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An investigation of the thermal stability and sulphur tolerance of Ag/γ-Al_2O_3 catalysts for the SCR of NO_x with hydrocarbons and hydrogen

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Abstract

The sulphur tolerance and thermal stability of a 2 wt% Ag/γ-Al_2O_3 catalyst was investigated for the H_2-promoted SCR of NO_x with octane and toluene. The aged catalyst was characterised by XRD and EXAFS analysis. It was found that the effect of ageing was a function of the gas mix and temperature of ageing. At high temperatures (800 °C) the catalyst deactivated regardless of the reaction mix. EXAFS analysis showed that this was associated with the Ag particles on the surface of the catalyst becoming more ordered. At 600 and 700 °C, the deactivating effect of ageing was much less pronounced for the catalyst in the H_2-promoted octane-SCR reaction and ageing at 600 °C resulted in an enhancement in activity for the reaction in the absence of H_2. For the toluene + H_2-SCR reaction the catalyst deactivated at each ageing temperature. The effect of addition of low levels of sulphur (1 ppm SO_2) to the feed was very much dependent on the reaction temperature. There was little deactivation of the catalyst at low temperatures ($\leq$235 °C), severe deactivation at intermediate temperatures (305 and 400 °C) and activation of the catalyst at high temperatures ($>$500 °C). The results can be explained by the activity of the catalyst for the oxidation of SO_2 to SO_3 and the relative stability of silver and aluminium sulphates. The catalyst could be almost fully regenerated by a combination of heating and the presence of hydrogen in the regeneration mix. The catalyst could not be regenerated in the absence of hydrogen.

Keywords: SCR-NO_x; Octane; Toluene; Silver; Ag/γ-Al_2O_3; EXAFS; XRD; Sulphur tolerance; Ageing

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1. Introduction

The recent discovery that the addition of small amounts of hydrogen to the feed during the selective catalytic reduction of NO_x with hydrocarbons can greatly improve the performance of Ag/γ-Al_2O_3 catalysts [1] has given added impetus to this area of research [2–10]. Hydrogen promotes the NO_x reduction over Ag/γ-Al_2O_3 catalysts when using a range of lower alkanes and alkenes [2] and higher alkanes [8] as reductants. The 'hydrogen' effect is limited to Ag-based catalysts and is support dependent; to date, Ag/γ-Al_2O_3 and Ag/MFI [3,4] are the only two metal/support combinations that have shown marked improvement in performance upon addition of hydrogen to the feed.

These results have, for the first time, made the commercial use of Ag-based catalysts in the abatement of NO_x emissions

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from lean burn engines a real possibility. However, there are still issues to be addressed, in particular, the thermal stability of the Ag/γ-Al_2O_3 catalyst and resistance to sulphur poisoning.

The effect of SO_x on the performance of the Ag/γ-Al_2O_3 catalyst for the SCR reaction has been well documented [11–21]. The recurrent theme in many of these papers, is that SO_x is detrimental to activity at low temperatures but that at higher temperatures the effect of SO_x is minimal or may even enhance NO_x conversion. Meunier and Ross [11] found that for a 1.2 wt% Ag/γ-Al_2O_3 catalyst the activity decreased rapidly in the presence of 100 ppm SO_2 in the reaction feed. The catalyst could be partially regenerated when SO_x was removed from the stream and could be almost fully regenerated by hydrogen. The extent of regeneration was very much dependent on the temperature of regeneration. The optimum temperature for regeneration was 650 and 750 °C in 10% H_2/Ar and in the reactant stream, respectively. They found that the sulphation of Ag rather than γ-Al_2O_3 was primarily responsible for the deactivation. Abe et al. [15] noted that silver sulphate decomposes at a lower temperature (427 °C) than aluminium sulphate (727 °C). This can at least partially explain why many of the catalysts tested in the literature maintain their activity in the presence of SO_x at higher temperatures (>427 °C) but tend to be inactive at temperatures lower than this. The effect of SO_x is also very much dependent on the nature of the reductant, Angelidis et al. [19,20] noted that SO_x enhanced the activity of their 5 wt% Ag/γ-Al_2O_3 catalyst when using propene as a reductant but caused severe deactivation when propane was used. This result finds some resonance in the work of Burch et al. [22–24] who found strong deactivation of a pre-sulphated Pt/Al_2O_3 catalyst when using propane as a reductant for the SCR reaction but little negative effect when using propene. This can be explained by differences in the sites at which the reactions take place for the two reactants, for propane the reaction occurs mainly on the support and is hindered by strongly bound sulphates on the support. In contrast, when using propene as a reductant, the reaction takes place predominantly on the Pt sites which do not adsorb sulphur strongly. Although, sulphates are much more stable on Ag than Pt, Angelidis et al. [20] have invoked reactive R–SO_x species as key intermediates in the SCR reaction with propene over a Ag/Al_2O_3 catalyst.

Given that hydrogen has a dramatic effect on NO_x conversion and that this effect is most pronounced at low temperatures (where SO_x has the greatest negative effect on conversions), it is timely to investigate the effect of SO_x on a Ag/γ-Al_2O_3 catalyst for the NO_x–SCR with hydrogen and hydrocarbon. To date, studies on the effect of SO_x have not encompassed the addition of hydrogen to the feed and have used high concentrations of SO_x, ranging from 18 to 100 ppm. A recent EU directive [25] requires that ‘‘sufficient quantities of petrol and diesel fuels with a maximum sulphur content of 10 ppm are available from 1st January 2005’’. Typically 1 ppm SO_x in the exhaust is generated from a fuel containing 25 ppm of S, this effectively means that for a fuel containing 10 ppm sulphur, the level of SO_x in the exhaust will not exceed 0.4 ppm. Given that the rate of adsorption and reaction for the majority of reactions are directly dependent on the partial pressure of the reactant gas and that in many cases the rate is not linear with concentration over an extended range of concentrations, it is important to study the effect of sulphur with realistic levels of SO_x. In this study, 1 ppm SO_x was added to the feed and its effect on the reaction was studied at different temperatures.

There are marked differences in the NO_x conversion obtained for a given catalyst when using different reductants. In particular, aromatics are significant constituents of diesel and petroleum and are known to have a negative effect on NO_x conversion during the SCR reaction over Pt/γ-Al_2O_3 [26] and Co/γ-Al_2O_3 [27] catalysts. Houel et al. [21] found that using real diesel fuel rather than model alkanes and alkenes resulted in deactivation by coking of their Ag/γ-Al_2O_3 catalyst. In this study, we investigate the effect of the addition of toluene to the SCR reaction over a Ag/γ-Al_2O_3 catalyst in the absence and presence of hydrogen.

We have also investigated the thermal stability of the catalyst when exposed to temperatures as high as 800 °C under different hydrogen-containing gas mixes. Nakatsuji et al. [16] found that their $AgAlO_2/Al_2O_3$ catalyst did not deactivate when exposed to a H_2O and O_2 mix at 900 °C for 24 h, however, this is probably due to the fact that the catalyst was a stable aluminate to start with. Houel et al. [21] found that their Ag/γ-Al_2O_3 deactivated to a small extent at reaction temperatures ≥350 °C after exposure to a H_2O and air mix at a temperature of 700 °C for 72 h.

2. Experimental

2.1. Kinetic evaluation

The catalyst, provided by Johnson Matthey plc., was prepared by the impregnation of γ-Al_2O_3 with a silver nitrate solution followed by drying and calcination to give a sample with a Ag metal loading of 2 wt% [28]. Catalyst testing was performed in a quartz tubular downflow reactor (i.d. 5 mm). The sample (with particle size of 250–425 μm) was held in place between two plugs of quartz wool and a thermocouple was placed in the centre of the catalyst bed. The reactant gases, NO, CO_2, H_2, O_2, SO_2, CO and the carrier gas He were fed from independent mass flow controllers, while *n*-octane, toluene and H_2O were fed using Razel syringe pumps. All reactor lines were heated to prevent condensation. The NO and total NO_x were determined by a Signal 4000 series chemiluminescence detector. In these studies NO_x conversion is defined as the reduction of NO and NO_2 to N_2 and N_2O. Unless otherwise stated, the total gas flow and catalyst mass were 276 $cm^3\ min^{-1}$ and 0.0825 g, respectively.

Several different gas mixes were used, details of these are given in Table 1.

2.1.1. Stability tests

The stability tests consisted of an initial temperature ramp to test the activity of the catalyst, the temperature range of the ramp depended on the gas mix used. The same sample was aged in situ in the gas mix at 600, 700 or 800 °C for 16 h and then the activity test was repeated.