ray Spectrometer (EDS) device attached to the microscope. In order for the EDS analysis to be carried out, microspheres were embedded in a carbon film.

3. Main catalyst

For testing the catalytic performance of ReSOx-PC, ReSOx-FC and SOx-COM catalysts in the pilot plant, they were blended with a conventional cracking catalyst. A RE-USY equilibrium catalyst (E-CAT), obtained from a refinery in Mexico, was used as main catalyst. An E-CAT actually corresponds to a mixture of various catalyst particles with a set of average properties. During a typical operation, periodically, fresh catalyst is added and spent catalyst is removed from the inventory, in order to maintain the feed conversion level. The physicochemical properties of the E-CAT employed are: particle size: 60-200 μm sieve, MAT activity = 69, total specific surface area = 140 m^2/g, unit cell size = 2.433

This journal is © The Royal Society of Chemistry 2011

nm, pore volume = 0.15 cm^3/g, average bulk density (ABD) = 0.88 g/cm^3, Ni = 424 ppm_w, V = 1425 ppm_w, and N a= 2102 ppm_w.

4. Analysis of flue gas and cracked products

The combustion gases out of the regenerator of the pilot unit were analyzed on-line by using California Analytical Instruments analyzers. CO_2, CO and SO_2 were analyzed via infrared detectors, O_2 via paramagnetics and NOx by chemiluminescence. Since a direct measurement of SO_3 is difficult, experimental SOx emissions essentially correspond to SO_2.

The composition of the riser effluent, which is required to accomplish the mass balances, was analyzed by gas chromatography. Beforehand, the cracked products leaving the riser of the pilot were separated into a gaseous and a liquid fraction in a stabilizer column operated at a temperature lower than 261 K. The gaseous fraction is composed of hydrogen, H_2S, C_1 to C_4 hydrocarbons and a small amount of non-condensed gasoline (mainly C_5-C_6). This was analyzed on-line in a HP-6890 GC equipped with FID and TCD detectors and a proper columns array, via the UOP-539 method. The liquid fraction consists of gasoline, light cyclic oil (LCO) and heavy cyclic oil (HCO); it was analyzed in a HP-6890 GC with a FID detector in accordance with ASTM-D-2887 method for simulated distillation.

In order to accomplish a full mass balance, gaseous and liquid products were accumulated and quantified for a specific period of time. The amount of coke deposited on the catalyst that is required to close the mass balance was indirectly quantified from the flow rate of the combustion gases. Mass recovery ranged between 98 and 101 wt%.