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A combination of NO_x trapping materials and urea-SCR catalysts for use in the removal of NO_x from mobile diesel engines

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Abstract

Preliminary studies on a series of nanocomposite BaO–Fe ZSM-5 materials have been carried out to determine the feasibility of combining NO_x trapping and SCR-NH_3 reactions to develop a system that might be applicable to reducing NO_x emissions from diesel-powered vehicles. The materials are analysed for SCR-NH_3 and SCR-urea reactivity, their NO_x trapping and NH_3 trapping capacities are probed using temperature programmed desorption (TPD) and the activities of the catalysts for promoting the $NH_{3\ ads} + NO/O_2 \rightarrow N_2$ and $NO_{x\ ads} + NH_3 \rightarrow N_2$ reactions are studied using temperature programmed surface reaction (TPSR).

Keywords: NO_x; NH_3; SCR; Urea; BaO

1. Introduction

The removal of NO_x from exhaust streams of a net oxidising nature such as stationary power sources, fuel-lean gasoline engine exhausts and diesel engine exhausts remains an intensively studied area of research within the heterogeneous catalysis community [1–7].

In the case of the stationary power sources SCR-NH_3, where NO_x (rather then O_2) is *selectively* reduced over catalyst with NH_3 as a reducing agent, is a technology used to deNO_x emissions [8,9]. This is possible under these conditions since (a) these facilities are by definition stationary and thus any problems with keeping a supply of $NH_{3(g)}$ on site are minimised and (b) the amount of combustion taking place within the power station and thus the amount of NO_x generated is generally constant (therefore the amount of NH_3 required to remove this NO_x is also constant). The dose of NH_3 to the reaction mixture is important since there must be sufficient NH_3 added to remove the NO_x but excess addition of NH_3 is undesirable. Any excess NH_3 over NO_x is either oxidised to N_2 or NO_x over the catalyst or oxidised to NO_x in the atmosphere if it ‘‘slips’’ beyond the catalyst, thereby rendering the entire process more expensive (if NH_3 is oxidised to N_2) or an entire waste of effort (if excess NH_3 is oxidised to NO_x).

The selective trapping of NO (via NO_2) onto BaO-containing materials followed by, once the trap is saturated, a reduction of $Ba(NO_3)_2$ and regeneration of BaO, using a pulse of hydrocarbons and CO (NO_x storage and reduction, NSR) is a technique that has found application in lean-burn gasoline vehicles [10,11].

There are problematic issues associated with the former technique (SCR-NH_3) since NH_3 is a gas which is difficult to both store and dose to the exhaust. The latter point is important since the formation of NO_x from a diesel engine is not at a constant level (since driving conditions vary). The former problem can be resolved through the use of solutions of urea and a suitable hydrolysis catalyst (to form NH_3 on board the vehicle) but the latter problem requires a sophisticated NO_x sensor coupled to the urea delivery system to ensure correct dosage of NH_3 to the catalyst and such systems are, as yet, unavailable.

The latter technique (NSR) is also unsuitable for direct use on a diesel engine due to the fact that it is unable to deliver the pulse of CO and hydrocarbons which the lean-burn gasoline engine can deliver since, due to its particular four-stroke cycle, a diesel engine is unable to run in a fuel-rich mode. However there are adjustments to the lean-burn gasoline NSR cycle that can be made in order to render it effective for the removal of NO_x from a diesel engine exhaust. One possibility would

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involve direct injection of the diesel (hydrocarbon) fuel over the catalyst while a second would be the on-board generation of H_2 and CO mixtures through on board reforming of the diesel by injection of the fuel into the combustion chambers directly following the fuel combustion step of the four-stroke cycle [12,13].

Here we propose one possible further method of removing NO_x emissions from the exhausts of diesel engines which is based on a combination of both of these approaches over a multi-component catalyst (Fig. 1). Using this proposed technique a catalyst would consist of several components, each of which would have a specific function within the NO_x removal cycle. In particular the catalyst would consist of: (a) BaO NO_x trapping sites, (b) hydrolysis sites to convert urea quantitatively into $NH_3 + CO_2$, (c) acid sites to trap any excess NH_3 and prevent NH_3 slip and (d) redox active sites to catalyse the NO + NH_3 reaction.

Specifically the cycle would operate as follows:

Beginning with the ''clean'' composite material

(a) Gaseous NO_x would be trapped on the material as $Ba(NO_3)_2$. This process would continue until the BaO is fully saturated. As is known [10] the first step in $Ba(NO_3)_2$ formation from NO is the oxidation of NO to NO_2. We would envisage that this function would be carried out by either the exchanged Fe cations [14] or any external FeO crystallites.

(b) Urea would be periodically injected over the material. This would hydrolyse to $NH_3 + CO_2$ with the NH_3 going on to reduce this $Ba(NO_3)_2$ to $BaO + N_2 + H_2O$.

(c) Any excess NH_3 formed would be trapped on the acid sites as NH_4^+ (or $NH_{3\ ads}$) preventing NH_3 slip. This would offer a certain amount of ''buffer'' capacity to the dosage of urea (NH_3) to the catalyst to compensate for the changes in [NO] formed under transient operation conditions, i.e. the dose of urea would not have to be as accurate as would be required in a straightforward SCR-NH_3 (or SCR-urea) deNO_x system.

(d) Gaseous NO_x would now have two possible courses of reaction, i.e. either reacting with the adsorbed NH_3 (''cleaning'' the NH_3-covered acid sites and forming N_2) or reacting with the ''clean'' BaO to form $Ba(NO_3)_2$, essentially restarting the cycle.

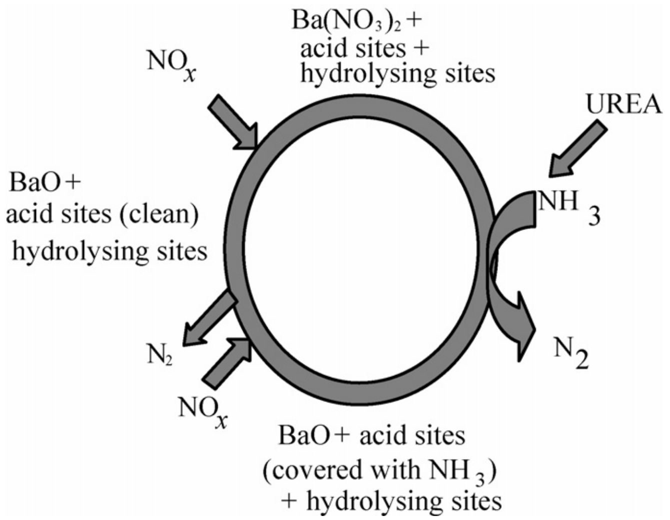

Fig. 1. Cycle showing the combination of a NO_x trapping material and an SCR-NH_3 catalyst for use in a proposed deNO_x system for mobile diesel engine exhausts.

We have tested various aspects of this cycle on composite materials using Ba containing Fe ZSM-5 catalysts as model materials. The Fe ZSM-5 portion of the composite material should possess SCR-NH_3 activity [15–17] (through redox active Fe ions) and NH_3-trapping capacity (through zeolitic acidity) while BaO (incorporated either as ion-exchanged or wet impregnated barium) should provide the NO_x trapping functionality [10–13].

Previous work within the group [18] has shown that urea solutions are not direct replacements for $NH_{3(g)}$ in terms of comparing the activity of a given catalyst for the SCR-NH_3 reaction and the SCR-urea reaction. This effect is not due to the presence of H_2O in the reaction stream (urea is dosed to the catalyst in an aqueous solution) since several sets of catalysts that proved active for deNO_x under wet SCR-NH_3 conditions show no activity in the SCR-urea reaction [19]. This suggests that the urea in these conditions is not hydrolysing to form NH_3 (via a HNCO intermediate [20]) as would be expected but rather is either oxidising to N_2 or is reacting through some other path.

Other work [21] has shown that Fe ZSM-5 catalysts can retain a large amount of activity in the SCR-urea reaction provided that the counter ion of the parent zeolite is Na^+ rather than NH_4^+. It is thought that in catalysts that are prepared with Brønsted acidity these acid sites promote the formation of melamine layers through the reaction of HNCO (an intermediate in urea decomposition to NH_3) with NH_3 [22].

The analysis has involved Temperature Programmed SCR activity using both NH_3 and urea as reducing agents, NO_x and NH_3 temperature programmed desorption and temperature programmed surface reactions (using pre-adsorbed NO_x and NH_3).

2. Experimental

2.1. Catalyst preparation

Fe ZSM-5 (0.8% Fe) and Ba ZSM-5 (4.3% Ba) were prepared by conventional ion-exchange method using Na ZSM-5 ($SiO_2/Al_2O_3 = 27$) obtained from Schwandorf. A quantity of 1.0 g zeolite was shaken for 2 h in 100 ml of either 0.01 M $FeSO_4.7H_2O$ or 0.01 M $Ba(C_2H_3O_2)_2$. The samples were filtered, washed in hot (80 °C) deionised water, dried at 110 °C and calcined at 500 °C for 2 h.

Two composite catalysts containing Fe and Ba (Fe Ba ZSM-5) were prepared using the Fe ZSM-5 prepared above followed by the introduction of Ba by both ion-exchange (ie) and wet impregnation (wi) techniques. The former catalyst was prepared first and subsequently the latter was prepared to