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Research paper

Remarkable enhancement of the selective catalytic reduction of NO at low temperature by collaborative effect of ethanol and NH_3 over silver supported catalyst

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ABSTRACT

The NO_x selective catalytic reduction (SCR) is extensively studied as an effective process for air pollutants abatement from lean burn and Diesel vehicles. In the implemented Urea-SCR technology, the NO_2/NO_x ratio is a key parameter that limits the deNO_x efficiency at low temperature (175–250 °C). We demonstrate that co-feeding of ammonia and ethanol on a Ag/Al_2O_3 catalyst enables a drastic enhancement of the NO_x conversion at temperatures below 200 °C using only NO as NO_x (standard SCR condition). Even if NO_2 is provided at low temperature by the NO oxidation over Ag/Al_2O_3 in presence of EtOH, the NO_x conversion improvement is not only due to a direct reaction between NH_3 and NO_x, but mainly attributed to the availability of hydrogen H* species resulting from EtOH oxidation (similar to a H_2 assisted NH_3-SCR process). Due to the presence of remaining NH_3 and NO_2 (formed over Ag/Al_2O_3 catalyst), further deNO_x efficiency improvement was obtained at low temperature by addition of a NH_3-SCR catalyst (WO_3/Ce-Zr). The critical dependence of the SCR process on the Diesel Oxidation Catalyst (DOC) efficiency at low temperature is thus avoided.

1. Introduction

Air pollution is responsible of direct harmful effects on human health with hundred thousand deaths per year throughout the world [1]. Consequently, stringent standards regulate pollutants emissions such as for nitrogen monoxide (NO) and nitrogen dioxide (NO_2) from stationary and mobile sources.

Worldwide, the introduction of three way catalyst (TWC) converters for gasoline spark ignition engines noticeably contributed to increasing the air quality [2–4]. However, for internal combustion engines operated in excess of air, such as Diesel engines, TWC converter is unable to efficiently reduce NO_x into N_2 and the implementation of selective catalytic reduction (SCR) technology, with a large choice of reductants, is described as one of the most promising way to control NO_x emissions in lean media.

Among the various possible reductants, ammonia (or urea used as NH_3 provider), hydrocarbons (propene, propane, decane...), ethanol (EtOH) were widely studied. Interestingly, whatever the considered reductant, the mechanistic studies generally suggest that N_2 is obtained *via* the formation of species like —CN and —NCO, which are known to be involved in ammonia formation. Indeed, such species were identified during the lean NO_x reduction by propene over $LaFe_{1-x}(Cu, Pd)xO_{3-\delta}$ perovskites [5], supported transition metals like $Cu/Ti_{0.7}Zr_{0.3}O_2$ [6], or supported noble metals like Rh/TiO_2 [7]. NH_3 intermediate species was also clearly identified over Cu-ZSM-5 exchanged zeolite when propane [8] or decane [9] are used, as well as during the NO_x reduction process by ethanol over Ag/Al_2O_3 catalyst [10]. These examples point out the key role of the ammonia-like intermediate species in the deNO_x pathway, whatever the considered reductant and the type of catalyst (noble metal, oxide, zeolite...).

To meet the current environmental standards limiting the NO_x emission from Diesel vehicles, the automotive industry has commonly adopted the Urea-SCR technology. The use of an aqueous urea solution as ammonia precursor is a safe and operational adaptation of the NH_3-SCR technology initially developed for stationary sources. Urea (NH_2—CO—NH_2) is theoretically decomposed in ammonia via two consecutives reactions: urea thermal decomposition and HNCO hydrolysis reactions. Thereafter, NO_x reduction is assumed to be correlated with NH_3 yield and supposed to follow

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similar pathways than those demonstrated with ammonia reductant:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (1)$$

More precisely, the fast-SCR reaction (Eq. (1)) results from sequences involving ammonium nitrate or related surface species as intermediates (Eqs. (2), (3)):

$$2NO_2 + 2NH_3 \rightarrow N_2 + NH_4NO_3 + H_2O \quad (2)$$

$$NO + NH_4NO_3 \rightarrow N_2 + NO_2 + 2H_2O \quad (3)$$

Firstly, ammonium nitrate formation (Eq. (2)) involves NO_2 reactivity by dimerization (Eq. (4)), disproportionation (Eq. (5)), and successive reaction to form N_2 (Eq. (6)) and ammonium nitrate (Eq. (7)). The second step of the fast-SCR chemistry (Eq. (3)) implies the NO reactivity with ammonium nitrate which proceeds via the NO oxidation by nitric acid (Eq. (8)) followed by reaction of NH_3 with nitrous acid to form N_2 (Eq. (6)). As a result, conversion of nitrogen oxides is optimized when NO, NO_2 and NH_3 respect a 1:1:2 ratio, enabling the stoichiometric reaction of fast SCR and is intimately related to HONO/HNO_3 reactional pathway [11,12–15]. Finally, N_2 is obtained by decomposition of ammonium nitrite (Eq. (6)). With many practical catalysts and regardless the used reductant, this reaction is commonly suggested to be the final step of deNO_x chemistry [16,17–19].

$$NO_2 \rightleftarrows N_2O_4 \quad (4)$$

$$N_2O_4 + H_2O \rightleftarrows HONO + HNO_3 \quad (5)$$

$$NH_3 + HONO \rightleftarrows NH_4^+ + NO_2^- \rightleftarrows NH_4NO_2 \rightarrow N_2 + 2H_2O \quad (6)$$

$$NH_3 + HNO_3 \rightleftarrows NH_4^+ + NO_3^- \rightleftarrows NH_4NO_3 \quad (7)$$

$$NO + HNO_3 \rightleftarrows NO_2 + HONO \quad (8)$$

Unfortunately, the on-board Urea-SCR technology suffers from a poor activity at low temperatures (200 °C) due to an insufficient NO_2/NO_x ratio to promote the fast SCR stoichiometry (Eq. (1)) [20]. NO_2 yield can be adjusted by the Diesel oxidation catalyst (DOC) upstream of the SCR converters, but the oxidation activity is also strongly dependent on both temperature and operating conditions. Recently an over-injection of aqueous solution of ammonium nitrate (Eq. (9)) was reported to enhance the deNO_x efficiency while avoiding NO pre-oxidation [11].

$$2NO + 2NH_3 + NH_4NO_3 \rightarrow 3N_2 + 5H_2O \quad (9)$$

EtOH-SCR process was also described as an attractive way to reduce NO_x, especially due to the practicality/availability of ethanol and its relative safety. Silver-based materials were found to be the most active and selective for the NO_x reduction by oxygenates reductant compounds [19,21]. With ethanol as reductant, the NO conversion is assumed to be strongly dependant of the nitromethane route, based on the ethanol oxidation to acetaldehyde via a variety of intermediates which are subsequently adsorbed, such as surface acetate and ethoxide ions leading to the global reaction (Eq. (10)):

$$C_2H_5OH + 6NO \rightarrow 3N_2 + 2CO_2 + 3H_2O \quad (10)$$

N-containing compounds as HNCO and ammonia are also eventually produced [10,22–26] as surface organic intermediate. A detailed surface mechanism for the SCR of NO_x with ethanol on silver alumina catalyst was proposed by Tham et al. [24]. In summary, the first step of the reaction framework results in C_2H_5OH dissociative adsorption into surface ethoxide $C_2H_5O^*$ and surface hydrogen H^* ad-species (Eq. (11)) [26]. Thereafter, ethoxide can be consumed either by the oxidation pathway to yield acetaldehyde (Eq. (12)) or by the NO_x reduction pathway via nitromethane route (Eqs. (13)–(16)).

$$C_2H_5OH \rightarrow C_2H_5O^*_{(ad)} + H^*_{(ad)} \quad (11)$$

$$C_2H_5O^*_{(ad)} \rightarrow CH_3CHO^*_{(ad)} + H^*_{(ad)} \rightarrow CH_3CHO \quad (12)$$

$$CH_3CHO^*_{(ad)} + O^*_{(ad)} \rightarrow CH_3COO^*_{(ad)} + H^*_{(ad)} \rightarrow CH_3COOH \quad (13)$$

$$CH_3COO^*_{(ad)} + NO_2 \rightarrow CH_3NO_2 + CO_2 \quad (14)$$

$$CH_3NO_2 \rightarrow HNCO + H_2O \quad (15)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \quad (16)$$

Interestingly, the formation of ammonia *via* the isocyanate hydrolysis route (Eq. (9)) takes place in this reaction pathway. It is assumed that the reaction pathway then follows very similar routes to those reported for the NH_3-SCR reaction, with N_2 formation from ammonium nitrite decomposition (Eq. (6)).

Unfortunately, the deNO_x activity of the EtOH-SCR technology at low temperatures appears not sufficient for a practical application to the next generation of the energy-efficient Diesel vehicles, especially due to the rate limiting step of CH_3NO_2 formation at T < 250–300 °C. However, some studies reported that an improvement of NO_x reduction efficiency of EtOH-SCR technology at low temperature is possible. For instance, addition of hydrogen into the reaction mixture allows an enhancement of the deNO_x efficiency. It was advanced that H_2 addition promotes the partial oxidation of C_2H_5OH to form enolic species which mainly contribute to accelerate NO_x reduction [27–29]. Note that Ag/Al_2O_3 catalysts were reported to exhibit a poor activity in NH_3-SCR but they become very active in case of H_2 addition [30–32]. An improvement of the N_2 yield can also be obtained modifying the alumina support to form surface zinc aluminates [21]. Indeed, an activation of the ethanol conversion in acetaldehyde was observed, but mainly from 250 to 300 °C.

Interestingly, the ethanol dehydrogenation leading to acetaldehyde appears concomitant with a high proportion of NO_2 emission from NO oxidation, as previously reported by Flura et al. [23]. This NO_2 formation at relatively low temperature (from 150 °C) may also favourably interfere in the SCR process, favouring the fast SCR reaction (Eq. (1)). Moreover, the formation of ammonia by the isocyanate hydrolysis route (Eq. (9)) appears in the EtOH-SCR reaction pathway. Ammonia was detected for temperature higher than 250 °C, when NO_x reach a high conversion level [23]. It could indicates that ammonia is a key intermediate species, but with a too low production rate at low temperature.

Obviously, N_2 yield of EtOH-SCR process seems to appear strongly dependant to subsequent ammonia route formation. Thus, in the present work, we studied the role of ammonia as co-reactant species for assisted EtOH-SCR process in NO rich media for future application in a coupled Urea/Ethanol-SCR process. Particular attention was paid to increasing the efficiency of EtOH-SCR system at low temperatures (T = 175–250 °C) while overcoming the NO_2 yield of the DOC.

2. Experimental part

2.1. Materials

Silver supported catalyst was selected to conduct EtOH-SCR experiments due to their high reactivity toward oxygenated compounds [33–35]. Alumina support was provided by Axens and exhibited a specific surface area of 170 $m^2\,g^{-1}$ after calcination 4 h under air at 700 °C. Silver (2.0 $_{wt.}$%, which is commonly described as the optimal loading [36]) was added by impregnation of $AgNO_3$ dissolved in ethanol [21,23,37]. Sample was finally calcined under synthetic air with 10% H_2O at 700 °C for 4 h and is noted Ag/Al.