ACTIVATED CARBON FIBER SUPPORTED TRANSITION METALS FOR LOW TEMPERATURE SELECTIVE CATALYTIC REDUCTION (SCR) OF NO.

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INTRODUCTION

Ever stricter emissions legislation has made selective catalytic reduction (SCR) of nitric oxide by ammonia an important technology for stationary combustion plant operators. Current commercial SCR systems operate at 300-450°C, necessitating their placement in the flue upstream from both sulphur and particulate extraction systems, which results in rapid poisoning of the catalyst. A catalyst capable of efficient NO_x reduction at <250°C, which can be retrofitted, downstream, in existing combustion systems, would offer an ideal solution. Some active carbons[1,2] or transition metal species[3-5] supported on active carbons exhibit this capability. Whilst previous systems have employed active carbon granules, activated carbon fibres (ACF) with diameters of *ca.* 10μm offer potentially higher SCR efficiencies, owing to their much more favourable mass transfer characteristics. This work investigates the effect of the different loading methods employed during metal impregnation of the ACF and the effect on subsequent SCR efficiency of the catalyst. Investigation of the ambient temperature NO reduction, also observed by other workers[6,7], has also been carried out.

EXPERIMENTAL

Enhanced catalytic activity is reported[8] for acid pre-treated carbon. Thus, active carbon fibre A-15 (*ex* Osaka Gas Co Ltd) was surface-oxidised by treatment with nitric acid for 1 hour at 75°C (1ox75N), then rinsed and dried. The acid treated ACF was then subjected to TPD and the BET surface area was measured both before, and again after, the TPD in order to establish whether there was any recovery of the surface area. ACF supported iron catalysts were then produced using either ion exchange (IE), incipient wetness (IW) or excess solution (XS) impregnation of iron (II) nitrate salt solution followed by calcination under N_2, using a horizontal tube furnace, at 300°C for two hours. The catalytic activity of the metal loaded ACF's was then tested in a plug-flow micro-reactor, i.d. 13mm, using on-line FTIR (Perkin-Elmer 1750 Infrared Fourier Transform Spectrometer) analysis of feed and flue gases. The experimental conditions were 800ppm NO, 800ppm NH_3 and 1 vol.% O_2 with He carrier and the total flow rate was 100ml min^{-1}. The temperature range studied was 25°C to 270°C. At ambient temperature the flue gases were also analysed using on-line GC/HID to establish the production of N_2. The production of N_2 at levels above the background would indicate that SCR is taking place at room temperature. This would confirm that there are two separate mechanisms at work within the catalyst, as has been postulated elsewhere[7].

RESULTS AND DISCUSSION

Nitric acid treatment of the ACF led to an irreversible loss of surface area via erosion of the carbon, leading to a loss of microporosity and pore widening. Metal loading by IE leads to an iron load of ~1wt. %. IW loads of 0.1, 0.5, 1.0 and 5.0wt. % were produced and their SCR efficiency for nitric oxide, as measured by on-line FTIR analysis of the flue gases, showed that the 1wt.% Fe catalyst produced the largest reduction in NO within the temperature range under investigation. The results are shown in Figure 1. The results obtained corresponded well with those obtained as a result of loading IE. This would tend to indicate that the optimum metal load is achieved at a weight loading of 1%. At this loading it can be assumed that the available oxygenated active sites on the surface of

the ACF are filled, and well-dispersed metal particles, which provide the optimum catalyst surface area to the reactants, is achieved. Excess solution impregnation gives the impression that increasing the metal load has the effect of improving the performance of the catalyst. However, even at a loading of 10wt. %, the XS catalyst is less efficient than the 1wt.% IW catalyst, as shown in Figure 2. This could be ascribed to a number of factors, namely, pore blocking of the ACF by the deposited metal, so that the reactant gases cannot gain access to the pores of the ACF. Agglomeration of the metal species leading to a loss of relative surface area available to the reactants, and, sintering of the metal particles which are chemisorbed at the acid sites (carboxyls, phenols) created during the acid pre-treatment of the ACF.

CONCLUSIONS

Nitric acid treatment of ACF results in a reduction in available surface area. The surface area appears to be lost *via* erosion of ACF microporosity rather than by pore blocking. Oxygen surface sites formed during acid pre-treatment, in particular the acidic carboxyls and phenols, facilitate iron loading of ~1wt. % by ion exchange. This weight loading is also the most efficient for SCR of NO when loading occurs by incipient wetness impregnation, leading to the conclusion that metal dispersion is optimised under these conditions. Although there is an increase in the SCR activity of the catalysts prepared by excess solution impregnation when increasing the metal load, the efficiency of these catalysts is poor and does not match the performance of the 1wt. % incipient wetness catalyst. This is probably due to pore

blocking and poor metal dispersion within the pore structure of the ACF, resulting in a low catalyst surface area available to the reactants at higher weight loading when using the excess solution method of impregnation. This, in turn, leads to reduced catalytic performance of the high metal load catalysts prepared in this way.

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Figure 1. The effect of varying metal loading on SCR efficiency of Fe/ACF catalysts prepared by incipient wetness impregnation
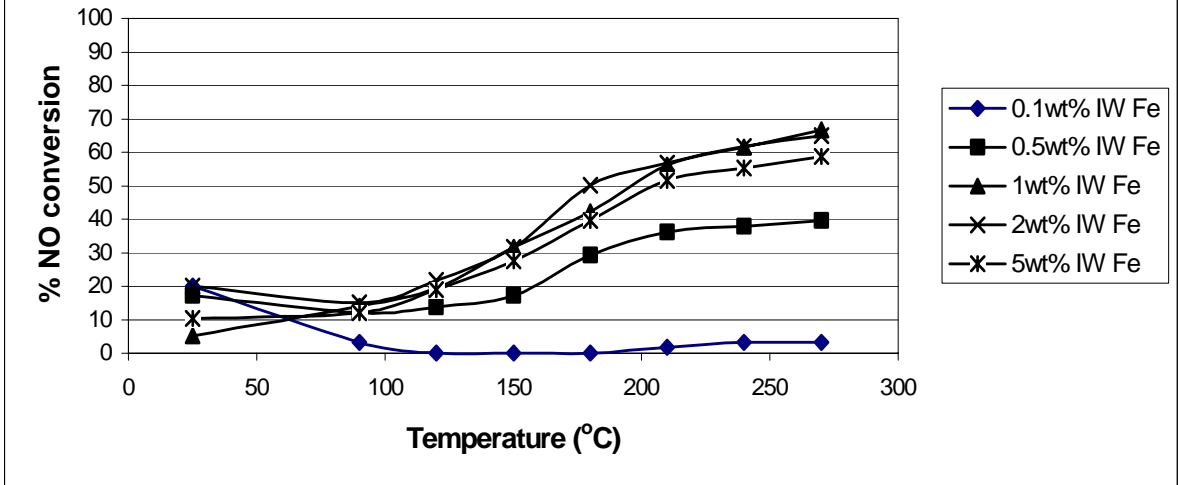

Figure 2. The effect of loading method on SCR efficiency of some iron loaded catalysts.