

New Development of De-NO_x SCR Catalyst Using Spent Petroleum Catalyst

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Summary

This study represents the feasibility of an alternative De-NO_x SCR catalyst using spent petroleum catalyst, a by-product of heavy oil upgrading facilities of an oil refinery, and introduces the pretreatment technology of spent petroleum catalyst to make useful sulfide alumina-vanadium oxide based catalyst body as an advanced raw material. And also, this new development focuses not only on the benefits of recycling the useful catalyst metals in lieu of waste disposal by land-filling, but also on environmental friendliness in consideration of the strict environmental management with 3R campaign; Reduce, Reuse, and Recycle, and cost-effective new production in SCR application.

SCR catalyst demonstrated in this study consists of two major components, a) sulfide alumina as a bulk phase and vanadium oxide as well as molybdenum from spent catalyst, b) commercially available TiO₂ in the anatase form impregnated with ammonium meta-tungstate (WO₃) as high surface area carrier to support the active components. The significant features of this new development are to remain high catalytic activity for longer periods of time due to the characteristic of catalyst's excellent durability, and substantially keeps better poison resistance to sulfur oxides compared to the commercially available SCR products. The activity test and poison resistance to sulfur oxides has been performed under various operating conditions, and it exhibits NO_x conversion efficiency as high as 90% or more at wide range of operation temperature. The summary of this particular pretreatment method and result of catalytic activity test is described as follows;

Pretreatment and Reactivity of "Spent Petroleum Catalyst"

After remove the impurities and/or unnecessary metals by way of heating and water washing, the pre-treated spent catalyst is reheated on the desired temperature at an elevation rate of 9°F/min by rotary kiln. The reheated pellet-typed spent catalyst are manually pulverized into a powder with a size of below 200

mesh that consists of the BET surface area of about 90~110m²/g with major diameter of pore size of about 190 ~ 230Å.

The pretreated spent catalyst mixed homogeneously with TiO₂/WO₃ to improve in NO_x removal efficiency. This mixing step gives the optimum dispersion of active metals on the mixed sulfide alumina and TiO₂ by chemical reaction to migrate metals and the bimodal pore structure by combined carriers. By means of this process, homogeneously mixed catalyst has excellent De-NO_x activity and long-term durability. The SO₂ adsorption test by thermal conductivity detector has been performed to compare poison resistance to sulfur oxide in use of alumina, zeolite, titania and a developed catalyst prepared from sample of pretreated spent catalyst. The adsorbed amounts at 320°C show in the order of alumina>zeolite>titania>pre-heated spent catalyst. From analysis of SO₂ adsorption test, the use of pre-heated spent catalyst represents two major effects, like less SO₂ to SO₃ oxidation and higher poison resistance to SO_x and other toxic substances.

Field Application of “Commercially Extruded Honeycomb SCR Catalyst”

Commercial SCR catalyst products with pulverized powder of pretreated spent catalyst are developed and available as extruded honeycomb type that is formed products yielding high efficiency of NO_x reduction at temperature window of 400 ~ 840 °F. This unique SCR catalyst manufactured has been applied in combined heat and power plant, nitric acid plant and diesel marine boilers. Through the experience of various field application for more than two years, the commercially developed SCR catalyst of using spent catalyst has been proven as an excellent activity of NO_x reduction at wide temperature window, durability for long catalyst life performance, and poison resistance to sulfur oxides.

In conclusion, this introduction of new alternative SCR catalyst using spent petroleum catalyst gives fully efficient for NO_x reduction in flue gas and must be able to treat flue gas from various combustion systems, such as coal, oil and gas fired boilers, gas turbines, diesel engines, solid waste incinerators, etc.