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A comparison of the activity and deactivation of Ag/Al_2O_3 and Cu/ZSM-5 for HC-SCR under simulated diesel exhaust emission conditions

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Abstract

The performances of two model HC-SCR catalysts, 5% Cu/ZSM-5 (Si/Al ratio of 30) and 2% Ag/Al_2O_3, are compared and contrasted under a variety of different operating conditions. We have examined the activity of these catalysts by using a wide range of hydrocarbons. The activity of the Cu/ZSM-5 catalyst is not significantly affected by the nature of the hydrocarbon species, whereas the Ag catalyst shows a strong dependence. The Ag catalyst displays poorer low-temperature activity with propene than with longer chain hydrocarbons, such as decane. The use of diesel fuel with the Ag catalyst induces deactivation at lower temperatures, because of coke deposition. The Ag catalyst is strongly deactivated by sulphur. The Cu/ZSM-5 catalyst is much more resistant to chemical deactivation. The Ag/Al_2O_3 catalyst is capable of withstanding high-temperature ageing conditions, whereas the Cu/ZSM-5 catalyst is significantly deactivated after such ageing because of a combination of Cu sintering and zeolite dealumination.

Keywords: Automotive emission control; Ag/Al_2O_3; Cu/ZSM-5; HC-SCR; NO_x

1. Introduction

The use of selective reduction of NO with hydrocarbons (HC-SCR) to reduce NO_x from diesel exhaust emissions has attracted considerable interest, and the subject has been extensively reviewed [1–7]. It probably represents one of the most challenging areas of environmental pollution control. Although a number of catalysts have been demonstrated to be effective for this reaction in the laboratory, the most effective catalysts are Pt/alumina, Cu-exchanged ZSM-5, and Ag/Al_2O_3, though a large variety of other Cu, zeolite, and platinum group metal (pgm)-based systems have also been studied. Cu/ZSM-5 and Ag/Al_2O_3 catalysts operate at higher temperatures and over a broader temperature range than Pt-based catalysts and so represent more likely options for automotive applications. However, the activity of HC-SCR catalysts, particularly after long-term ageing, has so far been insufficient to allow their widespread implementation [8].

The activity/durability of these catalysts reported in the academic literature varies widely. Discrepancies between the activities reported in the literature with simulated exhaust emissions and those demonstrated in engine testing are usually caused by differences in test conditions between laboratory measurements and real-world exhaust emissions. These differences include the nature of the hydrocarbon species, the inhibiting effect of H_2O or SO_2 (present in real-world exhaust but not always in laboratory tests), space velocity effects, and ageing conditions.

Though many papers have been published on both Cu/zeolite and Ag/alumina systems, they are rarely compared directly under conditions that are realistic for automotive applications and that require long-term durability. Here we compare and contrast the activity and deactivation mechanisms for these systems with the use of simulated exhaust gas conditions.

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2. Experimental

The alumina support for the silver catalyst was a γ-alumina with a surface area of $\sim 150\ m^2/g$. The ZSM-5 used was obtained from Zeolyst and had a SiO_2/Al_2O_3 ratio of ~ 30. The metal loadings for the Ag and Cu catalysts were 2 wt% and 5 wt%, respectively. These two catalysts are referred to here as 5% Cu/ZSM-5 and 2% Ag/Al_2O_3. The catalysts were prepared with traditional impregnation techniques and finally heated in air for 2 h at 500 °C. Catalysts were typically tested for HC-SCR activity with gas that was allowed to flow at 2 L/min over 0.4 g catalyst; the gas composition was 3000 ppm hydrocarbon (C1 equivalent), 500 ppm NO, 5% CO_2, 600 ppm CO, 12% O_2, 5% H_2O, and the balance in N_2. Lean hydrothermal ageing (LHA) of the zeolite catalysts was carried out in 5% H_2O/air. Experiments with diesel fuel used two different types of diesel fuel, MK1 and US06. MK1 is a Swedish grade fuel with < 10 ppm sulphur; US06 has a similar S content but a higher aromatic content.

3. Results and discussion

3.1. Cu/ZSM-5

Because of their high hydrocarbon trapping capacity, the NO_x conversion of zeolite-based catalysts for HC-SCR varies considerably between steady-state isothermal and transient temperature ramp measurements and between ramp-up and ramp-down measurements. Fig. 1 shows a comparison of a transient experiment (ramp up 10 °C/min) and an isothermal experiment (conversion taken after 20 min at constant temperature). The conversion is considerably higher at ~ 350 °C for the transient experiment, as the catalyst traps a large amount of hydrocarbon at low temperature, which can be utilised for NO_x conversion as the temperature is increased. The ramp-down measurement yields a result similar to that found in the steady-state experiment. Subsequent data were taken from the steady-state test.

3.1.1. Effect of hydrocarbon

Cu/ZSM-5 gives good NO_x conversion with a similar temperature window with a wide range of hydrocarbons. We have used, for example, propene, *n*-octane, decane, and diesel fuel. Fig. 2 shows the steady-state conversion of a fresh 5% Cu/ZSM-5 catalyst with propene, octane, and diesel fuel. The shapes of the conversion profiles as a function of temperature for all three fuels are very similar, showing that the catalyst is insensitive to the hydrocarbon.

3.1.2. Effect of thermal ageing

It is well established that the main cause of deactivation in the Cu/zeolite system for HC-SCR is an irreversible physical change that is a combination of copper sintering and zeolite dealumination [9–18]. Both become more severe with increasing temperature and ageing time. We shall not discuss the deactivation mechanism in detail here, but the activity data for a sample lean hydrothermally aged at 600 °C are shown in Fig. 3. After 1 week of ageing the most notable effect was the loss of low-temperature (350 °C) activity. When the ageing was extended to 3 weeks there was a considerable loss of NO_x conversion over the entire temperature window. We have extensively characterised the catalysts after ageing. The BET surface area was reduced slightly from 354 to 324 m^2/g. XRD showed very little change in the zeolite-related peaks, indicating that the basic zeolite matrix was

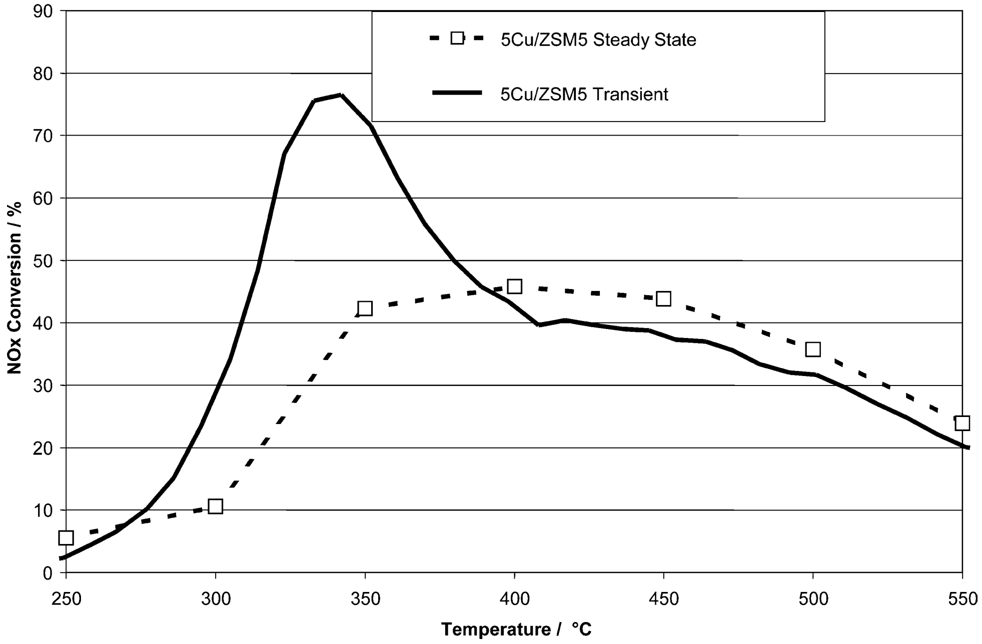

Fig. 1. Comparison of a transient (ramp up 10 °C/min) and isothermal experiment (conversion taken after 20 min at constant temperature) showing NO_x conversion as a function of temperature over 5% Cu/ZSM-5.

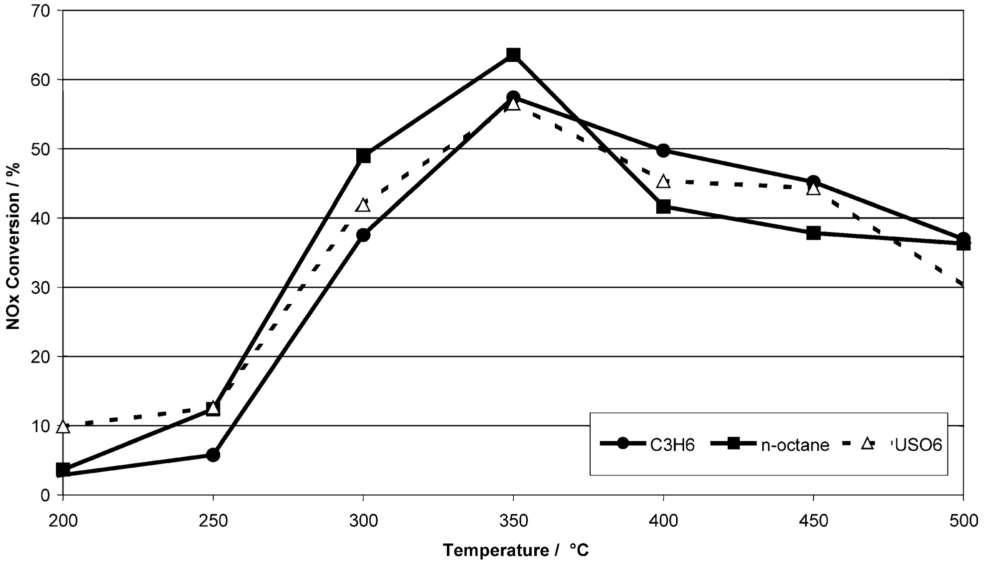

Fig. 2. Effect of hydrocarbon on steady-state NO_x conversion over fresh 5% Cu/ZSM-5.

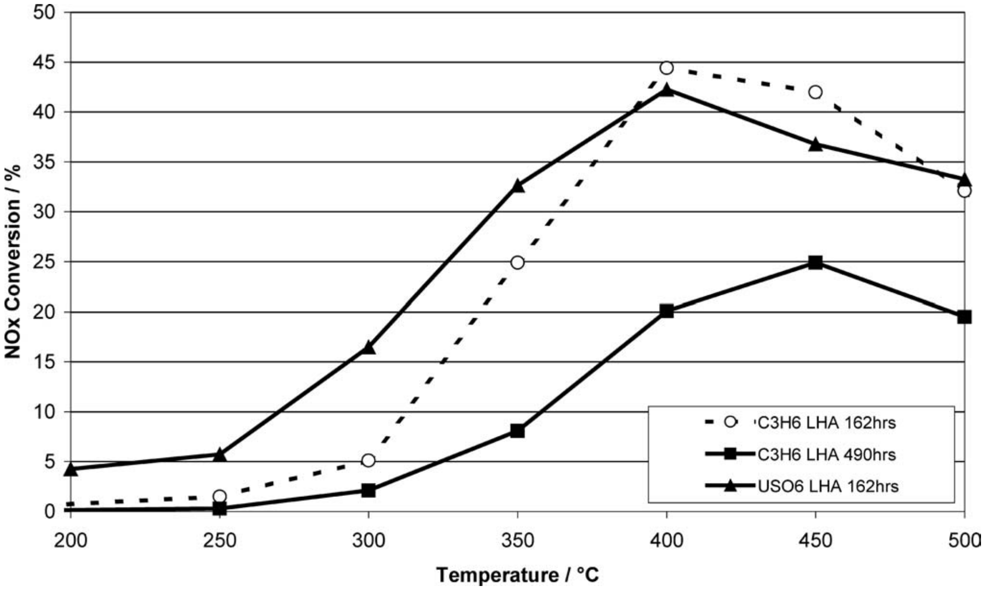

Fig. 3. Steady-state NO_x conversion of an aged (LHA 600 °C, 162 and 490 h) 5% Cu/ZSM-5 catalyst with propene and diesel fuel.

not decomposed by this type of ageing; however, there was an increase in the CuO peak intensity, indicating copper sintering. No clear evidence of CuO was visible in the XRD data for the fresh catalyst; after ageing the average Scherrer CuO crystallite size was estimated to be 31 nm. TEM also showed evidence for Cu sintering on ageing. MAS NMR [19] showed substantial changes with the formation of significant amounts of 5 and 6 coordinated Al as a result of dealumination.

3.1.3. *Effect of sulphur*

Chemical deactivation due to sulphur poisoning is not as significant a problem as dealumination/copper sintering. This is discussed in more detail below, where the effect of SO_2 is compared with that on the 2% Ag/Al_2O_3 catalyst.

3.2. *Ag/Al_2O_3*

3.2.1. *Effect of hydrocarbon*

Most studies of Ag/alumina catalysts have used short-chain hydrocarbons such as propene as a model hydrocarbon. Relatively few studies have used longer chain hydrocarbons or diesel fuel [20–22,26].

Model hydrocarbons. The nature of the hydrocarbon has a substantial effect on NO_x conversion; NO_x conversion activity for *n*-octane is substantially higher and occurs over a wider temperature range than for propene (Fig. 4). The dependence on hydrocarbon was much stronger than that observed with Cu/zeolite systems. The relatively poor NO_x conversion with propene, especially at lower temperatures,

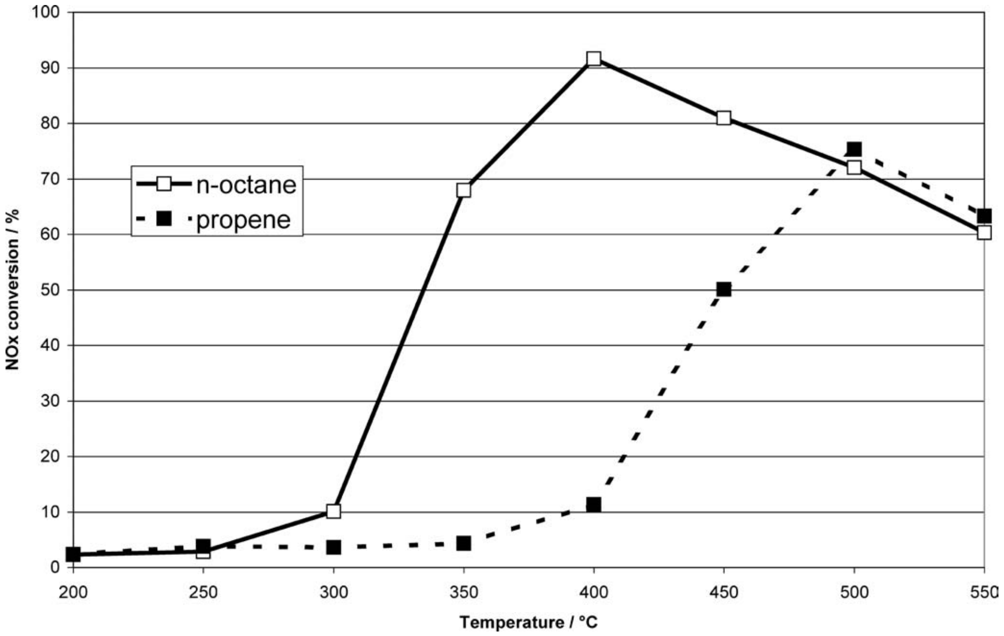

Fig. 4. NO_x conversion over fresh 2% Ag/Al_2O_3 with *n*-octane and propene.

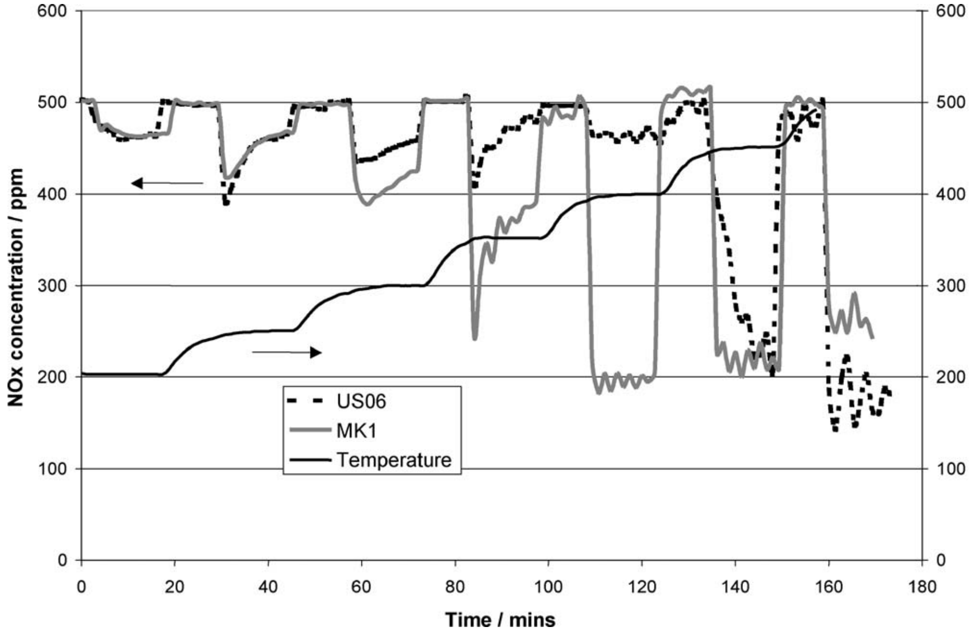

Fig. 5. Steady-state NO_x concentration as a function of time at different temperatures over 2% Ag/Al_2O_3 using diesel fuel.

may be a result of competitive adsorption of hydrocarbon and water. When propene was used the removal of the water in the gas feed led to substantially higher NO_x conversion (not shown). It may therefore be that higher chain hydrocarbons are able to compete with water more effectively than propene for adsorption at the active site. This is similar to the argument that has been used previously to account for the very high NO_x conversion activity that is observed for oxygenated hydrocarbons such as methanol when compared with propene [23]. The low temperature activity of Ag/Al_2O_3 catalysts with model hydrocarbons such as propane can also be improved by the addition of H_2 to the gas feed [24,25].

Diesel fuel. Both propene and octane can only be regarded as model fuels for HC-SCR, and the real challenge is for the catalyst to work effectively with diesel fuel. Fig. 5 shows the steady-state NO_x concentration as a function of time at different temperatures over 2% Ag/Al_2O_3 for diesel fuel. It is clear that the activity decays gradually with time at the lower temperatures of the measurement. However, when the catalyst was exposed to high temperature (∼ 500 °C), the initial

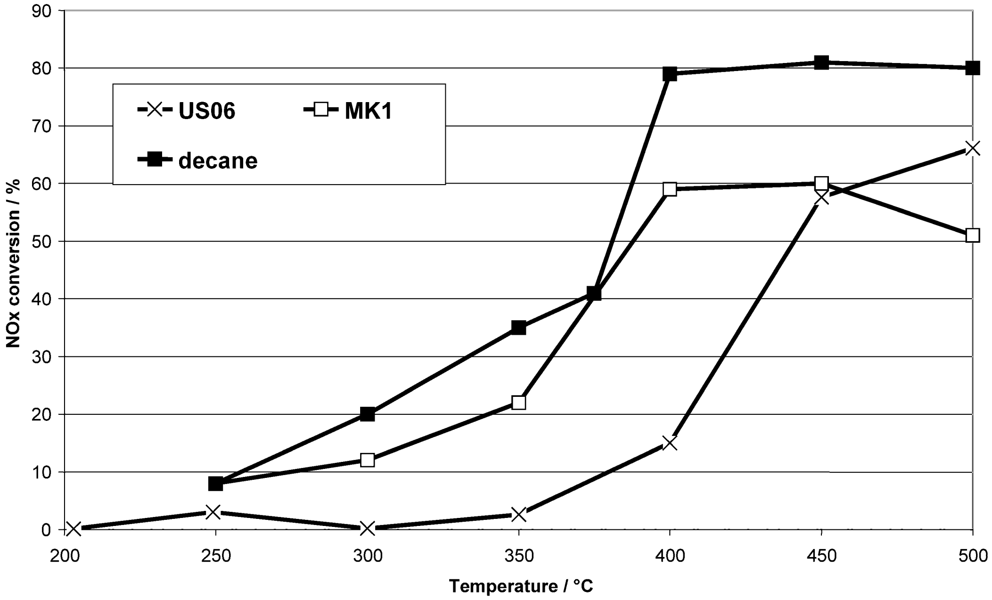

Fig. 6. Steady-state NO_x conversions over 2% Ag/Al_2O_3 using decane, and diesel fuel.

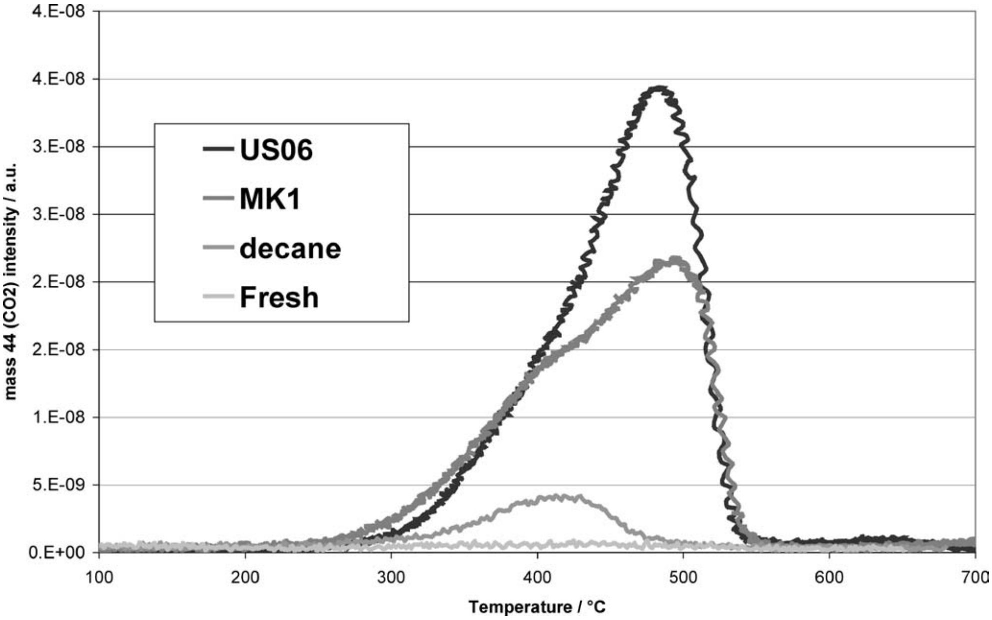

Fig. 7. TPO profile for a 2% Ag/Al_2O_3 sample fresh and following testing with diesel fuel and decane at 300 °C for 30 min.

activity at low temperatures was restored. A likely cause for this low-temperature deactivation is coking of the catalyst. This does not occur with the model fuels, which burn much more cleanly than diesel fuel. The effect of this can be seen in the steady-state data for different hydrocarbons, shown in Fig. 6. NO_x conversion varies in the order decane > MK1 > US06. Fig. 7 shows a TPO profile for a sample after testing with MK1, US06 diesel fuel, and n-decane. In the case of the diesel fuel test there was substantial release of CO_2 at ∼ 450–500 °C as the coke deposited during testing was burnt off. CO_2 release with n-decane is slight in comparison. Moreover, it is clear that the US06 diesel fuel produces more CO_2 than MK1, indicating that US06 induces more coking. This explains the poorer NO_x conversion at low temperatures obtained with US06 compared with MK1 in the steady-state conversion data.

3.2.2. *Effect of thermal ageing*

Fig. 8 compares the effect of LHA at 700 °C on the NO_x conversion of 2% Ag/Al_2O_3 and 5% Cu/ZSM-5. The fresh Ag catalyst was more active over most temperatures, the 5% Cu/ZSM-5 catalyst being much more active at 300 °C. After ageing the activity of the Cu catalyst was severely reduced at 300 and 350 °C but also significantly reduced at higher temperatures, whereas the Ag retained substantial activity.

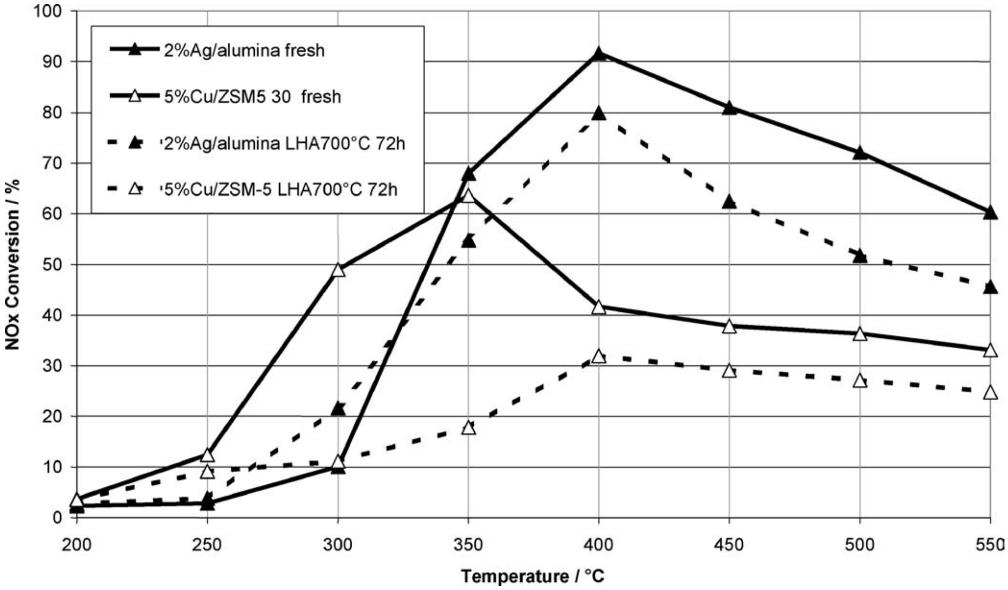

Fig. 8. Steady-state NO_x conversion as a function of temperature for 2% Ag/Al_2O_3 and 5% Cu/ZSM-5 fresh and after LHA 700 °C, 72 h using *n*-octane as the reductant.

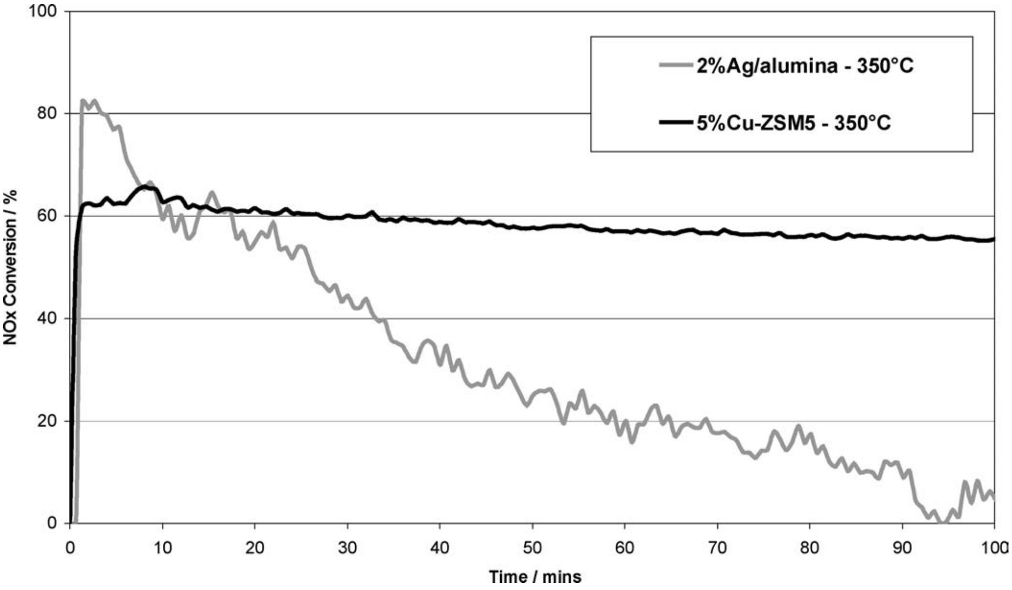

Fig. 9. NO_x conversion over 2% Ag/Al_2O_3 and 5% Cu/ZSM-5 catalyst as a function of time at 350 °C in the presence of 20 ppm SO_2, 3000 ppm (C1) *n*-octane.

The 2% Ag/Al_2O_3 catalyst was therefore substantially more effective than 5% Cu/ZSM-5 after LHA at 700 °C.

3.2.3. *Effect of sulphur*

A number of authors have demonstrated the deactivation of 2% Ag/Al_2O_3 systems due to poisoning with SO_2 [26–28]. However, other authors have observed a promotional effect with SO_2 [29]. Other authors have indicated a shift in the NO_x conversion window to a higher temperature, resulting in an increase in NO_x conversion at higher temperatures but a reduced NO_x conversion at lower temperatures [21,30].

Fig. 9 shows the NO_x conversion from a 2% Ag/Al_2O_3 catalyst as a function of time at 350 °C in the presence of 20 ppm SO_2, with *n*-octane as a model hydrocarbon. As no coking occurred with this hydrocarbon, there was a constant NO_x conversion without SO_2 at 350 °C. With SO_2 present there was a gradual decrease in NO_x conversion with time, indicating rapid sulphur poisoning. By comparison, there was essentially no effect of SO_2 in the feed with 5% Cu/ZSM-5 at 350 °C. This observation highlights the much higher sulphur tolerance of 5% Cu/ZSM-5 compared with 2% Ag/Al_2O_3.

Steady-state NO_x conversion data as a function of temperature for fresh and aged 2% Ag/Al_2O_3 are shown in

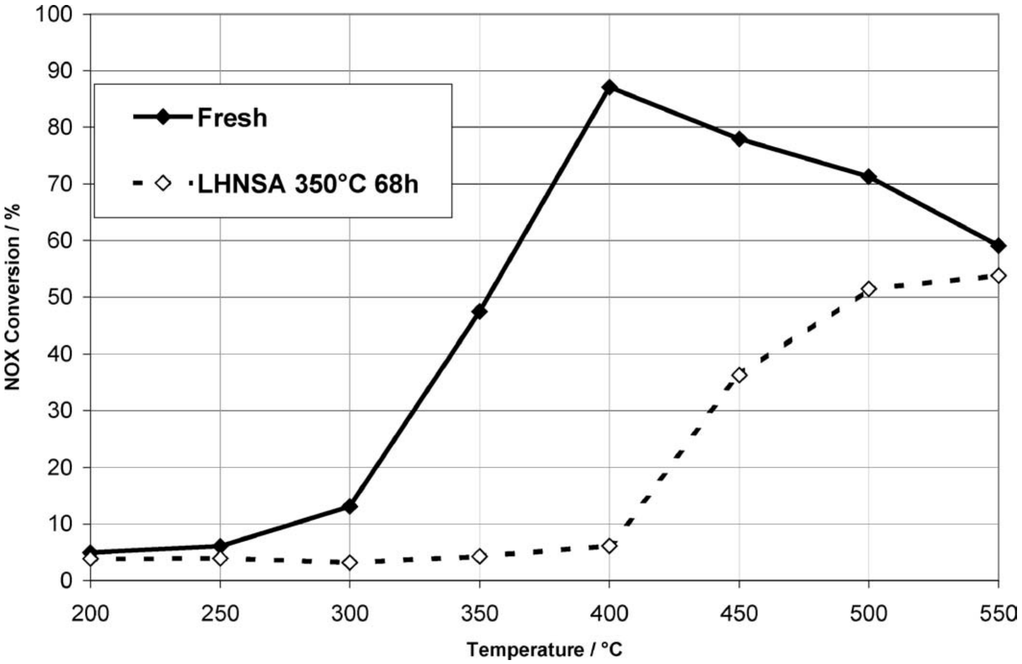

Fig. 10. Steady-state NO_x conversion data as a function of temperature for fresh and aged 2% Ag/Al_2O_3 using *n*-octane. Ageing condition: 350 °C, 68 h, 500 ppm NO, 20 ppm SO_2, 4.5% H_2O bal air, 2 g catalyst with 2 L/min flow rate.

Fig. 10. Samples were aged in the presence of 500 ppm NO (LHNSA), which leads to far more extensive sulphation than does a simple gas mix of $SO_2/H_2O/O_2/N_2$ [31]. Clearly the sulphation of the 2% Ag/Al_2O_3 catalyst causes severe deactivation.

4. Conclusions

The activity windows of NO_x conversion for fresh 2% Ag/Al_2O_3 and 5% Cu/ZSM-5 were quite similar, starting at ∼ 300 °C and extending to at least 550 °C. With *n*-octane as a model hydrocarbon, the maximum NO_x conversion for 2% Ag/Al_2O_3 (∼ 90% at 400 °C) was higher than that for 5% Cu/ZSM-5 (∼ 60% at 350 °C). The Ag catalyst was more active at temperatures of 350 °C and above, though the 5% Cu/ZSM-5 catalyst was substantially more active at 300 °C. The 2% Ag/Al_2O_3 catalyst is also substantially more active than 5% Cu/ZSM-5 after LHA at 700 °C.

The Ag catalyst was very sensitive to the nature of the hydrocarbon species, with longer chain hydrocarbons such as *n*-octane giving better lower temperature activity than propene, probably because of higher adsorption of the longer chain hydrocarbon relative to water at active sites. The variation in NO_x conversion with temperature for 5% Cu/ZSM-5 was almost invariant with hydrocarbon type.

The modes of deactivation (both chemical and thermal) of the two types of catalyst were quite different and can be summarised as follows:

- The 5% Cu/ZSM-5 catalyst was fairly insensitive to SO_2. However, the low-temperature (< 450 °C) activity of 2% Ag/Al_2O_3 catalyst was rapidly poisoned by SO_2.
- The main cause of deactivation for the 5% Cu/ZSM-5 catalyst after hydrothermal ageing was a combination of copper sintering and zeolite dealumination.
- When the Ag catalyst was tested with diesel fuel, coking occurred, leading to low-temperature (< 450 °C) deactivation. This is largely reversible at high enough temperatures. This effect contrasts with the behaviour of the 5% Cu/ZSM-5 catalyst, which can maintain activity at 300 °C with diesel fuel.

Although HC-SCR provides an attractive way of reducing NO_x emission from diesel engines, the conditions present in automotive exhaust require a robust catalyst to be developed. Both the 5% Cu/ZSM-5 and 2% Ag/Al_2O_3 catalysts have deficiencies that still need to be overcome for the successful implementation of these technologies in NO_x emission control from diesel vehicles. In particular, the issues that need to be addressed are the hydrothermal durability of the 5% Cu/ZSM-5 catalyst, the resistance to chemical poisoning (sulphur and coke) of the 2% Ag/Al_2O_3 catalyst, and the operating window of aged catalysts. This represents an important challenge in catalyst design.

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