Nitrogen Chemistry in Fluidized Bed Combustion of Coal

The present Ph.D thesis describes an experimental and theoretical investigation of the formation and destruction of nitrogen oxides (NOx and N2O) in fluidized bed combustion (FBC) of coal. A review of the current knowledge of nitrogen chemistry in FBC is presented. The review covers both laboratory studies and pilot and full-scale observations. In the experimental part of the work, the heterogeneous oxidation of HCN catalyzed by two Danish limestones was investigated in a fixed bed laboratory reactor to establish how the reduction of the SO2 emission by addition of limestone to FBC influences the emission of NO and N2O. The results show that calcined limestone is an excellent catalyst for oxidation of HCN. The selectivity for the formation of NO is high, 50 to 70 % at typical FBC temperatures and concentrations. On the other hand the selectivity for the formation of N2O is very low, typically less than 5 %. Under conditions with high HCN concentrations at low O2 concentrations or at low temperatures, the selectivity for the formation of N2O is significantly higher, whereas the selectivity for NO formation is lower than it is under high temperature-high O2 conditions. Furthermore, HCN may react with CaO forming CaCN2. Separate experiments with oxidation of CaCN2 showed that the selectivity for the formation of N2O was 20 to 25 %. The selectivity for the formation of NO was similar. These results indicate that simultaneous formation and oxidation of CaCN2 leads to the high selectivity for N2O observed under conditions where CaCN2 is formed. It was also found that the presence of NO enhanced the formation of N2O while NO was reduced. A preliminary reaction mechanism and mathematical model, considering the simultaneous catalytic oxidation of HCN and the formation and oxidation of CaCN2, was proposed and compared to experimental data. The agreement between model and experimental data was fair. Experiments were also conducted with simultaneous oxidation of HCN and sulphation of seven different types of limestone. The catalytic activity of the limestones decreases to a non-zero level with an increasing degree of sulphation. The selectivity for NO decreases with an increasing degree of sulphation of the limestone, but the N2O selectivity increases. The N2O selectivity by HCN oxidation over sulphated limestone is higher in the presence of NO. Furthermore, the catalytic activity decreases with an increasing inlet concentration of SO2. In the absence of O2 and SO2, CaSO4 decomposes to CaO and CaS in the presence of HCN. The results indicate that HCN is oxidized on two different types of site on the sulphated limestone. On one site there is competition between SO2 and HCN which results in the dependence of the catalytic activity on the SO2 concentration. It is possible that these sites are CaO, formed by decomposition of CaSO4 even in the presence of O2. These results partly explain the frequent observation that limestone addition to fluidized bed combustors results in a higher NO emission and a lower N2O emission. When limestone is added, the oxidation path for HCN changes from homogeneous oxidation with a high selectivity for N2O and a low selectivity for NO to a heterogeneous oxidation path over the limestone with a high NO selectivity and a low N2O selectivity. A mathematical model for the emission of NOx from FBC has been developed as part of a JOULE project. The model is based on the two-phase theory of fluidization for the bed with a Kunii-Levenspiel type freeboard model and includes submodels for coal devolatilization, combustion of volatiles and char and a detailed model of NO formation and reduction by homogeneous and heterogeneous reactions. The data for the estimation of kinetics of the heterogeneous reactions were measured by one of the partners in the project for char and bed material sampled from a pressurized FBC pilot plant burning Kiveton Park coal. Experimental data from the pilot plant were used for model verification. The simulations of the NO emission during staged combustion and NH3 injection for NO reduction were in qualitative agreement with the experimental data. A parametric study of the influence of operating conditions on the conversion of fuel-N to NO showed that in most cases the trends predicted by the model are in agreement with experimental observations in the literature. The simulations gave an increased insight into how and why different operating conditions influence the NO emission. The model contains a number of parameters the values of which are subjected to some uncertainty, and a sensitivity analysis of the predicted NO emission was carried out. The analysis showed that the predicted NO emission is sensitive to both hydrodynamic and combustion-related parameters. The most important hydrodynamic parameters were the minimum fluidization velocity, the gas interchange coefficient, the bubble size and the bubble rise velocity. The most important combustion parameters were the rate of CO and CH4 combustion and the fraction of CO produced from char combustion. By using a rate of production analysis, the important reactions in the NO model were identified. Laboratory measurements showed that 50 % of the fuel-N stays in the char after devolatilization and in the model it is assumed that this is oxidized to NO during char combustion. A significant amount of NO, 10-18 % of the fuel-N, was formed by oxidation of NH3 catalyzed by bed material. The reaction between NO and CO catalyzed by bed material is the most important reaction for reduction of NO at low to intermediate temperatures. At high temperatures, the reduction of NO by char and by CO catalyzed by char and the homogeneous reduction of NO by NH3 are also important. The oxidation of NH3 to N2 catalyzed by bed material is important for a low NO formation. The catalytic oxidation of NH3 over char to NO and N2 is not important because of the low char content in the bed. The results have demonstrated that mathematical modelling is a powerful tool to gain an increased understanding of the complicated process of NO formation and reduction in fluidized bed combustion.

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