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In order to meet national and European targets regarding reduction of the emission of greenhouse gases, fossil fuels are gradually being substituted with biomass, such as straw, wood chips and wood pellets, in Danish combined heat and power plants. The release of inorganic elements, present in such biomass fuels, however, causes enhanced strain on the different equipment in these power plants. One of the affected units is the catalyst for selective catalytic reduction (SCR) of nitrogen oxides, which undergoes accelerated deactivation due to deposition of potassium rich particles and subsequent poisoning. The potassium poisoning of commercial vanadia based SCR catalysts have been studied for more than two decades, and a broad understanding have been obtained. However, more detailed information on the overall mechanism of deposition, reaction and transport of potassium, and its function of catalyst composition and operating conditions, is not available. The main objective of the work presented in this thesis has been to conduct an in depth investigation of the deactivation mechanism of vanadia based SCR catalysts, when subjected to potassium rich aerosols. It has furthermore been a goal to suggest and test new alkali resistant catalyst formulations, coatings and/or improved means of operation which can extend the life-time of SCR catalysts in biomass fired power plants. Plate-type V_2O_5-(WO_3)/TiO_2 SCR catalysts have been exposed to KCl and K_2SO_4 aerosols in a bench-scale reactor at 150, 300 or 350 °C for up to 600 hours. The activity of fresh and exposed catalysts was measured in the temperature range 250-400 °C in a laboratory-scale reactor. All samples exposed for more than 240 hours proved to have deactivated significantly, however, catalysts exposed at 150 °C showed higher remaining activity compared to samples exposed at 300-350 °C. This indicates that the deactivation rate increases with the exposure/operating temperature. The majority of the catalysts exposed to KCl aerosols at high temperatures had lost more than 90 % of their initial activity. Increasing the mass of the mass based KCl particle size distribution, from an aerodynamic diameter of 0.12 to 2.6 μm, showed no effect on the catalyst deactivation rate. This may be attributed to a continued presence of a significant number of ultrafine KCl particles in the flue gas. The K_2SO_4 aerosols caused a slower rate of deactivation compared to the KCl aerosols. This indicates that potassium bound in K_2SO_4 deposits, on the catalyst surface, is less mobile than that bound KCl. However, an effect of particle size on the catalyst deactivation cannot be excluded, as the obtained K_2SO_4 aerosols generally were shifted towards larger particles (mass based diameter mode: 1.3 μm) compared to the KCl aerosols. Activity measurements on the exposed catalysts indicated that WO3 promoted samples, which in general showed higher NH_3 adsorption capacities, had lost larger fractions of their initial activities compared to unpromoted ones. This is likely due to the enhanced Brønsted acidity which appears to facilitate the transport of potassium in SCR catalysts. The potassium mobility has further been studied using a new experimental protocol. This involves two-layer pellets of vanadia based SCR catalysts, where one side has been impregnated with KCl or K_2SO_4. SEM-WDS measurements on pellets heat treated at 350 °C showed that potassium bound in KCl readily left its counter ion, causing a faster transport into the undoped catalyst compared to potassium from K_2SO_4. Furthermore, only half of the sulfate bound potassium seemed to be able to leave its solid matrix. These observations are in agreement with the results from the plate exposure experiments. Likewise as indicated by the bench-scale experiments, the presence of WO_3 in the two-layer pellets appeared to facilitate the potassium transport. The potassium blocking abilities of potential coating materials have been tested using three-layer pellets. Here, layers of MgO, sepiolite, a mixture of the two, or Hollandite manganese oxide have been introduced in between the two (respectively potassium impregnated and unpromoted) catalyst layers. Pure MgO proved to be the most effective barrier of the tested candidates, and was able to retain the potassium in the impregnated side of the pellet, even after 7 days of exposure at SCR conditions. Partial or full potassium penetration of layers of the other tested materials was observed. Half-length monoliths have been exposed to KCl aerosols in the bench-scale setup at 350 °C for up to 1100 hours, and their activities were followed by in situ measurements. A 3%V_2O_5-7%WO_3/TiO_2 reference catalyst deactivated with a rate of 0.91 %/day during 960 hours of exposure, and a subsequent SEM-EDS analysis showed complete potassium penetration of the catalyst wall with average K/V molar ratios of 0.38-0.51. During 1100 hours of exposure, a similar monolith coated with 8.06 wt.% MgO deactivated with a rate of 0.24 %/day, relative to the fresh activity of the reference, but showed a 42 % lower start activity due to enhanced transport limitations. The MgO coat proved to have protected the SCR catalyst against potassium poisoning, however, SEM-EDS analysis showed that some potassium had penetrated the coat. The SEM analysis also indicated that the MgO coat was rather fragile and adhered weakly to the catalyst substrate, indicating the need for a binder material. A catalyst coated with a 1:1 mixture of MgO and TiO_2 showed insufficient start activity (30 % of that of the reference) when tested in the bench-scale setup, likely due to a low porosity of the coat. A deactivation model describing the potassium poisoning of an SCR monolith catalyst has been derived. The model accounts for deposition and consumption of potassium rich particles on the external catalyst surface, the build-up of potassium, bound to Brønsted acid sites, throughout the catalyst wall, and the resulting loss in SCR activity. Simulations show that the particle deposition rate, and hence the deactivation rate, decreases if the particle size of the incoming aerosol is increased. The results obtained in this work indicate that the life-time of SCR catalysts used in biomass fired power plants can be improved by ensuring a high conversion of KCl to K_2SO_4 aerosols, by reducing the operating temperature, and by increasing the size of the incoming, potassium rich aerosol particles to above 200 nm. While it may not be mechanically durable in its current state of development, applying an MgO coat to the SCR catalyst will also protect it against potassium poisoning.

General information

State: Published
Organisations: Department of Chemical and Biochemical Engineering, CHEC Research Centre
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Number of pages: 140
Publication date: 2015