Recycling of Spent FCC Catalyst to Zeolite ZSM-5

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Abstract

To date Fluid Catalytic Cracking (FCC) is one of the most important petrochemical processes. Over 400 operating units all over the world handle more than 20 million barrels of oil per day resulting in approximately 2300 tons of spent catalyst each day, which is mainly disposed of in landfills or used as cement additive. During commercial recycling the main focus lies on leaching of high-priced rare earth elements (REE), that make up just 1-3 wt.-% of the entire catalyst. Recent literature showed that conversion of the catalyst residues into zeolites A, X and Y could be performed. As ZSM-5 has a higher economic value compared to zeolites A, X and Y, the aim of this work is to convert the residues from spent FCC catalyst after leaching of REE into a competitive ZSM-5 product, and thus, avoid landfilling.

The methods used include a leaching with HNO_3 to remove all REE such as La, solvothermal leaching with HCl to remove large amounts of Al and impurities like Fe, Ni and V and a final leaching with H_2SO_4 to remove Ti. The solid residues were activated with sodium hydroxide after the leaching steps to finally end-up with a subsequent synthesis of ZSM-5. As a highlight, this method does not require additional aluminium or silicon sources. A variation of the leaching time with sulphuric acid revealed the importance of titanium removal regarding crystallinity, surface area, acidity, hydrocarbon cracking properties and particle size. The synthesized ZSM-5 samples, on the one hand, demonstrate comparable properties to a commercial reference and, on the other hand, this strategy enhances the final re-use of spent FCC catalyst from 3 wt.-% up to 39 wt.-%.

To further improve the recycling procedure, spray drying of ZSM-5 has been performed to directly reuse the catalyst as an additive for increasing the yield of light olefins in the product stream of FCC process. The optimal spray drying formulation regarding selectivity and conversion was shown to be a mixture of ZSM-5 as active component, kaolin as filler and a combined mixture of aluminiumphosphates and silica as binder.

The aluminium-rich solution from the second leaching step with hydrochloric acid can act as raw material to synthesize the aluminiumphosphate binder to reduce costs and decrease the waste stream with a re-use up to 88 wt.-%. Finally, recycling of side-streams of base and acid show potential to end-up with a re-use of up to 97 wt.-% of spent FCC catalyst.