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**Lean NO<sub>x</sub> Removal by a Bifunctional (EtOH + NH<sub>3</sub>)  
Mixture Dedicated to (Ag/Al<sub>2</sub>O<sub>3</sub> + NH<sub>3</sub>-SCR)  
Dual-Bed Catalytic System: Comparison Between  
WO<sub>3</sub>/CeZrO<sub>2</sub> and Cu-FER as NH<sub>3</sub>-SCR Catalyst**

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## Lean NO<sub>x</sub> removal by a bifunctional (EtOH+NH<sub>3</sub>) mixture dedicated to (Ag/Al<sub>2</sub>O<sub>3</sub>+NH<sub>3</sub>-SCR) dual-bed catalytic system. Comparison between WO<sub>3</sub>/CeZrO<sub>2</sub> and Cu-FER as NH<sub>3</sub>-SCR catalyst.

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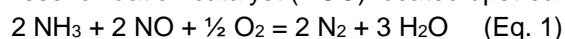
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**Abstract:** In a previous study, a drastic enhancement of the NO<sub>x</sub> conversion in EtOH-SCR process was achieved by means of ammonia and ethanol co-feeding over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to avoid the NO<sub>2</sub>/NO<sub>x</sub> ratio dependency of conventional implemented urea-SCR technology. The ammonia activation was mainly attributed to the availability of hydrogen H\* species resulting from EtOH dehydrogenation, which promoted the H<sub>2</sub> assisted NH<sub>3</sub>-SCR over Ag/Al<sub>2</sub>O<sub>3</sub>. Additional conversion gain was reached with a dual-bed configuration in which a NH<sub>3</sub>-SCR catalyst (WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>) was added downstream to the silver-based sample (Ag/Al<sub>2</sub>O<sub>3</sub> + NH<sub>3</sub>-SCR catalyst). This study deals with the influence of the SCR catalyst formulation on the catalytic performances of the dual-bed system. Oxide-based sample (WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>) and exchanged copper zeolite (Cu<sub>2.5</sub>-FER) were selected as model NH<sub>3</sub>-SCR catalysts. Results shows that WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> is more appropriate in dual-bed configuration for (EtOH+NH<sub>3</sub>)-SCR process because ammonia and ethanol (or its by-products) strongly interacted together on Cu<sub>2.5</sub>-FER.

**Keywords:** SCR, DeNO<sub>x</sub>, Ag/Al<sub>2</sub>O<sub>3</sub>, ethanol, NH<sub>3</sub>.

### 1. Introduction

NO<sub>x</sub> reduction from Diesel and lean burn engines remains a major challenge at low temperature. Currently, NO<sub>x</sub> conversion is achieved by the urea/NH<sub>3</sub> selective catalytic reduction (SCR) process, which is strongly dependent on the NO<sub>2</sub>/NO<sub>x</sub> ratio (Eq. 1: standard-SCR; Eq. 2: Fast-SCR), itself imposed by the Diesel oxidation catalyst (DOC) located upstream the SCR converter.



Unfortunately, the DOC activity also undergoes kinetic limitation at low temperature (175-250°C) and then penalizes the deNO<sub>x</sub> efficiency of the SCR converter downstream.

EtOH-SCR process was also described as an attractive way to reduce NO<sub>x</sub> over silver-based catalyst [1]. The NO conversion is assumed to be dependent on the nitromethane route formation, based on the ethanol oxidation to acetaldehyde *via* a large variety of adsorbed intermediates. N-containing compounds such as HNCO and NH<sub>3</sub> are also involved in the NO<sub>x</sub> reduction mechanism [2]. Unfortunately, this system also suffers from limited activity at low temperature, although partial oxidation of ethanol leads to significant NO<sub>2</sub> emission in the 175-300°C temperature range [3].

In a recent work [4], it was reported that co-feeding of ethanol and ammonia over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst is a promising way to enhance the deNO<sub>x</sub> efficiency at low temperature (175-250°C), while avoiding the NO<sub>2</sub> dependency. The (EtOH+NH<sub>3</sub>)-SCR process avoids the rate-limiting step of nitromethane route formation encountered in the conventional EtOH-SCR mechanism, by three different pathways: the original EtOH-SCR, the NH<sub>3</sub>-SCR process (poorly active, even if NO<sub>2</sub> is formed during EtOH-SCR) and more remarkably, by the H<sub>2</sub>-assisted NH<sub>3</sub>-SCR (H\* species were provided by ethanol dehydrogenation into acetaldehyde) *via* the formation of HNO<sub>x</sub> intermediate.

However, in this case, the outlet exhaust gas still contained some NH<sub>3</sub> and NO<sub>x</sub> (including NO<sub>2</sub>) in this low temperature range. Consequently, the DeNO<sub>x</sub> efficiency at low temperature (175-300°C) was

supplementary improved by means of the addition of a dedicated NH<sub>3</sub>-SCR catalyst (WO<sub>3</sub>/CeZrO<sub>2</sub>) downstream the Ag/Al<sub>2</sub>O<sub>3</sub> sample. This dual-bed configuration achieved NO<sub>x</sub> conversions similar to that obtained in the most favorable fast SCR stoichiometry over WO<sub>3</sub>/CeZrO<sub>2</sub> catalyst, while only NO was initially introduced, avoiding the DOC dependency. The choice of WO<sub>3</sub>/CeZrO<sub>2</sub> as NH<sub>3</sub>-SCR catalyst was justified by the need to develop new generations of vanadium free NH<sub>3</sub>-SCR catalysts to avoid vanadia sublimation of usual V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> materials [5,6]. 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> [7], MnO<sub>x</sub>-CeO<sub>2</sub> [8] also including WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> [9] were likewise proposed. However, iron or copper exchanged zeolite with small pore size to assure a suitable thermal stability, are usually implemented as SCR catalyst for automotive application [10], even if the deNO<sub>x</sub> activity of these materials is also strongly dependant on the NO<sub>2</sub>/NO<sub>x</sub>.

This work aims to examine the influence of the NH<sub>3</sub>-SCR catalyst formulation on the deNO<sub>x</sub> efficiency of the dual-bed system devoted to (EtOH+NH<sub>3</sub>)-SCR process. A copper exchanged ferrierite zeolite (Cu<sub>2.5</sub>-FER) was associated to Ag/Al<sub>2</sub>O<sub>3</sub> and results were compared with those previously obtained with WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> as SCR catalyst. Specific attention was paid to the reactivity of carbon and nitrogen compounds on the downstream WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> or Cu-FER sample.

## 2. Experimental part

### 2.1 Materials

Ag/Al<sub>2</sub>O<sub>3</sub> (noted Ag/Al; specific surface area: 160 m<sup>2</sup> g<sup>-1</sup>) and WO<sub>3</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (noted WO<sub>3</sub>/Ce-Zr; specific surface area: 52 m<sup>2</sup> g<sup>-1</sup>) were the same than those used and detailed in [4]. For Ag/Al sample, silver (2.0 wt-%) was added on alumina (Axens) by impregnation of AgNO<sub>3</sub> dissolved in ethanol. After drying, the resulting powder was calcined under synthetic air with 10 % H<sub>2</sub>O at 700°C for 4 h. XRD analyses collected using an Empyrean (PANalytical) diffractometer showed no visible reflection assigned to silver species (Ag<sup>0</sup>, Ag<sub>2</sub>O, AgO, Ag<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>...). H<sub>2</sub>-TPR experiment, performed on a Micromeritics Autochem 2920 after *in-situ* calcination at 450°C, showed a broad H<sub>2</sub> consumption peak, with a maximum at around 260°C. Hydrogen consumption indicated that 67 % of the deposited silver was in metallic state, according to results previously reported by Flura *et al* [11].

For WO<sub>3</sub>/Ce-Zr sample, tungsten (6.0 wt-% WO<sub>3</sub>) was added on a ceria-zirconia support (40 wt-% of CeO<sub>2</sub>, provided by Solvay) by impregnation at 60°C using an aqueous solution of ammonium metatungstate. After drying, the same hydro-treatment that applied to Ag/Al was carried out (700°C, 4 h). No modification of the XRD pattern of the CeZr support was recorded after WO<sub>3</sub> impregnation, and no diffraction peaks attributable to WO<sub>3</sub> was observed, suggesting a good dispersion of tungsten trioxide on WO<sub>3</sub>/Ce-Zr.

Copper exchanged zeolite sample was prepared from a ferrierite (FER) zeolite which exhibits a channel system of 10 and 8 member rings (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 20, provided by Alfa Aesar). Copper addition (2.5 wt-%, measured by ICP elemental analysis after preparation of the sample) was performed by the ion exchange at pH = 5 as reported in [12]. The resulting powder was finally hydro-treated at 600 °C for 16 hours. The corresponding stabilized samples (denoted Cu<sub>2.5</sub>-FER) exhibited a specific surface area of 252 m<sup>2</sup> g<sup>-1</sup>. No evolution of the ferrierite zeolite structure was observed by XRD analysis after copper exchange and the stabilization treatment. Moreover, CuO phase (2θ = 35.5° and 38.7°) was not detected. H<sub>2</sub>-TPR profile of Cu-FER exhibited two main reductions peaks. The first one (200-350°C) is attributed to the reduction of Cu<sup>2+</sup> species to Cu<sup>+</sup> and the second one at higher temperature (950°C) corresponds to the reduction of the formed Cu<sup>+</sup> species into Cu<sup>0</sup> [13]. These both peaks must exhibit the same H<sub>2</sub> consumption. If present on the catalyst surface, the reduction of CuO species into metallic copper should be also observed in the 200-400°C temperature range [13,14], while copper aluminate (CuAl<sub>2</sub>O<sub>4</sub>) reduction possibly occurs around 500°C [15]. H<sub>2</sub>-TPR profiles were deconvoluted and integrated to assess to the copper distribution: Cu<sub>2.5</sub>-FER exhibited more than 90% of copper as Cu<sup>2+</sup> in exchanged position. No CuO was evidenced (in accordance with XRD results), only few percent of copper aluminate were deduced from the deconvolution of the TPR profile. This species may be formed because the zeolite sample exhibited traces of extra-framework aluminium (EFAL).

## 2.2 Catalytic tests

Catalytic test set up was previously described in [4]. Tests were performed in a quartz tubular micro-reactor under various realistic reaction mixtures depending on the implemented reductant(s): ethanol (EtOH), ammonia (NH<sub>3</sub>), and a blend of both (EtOH+NH<sub>3</sub>) (Table 1). The total flow rate was fixed at 333 mL min<sup>-1</sup> for 100 mg of powdered catalyst diluted in 100 mg SiC, both sieved between 100 μm and 250 μm, corresponding to a GHSV of 130 000 h<sup>-1</sup> toward the catalyst (200 L.h<sup>-1</sup>.g<sub>catalyst</sub><sup>-1</sup>; 100 L.h<sup>-1</sup>.g<sub>powder</sub><sup>-1</sup>). For the dual-bed configuration, 100 mg of NH<sub>3</sub>-SCR sample (WO<sub>3</sub>/Ce-Zr or Cu<sub>2.5</sub>-FER) were placed downstream 100 mg of Ag/Al catalyst (no SiC was used for these experiments).

Gaseous NO/NO<sub>2</sub>/NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures were adjusted by mass-flow controllers (Bronkhorst). For ethanol addition, an aqueous solution containing 8.02 10<sup>-1</sup> mol L<sup>-1</sup> ethanol was vaporized and mixed upstream the SCR catalyst *via* a micro-nozzle (The Lee Company, Ø<sub>nozzle</sub>= 50 μm) connected to a HPLC pump (Jasco, PU-2085, 22 μL min<sup>-1</sup>, ΔP=10 bar). The composition of the inlet and outlet gases were monitored using online MKS 2030 Multigas infrared analyser for NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, 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>, CO, CO<sub>2</sub> and In fact, CH<sub>3</sub>CHO is the main observed C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-compounds from ethanol conversion and the records of the other C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> products are not presented in this study.

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

Catalytic test	NO (ppm)	NO <sub>2</sub> (ppm)	NH <sub>3</sub> (ppm)	EtOH (ppm)	O <sub>2</sub> (%)	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	balance
EtOH-SCR	400	-	-	1200	10	10	8	
(EtOH+NH <sub>3</sub> )-SCR	400	-	400	1200	10	10	8	
(EtOH+NH <sub>3</sub> )-SCO*		-	400	1200	10	10	8	

\*oxidation test, referred as selective catalytic oxidation (SCO) experiment.

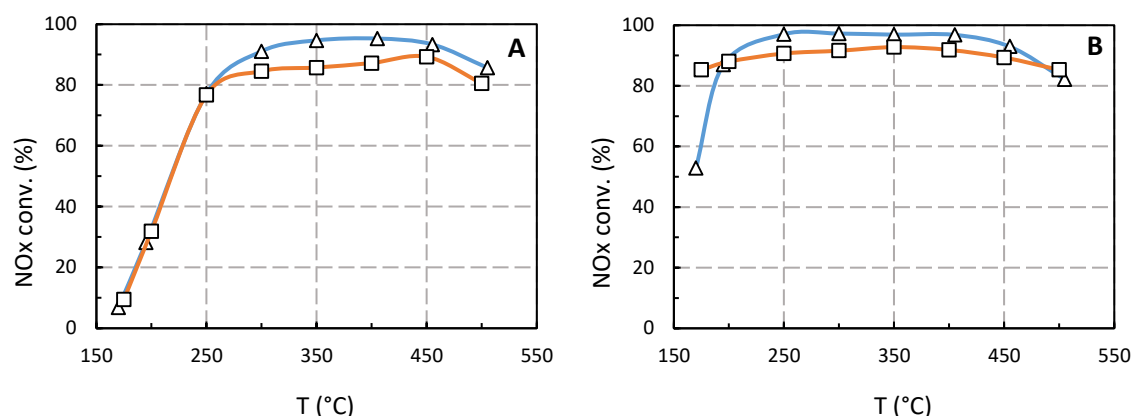
## 3. Results and discussion

### 3.1 Single NH<sub>3</sub>-SCR catalyst behaviors: WO<sub>3</sub>/Ce-Zr and Cu<sub>2.5</sub>-FER

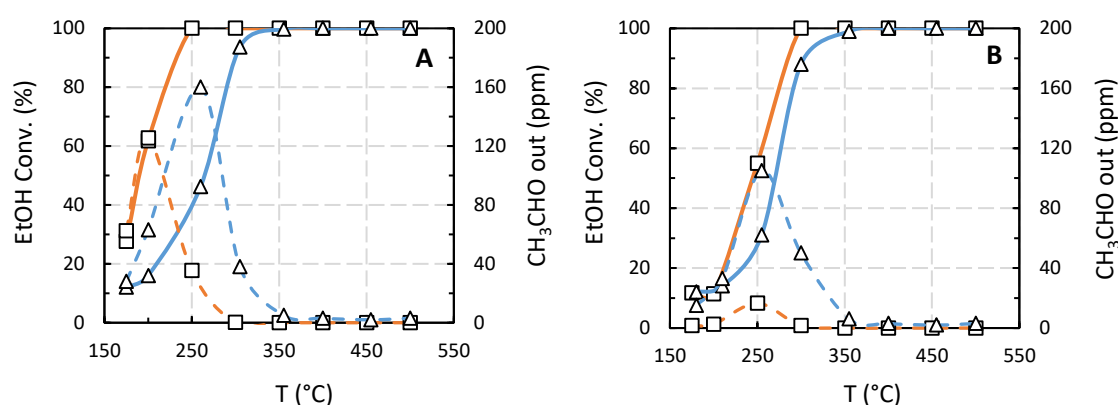
Both studied NH<sub>3</sub>-SCR catalysts were firstly evaluated in standard and fast NH<sub>3</sub>-SCR conditions. In standard-SCR condition (only NO as inlet NO<sub>x</sub>, Figure 1A), the NO<sub>x</sub> conversions recorded with WO<sub>3</sub>/Ce-Zr (Δ) and Cu<sub>2.5</sub>-FER (□) were very close, from approximately 10 % at 175°C and near to 90 % in the 300-450°C temperature range. At temperature higher than 450°C, the NO<sub>x</sub> conversion decreased, which was attributed to a competition with the ammonia oxidation reaction, in agreement with previous reported work [9,12]. As expected, the NO<sub>x</sub> conversion was considerably improved in fast-SCR condition for both catalysts (Figure 1B), pointing out the major interest to gain NO<sub>2</sub> at low temperature, whereas the usual DOC placed upstream the SCR system is then generally poorly active in NO oxidation. Interestingly, in "fast" SCR condition, Cu<sub>2.5</sub>-FER sample exhibited significantly higher NO<sub>x</sub> conversion rate at 175°C, at 88 % versus 53 % for WO<sub>3</sub>/Ce-Zr. This is a promising behavior for a higher deNO<sub>x</sub> efficiency at low temperature in the dual-bed configuration. For higher temperatures, both catalysts exhibited high NO<sub>x</sub> conversions. However, for both fast and standard SCR conditions, WO<sub>3</sub>/Ce-Zr catalyst presented higher maximum NO<sub>x</sub> conversion rates in the 250-450°C temperature range, while the NH<sub>3</sub> conversions were close to 100 % for both catalysts.

Both single NH<sub>3</sub>-SCR catalysts were also evaluated in EtOH-SCR and (EtOH+NH<sub>3</sub>)-SCR conditions (Figure 2). In EtOH-SCR condition (Figure 2A), the WO<sub>3</sub>/Ce-Zr sample exhibited 12 % ethanol conversion at 175°C and the full conversion was recorded from 350°C. However, the NO<sub>x</sub> conversion was very limited, with a maximum of only 7 % at 300°C (Table 2). It results that WO<sub>3</sub>/Ce-Zr catalyst is not efficient to reduce NO<sub>x</sub> by ethanol. Compared with WO<sub>3</sub>/Ce-Zr sample, higher activity in ethanol conversion was recorded for Cu<sub>2.5</sub>-FER catalyst, with 100 % ethanol conversion since 250°C. The maximum NO<sub>x</sub> conversion was also improved, but remained moderate with a maximum of 20 % at

450°C. Concomitantly, acetaldehyde outlet concentration reached a maximum of 160 ppm at 250°C for WO<sub>3</sub>/Ce-Zr and 120 ppm at 200°C for Cu<sub>2.5</sub>-FER sample (Figure 2A).



**Figure 1.** NO<sub>x</sub> conversion in NH<sub>3</sub>-SCR over WO<sub>3</sub>/Ce-Zr (Δ) and Cu<sub>2.5</sub>-FER (□) catalysts for standard NH<sub>3</sub>-SCR (A) and fast NH<sub>3</sub>-SCR condition. Reaction mixtures are depicted in Table 1.



**Figure 2.** EtOH conversion (full line) and CH<sub>3</sub>CHO emissions (dotted line) over WO<sub>3</sub>/Ce-Zr (Δ) and Cu<sub>2.5</sub>-FER (□) catalysts for EtOH-SCR (A) and (EtOH+NH<sub>3</sub>)-SCR condition. Reaction mixtures are depicted in Table 1.

**Table 2.** NO<sub>x</sub> conversion and NH<sub>3</sub>/NO<sub>x</sub> outlet ratio over WO<sub>3</sub>/Ce-Zr or Cu<sub>2.5</sub>-FER catalysts for EtOH-SCR and (EtOH+NH<sub>3</sub>)-SCR experiments.

T (°C)	WO <sub>3</sub> /Ce-Zr			Cu <sub>2.5</sub> -FER		
	EtOH-SCR	(EtOH+NH <sub>3</sub> )-SCR		EtOH-SCR	(EtOH+NH <sub>3</sub> )-SCR	
	NO <sub>x</sub> Conv. (%)	NO <sub>x</sub> Conv. (%)	NH <sub>3</sub> /NO <sub>x</sub> out	NO <sub>x</sub> Conv. (%)	NO <sub>x</sub> Conv. (%)	NH <sub>3</sub> /NO <sub>x</sub> out
175	1	13	1.0	4	12	0.9
200	0	24	1.0	3	21	0.8
250	3	38	1.0	3	53	0.3
300	7	60	0.8	3	69	0.1
350	4	71	0.2	6	79	0.1
400	2	71	0.1	13	82	0.1
450	0	70	0.1	20	84	0.1
500	1	64	0.1	16	73	0.0

With NH<sub>3</sub> co-injection ((EtOH+NH<sub>3</sub>)-SCR experiments, Figure 2B), ethanol conversion decreased for both catalysts together with lower acetaldehyde emissions compared to EtOH-SCR experiments. However, the impact of NH<sub>3</sub> co-feeding was significantly more pronounced over Cu<sub>2.5</sub>-FER sample. The temperature for 50 % EtOH conversion increased from approximately 263°C to 268°C for WO<sub>3</sub>/Ce-Zr, and from 188°C to 245°C for Cu<sub>2.5</sub>-FER. As expected, the presence of ammonia in the reaction gas mixture also caused an increase of the NO<sub>x</sub> conversion (Table 2). Nevertheless, it remained lower than the activity measured in standard NH<sub>3</sub>-SCR (Figure 1). For instance at 250°C, the NO<sub>x</sub> conversion reached 77 % in standard NH<sub>3</sub>-SCR for both catalysts, while only 38 % and 53 % was obtained in (EtOH+NH<sub>3</sub>)-SCR condition with WO<sub>3</sub>/Ce-Z and Cu<sub>2.5</sub>-FER, respectively. In addition, the NH<sub>3</sub>/NO<sub>x</sub> outlet ratio reported in Table 2 clearly illustrates an over ammonia consumption for Cu<sub>2.5</sub>-FER catalyst even at low temperature (T<300°C).

Globally, these results suggest a competitive adsorption of ethanol (or these by-products) with NH<sub>3</sub> for both catalysts. However, compared with WO<sub>3</sub>/Ce-Zr, the exchanged copper-based catalyst presented both stronger interactions between both reductants on the Cu<sup>2+</sup> active sites and a higher ammonia conversion ability in presence of ethanol.

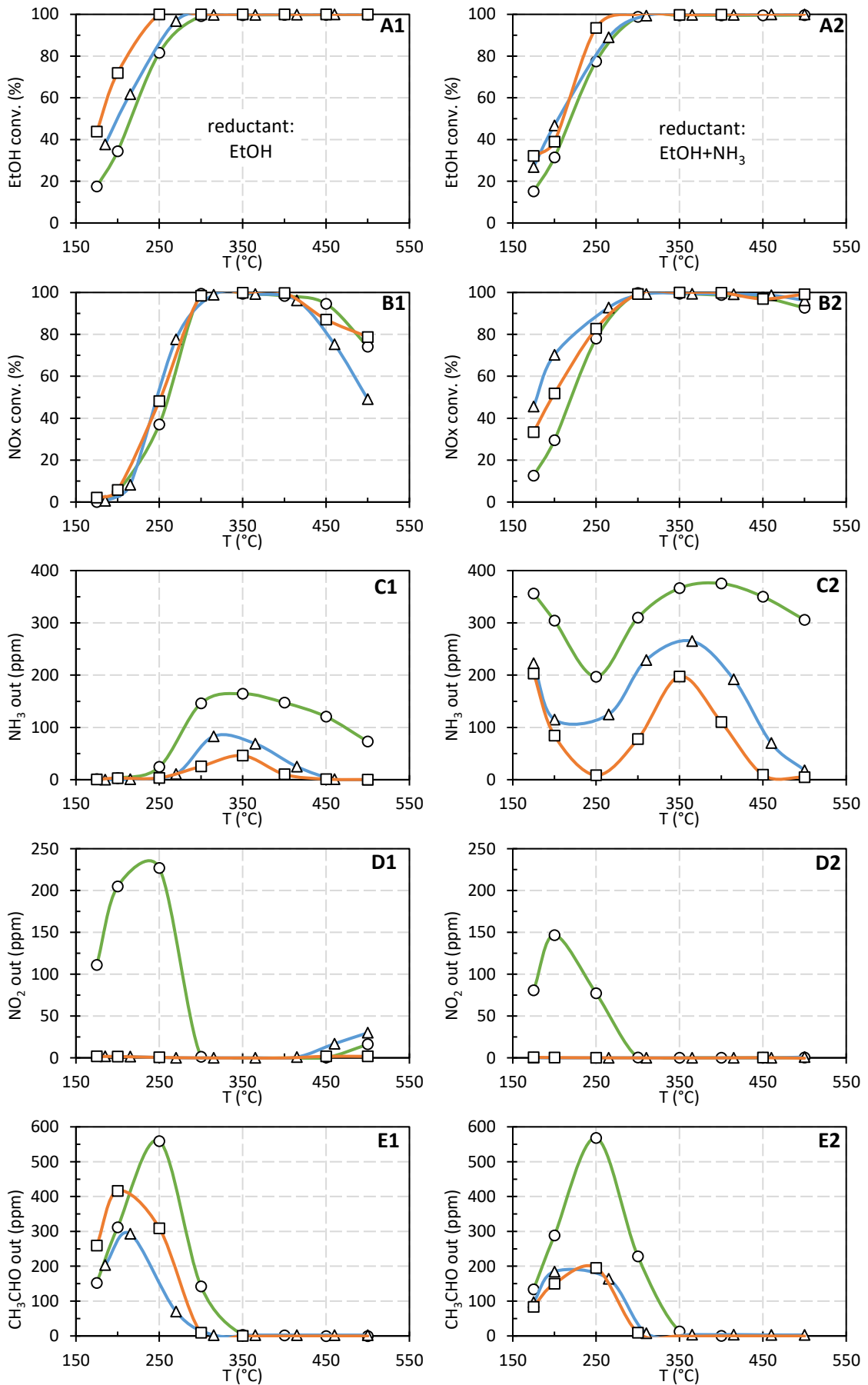
### 3.2 Dual-bed system: (Ag/Al+ WO<sub>3</sub>/Ce-Zr) vs. (Ag/Al+Cu<sub>2.5</sub>-FER)

Results obtained with Ag/Al (100 mg) and with the two dual-bed configuration depending on the implemented NH<sub>3</sub>-SCR catalyst (100 mg of WO<sub>3</sub>/Ce-Zr or Cu<sub>2.5</sub>-FER placed downstream) are compared in Figure 3 for both EtOH-SCR (1) and (EtOH+NH<sub>3</sub>)-SCR (2) conditions. Results are compared in terms of ethanol and NO<sub>x</sub> conversion (Figure 3 A and B), and NH<sub>3</sub>, NO<sub>2</sub> and acetaldehyde outlet concentrations (Figure 3 C, D, E, respectively).

#### 3.2.1 EtOH-SCR condition

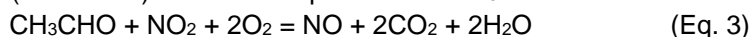
In EtOH-SCR condition, whatever the NH<sub>3</sub>-SCR catalyst formulation, the ethanol conversion (Figure 3-A1) was enhanced over the dual bed system compared with single Ag/Al catalyst. The combination with Cu<sub>2.5</sub>-FER (□) clearly led to the largest improvement. For instance, the ethanol conversion at 200°C was increased from 34 % over single Ag/Al (○) to 60 and 72 % for Ag/Al+WO<sub>3</sub>/Ce-Zr (△) and Ag/Al+Cu<sub>2.5</sub>-FER (□), respectively. This result highlighted the higher reactivity of ethanol over the Cu<sub>2.5</sub>-FER sample. Interestingly, the corresponding CH<sub>3</sub>CHO emission (Figure 3-E1) was lower over the dual bed system with WO<sub>3</sub>/Ce-Zr than on single Ag/Al sample, suggesting a specific reactivity of acetaldehyde over the SCR catalyst. Note that the higher CH<sub>3</sub>CHO emission at 200°C over Cu<sub>2.5</sub>-FER is correlated to the gain in ethanol conversion.

The addition of a SCR catalyst downstream Ag/Al led to a limited NO<sub>x</sub> conversion improvement (Figure 3 B1) despite the full conversion of the emitted NO<sub>2</sub> from the Ag/Al catalyst in the 150-300°C temperature range (Figure 3-D1). The NO<sub>2</sub> consumption was not consistent with the increase of DeNO<sub>x</sub> efficiency and, unfortunately, the Cu<sub>2.5</sub>-FER sample did not present an optimal use of the available NO<sub>2</sub>. In fact, higher NO outlet concentration was observed over dual-bed system whatever the NH<sub>3</sub>-SCR formulation compared to single Ag/Al sample (results not shown) which suggests a specific reactivity of NO<sub>2</sub> with EtOH by-products to produce NO, in accordance to acetaldehyde yield presented in Figure 3-E1.



**Figure 3.** Comparison of Ag/Al (○) and dual-bed Ag/Al+WO<sub>3</sub>/Ce-Zr (△) or Ag/Al+Cu<sub>2.5</sub>-FER (□) system for EtOH-SCR (1) and (EtOH+NH<sub>3</sub>)-SCR (2) condition.

Complementary tests were performed using acetaldehyde instead of ethanol as reductant. The activities in fast-SCR conditions ( $\text{NO}_2/\text{NO}_x = 0.5$ ) and in  $\text{CH}_3\text{CHO}$  oxidation by  $\text{O}_2$  (without  $\text{NO}_x$ ) were investigated. Results (not shown) would correspond to the  $\text{CH}_3\text{CHO} - \text{NO}_2$  stoichiometry of Eq. 3:



Note that ammonia emitted from Ag/Al was also partially converted after addition of a SCR catalyst, with a higher activity over  $\text{Cu}_{2.5}$ -FER. However, this conversion mostly occurred in a temperature range for which the  $\text{NO}_x$  conversion was already completed over Ag/Al.

### 3.2.2 (EtOH+ $\text{NH}_3$ )-SCR condition

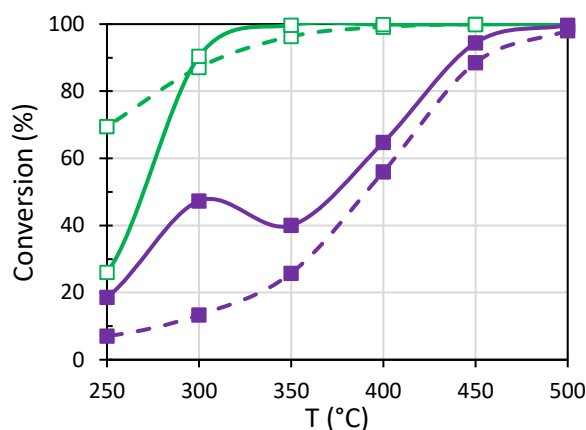
When  $\text{NH}_3$  was additionally injected with ethanol in the inlet gas mixture, similar ethanol conversions were observed over Ag/Al+ $\text{WO}_3/\text{Ce-Zr}$ , combination, compared to the EtOH-SCR condition (Figure 3-A2 vs. Figure 3-A1). To the opposite, the association of Ag/Al+ $\text{Cu}_{2.5}$ -FER led to a decrease in EtOH conversion in the 175-300°C temperature range, probably associated to a strong competition between ethanol and ammonia since  $\text{NH}_3$  is highly converted on  $\text{Cu}_{2.5}$ -FER in this temperature range (Figure 3-C2). This assumption is consistent with results obtained when the catalytic tests were performed over the single  $\text{Cu}_{2.5}$ -FER sample (Table 2). Co-injection of (EtOH+ $\text{NH}_3$ ) also led to a lower  $\text{CH}_3\text{CHO}$  outlet concentration (Figure 3-E2) than that observed in EtOH-SCR condition, suggesting again a competitive reactivity of acetaldehyde with co-fed ammonia over  $\text{NH}_3$ -SCR sample. Acetaldehyde may be either consumed to reduce  $\text{NO}_x$  or oxidized over  $\text{WO}_3/\text{Ce-Zr}$  and  $\text{Cu}_{2.5}$ -FER. Nevertheless, the single  $\text{WO}_3/\text{Ce-Zr}$  and  $\text{Cu}_{2.5}$ -FER catalysts presented a poor activity for  $\text{NO}_x$  reduction in EtOH-SCR experiments (maximum  $\text{NO}_x$  conversion lower than 20 %, Table 2), that tends to validate the oxidation route of  $\text{CH}_3\text{CHO}$  by  $\text{NO}_2$ , as previously proposed (Eq. 3).

Figure 3-B2 recalls that a remarkable de $\text{NO}_x$  activity was reached at low temperature with the co-injection of ethanol and  $\text{NH}_3$  using the (Ag/Al+ $\text{WO}_3/\text{Ce-Zr}$ ) dual bed configuration ( $\Delta$  symbols). The  $\text{NO}_x$  conversion was then ranked between 46 and 95 % in the 175-250°C temperature range, close to the activity observed in the most favourable fast-SCR stoichiometry, while only NO was initially injected. Unfortunately, addition of  $\text{Cu}_{2.5}$ -FER downstream Ag/Al sample did not allow the expected improvement in the de $\text{NO}_x$  efficiency, which remained lower than that observed with  $\text{WO}_3/\text{Ce-Zr}$ . The obtained  $\text{NO}_x$  conversion reached only 33 % and 52 % at 175°C and 200°C, respectively. The gain in  $\text{NO}_x$  conversion appeared then not directly correlated with the  $\text{NH}_3$  consumption. Finally, it appears that  $\text{Cu}_{2.5}$ -FER zeolite-based catalyst (i) was highly reactive towards oxygenated hydrocarbon compounds (ethanol and its by-products) and (ii) exhibited interaction between ethanol (and its by-products) and  $\text{NH}_3$ , which inhibited the expected NO- $\text{NO}_2$ - $\text{NH}_3$  reactivity to improve the de $\text{NO}_x$  efficiency. To highlight this interactions, supplementary tests were performed over  $\text{Cu}_{2.5}$ /FER without  $\text{NO}_x$  in the feed stream

### 3.2.3 EtOH(+ $\text{NH}_3$ )-SCO condition

The ammonia and ethanol conversions recorded in oxidation conditions (referred as SCO tests in Table 1) are plotted in Figure 4. Firstly, with a blend of EtOH+ $\text{NH}_3$  (full line), the ammonia conversion exhibited a maximum near 300°C, then decreased before rose again when ethanol conversion reached 100 %. This behavior clearly indicates that both reductants competed on similar active sites. This assumption is also supported by the fact that the ethanol conversion was dramatically affected at low temperature when ethanol was mixed with ammonia. On the contrary, the ammonia conversion was strongly favored on  $\text{Cu}_{2.5}$ -FER when  $\text{NH}_3$  was mixed with ethanol, in accordance with results previously reported in Figure 3-C2. A direct reaction between ammonia and ethanol (or its by-products) is then suspected. This point have to be investigated to potentially observe amination/imination reactions such as  $\text{C}_2\text{H}_5\text{OH} + \text{NH}_3 = \text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O}$  or  $\text{CH}_3\text{CHO} + \text{NH}_3 = \text{CH}_3\text{CHNH} + \text{H}_2\text{O}$ .





**Figure 4.** Oxidation tests (400 ppm NO and/or 1200 ppm EtOH, 10 % O<sub>2</sub>, 10 % CO<sub>2</sub>, 8 % H<sub>2</sub>O) over Cu<sub>2.5</sub>-FER sample. Ethanol (□) and ammonia (■) conversion depending on the considered mixture: single reductant mixture (dotted lines) or with a mix of them (full lines).

#### 4. Conclusion

This aim of this work was to compare two SCR catalysts formulation in the dual-bed system devoted to the (EtOH+NH<sub>3</sub>)-SCR process working with only NO as introduced NO<sub>x</sub>. Compared with WO<sub>3</sub>/CeZrO<sub>2</sub>, the studied Cu<sub>2.5</sub>-FER catalyst exhibited similar standard-SCR behaviour but promising higher fast-SCR activity at low temperature. Unfortunately, in the dual-bed system, the Cu<sub>2.5</sub>-FER sample led to a lower deNO<sub>x</sub> efficiency than WO<sub>3</sub>/CeZrO<sub>2</sub>, despite a significantly higher ammonia conversion rate. Results showed that ammonia and ethanol strongly interacted together on Cu<sub>2.5</sub>-FER. Possible products formation from amination/imination reactions have to be investigated.

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#### References

- [1] Miyadera T (1993) Appl. Catal B 2:199-205
- [2] Flura A, Courtois X, Can F, Royer S, Duprez D (2013) Top. Catal. 56:94-103
- [3] Johnson II WL, Fisher GB, Toops TJ (2012) Catal. Today 184:166-177
- [4] Barreau M, Tarot M-L, Duprez D, Courtois X, Can F (2018), Appl. Catal. B 220:19-30
- [5] Michalow-Mauke KA, Lu Y, Kowalski K, Graule T, Nachtegaal M, Krocher O, Ferri D (2015) ACS catalysis 5:5657-5672
- [6] Liu X, Wu X, Xu T, Weng D, Si Z, Ran R (2016) Chin. J. Cat. 37:1340-1346
- [7] Apostolescu N, Geiger B, Hizbullah K, Jan MT, Kureti S, Reichert D, Schott F, Weisweiler W (2006) Appl. Catal., B 62:104-114
- [8] Qi G, Yang RT, Chang R (2001) Appl. Catal. B. 51:93-106
- [9] Can F, Berland S, Royer S, Courtois X, Duprez D (2013) ACS Catal. 3:1120-1132
- [10] Nova I, Tronconi E (2014) Urea-SCR Technology for deNO<sub>x</sub> After Treatment of Diesel Exhausts, Springer, New York
- [11] Flura A, Can F, Courtois X, Royer S, Duprez D (2012) Appl. Catal. B 126:275-289
- [12] Tarot M-L, Barreau M, Duprez D, Lauga V, Iojoiu EE, Courtois X, Can F (2018) Catalysts 8:3
- [13] Bulánek R, Wichterlová B, Sobalík Z, Tichý J (2001) Appl. Catal. B. 31:13-25
- [14] Delahay G, Coq B, Broussous L (1997) Appl. Catal. B 12:49-59
- [15] Dumas JM, Geron C, Kribii A, Barbier J (1989) Appl. Catal. B 47:9-15