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# Selective Catalytic Reduction of NO at low temperature using a (ethanol+ammonia) mixture over a Ag/Al<sub>2</sub>O<sub>3</sub> + WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub> dual-bed catalytic system: reactivity insight of WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub>.

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**Abstract:** The Selective Catalytic Reduction (SCR) is one of the most efficient process for NO<sub>x</sub> removal from Diesel exhaust gas. However, the urea/NH<sub>3</sub>-SCR process implemented in recent vehicles still suffers from a poor activity in the low temperature range (T < 250°C). One main reason is its dependency against the NO<sub>2</sub>/NO<sub>x</sub> ratio, limiting the expected fast-SCR reaction in this temperature range. Recently, we shown that the addition of ethanol to ammonia led to a significant increase of the activity of a Ag/Al<sub>2</sub>O<sub>3</sub> catalyst in this low temperature range. Moreover, in a dual-bed configuration (Ag/Al<sub>2</sub>O<sub>3</sub>+WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub>), a remarkable improvement was achieved at low temperature using only NO as NO<sub>x</sub>. The present work aims to highlight the DeNO<sub>x</sub> chemistry encountered over the WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub> catalyst in a bifunctional (EtOH+NH<sub>3</sub>) mixture. In addition to the fact that this process takes advantage of the low temperature NO<sub>2</sub> formation over the upstream Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, this work also puts in evidenced unexpected interactions between NO<sub>2</sub> and CH<sub>3</sub>CHO (resulting from ethanol oxidation over Ag/Al<sub>2</sub>O<sub>3</sub>) thus leading to NO emission.

Keywords: DeNO<sub>x</sub>; SCR; ethanol; ammonia; Ag/Al<sub>2</sub>O<sub>3</sub>; WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub>

#### 1. Introduction

Air pollution is now recognized as a major health risk. In 2013, the World Bank estimated that one in ten deaths in the world could be the result of air pollution. In addition to particulate matter (PM) and tropospheric ozone ( $O_3$ ), nitrogen oxides ( $NO_x$ , *i.e.* NO and  $NO_2$ ) are also considered as first-order pollutants.  $NO_x$  arise mainly from anthropogenic sources and result largely from combustion reactions. Vehicles, especially with Diesel engines, play a major concern in these emissions (39 % in 2013) [1].

Consequently more and more drastic legislations were adopted to limit the emission of air pollutants. To reach the recent Euro 6 standard about the  $NO_x$  emission limitations, manufacturers implement a dedicated catalytic system. Two main processes are commonly envisaged: the  $NO_x$  storage reduction (NSR) process [2,3] and the selective catalytic reduction (SCR) process [4]. Currently, the SCR process is the most commonly used system. In this case, an aqueous urea solution (AdBlue®) is directly injected into the exhaust pipe [5]. Urea is then decomposed into ammonia and reacts which  $NO_x$  leading to dinitrogen formation, according to the so-called "standard-SCR" reaction (1):

 $2 \text{ NH}_3 + 2 \text{ NO} + \frac{1}{2} \text{ O}_2 \rightarrow 2 \text{ N}_2 + 3 \text{ H}_2\text{O}$  (1)

However, in standard-SCR condition, the activity at low temperatures (T <  $250^{\circ}$ C) appears limited, which induces significant NO<sub>x</sub> emissions during the cold start of the vehicles. A DeNO<sub>x</sub> improvement is obtained by a previous oxidation of NO to NO<sub>2</sub> in order to obtain an optimal NO<sub>2</sub>/NO<sub>x</sub> ratio of 0.5. The corresponding NO<sub>x</sub> reduction stoichiometry is known as the "fast-SCR" reaction (2) [6]:

 $2 \text{ NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2 \text{ N}_2 + 3 \text{ H}_2\text{O}$  (2)

Conventional NH<sub>3</sub>-SCR catalysts are made of oxide-based materials consisting of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> [7]. However, because of the possibility of vanadia sublimation [8,9], extensive efforts were made to develop vanadium free catalysts for mobile sources. Supported transition metal or ceria-based oxides such as Fe<sub>2</sub>O<sub>3</sub>/WO<sub>3</sub>/ZrO<sub>2</sub> [10], MnO<sub>x</sub>-CeO<sub>2</sub> [11], Nb-MnO<sub>x</sub> [12] or WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> [13,14] were proposed. Regarding WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>, tungsten addition was found to enhance the NO<sub>x</sub> removal efficiency through the increase of the surface acidity and NH<sub>3</sub> adsorption properties [15]. Metal exchanged zeolites were also reported as highly active materials. Zeolites are generally promoted by transition metals, such as iron or copper and should offer small pore size to assure a suitable thermal stability [5,16,17]. Impressive DeNO<sub>x</sub> efficiencies were reported for these materials which remain however strongly dependant to the NO<sub>2</sub>/NO<sub>x</sub> inlet ratio.

In the exhaust pipe, the Diesel Oxidation Catalyst (DOC), originally dedicated to the treatment of carbon monoxide (CO) and unburned hydrocarbons (HC), is usually placed upstream the SCR catalyst to also partially oxidizes NO into NO<sub>2</sub> [18]. Unfortunately, this catalyst also exhibits kinetic limitation at low temperature, which limits the NO<sub>2</sub> emission and consequently impacts the efficiency of the NH<sub>3</sub>-SCR process. As a result, new approaches are explored to avoid the DOC dependency, by developing catalytic systems more efficient at low temperatures (T < 250°C) in NO rich media.

Among the large choice of available reducing agent (unburned hydrocarbons, urea, ammonia, hydrogen... [19,20]), oxygenated HC like ethanol (EtOH), acetone or propanol [21] were also mentioned as attractive reductants. Supported silver materials, mainly  $Ag/Al_2O_3$  catalysts, were reported as particularly active for this EtOH-SCR process [22–25]. It allows high DeNO<sub>x</sub>

performances using a relatively safe and low-cost reductant. The EtOH-SCR mechanism involves numerous reactions [24]. The admitted reaction pathway is based on the ethanol oxidation into acetaldehyde, which then reacts with NO<sub>x</sub> to form nitromethane (CH<sub>3</sub>NO<sub>2</sub>). Finally, nitromethane is decomposed into intermediate N-containing species such as HNCO or NH<sub>3</sub>, reactive towards NO<sub>x</sub> reduction into nitrogen. An important characteristic of this system is the ability of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to oxidize NO into NO<sub>2</sub>, even at low temperature, concomitant with the ethanol dehydrogenation into acetaldehyde [22,26]. Unfortunately, EtOH-SCR process still suffers from a relatively poor DeNO<sub>x</sub> activity at T < 250°C, linked to the rate limiting step of nitromethane route formation [27,28].

In a recent work [29], we reported that co-feeding of ethanol and ammonia ((EtOH+NH<sub>3</sub>)-SCR) over a Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was a promising way to enhance the DeNO<sub>x</sub> efficiency at low temperature ( $175 - 250^{\circ}$ C), while avoiding NO<sub>2</sub> and DOC dependencies. (EtOH+NH<sub>3</sub>)-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst had superior NO<sub>x</sub> reduction efficiency than both NH<sub>3</sub>-SCR and EtOH-SCR performed on the same sample in the 175 - 500°C temperature range. This synergetic effect observed at low temperature was explained by the activation of three different DeNO<sub>x</sub> pathways: (i) the original EtOH-SCR, (ii) the NH<sub>3</sub>-SCR process, activated by NO<sub>2</sub> formed during EtOH-SCR (fast-SCR condition); and (iii) mainly by the H<sub>2</sub>-assisted NH<sub>3</sub>-SCR [30], occurring thanks to the H<sup>\*</sup> species provided by the ethanol dehydrogenation into acetaldehyde over the silver supported catalyst.

Even though a significant DeNO<sub>x</sub> enhancement was obtained by ammonia co-feeding in EtOH-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, the outlet exhaust gas still contained residual ammonia and NO<sub>x</sub>. Interestingly, NO<sub>2</sub> composed a high proportion of the remaining NO<sub>x</sub> in the 175 – 300°C temperature range. The composition of the outlet exhaust gas being close to the fast-SCR condition, the addition of a conventional NH<sub>3</sub>-SCR catalyst (WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub>) downstream the EtOH-SCR catalyst was thus implemented. The DeNO<sub>x</sub> efficiency at low temperature range while only NO was injected as NO<sub>x</sub> in the feed stream. This high DeNO<sub>x</sub> efficiency was then very similar to that recorded over NH<sub>3</sub>-SCR materials in the most favourable fast-SCR condition.

The WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalyst was selected as NH<sub>3</sub>-SCR material because it appeared active with various NO<sub>2</sub>/NO<sub>x</sub> inlet ratios and it could act as an Ammonia Slip Oxidation Catalyst (ASC) to avoid ammonia release with a high selectivity towards N<sub>2</sub>[13]. We recently compared WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and exchanged Cu–FER as NH<sub>3</sub>-SCR catalyst in the dual-bed configuration [31]. Compared to WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>, Cu-FER catalyst exhibited similar standard NH<sub>3</sub>-SCR behaviour and promising higher fast-SCR activity at low temperature. Unfortunately, in the dual-bed configuration, the Cu-FER sample led to a lower DeNO<sub>x</sub> efficiency than WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>, despite higher ammonia conversion rates. Then, the Cu exchanged zeolite exhibited a less attractive use of ammonia compared to WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>.

In the present work, the  $Ag/Al_2O_3 + WO_3/Ce_x-Zr_yO_2$  dual-bed reactivity was investigated with the aim to have a better understanding of the  $WO_3/Ce_xZr_{1-x}O_2$  catalytic behaviour, especially toward the reactivity of carbon and nitrogen compounds.

#### 2. Materials and methods

#### 2.1. Catalysts preparation

Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, dedicated to NO<sub>x</sub> reduction by ethanol, was prepared by silver impregnation (from AgNO<sub>3</sub> salt, Sigma Aldrich) on alumina (provided by Axens, previously calcined 4 hours under air at 700°C) in order to obtain of  $2_{wt}$ % Ag. This silver content was selected because it is commonly described as an optimal loading [32]. The preparation method, detailed in [29], was inspired by the work of Sato *et al.* [33] in which ethanol was used as impregnation solvent rather than water because it allows a better silver dispersion thus a better DeNO<sub>x</sub> activity. The catalyst was finally calcined under wet air (10 vol% H<sub>2</sub>O) at 700°C for 4 h (heating rate of 5°C min<sup>-1</sup>) and it is denoted Ag/Al in this article.

 $6_{wt}$ % WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalyst (noted as WO<sub>3</sub>/Ce-Zr), was selected as NH<sub>3</sub>-SCR material. The method of preparation was inspired by a previous study [13]. First, ceria-zirconia support (40 wt% of CeO<sub>2</sub>, supplied by Solvay) was aged 4 hours under air at 700°C. After dissolution of the desired amount of ammonium metatungstate ((NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>, 5H<sub>2</sub>O) in water, this solution was added to the Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub> support and maintained at 60°C under continuous stirring for 30 minutes. After a drying step at 120°C for 12 hours, the obtained solid was finally calcined 4 hours at 700°C in wet air, as well as the Ag/Al material.

#### 2.2. Characterizations

#### N<sub>2</sub> physisorption.

N<sub>2</sub> physisorption experiments were conducted with a Tristar 3000 (Micromeritics). The sample was firstly degassed 2 hours under vacuum at 250°C. N<sub>2</sub> adsorption was then realized at -196°C and the specific surface areas were determined from the Brunauer-Emmett-Teller (BET) method in the 0.05 – 0.25 p/p<sup>0</sup> range. *X-Ray Diffraction*. X-Ray Diffraction (XRD) patterns were collected using an Empyrean diffractometer (PANalytical) operating in the  $\theta$ -2 $\theta$  mode, using the Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The patterns were recorded from 2 $\theta$ =20 to 120° with a scanning step of 0.1°.

#### H<sub>2</sub>-Temperature Programmed Reduction.

Temperature Programmed Reduction (TPR) experiments were carried out using a Micromeritics Autochem 2920 device, equipped with a thermal conductivity detector (TCD). The sample (between 100 and 200 mg) was placed in a U-shaped reactor between two layers of quartz wool. Prior to the TPR measurement, the sample was first treated under pure  $O_2$  at 500°C for 60 min (heating rate of 5°C min<sup>-1</sup>). After cooling down to room temperature, the sample was purged under Ar flow for 45 minutes. The reduction step was then carried out under 1 % H<sub>2</sub> in Ar flow up to 900°C, with a heating rate of 5°C min<sup>-1</sup>. Since the TCD signal is sensitive to water, a trap (magnesium perchlorate) was added downstream of the reactor.

#### 2.3. Catalytic tests

Tests were carried out in a quartz tubular micro-reactor under a flow representative of a Diesel exhaust gas (including CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>) in which were added, alone or combined, various reductants: ammonia (NH<sub>3</sub>), ethanol (EtOH) or acetaldehyde (CH<sub>3</sub>CHO). All the catalytic test types are listed in Table 1. All tests were performed at a total flow rate of 333 mL

min<sup>-1</sup>. For catalytic tests with single catalyst, 100 mg of powdered catalyst were diluted in 100 mg SiC, both sieved between 100 µm and 250 µm. The corresponding GHSV were of 130,000 h<sup>-1</sup> toward Ag/Al and 230,000 h<sup>-1</sup> toward WO<sub>3</sub>/Ce-Zr catalysts (200 L h<sup>-1</sup> g<sub>cata</sub><sup>-1</sup>; 100 L h<sup>-1</sup> g<sub>powder</sub><sup>-1</sup>). Regarding the dual-bed configuration, 100 mg of WO<sub>3</sub>/Ce-Zr catalyst were placed downstream 100 mg of Ag/Al catalyst. Consequently, the GHSV was of 180,000 h<sup>-1</sup> (100 L h<sup>-1</sup> g<sub>cata</sub><sup>-1</sup>). The experimental setup has been previously described in [36,37]. The gas mixture was adjusted using Bronkhorst mass-flow controllers, except for ethanol, acetaldehyde and water which were vaporized into the reactor *via* a micro-nozzle (The Lee Company ( $\emptyset_{nozzle}$ = 50 µm)) placed into the quartz reactor in a heated zone at 200°C. The micro-nozzle was connected to a HPLC pump (Jasco, PU-2085) operating at a flow rate of 22 µL min<sup>-1</sup>, ( $\Delta$ P= 10 bar). Before injection, EtOH and CH<sub>3</sub>CHO were diluted into water at a concentration of 8.02 10<sup>-1</sup> mol L<sup>-1</sup>, in order to achieve the desired amounts of reductant and water in the gas phase. Note that the theoretical residence time between the injection zone and the catalytic bed is 5.2 s.

The inlet and outlet gas compositions were monitored using a MKS 2030 Multigas infrared analyser, recording the concentrations of CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CHO, CH<sub>3</sub>OH, CH<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, HCOOH, CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, HNCO and H<sub>2</sub>O.

Catalytic test	NO (ppm)	NO <sub>2</sub> (ppm)	NH <sub>3</sub> (ppm)	C <sub>2</sub> -comp. <sup>1</sup> (ppm)	O2 (%)	CO <sub>2</sub> (%)	H <sub>2</sub> O (%)	N <sub>2</sub>
Standard-NH <sub>3</sub> - SCR	400	-	400	-	10	10	8	_
Fast-NH <sub>3</sub> -SCR	200	200	400	-	10	10	8	
EtOH-SCR	400	-	-	1200	10	10	8	-
(EtOH+NH <sub>3</sub> )-SCR	400	-	400	1200	10	10	8	-
Fast-CH <sub>3</sub> CHO- SCR	200	200	-	600	10	10	8	balance
Fast- (CH <sub>3</sub> CHO+NH <sub>3</sub> )- SCR	200	200	400	600	10	10	8	-
CH <sub>3</sub> CHO oxidation	-	-	-	600	10	10	8	-

Table 1. Gas mixtures for SCR catalytic tests (total flow rate: 333 mL min<sup>-1</sup>).

<sup>1</sup> C<sub>2</sub>-compounds are C<sub>2</sub>H<sub>5</sub>OH (EtOH) or CH<sub>3</sub>CHO

#### 3. Results and discussion

3.1 Physical and chemical characterizations of Ag/Al and WO<sub>3</sub>/Ce-Zr single catalysts

#### 3.1.1. Ag/Al catalyst

The Ag/Al sample exhibited a specific surface area of 160 m<sup>2</sup> g<sup>-1</sup>, which was very similar to the surface area of the host alumina support before the addition of 2 wt% Ag (Table 2). The XRD analysis of this catalyst evidenced the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase (ICDD PDF n° 00-050-0741(1)) and no peaks assigned to silver species such as Ag<sup>0</sup>, Ag<sub>2</sub>O or AgO were evidenced (Figure 1). TPR

profile of Ag/Al (not shown) exhibited a broad H<sub>2</sub> consumption peak centred at 260°C. The corresponding hydrogen consumption (Table 2) indicated that silver species were initially composed of 33 % of Ag<sup>I</sup> species, in accordance with data reported by Musi *et al.* [35] for such samples. As previously reported in [29], TEM analysis showed that Ag/Al sample presented a homogeneous repartition of small silver particles, most of them ranging below 3 nm.

Catalyst	$\begin{array}{c} S_{BET} \\ (m^2.g^{-1}) \end{array}$	porous volume (cm <sup>3</sup> .g <sup>-1</sup> )	mean pore diameter (Å)	TPR H <sub>2</sub> cons. (20-800°C range) $(\mu mol_{H2}.g^{-1})$
Al	176	0.53	120	-
Ag/Al	160	0.49	128	119
Ce-Zr	73	0.32	175	795
WO <sub>3</sub> /Ce-Zr	52	0.26	197	785

Table 2. Textural properties and hydrogen consumption from H<sub>2</sub>-TPR experiments.



Figure 1: XRD patterns of the studied catalysts and corresponding host supports.

#### 3.1.2. WO<sub>3</sub>/Ce-Zr catalyst

The addition of 6 wt% WO<sub>3</sub> to the ceria-zirconia support led to a significant decrease of the specific surface area, from 73 to 52 m<sup>2</sup> g<sup>-1</sup>. This decline was associated with a decrease in the porous volume from 0.32 to 0.26 cm<sup>3</sup>.g<sup>-1</sup> and with an increase in the mean pore diameter from 175 to 197 Å (Table 2). The XRD analysis of WO<sub>3</sub>/Ce-Zr revealed no modification of the XRD pattern of the support after WO<sub>3</sub> impregnation (Figure 1). No WO<sub>3</sub> XRD peaks were detected, suggesting a good dispersion of tungsten trioxide phase, in accordance with Xiaowei *et al.* [34] which reported that tungsten oxide can be highly dispersed on Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> solid solution. The

H<sub>2</sub>-TPR profile of WO<sub>3</sub>/Ce-Zr (not shown) revealed a broad H<sub>2</sub> consumption peak between 350 and 750°C, with a maximum hydrogen consumption recorded at 660°C. The shoulder recorded in the low temperature range (350- 600°C) was attributed to the reduction of Ce<sup>4+</sup> into Ce<sup>3+</sup> from the first layers of the support, while the high temperature H<sub>2</sub> consumption was associated to the bulk reduction. No peak attributable to WO<sub>3</sub> was observed in the studied temperature range. A TPR experiment conducted over the Ce<sub>40</sub>Zr<sub>60</sub>O<sub>2</sub> support resulted in similar profile, with an identical H<sub>2</sub> consumption (Table 2). Only a shift of approximately 50°C to lower temperatures was observed. It suggests interactions between deposited WO<sub>3</sub> and the support which slowed down the support reducibility, in accordance with a previous study [13]. These results together with XRD patterns allow to assume that WO<sub>3</sub> covered the Ce-Zr support without causing any structural change for the support.

#### 3.2. Catalytic activity of WO<sub>3</sub>/Ce-Zr in NO<sub>x</sub> SCR by NH<sub>3</sub> and/or EtOH.

In order to have a better understanding of the WO<sub>3</sub>/Ce-Zr behaviour in the Ag/Al + WO<sub>3</sub>/Ce-Zr dual-bed system, the catalytic activity of single WO<sub>3</sub>/Ce-Zr was examined with various gas mixtures detailed in section 2.3.

#### 3.2.1. Standard and fast-NH<sub>3</sub>-SCR conditions

Single WO<sub>3</sub>/Ce-Zr catalyst was firstly evaluated in NH<sub>3</sub>-SCR with two different NO<sub>2</sub>/NO<sub>x</sub> inlet ratios corresponding to the standard-SCR condition (NO<sub>2</sub>/NO<sub>x</sub>= 0) and to the fast-SCR condition (NO<sub>2</sub>/NO<sub>x</sub>= 0.5). Obtained NO<sub>x</sub> and NH<sub>3</sub> conversions are reported in Figures 2a and 2b, respectively. In standard-SCR condition (Figure 2a), the NO<sub>x</sub> conversion was ranked between 15 % and 90 % in the 175 - 300°C temperature range. In this temperature range, the NH<sub>3</sub> conversion followed the same trend, in accordance with the standard-SCR stoichiometry (reaction (1)), corresponding to an ammonia to NO<sub>x</sub> ratio (ANR) of 1. A decrease in the NO<sub>x</sub> conversion was then observed for temperatures higher than 450°C, while ammonia was totally converted. The NO<sub>x</sub> reduction then competed with the ammonia oxidation, which can lead to either N<sub>2</sub> or NO<sub>x</sub> as described by reactions (3) and (4) [6]:

 $4 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O}$  (3)

 $4 \text{ NH}_3 + 5 \text{ O}_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}$  (4)

Note that  $N_2O$  could be a by-product of both the  $NH_3$  oxidation and the  $NO_x$  reduction. However, these pathways were very limited since  $N_2O$  was detected only in small amounts in both standard and fast-SCR condition (less than 10 ppm over the full studied temperature range).

As expected, the NO<sub>x</sub> conversion was significantly improved in fast-SCR condition (Figure 2b). Compared to the standard-SCR condition, the NO<sub>x</sub> conversion was increased by around 30 and 50 % at 175°C and 200°C, respectively. The 90 % NO<sub>x</sub> conversion was reached from 200°C in fast-SCR condition while a temperature higher than 250°C was needed in standard-SCR condition. The ammonia conversion still followed the NO<sub>x</sub> conversion until 400°C, according to the 1:1 stoichiometric ratio resulting from the fast-SCR reaction (2). Again, a decrease in the NO<sub>x</sub> conversion was observed for temperature higher than 450°C due to the competition with the ammonia oxidation.

Finally, as expected, a clear improvement in the  $NO_x$  conversion was obtained when NO and  $NO_2$  were fed together. Mechanistic studies highlighted that the concomitance of NO and  $NO_2$ 

favours the formation of surface  $HNO_x$  species, which are very reactive towards ammonia [38]. When only NO is introduced in the gas mixture, the limiting step corresponds to the oxidation of NO to NO<sub>2</sub> [39] to further obtain the formation of  $HNO_x$  species. To characterize the NO oxidation ability of the WO<sub>3</sub>/Ce-Zr sample, a supplementary test was performed without ammonia in the feed stream. Results (not shown) showed that this catalyst was unable to significantly oxidize NO in NO<sub>2</sub> below 350°C, which explains the lack of activity in standard-SCR condition at low temperature.



Figure 2.  $NO_x$  (—) and  $NH_3$  (—) conversions in  $NH_3$ -SCR over  $WO_3$ /Ce-Zr catalyst for standard- $NH_3$ -SCR condition (**a**) and fast- $NH_3$ -SCR condition (**b**). Reaction mixtures are depicted in Table 1.

#### 3.2.2. EtOH and (EtOH+NH<sub>3</sub>)-SCR conditions

In the dual-bed (Ag/Al+WO<sub>3</sub>/Ce-Zr) catalytic system, the silver-based catalyst is dedicated to the EtOH-SCR purpose (see section 3.3). However, mixtures including ethanol (and its by-products) may reach the WO<sub>3</sub>/Ce-Zr catalyst placed downstream. Consequently, the single WO<sub>3</sub>/Ce-Zr catalyst was also evaluated in EtOH-SCR and (EtOH+NH<sub>3</sub>)-SCR conditions with only NO as injected NO<sub>x</sub>, as reported in Table 1.

EtOH-SCR tests were performed by injecting 1200 ppm of EtOH in the feed-stream (without ammonia). NO<sub>x</sub> and EtOH conversion profiles recorded over WO<sub>3</sub>/Ce-Zr are presented in Figure 3a, while outlet concentrations of NO<sub>2</sub> and C-compounds are presented in Figure 3b. The catalyst allowed the ethanol conversion from the starting temperature (175°C) and EtOH was completely converted at 320°C (Figure 3a). However, the NO<sub>x</sub> conversion was then very limited, with a maximum of 7 % around 300°C. For temperatures higher than 350°C, few amounts of NO<sub>2</sub> were emitted, with a maximum of 30 ppm observed at 500°C (Figure 3b, blue line). In this temperature range, NO oxidation into NO<sub>2</sub> was probably resulting from the reaction between NO and ethanol in the gas phase, as already mentioned in the literature [22].

The ethanol conversion over WO<sub>3</sub>/Ce-Zr was firstly characterized by the formation of small amounts of acetaldehyde, with a maximum of 160 ppm recorded at 250°C (Figure 3b). The ethanol reactivity was also characterized by the emission of high concentrations of ethylene and CO from 300°C. In this temperature range, the catalyst thus promoted the dehydration reaction

rather than the dehydrogenation reaction of ethanol. Moreover, ammonia was not detected as a reaction product. As discussed in the introduction part, ammonia emission is usually observed over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts in EtOH-SCR condition. Its formation is due to the decomposition of nitromethane, an intermediate species involved in the N<sub>2</sub> formation route. Ammonia absence over WO<sub>3</sub>/Ce-Zr indicates that nitromethane formation was then limited or did not occur. It results that WO<sub>3</sub>/Ce-Zr catalyst is not efficient to reduce NO<sub>x</sub> by ethanol, probably because of the acidity procured by WO<sub>3</sub>, which generally promotes alcohols dehydration [40,41].



Figure 3. EtOH-SCR over WO<sub>3</sub>/Ce-Zr catalyst: NO<sub>x</sub> (-) and EtOH (-) conversions (**a**) and CH<sub>3</sub>CHO (-), CO (-), CH<sub>2</sub>O (-), C<sub>2</sub>H<sub>4</sub> (-) and NO<sub>2</sub> (-) distributions (**b**). Reaction mixture is depicted in Table 1.

The single WO<sub>3</sub>/Ce-Zr catalyst was also evaluated in (EtOH+NH<sub>3</sub>)-SCR condition (Figure 4). To the opposite of EtOH-SCR (Figure 3), the NO<sub>x</sub> conversion was significant in (EtOH+NH<sub>3</sub>)-SCR condition, from 13 to 70 % in the 175 – 450°C temperature range (Figure 4a). Above 450°C, the conversion dropped slightly. This reactivity was correlated with the conversion of ammonia. From 175 to 250°C, the NH<sub>3</sub> conversion was close to the NO<sub>x</sub> conversion, indicating that the standard-SCR reaction was achieved. From 250°C, the NH<sub>3</sub> conversion became higher than the NO<sub>x</sub> conversion, reaching 93 % at 350°C. The NO<sub>x</sub> conversion loss at T > 450°C was thus correlated to the probable oxidation of a part of the added ammonia, according to reaction (3) and (4).

However, in comparison to the standard-NH<sub>3</sub>-SCR test reported in Figure 2a, the NO<sub>x</sub> conversion in (EtOH+NH<sub>3</sub>)-SCR was significantly lower. For instance, the NO<sub>x</sub> conversion at 250°C was more than two times lower in presence of ethanol, at around 40 % compared to 85 % in NH<sub>3</sub>-SCR. Thus, the presence of ethanol did not allow NO<sub>x</sub> conversion but also inhibited the NH<sub>3</sub>-SCR over WO<sub>3</sub>/Ce-Zr. This statement was confirmed by the comparison of the EtOH conversion profiles. Compared to EtOH-SCR experiments (Figure 3a), NH<sub>3</sub> co-injection induced a slight decrease in the ethanol conversion, especially in the 250-300°C temperature range. As a result, lower amounts of acetaldehyde were also observed (Figure 4b). Similarly, NH<sub>3</sub> conversion also decreased in presence of ethanol. A competitive adsorption between the two reductants is thus presumed, probably occurring on the acid sites. As for EtOH-SCR

condition, NO<sub>2</sub> emissions were recorded in (EtOH+NH<sub>3</sub>)-SCR, but in a lower extent. A maximum of 15 ppm was observed at 500°C, suggesting a consumption of emitted NO<sub>2</sub> with NH<sub>3</sub>.



Figure 4. (EtOH+NH<sub>3</sub>)-SCR over WO<sub>3</sub>/Ce-Zr catalyst: NO<sub>x</sub> (-), NH<sub>3</sub> (-) and EtOH (-) conversions (**a**) and CH<sub>3</sub>CHO (-), CO (-), CH<sub>2</sub>O (-), C<sub>2</sub>H<sub>4</sub> (-) and NO<sub>2</sub> (-) distributions (**b**). Reaction mixtures are depicted in Table 1.

To conclude, the WO<sub>3</sub>/Ce-Zr catalyst is quite inactive for reducing NO<sub>x</sub> with ethanol. In addition, the comparison of the DeNO<sub>x</sub> efficiency over WO<sub>3</sub>/Ce-Zr catalyst in (EtOH+NH<sub>3</sub>)-SCR (Figure 4a) and NH<sub>3</sub>-SCR (Figure 2a) with only NO as NO<sub>x</sub> injected revealed a lower NO<sub>x</sub> conversion when ethanol was co-fed with ammonia. It suggests a competitive adsorption of ethanol or these by-products with NH<sub>3</sub>. This assumption is also consistent with the lower ethanol conversion reported for (EtOH+NH<sub>3</sub>)-SCR compared to EtOH-SCR. In the context of the dual-bed catalytic system, there is therefore a risk that residual ethanol and carbonaceous by-products (after passing through the first Ag/Al catalytic bed) partially inhibit the activity of the second bed (WO<sub>3</sub>/Ce-Zr).

#### 3.3. Catalytic behaviours of Ag/Al and Ag/Al + WO<sub>3</sub>/Ce-Zr dual-bed

In order to highlight the reactivity of the WO<sub>3</sub>/Ce-Zr in the dual-bed configuration (composed of 100 mg of Ag/Al as EtOH-SCR catalyst placed upstream 100 mg of WO<sub>3</sub>/Ce-Zr as NH<sub>3</sub>-SCR catalyst), results were compared with those obtained over single Ag/Al catalyst (100 mg diluted in 100 mg of SiC). The DeNO<sub>x</sub> chemistry of Ag/Al sample in EtOH-SCR and (EtOH+NH<sub>3</sub>)-SCR was already discussed in a previous work [29]. As presented in the introduction section, one interesting point is the significant NO<sub>2</sub> emission recorded at low temperature (175 – 300°C) concomitantly with ethanol oxidation into CH<sub>3</sub>CHO.

#### 3.3.1. EtOH-SCR condition

Ag/Al and the dual-bed configuration were firstly evaluated in EtOH-SCR (1200 ppm EtOH, 400 ppm NO, 10 % O<sub>2</sub>, 10 % CO<sub>2</sub>, 8 % H<sub>2</sub>O, N<sub>2</sub>).

#### 3.3.1.1. Evolution of C-compounds (ethanol and acetaldehyde)

Figure 5 reports the ethanol conversions and the acetaldehyde emission obtained in EtOH-SCR for both catalytic configuration. Compared with single Ag/Al catalyst, the ethanol conversion was enhanced over the dual-bed system, by 10 to 20 % in the 175 - 350°C temperature range. This improvement is explained by the ability of the WO<sub>3</sub>/Ce-Zr catalyst to activate the oxidation of ethanol from 175°C, as previously illustrated in Figure 3a. Interestingly, the acetaldehyde concentration was also impacted by the addition of WO<sub>3</sub>/Ce-Zr. A significant decrease was observed from 200°C. At 250°C, a maximum of 420 ppm was reached over Ag/Al, while the concentration was almost three times lower (150 ppm) over the dual-bed system. Instead, according to Figure 3b, an additional release of CH<sub>3</sub>CHO was rather expected by the addition of the second bed. Therefore, this consumption, recorded over a wide temperature range, suggests a specific reactivity of acetaldehyde over WO<sub>3</sub>/Ce-Zr sample. This point is discussed thereafter in section 3.3.2.

Note that the CO emission from the dual-bed configuration (not shown) was close to that observed with Ag/Al alone and significantly lower than values recorded with WO<sub>3</sub>/Ce-Zr sample. For instance, at 350°C (temperature for which the ethanol conversion reached 100 % for the three studied catalytic beds), the CO emissions reached 245, 765 and 325 ppm over the Ag/Al, WO<sub>3</sub>/Ce-Zr and Ag/Al+WO<sub>3</sub>/Ce-Zr catalytic systems, respectively. Then, the addition of WO<sub>3</sub>/CeZr downstream Ag/Al led only to a small increase of the CO emissions, indicating that other by-products from ethanol decomposition, typically CH<sub>3</sub>CHO, were partially converted into CO over WO<sub>3</sub>/CeZr (see also section 3.3.3).



Figure 5. EtOH-SCR over Ag/Al (—) and (Ag/Al+WO<sub>3</sub>/Ce-Zr) dual-bed system (—): EtOH conversions (full line) and CH<sub>3</sub>CHO emissions (dotted line). Reaction mixtures are depicted in Table 1.

#### 3.3.1.2. Evolution of N-compounds

The NO<sub>x</sub> conversion and NO<sub>2</sub> concentration profiles recorded during the EtOH-SCR experiments are depicted in Figure 6 depending on the nature of the catalyst bed,. As expected, the addition of WO<sub>3</sub>/Ce-Zr downstream Ag/Al catalyst led to an enhancement in the DeNO<sub>x</sub> efficiency in the 230 - 400°C temperature range.

This improvement can be related to the capacity of the Ag/Al catalyst to generate  $NH_3$  *in situ* as reported by Flura *et al.* [22], which can be used by the  $NH_3$ -SCR catalyst. Indeed the  $NH_3$  emission was significantly decreased after the addition of the  $WO_3$ /Ce-Zr. For instance, 19 ppm  $NH_3$  were converted on  $WO_3$ /Ce-Zr at 300°C, close to the supplementary  $NO_x$  conversion (16 ppm). At higher temperature, when the  $NO_x$  conversion already reached 100 % over Ag/Al, the  $WO_3$ /Ce-Zr catalyst also acted as an ammonia slip catalyst, limiting the ammonia emissions: at 400°C, 98 ppm  $NH_3$  were converted while the  $NO_x$  conversion remained total. Unfortunately, for temperature higher than 450°C, the ammonia oxidation appeared leading to  $NO_x$  formation, since a decrease in the  $NO_x$  conversion was then observed (Figure 6).

Besides, Figure 6 shows that the outlet concentration of NO<sub>2</sub> was also strongly affected by the addition of the second catalytic bed. Indeed, NO<sub>2</sub> was fully consumed from 175 to 400°C whereas amounts higher than 220 ppm were emitted from Ag/Al catalyst between 200 and 250°C. Thanks to ammonia formation on the first bed, NO<sub>2</sub> could be potentially reduced, according to the fast SCR reaction (reaction (2)). This result would be in accordance with the strong activity of the WO<sub>3</sub>/Ce-Zr catalyst in fast condition (section 3.2.1). However, the NO<sub>2</sub> consumption on WO<sub>3</sub>/Ce-Zr was too important to be only explained by the fast SCR reaction, with respect to the gain of NO<sub>x</sub> conversion observed by adding the NH<sub>3</sub>-SCR catalyst. Then, a realistic assumption is that NO<sub>2</sub> was also reduced into NO over WO<sub>3</sub>/Ce-Zr catalyst. Moreover, the NO<sub>2</sub> consumption (Figure 5), suggesting that both species could be involved in an additional reaction. This assumption is examined in section 3.3.3.



Figure 6. EtOH-SCR over Ag/Al (—) and (Ag/Al+WO<sub>3</sub>/Ce-Zr) dual-bed system (—): NO<sub>x</sub> conversions (full line) and NO<sub>2</sub> emissions (dotted line). Reaction mixtures are depicted in Table 1.

#### 3.3.2. (EtOH+NH<sub>3</sub>)-SCR condition

Both Ag/Al and Ag/Al+WO<sub>3</sub>/Ce-Zr catalytic systems were also compared in (EtOH+NH<sub>3</sub>)-SCR (1200 ppm EtOH, 400 ppm NH<sub>3</sub>, 400 ppm NO, 10% O<sub>2</sub>, 10% CO<sub>2</sub>, 8% H<sub>2</sub>O).

#### 3.3.2.1. Evolution of C-compounds (ethanol and acetaldehyde)

Figure 7 shows the influence of the addition of the WO<sub>3</sub>/Ce-Zr catalyst to Ag/Al toward both ethanol conversion and acetaldehyde emission measured in (EtOH+NH<sub>3</sub>)-SCR condition. When NH<sub>3</sub> was added to the inlet mixture, similar ethanol conversion profiles were obtained whatever the catalytic bed configuration. Compared to single Ag/Al, the dual-bed led to a slight increase in the alcohol conversion, as already reported in EtOH-SCR condition. Again, the acetaldehyde emission was decreased by addition of the WO<sub>3</sub>/Ce-Zr catalyst. Nevertheless, over the dual-bed system, co-injection of (EtOH+NH<sub>3</sub>) led to a lower acetaldehyde outlet concentration than that observed in EtOH-SCR condition, suggesting a competitive reactivity of acetaldehyde with co-fed ammonia. However, whatever the considered catalytic system, the addition of NH<sub>3</sub> in the inlet mixture has no significant impact on CO emissions.



Figure 7. (EtOH+NH<sub>3</sub>)-SCR over Ag/Al (—) and (Ag/Al+WO<sub>3</sub>/Ce-Zr) dual-bed system (—): EtOH conversions (full line) and CH<sub>3</sub>CHO emissions (dotted line). Reaction mixtures are depicted in Table 1.

#### 3.3.2.2. Evolution of N-compounds

Figure 8 reports the evolution of the N-compounds, expressed as the NO<sub>x</sub> conversion and the NO<sub>2</sub> emission profiles for both catalytic systems. As expected, the addition of ammonia to the feed-stream led to a remarkable enhancement of the DeNO<sub>x</sub> activity compared to the NO<sub>x</sub> conversions obtained over the single Ag/Al catalyst, especially at low temperature (T < 300°C). The NO<sub>x</sub> conversion was then ranked between 45 and 90 % in the 175 - 250°C temperature range, while only NO was initially injected. Interestingly, the DeNO<sub>x</sub> efficiency obtained in (EtOH+NH<sub>3</sub>)-SCR condition over the dual-bed system became close to the activity observed in the most favourable fast-SCR stoichiometry recorded with single WO<sub>3</sub>/Ce-Zr sample (Figure 2a).



Figure 8. (EtOH+NH<sub>3</sub>)-SCR over Ag/Al (—) and (Ag/Al+WO<sub>3</sub>/Ce-Zr) dual-bed system (—): NO<sub>x</sub> conversions (full line) and NO<sub>2</sub> emissions (dotted line). Reaction mixtures are depicted in Table 1.

As previously observed in EtOH-SCR condition, NO<sub>2</sub> emitted from Ag/Al was fully converted in the dual-bed configuration. Table 3 reports, for each studied temperature, the amounts of NH<sub>3</sub>, NO<sub>2</sub> and NO<sub>x</sub> converted by the second WO<sub>3</sub>/Ce-Zr bed by subtraction between the remaining amounts measured after single Ag/Al bed and the dual-bed (remind that 400 ppm NH<sub>3</sub> were then added in the feed stream). Table 3 clearly evidenced that the addition of the NH<sub>3</sub>-SCR catalyst led to a significant supplementary ammonia consumption. For a temperature higher than 300°C, for which the gain in NO<sub>x</sub> conversion is negligible, WO<sub>3</sub>/Ce-Zr catalyst acted as an ammonia slip catalyst, limiting the ammonia emissions. In the 175 – 250°C temperature range, the improvement in the ammonia conversion was associated with an improvement in the NO<sub>x</sub> conversion. However, data clearly evidenced that the involved NO<sub>x</sub> and NH<sub>3</sub> quantities did not correspond to the stoichiometry of the fast or standard SCR reactions described in reactions (1) and (2).

Temperature – (°C)	NH3 outl	et (ppm)	ANIL.	ANO	ANO
	Ag/Al	Dual- bed	(ppm)	(ppm)	(ppm)
175	363	223	140	49	127
200	300	115	185	137	124
250	195	125	70	52	36
300	304	229	75	1	1
350	351	265	86	0	3
400	339	192	147	0	6
450	306	70	236	0	19
500	256	18	238	2	47

Table 3. NH<sub>3</sub> outlet emissions recorded in (EtOH+NH<sub>3</sub>)-SCR over Ag/Al catalyst and the dual-bed catalytic system (Ag/Al+WO<sub>3</sub>/Ce-Zr); NH<sub>3</sub>, NO<sub>x</sub> and NO<sub>2</sub> consumptions resulting from the addition of WO<sub>3</sub>/Ce-Zr catalyst downstream Ag/Al (for instance,  $\Delta$ NH<sub>3</sub>= NH<sub>3</sub>(Ag/Al)-NH<sub>3</sub>(dual-bed)).

In order to obtain a better understanding of the reactions involved, the amounts of NO<sub>2</sub> and NH<sub>3</sub> consumed by the addition of WO<sub>3</sub>/Ce-Zr were used to predict the NO<sub>x</sub> conversion. The theoretical NO<sub>x</sub> conversion was calculated assuming two different hypothesis: (i) the supplementary NO<sub>2</sub> consumption was only used to carry out the fast SCR reaction; the consumption of NO<sub>2</sub> was therefore doubled to obtain the theoretical NO<sub>x</sub> conversion, to take into account that NO was also equally consumed by the fast SCR reaction; (ii) the supplementary consumed NH<sub>3</sub> was only used to reduce NO<sub>x</sub>, with a NH<sub>3</sub>:NO<sub>x</sub> ratio of 1:1. These estimations of NO<sub>x</sub> conversion were then added to the experimental values obtained in (EtOH+NH<sub>3</sub>)-SCR over the single Ag/Al catalyst to obtain a theoretical NO<sub>x</sub> conversion over the dual-bed system. Results from these calculations are presented in Figure 9 as a function of temperature, and compared to the experimental NO<sub>x</sub> conversion obtained with the dual-bed configuration. When the NO<sub>x</sub> conversion was estimated from the quantity of consumed NH<sub>3</sub> (green bares), the comparison to the experimental value (blue bares) shows rather close NO<sub>x</sub> conversion in the 175-250°C temperature range, which suggests that the supplementary NO<sub>x</sub> conversion was mainly governed by the standard or, more probably, the fast-SCR reaction (both respecting a NH<sub>3</sub>:NO<sub>x</sub> ratio of 1). However, at  $T \ge 300^{\circ}$ C, the calculated NO<sub>x</sub> conversion was then higher than 100%, reaching up to 155% at 450°C. This result induces an overconsumption of ammonia that could be attributed to its oxidation (SCO) into  $N_2$ , according to reaction (3). This reaction is usually undesired because it leads to an overconsumption of the reductant. Moreover, depending on the catalyst and the temperature, ammonia SCO can lead to NOx formation, according to reaction (4). The efficiency of the WO<sub>3</sub>/Ce-Zr catalysts toward SCO reaction was already described in [13]. The ammonia conversion started near 250°C and reached approximately 80 % at 500°C. N<sub>2</sub>O was not detected and traces of NO<sub>x</sub> (in fact NO) were only detected at 500°C. The corresponding NO selectivity was then lower than 5 %. When the  $NO_x$  conversion was estimated from the amount of  $NO_2$  consumed (red-grey bares) by considering a fast-SCR stoichiometry, the only calculation closed to the experimental value

by considering a fast-SCR stoichiometry, the only calculation closed to the experimental value was obtained at  $175^{\circ}$ C and thus could characterize a fast-SCR type reaction. The values calculated at 200°C and 250°C were significantly higher than the experimental values, even exceeding a theoretical conversion of 100 %. These results highlight that NO<sub>2</sub> was not only consumed for the NO<sub>x</sub> reduction, but NO<sub>2</sub> was partially reduced into NO. Indeed, NO<sub>2</sub> reduction is possibly related to the oxidation of acetaldehyde, its consumption (Figure 7) being also significant in the same temperature range. This hypothesis is developed in the following section.



Figure 9. Additional NO<sub>x</sub> conversion expected from N-balance during (EtOH+NH<sub>3</sub>)-SCR test over the dual-bed configuration (Ag/Al+WO<sub>3</sub>/Ce-Zr). ( $\mathbb{N}$ ): additional NO<sub>x</sub> conversion estimated from NO<sub>2</sub> consumption by WO<sub>3</sub>/Ce-Zr (according to the fast SCR stoichiometry); ( $\mathbb{Z}$ ): additional NO<sub>x</sub> conversion estimated from NH<sub>3</sub> consumption over WO<sub>3</sub>/Ce-Zr; ( $\square$ ): experimental NO<sub>x</sub> conversion measured in (EtOH+NH<sub>3</sub>)-SCR over the dual-bed system.

#### 3.3.3. Acetaldehyde - NO2 reactivity

Results obtained in dual-bed configuration in both EtOH-SCR and (EtOH+NH<sub>3</sub>)-SCR conditions (sections 3.3.1 and 3.3.2, respectively) showed that the NO<sub>2</sub> consumption over WO<sub>3</sub>/Ce-Zr was not only involved in the NO<sub>x</sub> reduction respecting the fast-SCR reaction, and was also concomitant with the increase in the acetaldehyde consumption. Focussing on the (EtOH+NH<sub>3</sub>)-SCR condition and according to Table 3, 137 ppm of NO<sub>2</sub> were consumed at 200°C after addition of WO<sub>3</sub>/Ce-Zr to Ag/Al. Assuming that the NO<sub>x</sub> conversion gain was exclusively associated with the fast-SCR reaction, it would correspond to the conversion of 64 ppm NO<sub>2</sub> + 64 ppm NO. Around 70 ppm of remaining NO<sub>2</sub> were then converted into NO. This value being in the same order than the acetaldehyde consumption after the addition of the second bed, the reaction (5) was then hypothetically proposed:

 $CH_3CHO + NO_2 + 2 O_2 \rightarrow NO + 2 CO_2 + 2 H_2O \quad (5)$ 

 $NO_2$  is well known to be a stronger oxidizer than  $O_2$ . For instance,  $NO_2$  is commonly used for particulate matter removal in vehicles [4,42], it favours the continuous regeneration of the diesel particulate filter (DPF). Consequently, the improvement in the acetaldehyde oxidation in presence of  $NO_2$  is actually conceivable.

Even if reaction (5) probably occurred at 200°C over WO<sub>3</sub>/Ce-Zr, it did not reflect the NO<sub>2</sub>-CH<sub>3</sub>CHO reactivity in the whole studied temperature range. Indeed, the ratio between consumed CH<sub>3</sub>CHO and NO<sub>2</sub> over WO<sub>3</sub>/Ce-Zr was temperature dependant. Furthermore, this reaction supposes a complete CH<sub>3</sub>CHO oxidation into CO<sub>2</sub>. The fact that other compounds such as remaining ethanol but also CO,  $C_2H_4$  and CH<sub>2</sub>O produced over the first bed could also reacted on the second bed impedes in determining if CH<sub>3</sub>CHO oxidation by NO<sub>2</sub> was completed or not. In addition, over the dual-bed system, supplementary formaldehyde emissions of 20 and 63 ppm were observed at 200°C and 250°C, respectively, compared to single Ag/Al. Then, the complex mixture reaching the WO<sub>3</sub>/Ce-Zr catalyst led to numerous secondary reactions.

In order to investigate in greater depth the reaction between acetaldehyde and NO<sub>2</sub> over WO<sub>3</sub>/Ce-Zr catalyst, supplementary catalytic tests were performed over single WO<sub>3</sub>/Ce-Zr using acetaldehyde instead of ethanol as introduced reductant. The CH<sub>3</sub>CHO concentration for these tests was fixed at 600 ppm to be consistent with the acetaldehyde concentration recorded from Ag/Al sample. Figure 10 reports the CH<sub>3</sub>CHO conversion evaluated under different conditions reported in Table 1: (i) oxidation test with O<sub>2</sub> (600 ppm CH<sub>3</sub>CHO, without NO<sub>x</sub>), (ii) fast-CH<sub>3</sub>CHO-SCR (600 ppm CH<sub>3</sub>CHO, 200 ppm NO, 200 ppm NO<sub>2</sub>) and (iii) fast-(CH<sub>3</sub>CHO+NH<sub>3</sub>)-SCR (400 ppm NH<sub>3</sub> supplementary added). Note that the conversions are only reported at low temperatures (between 175 and 300°C), because total CH<sub>3</sub>CHO conversion was recorded at a higher temperature over Ag/Al.

It clearly appears that WO<sub>3</sub>/Ce-Zr is active in CH<sub>3</sub>CHO oxidation with O<sub>2</sub>, with 90 % conversion at 300°C (blue bare). Interestingly, for temperature ranked between 175 and 250°C, higher acetaldehyde conversions were denoted in the fast-CH<sub>3</sub>CHO-SCR condition (grey bare). Consequently, these results are in accordance with the hypothesis of a NO<sub>x</sub>-CH<sub>3</sub>CHO reactivity. When NH<sub>3</sub> was co-fed with CH<sub>3</sub>CHO (green bare), the conversion was slightly lower. Thus, a competitive adsorption between CH<sub>3</sub>CHO and NH<sub>3</sub> was highlighted, such as already observed with ethanol.



Figure 10. Comparison of the CH<sub>3</sub>CHO conversion *vs* the temperature, recorded over WO<sub>3</sub>/Ce-Zr for three different tests: CH<sub>3</sub>CHO oxidation with O<sub>2</sub> ( $\blacksquare$ ), fast-CH<sub>3</sub>CHO-SCR ( $\blacksquare$ ) and fast-(CH<sub>3</sub>CHO+NH<sub>3</sub>)-SCR ( $\blacksquare$ ).



Figure 11. Comparison of the  $NO_x$  conversion ((a), full line) and the NO outlet emission ((b), dotted line) *vs* the temperature, recorded over single WO<sub>3</sub>/Ce-Zr catalyst in fast-CH<sub>3</sub>CHO-SCR (—) and in fast-(CH<sub>3</sub>CHO+NH<sub>3</sub>)-SCR (—). Reaction mixtures are depicted in Table 1.

The NO<sub>x</sub> conversion and the NO outlet emission recorded over single WO<sub>3</sub>/Ce-Zr catalyst in fast-CH<sub>3</sub>CHO-SCR and fast-(CH<sub>3</sub>CHO+NH<sub>3</sub>)-SCR conditions are reported in Figure 11a and Figure 11b, respectively. In fast-CH<sub>3</sub>CHO-SCR condition, the DeNO<sub>x</sub> efficiency was limited to 7 % between 250°C and 300°C (full grey line). Interestingly, this result could explain a part of the DeNO<sub>x</sub> enhancement recorded in the same temperature range in EtOH-SCR condition over the dual-bed system (see section 3.3.1). In parallel, from 175°C, a major part of the introduced NO<sub>2</sub> was reduced into NO (Figure 11b) since NO emission was superior to 370 ppm over the whole studied temperature range, while only 200 ppm were introduced. This result confirms once again the reaction between acetaldehyde and NO<sub>2</sub>, as proposed in reaction (5).

However, the CH<sub>3</sub>CHO-NO<sub>2</sub> stoichiometry appeared varying with temperature. For instance, at 175°C in the fast-CH<sub>3</sub>CHO-SCR condition, 175 ppm of NO<sub>2</sub> were consumed for the oxidation of 100 ppm of CH<sub>3</sub>CHO (16 % of CH<sub>3</sub>CHO conversion, grey bare Figure 10), which results in a NO<sub>2</sub>/CH<sub>3</sub>CHO ratio of 1.75. Besides, this ratio seems to be the most precise we can determine because no consumption of CH<sub>3</sub>CHO by O<sub>2</sub> was denoted at this temperature in oxidation reaction (blue bare, Figure 10). Only the CH<sub>3</sub>CHO conversion linked with NO<sub>2</sub> was involved. It should also be noted that the stoichiometry proposed in reaction (5) assumes a total oxidation of acetaldehyde by NO<sub>2</sub>, which is not entirely correct. Indeed, other carbon by-products than CO<sub>2</sub> were detected, mainly HCOOH, CO and CH<sub>2</sub>O, showing an incomplete oxidation of CH<sub>3</sub>CHO. Taking into account (i) all these detected carbon by-products and (ii) the observed NO<sub>2</sub>/CH<sub>3</sub>CHO consumption ratio, the experimental stoichiometry calculated at 175°C would correspond to reaction (6):

 $35 \text{ NO}_2 + 20 \text{ CH}_3\text{CHO} + 10 \text{ O}_2 \rightarrow 35 \text{ NO} + 12 \text{ CH}_2\text{O} + 13 \text{ H}_2\text{O} + 6 \text{ CO} + 15 \text{ HCOOH} + 7 \text{ CO}_2$ (6)

Clearly, this equation includes several reactions occurring on the catalyst surface, going from the partial CH<sub>3</sub>CHO oxidation to its complete oxidation into CO<sub>2</sub>.

Figure 11b also revealed that the  $NO_x$  conversion was enhanced in presence of  $NH_3$  (green curve), assigned to the activity of  $WO_3$ /Ce-Zr sample in  $NH_3$ -SCR (Figure 2). For instance, a

NO<sub>x</sub> conversion of 50 % was achieved at 175°C, close to the value obtained with only ammonia as reducer (about 55 %). In this case, the over-emission of NO was not observed, with a preferentially NO<sub>2</sub> reduction into N<sub>2</sub>. It induced that the NO<sub>x</sub> reduction by NH<sub>3</sub> appeared more favoured than the acetaldehyde oxidation by  $NO_2$ . However, the  $NO_x$  conversion reached only 50-60 % between 200°C and 300°C, indicating an inhibitory effect from acetaldehyde on the fast-NH<sub>3</sub>-SCR reaction. Finally, these specific tests confirmed both the reactivity of CH<sub>3</sub>CHO with  $NO_2$  and the competitive adsorption of  $CH_3CHO$  with ammonia over  $WO_3$ /Ce-Zr. To summarize, an overview of the various reaction pathways identified in the (EtOH+NH<sub>3</sub>)-SCR process over the (Ag/Al + WO<sub>3</sub>/Ce-Zr) dual-bed system is presented in Figure 12. Pathways over Ag/Al catalyst originate from our previous work [29]. Despite the beneficial collaborative effect of ethanol and  $NH_3$  on the NO<sub>x</sub> conversion over silver supported catalyst, mainly attributed to the so-called "H2 assisted" NH3 -SCR, some NO, NO2 and NH3 remained at low temperature, as well as few hundreds ppm of acetaldehyde from ethanol decomposition. The reactivity of these remaining compounds results in three main reaction pathways on WO<sub>3</sub>/Ce-Zr catalyst. Firstly, as expected, the addition of this NH<sub>3</sub>-SCR catalyst allowed the improvement of the low temperature deNO<sub>x</sub> efficiency via the favorable fast-SCR reaction, but an inhibiting effect of traces of acetaldehyde was also highlighted. Secondly, a part of NO<sub>2</sub> emitted from Ag/Al was not used for the fast-SCR reaction but reacted with CH<sub>3</sub>CHO to form NO, with also formation of traces of HCOOH, CO and CH<sub>2</sub>O. Thirdly, note that for temperature higher than 250-300°C, NH<sub>3</sub> is also emitted from Ag/Al [22,29] while the NO<sub>x</sub> conversion was total. The added WO<sub>3</sub>/Ce-Zr catalyst then acted as an ammonia slip catalyst (ASC) allowing the selective ammonia oxidation into N<sub>2</sub>.



Figure 12. Schematic view of the various reaction pathways identified in the (EtOH+NH<sub>3</sub>)-SCR process over the  $(Ag/Al + WO_3/Ce-Zr)$  dual-bed system.

#### 4. Conclusions

The (EtOH+NH<sub>3</sub>)-SCR process is an efficient way to reach stricter NO<sub>x</sub> emission regulations without dependency to the NO<sub>2</sub>/NO<sub>x</sub> ratio provided by the DOC upstream. This high DeNO<sub>x</sub> performance was achieved by a dual-bed configuration composed of an EtOH-SCR catalyst upstream a NH<sub>3</sub>-SCR catalyst (Ag/Al<sub>2</sub>O<sub>3</sub>+WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub>). The emitted NO<sub>2</sub> by the EtOH-SCR sample allowed the favorable fast-SCR reaction on the downstream NH<sub>3</sub>-SCR catalyst. Unfortunately, the NH<sub>3</sub>-SCR reactivity over WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub> was not optimal because of (i) a competitive adsorption between ammonia and ethanol/acetaldehyde and (ii) an undesired NO<sub>2</sub> reactivity with CH<sub>3</sub>CHO to form NO. In addition, CH<sub>3</sub>CHO-SCR experiments over single WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub> also pointed out the formation of several by-products from the partial oxidation of CH<sub>3</sub>CHO such as HCOOH, CO, CH<sub>2</sub>O. Then, the beneficial effect of WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub> as the second bed appeared not optimal, but this (Ag/Al<sub>2</sub>O<sub>3</sub>+WO<sub>3</sub>/Ce<sub>x</sub>-Zr<sub>y</sub>O<sub>2</sub>) combination remained significantly more attractive than (Ag/Al<sub>2</sub>O<sub>3</sub>+Cu-FER) previously studied in (EtOH+NH<sub>3</sub>)-SCR.

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