



HAL
open science

A Study of the NO_x Selective Catalytic Reduction with Ethanol and Its By-products

A. Flura, X. Courtois, F. Can, S. Royer, D. Duprez

► **To cite this version:**

A. Flura, X. Courtois, F. Can, S. Royer, D. Duprez. A Study of the NO_x Selective Catalytic Reduction with Ethanol and Its By-products. *Topics in Catalysis*, 2013, 56 (1-8), pp.94-103. 10.1007/s11244-013-9935-2 . hal-00840145

HAL Id: hal-00840145

<https://hal.science/hal-00840145>

Submitted on 22 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Topics in catalysis 56 (2013) 94–103.
DOI: 10.1007/s11244-013-9935-2

A study of the NO_x selective catalytic reduction with ethanol and its by-products.

A. Flura, X. Courtois*, F. Can, S. Royer, D. Duprez

Institut de Chimie des Milieux et des Matériaux de Poitiers (IC2MP), UMR 7285 Université de Poitiers-CNRS, 4 rue Michel Brunet, F-86022 Poitiers Cedex, France

*Corresponding author: Tel.: 33(0)549453994, e-mail: xavier.courtois@univ-poitiers.fr.

Abstract

The NO_x Selective Catalytic Reduction (SCR) with ethanol has been investigated over alumina supported silver catalyst with a special attention to the main involved reactions depending on the temperature test. With this aim, the possible reducers from ethanol transformations were also evaluated (C₂H₅OH, CH₃CHO, C₂H₄, CO). In addition, the contributions of the gas phase reactions and the alumina support were also pointed out.

Based on the C-products and N-compounds distributions, it is assumed that at low temperature (T<300°C), ethanol reacts firstly with NO+O₂ to produce acetaldehyde and N₂. For higher temperatures, two reaction pathways have been proposed, supported by the CH₃CHO-SCR results: a direct reaction between NO₂ and CH₃CHO, or via –NCO species.

Keywords: NO_x, SCR, ethanol, Ag/Al₂O₃, NH₃, acetaldehyde

1. Introduction

In addition to the emission control of pollutants such as CO, hydrocarbons, NO_x and particulates, the reduction of the greenhouse gases emission, as CO₂, also becomes stricter. As a consequence, the use of engines working in lean condition is very attractive. However, the usual three way-catalyst is not able to reduce NO_x in excess of oxygen and other catalytic processes were proposed to achieve expected NO_x abatement. One possible solution is to use NO_x storage reduction (NSR) catalysts [1], which works in lean/rich cycling condition. The major drawback of this system is the possible deactivation of the catalyst, mainly due to sulfur poisoning [2,3] or thermal ageing [4-6]. Moreover, possible emission of NH₃ and N₂O, a strong greenhouse gas, were also reported [7,8].

The second way to reduce NO_x is the Selective Catalytic Reduction (SCR). For this process, numerous reducers have been investigated, such as hydrocarbons [9-11], oxygenated compounds [11-13] or nitrogen containing compounds (ammonia, urea,...) [14-16]. Recently, development of bio-ethanol gasoline aroused the interest for NO_x SCR by ethanol. Alumina supported silver materials are reported to be the more efficient catalysts [17-19], and the reaction mechanism has been investigated in numerous studies [17,20-22]. A global overview is presented Figure 1. In this work, the NO_x SCR with ethanol (EtOH-SCR) was studied over a 2wt.% Ag/Al₂O₃ catalyst with a special attention to the main reactions involved depending on the temperature. With this aim, the possible reducers derived from ethanol (*i.e.* CH₃CHO, C₂H₄, CO) were also evaluated. In order to understand the role of the gas phase reactions, as well as the catalytic reactions on the alumina support and the silver active phase, experiments were performed using three different conditions: i) without catalyst; ii) in presence of the Al₂O₃ support and iii) in presence of the Ag/Al₂O₃ catalyst.

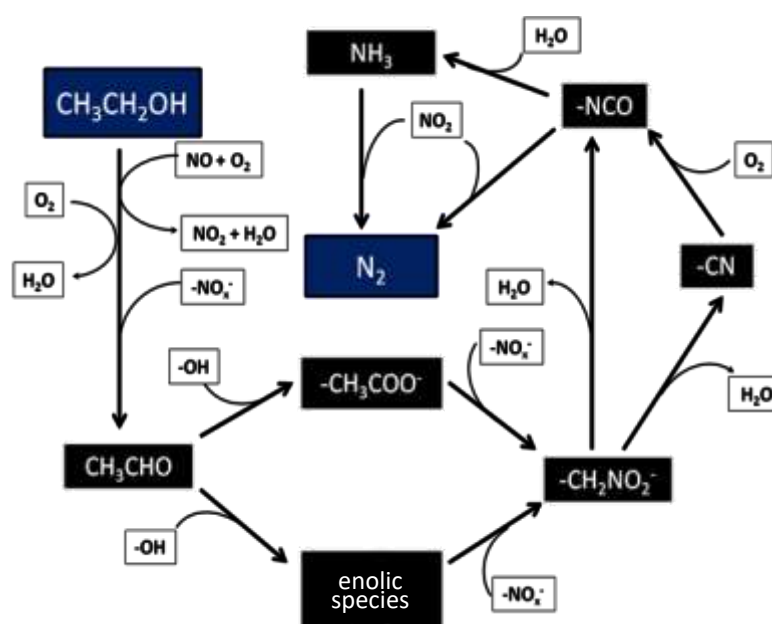


Figure 1: Global overview of EtOH-SCR mechanism

2. Experimental

The alumina support was synthesized using a sol-gel route [23]. Silver (2.0wt.%) was added by impregnation in ethanol [24]. Sample was finally calcined under air +10% H₂O at 600°C for 4 h, and exhibits a specific surface area of 263 m²g⁻¹ (pore volume 1.13 cm³g⁻¹). X-ray diffraction pattern evidences the γ -Al₂O₃ phase [ICDD PDF n° 00-050-0741(I)] with no visible reflection assigned to silver species (Ag⁰, Ag₂O, AgO, Ag₂Al₂O₄...). H₂-TPR result reveals that 66% of the deposited silver is in metallic state, according to Musi *et al* [25]. TEM experiments show that Ag/Al₂O₃ presents a low silver particles size distribution, most of the particles ranging below 10 nm.

Standard catalytic tests were performed under mixture of 400ppm NO, 500ppm CO, 167ppm H₂, 1200ppm C₂H₅OH, 8% O₂, 10% H₂O, 10% CO₂ balanced in N₂. The GHSV is fixed at 150,000 h⁻¹. Catalytic tests were also performed with other reducers, keeping the C/N ratio constant (C/N = 6). Systematically, thermal decomposition (without catalyst) and catalytic reaction (alumina support alone or Ag/Al₂O₃ catalyst) were performed for each gas mixture depicted in Table 1. Results are expressed as conversion or yield. Note that the NO conversion represents the global NO disappearance, *i.e.* taking into account both the NO oxidation into NO₂ and the NO reduction.

Table 1: Gas mixtures of the main catalytic tests at constant GHSV of 150 000 h⁻¹.

| Gas mixture | HC * (ppm) | NO (ppm) | CO (ppm) | H ₂ (ppm) | O ₂ (%) | CO ₂ (%) | H ₂ O (%) | N ₂ |
|----------------------|------------|----------|----------|----------------------|--------------------|---------------------|----------------------|----------------|
| HC*-SCR (standard) | 1200 | 400 | 500 | 167 | 8 | 10 | 10 | balance |
| HC*-SCR (simplified) | 1200 | 400 | - | - | 8 | - | - | balance |
| HC*-NO | 1200 | 400 | - | - | - | - | - | balance |
| HC* decomposition | 1200 | - | - | - | - | - | - | balance |
| HC* oxidation | 1200 | - | - | - | 8 | - | - | balance |
| NO oxidation | - | 400 | - | (167) | 8 | - | (10) | balance |
| CO-SCR | - | 400 | 500 | - | 8 | - | - | balance |

HC*: CH₃CH₂OH or CH₃CHO or C₂H₄

Most gases (NO, NO₂, N₂O, NH₃, CO, CO₂, C₂H₅OH, CH₃CHO, C₂H₄) were analyzed using a Multigas FTIR detector (MKS 2030). The N₂ selectivity is calculated assuming that no other N-compounds than NO, NO₂, N₂O, NH₃ are emitted. In fact, no N₂O emission was detected whatever the catalytic test conditions.

3. Results and discussion

3.1 Standard-SCR behaviors over Ag/Al₂O₃ (C₂H₅OH-SCR, CH₃CHO-SCR, C₂H₄ –SCR)

Catalytic results obtained on Ag/Al₂O₃ catalyst for the standard C₂H₅OH-SCR test (Table 1) are presented in Figure 2A and Figure 2B for C-compounds and N-compounds yields, respectively. A comparison of the NO_x conversion depending on the introduced hydrocarbon (C₂H₅OH, CH₃CHO or C₂H₄) is also illustrated in Figure 2C.

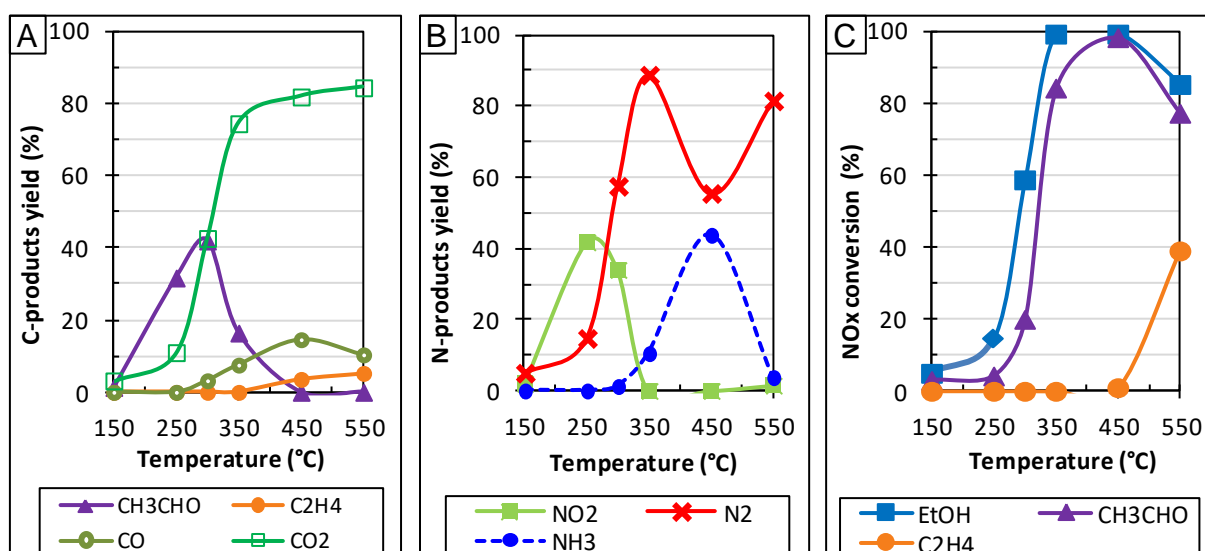


Figure 2: Standard-SCR tests over Ag/Al₂O₃. (A) C-compound yields and (B) N-compound yields with EtOH as reducer. (C) NO_x conversion in SCR with C₂H₅OH, CH₃CHO or C₂H₄ as reducer.

C₂H₅OH-SCR test over Ag/Al₂O₃ (Figure 2A) shows that acetaldehyde is the main C-product emitted at low temperature (250°C). Low ethylene concentration is also observed at high temperature (450-550°C). Maximum CO yield (17%) is observed at 450°C. The N-compounds distribution (Figure 2B) shows the emission of NO₂ and NH₃, in addition to N₂. In fact, the main N-compound product is nitrogen from 300°C, whereas, at 250°C, important amount of NO₂ is detected. An important NH₃ formation is observed at 450°C (NH₃ yield: 43%), which induces a strong decrease of the N₂ yield at this temperature.

Using the standard condition (Table1), Figure 2C shows that both ethanol and acetaldehyde are efficient to reduce NO_x. Total NO_x conversion is achieved at 350°C with ethanol. A shift of 25-50°C to higher temperatures is observed when acetaldehyde is used. Ethylene is not active until 450°C, but NO_x conversion reaches 38% at 550°C. Indeed, it appears from Figure 2C, that ethanol, acetaldehyde and, to a lesser extent ethylene, are effective reducers for the NO_x abatement in excess of O₂. Thereafter, in order to clarify the role of each reducer, the reactivity of the C-containing reducers (C₂H₅OH, CH₃CHO, C₂H₄, CO) has been examined in detail using simplified gas mixtures, with special attention to the N-compounds distribution.

3.2 Understanding the role of the gas phase reaction, alumina and silver supported catalyst: simplified-SCR behaviors (C_2H_5OH -SCR, CH_3CHO -SCR, C_2H_4 –SCR)

Efficiency of various hydrocarbons (C_2H_5OH , CH_3CHO , C_2H_4) in NO_x SCR in simplified condition ($HC + NO + O_2$, Table 1) is studied in this section. Catalytic tests were carried out always keeping the same introduced C/N ratio and GHSV. The CO behavior toward NO in excess of oxygen was also examined. In order to understand the role of each parameter, a special attention is focused on the influence of the condition test: without catalyst, in presence of alumina, or with Ag/Al_2O_3 .

Firstly, with CO as reducer (400ppm NO + 500ppm CO + 8% O_2 gas mixture), no SCR activity is observed in thermal condition as well as with Al_2O_3 or Ag/Al_2O_3 catalyst. CO_2 is nevertheless detected, but only with Ag/Al_2O_3 and at high temperature (550°C).

With C_2H_4 as reducer, it is concluded that ethylene is not thermally decomposed and does not react with NO or O_2 alone. It was observed that C_2H_4 is converted (30%) only at 550°C in presence of both NO + O_2 . The main product is then CO and NO_2 . The N_2 formation is negligible (9ppm). On alumina C_2H_4 also reacts with NO + O_2 , but only at 550°C. Comparison with the gas phase test indicates that NO_2 produced in the gas phase is converted on alumina, and the N_2 yield reaches 43% at 550°C. Finally, with Ag/Al_2O_3 , NO conversion is detected from 450°C (20%), but NO_2 is the major product. At 550°C, the N_2 yield (53%) is just a little improved with silver.

Comparative results in CH_3CHO -SCR and C_2H_5OH -SCR at different temperatures are presented in Table 2.

Concerning CH_3CHO -SCR tests, surprisingly, NO conversion is similar either in thermal condition or with Al_2O_3 sample, but the N-compounds selectivity is greatly modified, as reported in Table 2. In fact, in thermal condition, NO conversion mainly leads to NO_2 formation, even if N_2 concentration also calculated. With Al_2O_3 , NO_2 emission is not observed before 450°C, and the drop of NO_2 yield observed with alumina is concomitant with a significant increase in N_2 emission. This result suggests that, using CH_3CHO as reducer, the N_2 formation on alumina is correlated with the amount of NO_2 produced in thermal condition, upstream of the catalyst. Note that the NO_2 yields observed in thermal condition is in accordance with the NO/NO_2 thermodynamic equilibrium.

Compared with alumina, CH_3CHO and NO conversions are enhanced with silver supported catalyst. Addition of silver on alumina leads to an increase of the N_2 yield from 50% to 88% at 450°C, whereas the NO_2 yields are nil for both samples (Table 2). In this case, N_2 emission is not limited by the NO_2 formed upstream of the catalyst. This result clearly implies that silver species are active for NO oxidation into NO_2 . These results seem to indicate that the NO_2

formation is an important step of the CH₃CHO-SCR mechanism, as reported in the literature [26].

For C₂H₅OH-SCR, in thermal condition, NO conversion is effective essentially at 550°C (conv.: 92%) and it mainly leads to NO₂ (Table 2). On Al₂O₃, the NO conversion varies from 55% to 80% between 350°C and 550°C. The N₂ yield reaches a maximum of 48% at 450°C. Interestingly, the NO₂ yield at 550°C is lower on alumina (45%), than without any catalyst (78%). Ammonia is never observed in thermal condition, or with Al₂O₃.

Table 2: Comparative results in CH₃CHO and C₂H₅OH-SCR in simplified condition (reducer + NO + O₂). Reducer conversion, NO_x conversion and N-compound yields for reaction in thermal condition, with Al₂O₃ or with Ag/Al₂O₃.

| | | CH ₃ CHO + NO + O ₂ | | | | C ₂ H ₅ OH + NO + O ₂ | | | |
|---------------------------|-----------------------------------|---|-------|-------|-------|--|-------|-------|-------|
| | | 250°C | 350°C | 450°C | 550°C | 250°C | 350°C | 450°C | 550°C |
| C-reducer conv. (%) | Thermal | 0 | 1 | 9 | 62 | 0 | 0 | 8 | 49 |
| | Al ₂ O ₃ | 0 | 22 | 89 | 100 | 38 | 95 | 100 | 100 |
| | Ag/Al ₂ O ₃ | 2 | 54 | 100 | 100 | 46 | 100 | 100 | 100 |
| NO conv. (%) | Thermal | 0 | 10 | 48 | 79 | 0 | 0 | 3 | 92 |
| | Al ₂ O ₃ | 0 | 10 | 50 | 83 | 3 | 55 | 60 | 80 |
| | Ag/Al ₂ O ₃ | 8 | 22 | 99 | 90 | 28 | 69 | 100 | 90 |
| N ₂ yield (%) | Thermal | 0 | 2 | 9 | 27 | 0 | 0 | 1 | 14 |
| | Al ₂ O ₃ | 0 | 10 | 50 | 48 | 2 | 35 | 48 | 35 |
| | Ag/Al ₂ O ₃ | 1 | 22 | 88 | 55 | 14 | 65 | 76 | 58 |
| NO ₂ yield (%) | Thermal | 0 | 8 | 39 | 52 | 0 | 0 | 2 | 78 |
| | Al ₂ O ₃ | 0 | 0 | 0 | 35 | 1 | 20 | 12 | 45 |
| | Ag/Al ₂ O ₃ | 7 | 0 | 0 | 35 | 14 | 0 | 0 | 32 |
| NH ₃ yield (%) | Thermal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Al ₂ O ₃ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Ag/Al ₂ O ₃ | 0 | 0 | 11 | 0 | 0 | 4 | 24 | 0 |

Silver supported catalyst promotes the NO conversion and N₂ yield in the whole temperature range. NO₂ emission is lower than the one observed with alumina. In fact, NO₂ is not detected at 350°C or 450°C and reaches a yield of 32% at 550°C, compare to 45% for Al₂O₃. On Ag/Al₂O₃ sample, NH₃ emission is likewise detected. The higher is the NH₃ yield, the higher is the NO conversion. In fact, total NO conversion is achieved at 450°C, when ammonia yield reaches about 25%. Such emission of ammonia is rarely reported in literature and was discussed in a previous work [23].

These first results indicate that NO oxidation into NO₂ plays an important role in the NO reduction mechanism. The reactivity of the SCR mechanism is complex and specific supplementary tests have been performed in order to understand and highlight the SCR mechanism.

3.3 Specific tests

3.3.1 NO oxidation

The reactions were carried out with 400ppm NO and 8% O₂ (Table 1) in the presence or not of 167ppm H₂. Dry condition (no water) or addition of 10% H₂O was also used for comparison.

NO oxidation in absence of H₂

In absence of H₂ and in dry condition (*i.e.* NO oxidation conditions presented in Table 1), the oxidation of NO into NO₂ is never observed in the gas phase. On the contrary, on Al₂O₃, NO₂ is observed, but only at high temperature (550°C), and with a low yield (5%). No other compounds are detected, namely N₂O, NH₃ or N₂. Surprisingly, similar result is obtained with silver supported catalyst (Ag/Al₂O₃ sample).

It is reported in literature that NO oxidation starts by an adsorption step on acidic surface sites over Al₂O₃ [27-32]. NO is furthermore oxidized to nitrites species which involve basic oxygen of alumina support, and is thereafter desorbed into NO₂. This assumption was confirmed by O₂ isotopic exchange experiments (not shown), which show that gas ¹⁸O₂ is exchanged with ¹⁶O₂ of alumina matrix from 500°C. In presence of H₂O, the water dissociation on Lewis acid-base sites blocks this mechanism, and no NO₂ emission is then observed in this condition (NO + O₂ + H₂O) over alumina in the studied temperature range.

NO oxidation in presence of H₂

As mentioned above, without H₂ and H₂O in the gas mixture (NO+O₂), similar NO₂ yield is obtained at 550°C with alumina or with Ag/Al₂O₃. Silver is then not involved in the NO oxidation mechanism. If H₂ is added to the gas mixture (NO+O₂+H₂), no effect of H₂ is observed on Al₂O₃. On the contrary, NO₂ emission is detected from 150°C on Ag/Al₂O₃ catalyst (*vs.* 550°C in absence of H₂) and the NO₂ yield reaches about 60% at 550°C. Then, hydrogen favors the NO oxidation, but only with silver supported material. No other compound than NO₂ is detected (no N₂O or NH₃). It is proposed that, even in small amount (167 ppm), hydrogen is able to reduce silver particles, leading to higher oxidation performances. It is also likely that hydrogen favors the desorption of nitrate species adsorbed on silver, giving NO₂. Besides, in presence of water (NO+O₂+H₂O), NO₂ yield increases up to 20% at 550°C over Ag/Al₂O₃ catalyst, whereas NO₂

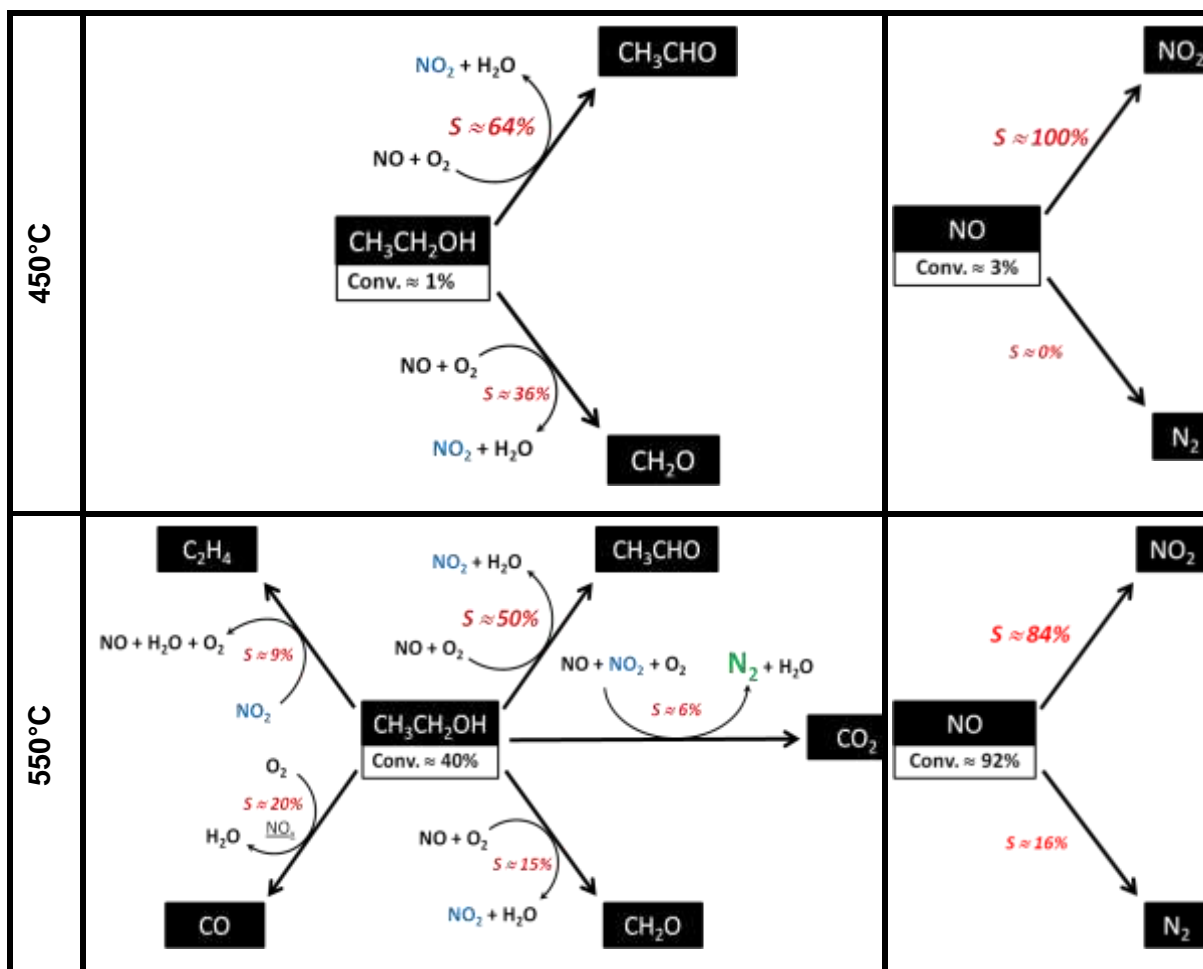
is not emitted on Al_2O_3 with these conditions. This result seems to support the assumption of nitrates desorption, since water cannot reduce silver species.

3.3.2 Investigation on $\text{C}_2\text{H}_5\text{OH}$ -SCR

The $\text{C}_2\text{H}_5\text{OH}$ -SCR was studied in detail, with a special attention concerning the thermal decomposition and the catalytic results in regards on simplified reaction.

Thermal decomposition and oxidation of $\text{C}_2\text{H}_5\text{OH}$

In thermal condition (without any sample), $\text{C}_2\text{H}_5\text{OH}$ is not decomposed and does not react with O_2 or NO . Nevertheless, if NO and O_2 are both present in the gas mixture (simplified SCR tests, Table 2), a small conversion is observed from 450°C and, at 550°C , the NO and $\text{C}_2\text{H}_5\text{OH}$ conversions reach 92% and 40%, respectively. Similar results are obtained in standard SCR tests. N_2 is observed only at 550°C (N_2 yield about 16%) whatever the gas mixture (i.e. simplified or standard $\text{C}_2\text{H}_5\text{OH}$ -SCR). The following suggested scheme is then proposed:



Scheme 1: Reaction mechanism pathway for $\text{C}_2\text{H}_5\text{OH}$ -SCR in thermal condition for $\text{C}_2\text{H}_5\text{OH} + \text{NO} + \text{O}_2$ gas mixture. S: selectivity.

To conclude, thermal C₂H₅OH-SCR reaction is active essentially at high temperature (550°C), leading to a maximum of about 90% of NO conversion, with N₂ selectivity close to 16% and an important amount of NO₂ detected (S≈85%). Ethanol is mainly oxidized into CH₃CHO (50% of selectivity at 550°C), but also into CO, CH₂O, C₂H₄ and CO₂.

C₂H₅OH reactivity over (Ag)/Al₂O₃

Different results were obtained on Al₂O₃ or Ag/Al₂O₃ catalyst. Firstly, ethanol (alone) is decomposed on alumina from 150°C (5% of conversion), and the conversion is total at 350°C. The main product is ethylene, with a yield of about 85% in the 350-550°C temperature range. Similar results (conversion and selectivity) are obtained on Ag/Al₂O₃. However, addition of O₂ in the gas mixture (C₂H₅OH + O₂) dramatically modifies the C-compound selectivities between Al₂O₃ and Ag/Al₂O₃ catalysts (Table 3).

Table 3: C₂H₅OH conversion and C-compound yields for (C₂H₅OH + O₂) and (C₂H₅OH + NO + O₂) reaction in thermal condition, with Al₂O₃ or with Ag/Al₂O₃.

| Reaction | | C ₂ H ₅ OH + O ₂ | | | | C ₂ H ₅ OH + NO + O ₂ | | | |
|---|-----------------------------------|---|-------|-------|-------|--|-------|-------|-------|
| Temperature (°C) | | 250°C | 350°C | 450°C | 550°C | 250°C | 350°C | 450°C | 550°C |
| C ₂ H ₅ OH conv. (%) | Thermal | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 40 |
| | Al ₂ O ₃ | 48 | 100 | 100 | 100 | 38 | 95 | 100 | 100 |
| | Ag/Al ₂ O ₃ | 35 | 100 | 100 | 100 | 46 | 100 | 100 | 100 |
| CH ₃ CHO yield (%) | Thermal | 0 | 0 | 0 | 0 | 0 | 0 | <1 | 20 |
| | Al ₂ O ₃ | 2 | 2 | 0 | 0 | 4 | 21 | 1 | 0 |
| | Ag/Al ₂ O ₃ | 31 | 61 | 0 | 0 | 38 | 25 | 0 | 0 |
| C ₂ H ₄ yield (%) | Thermal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| | Al ₂ O ₃ | 12 | 81 | 85 | 73 | 7 | 17 | 53 | 33 |
| | Ag/Al ₂ O ₃ | 0 | 2 | 17 | 39 | 0 | 1 | 10 | 0 |
| CO ₂ yield (%) | Thermal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| | Al ₂ O ₃ | 34 | 16 | 13 | 21 | 28 | 46 | 25 | 35 |
| | Ag/Al ₂ O ₃ | 3 | 33 | 64 | 46 | 5 | 59 | 67 | 94 |

On alumina, no effect of O₂ is observed on the ethanol conversion, similar catalytic results are observed with C₂H₅OH alone or C₂H₅OH + O₂ (Table 3). In presence of NO+O₂ the selectivity is strongly modified and CH₃CHO yield is greatly enhanced, especially at 350°C. Acetaldehyde yield then reaches 21%, compare to 2% in absence of NO in the gas mixture. In parallel, N₂ conversion over alumina is 2% and 35% at 250°C and 350°C, respectively (results reported in Table 2). Thus, it seems that NO+O₂ reacts with C₂H₅OH to produce both N₂ and CH₃CHO on

alumina active sites. This way is assumed to be the first reaction path to produce N₂ at low temperature on alumina active sites.

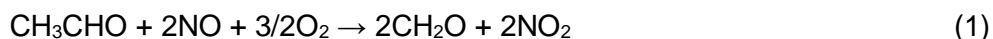
Using Ag/Al₂O₃, ethanol oxidation (C₂H₅OH + O₂) leads mainly to acetaldehyde at low temperature (61% of CH₃CHO yield at 350°C), whereas CO₂ and C₂H₄ are the major products at 450°C and 550°C, with ethylene yields of 17% and 39%, respectively. Ethylene is no more observed at 550°C, whereas a yield of 33% is obtained with alumina without silver. When NO is added to the gas mixture, CH₃CHO yield increases from 30% (C₂H₅OH + O₂) to 40% (C₂H₅OH + NO + O₂) at 250°C (Table 3). This higher acetaldehyde formation is directly correlated with the ethanol conversion which is 10% higher in presence of NO with Ag/Al₂O₃ catalyst. Note that using acetaldehyde (simplified CH₃CHO-SCR tests, Table 2), NO conversion is about 8% at 250°C, but mainly into NO₂. Finally, acetaldehyde reactivity in NO reduction is a key parameter in C₂H₅OH-SCR, and investigation of CH₃CHO-SCR behaviors is presented thereafter.

3.3.3 Investigation on CH₃CHO-SCR

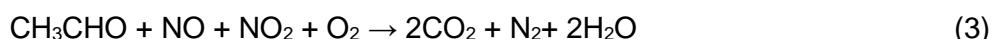
It was showed previously that acetaldehyde is as an active reducer in standard SCR condition (Figure 2C). Besides, during the C₂H₅OH-SCR experiments on silver supported material, CH₃CHO is the main by-product, obtained by dehydrogenation. Thus reactivity of CH₃CHO was carefully studied.

Thermal decomposition and reaction of CH₃CHO

It was firstly checked that acetaldehyde is not thermally decomposed (CH₃CHO alone) and it does not react with NO (CH₃CHO + NO) from 150°C to 550°C. However, in presence of both NO + O₂ (CH₃CHO + NO + O₂) a low acetaldehyde conversion (2%) with NO₂ production (3%) is observed starting from 350°C. It is important to note that the thermal oxidation of NO to NO₂ (without reducer, part 3.3.1) is not observed. Then, at 350°C, CH₃CHO reacts with both NO and O₂ to produce NO₂, formaldehyde (CH₂O) and CO, according to the following reactions:

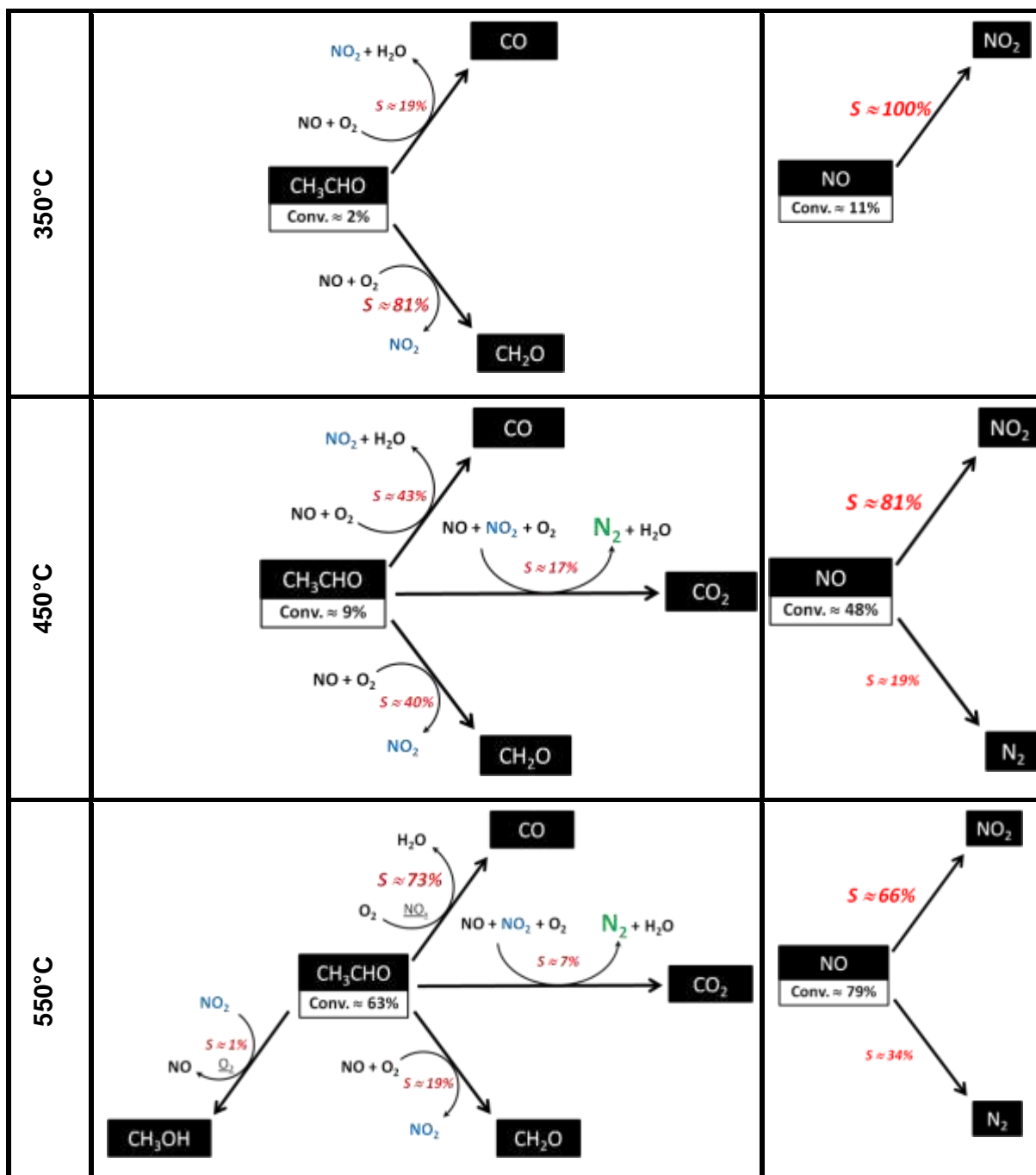


The thermal conversion of CH₃CHO increases with the temperature, to 9% at 450°C. Besides, at 450°C, N₂ formation is also observed according to reaction (3):



At higher temperature (550°C), the thermal conversion of acetaldehyde reaches 63%. Contrary to results obtained at 350°C and 450°C, CH₃CHO can be directly oxidized by O₂ at 550°C (CH₃CHO + O₂), mainly into formaldehyde and CO.

Based on the whole of results, the following reaction pathway for CH₃CHO-SCR in thermal condition is proposed:



Scheme 2: Reaction mechanism pathway for CH₃CHO-SCR in thermal condition for CH₃CHO + NO + O₂ gas mixture.

Catalytic decomposition and oxidation of CH₃CHO

Acetaldehyde decomposition or oxidation (Table 1) was firstly studied over alumina and then over Ag/Al₂O₃. On Al₂O₃, the CH₃CHO conversion starts from 300°C, and it is total at 550°C,

with or without O₂ in the gas mixture. However, selectivity depends on the presence of O₂. Indeed, without oxygen, an important amount of CO is observed. With O₂, the main oxidative compound detected at 550°C is CO₂. Addition of silver to alumina (Ag/Al₂O₃) enhances the acetaldehyde decomposition (CH₃CHO alone) from 75% to 100% at 450°C, and favors the CO₂ formation at 550°C.

Catalytic reduction of NO with CH₃CHO (CH₃CHO + NO + O₂), effect of water

Catalytic results for the (CH₃CHO + NO + O₂) reaction, mentioned as simplified CH₃CHO-SCR tests in Table 1, was previously presented in Table 2 for Ag/Al₂O₃. Conversions of CH₃CHO and NO obtained over Al₂O₃ and Ag/Al₂O₃ are compared in Figures 3A and 3B, and the effect of H₂O is depicted in Figure 3C.

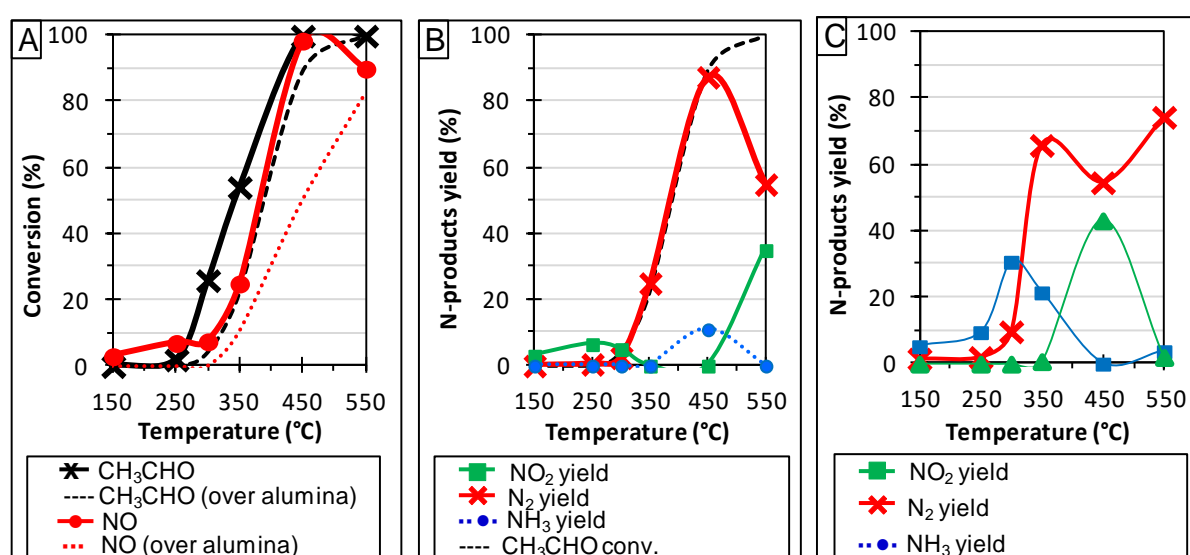


Figure 3: Simplified CH₃CHO-SCR tests on Ag/Al₂O₃. (A) CH₃CHO and NO conversion. (B) N-compound yields; (C) Effect of water: N-compound yields for (NO + O₂ + H₂O) condition. Catalytic results obtained over Al₂O₃ are plotted in dotted line (CH₃CHO yields in Fig B and C). Gas mixture: 1200 ppm CH₃CHO, 400 ppm NO, 8% O₂, (10% H₂O) balanced with N₂.

As expected, CH₃CHO and NO conversions are enhanced with Ag/Al₂O₃ catalyst, compare to Al₂O₃. Figure 3B also reveals that the N₂ yield observed with Ag/Al₂O₃ catalyst is correlated with the CH₃CHO conversion obtained with alumina (in dotted line), in a large temperature range (150-450°C). This result seems to indicate that the N₂ formation in CH₃CHO-SCR is linked to the activation of acetaldehyde over the alumina support.

Addition of water in the feed stream (CH₃CHO + NO + O₂ + H₂O mixture) significantly changes the N-compound yields (Figure 3C). The N₂ yield is then improved in the low temperature range. For instance, at 350°C, the N₂ yield reaches 67%, compared to 22% without water. In opposition, the N₂ yield is strongly decreased at 450°C, which is correlated with the enhancement of the ammonia yield with water. Another important point is that NO₂ yield is also

enhanced with H₂O around 300°C, from 7% to 30% at this temperature. Besides, the N₂ yield is no more correlated with the CH₃CHO conversion obtained with alumina (in dotted line, Figure 3C), as it was reported in absence of H₂O in the gas mixture (Figure 3B).

3.4 Highlights on the EtOH-SCR mechanism with Ag/Al₂O₃

3.4.1 Low temperature limitation in EtOH-SCR with Ag/Al₂O₃ (T≤300°C)

At 250°C, the presence of NO in the gas mixture increases the ethanol conversion on Ag/Al₂O₃, from 35% to 46% (Table 3). In fact, in absence of NO, a higher C₂H₅OH conversion is observed on Al₂O₃ support than on Ag/Al₂O₃ catalyst. Besides, NO conversion is effective at 250°C on Ag/Al₂O₃ (28%, Table 2), but is very low on alumina (3%). At this temperature, Table 3 reveals that on Ag/Al₂O₃ catalyst, ethanol activation leads mainly to the formation of CH₃CHO (yield about 38%) when NO is present on the gas mixture. In absence of NO (C₂H₅OH + O₂), CH₃CHO yield drops to 31%. Note that acetaldehyde is produced in very low amount on alumina (C₂H₅OH + O₂ mixture). Thus on Ag/Al₂O₃ catalyst, it appears that the dehydrogenation reaction (4), leading also to the formation of hydrogen, becomes faster than the dehydration one.



It was previously reported in section 3.3.1 that Ag/Al₂O₃ and Al₂O₃ samples act differently in presence of H₂, especially for the NO oxidation reaction. In fact the presence of a low concentration of H₂ (167 ppm,) enables the oxidation of NO into NO₂ on Ag/Al₂O₃ at low temperature (starting from 150°C). Without hydrogen in the gas mixture, NO₂ is not observed at low temperature (T≤300°C). Then, the use of C₂H₅OH leads to the formation of NO₂ at low temperature (i.e 250°C) on Ag/Al₂O₃ (yield about 14%, Table 2).

It is thus assumed that the NO₂ formation is the rate-determining step in N₂ formation. In fact, based on the work of Sachtler et al. [22], it is proposed that the first reaction step of NO oxidation into NO₂ leads to the formation of adsorbed nitrates species at low temperature. As reported in literature [30,33], NO₂ adsorption on alumina support leads to the formation of three kinds of nitrate species (bridging, monodentate and bidentate). The C₂H₅OH-SCR reaction is thereafter limited by the low reactivity between adsorbed nitrates and ethanol. The deduced N₂ formation at T < 300°C may be due to few active nitrite species [34].

In fact, nitrites are reported to be very reactive but formed with a very low extent over alumina [34]. Over alumina, NO₂ is much more active than NO [26], especially for T>300°C. At lower temperature, nitrates are too strongly adsorbed [28,35,36], but addition of H₂ allows the increase of the low temperature activity due to the nitrates reduction into highly active nitrites [37,38,39]

3.4.2 High temperature mechanism

A comparative study of the effect of water over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst is presented in Figure 4 for the $\text{C}_2\text{H}_5\text{OH}$ -SCR and CH_3CHO -SCR tests in simplified condition (reducer + NO + O_2). It appears that the profile distribution of N-compound is quite similar whatever the reducer (ethanol or acetaldehyde, Figure 4A and 4C). In fact, for both reducers, the maximum N_2 yield is obtained at 450°C , at about 75% and 88% for $\text{C}_2\text{H}_5\text{OH}$ -SCR and CH_3CHO -SCR tests, respectively. Total NO_x conversion is achieved in both cases and the lower N_2 yield obtained with ethanol as reducer is associated with the higher ammonia emission. The presence of water (Figure 4B and 4D) increases the ammonia yield with still a maximum at 450°C . As a consequence, the N_2 yield at this temperature is strongly decreased and maximum N_2 yield is then obtained at 350°C . NO_2 emission in the low temperature range is also favored if H_2O is introduced in the feed stream.

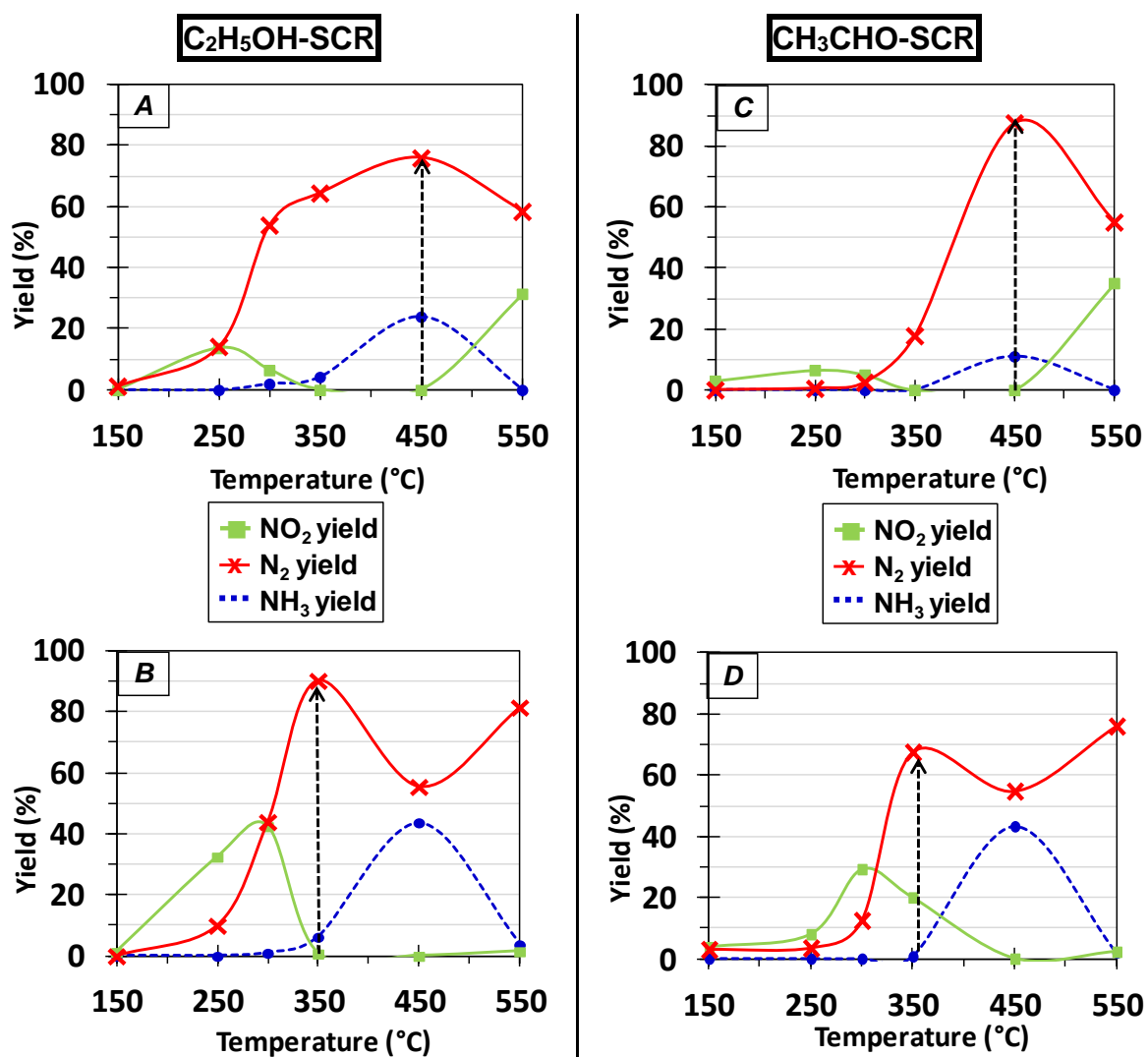
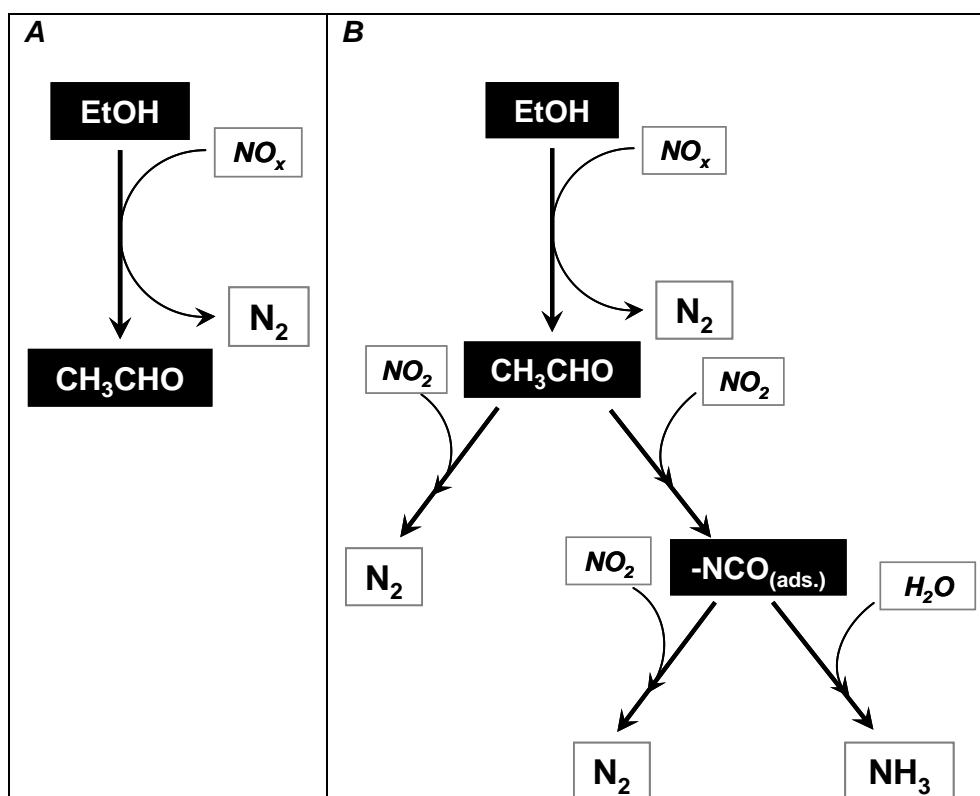


Figure 4: N-compound yields for $\text{C}_2\text{H}_5\text{OH}$ -SCR (A) and CH_3CHO -SCR (C) tests in simplified condition over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst. Effect of water on $\text{C}_2\text{H}_5\text{OH}$ -SCR (B) and CH_3CHO -SCR (D).

Ammonia formation mechanism is well established in literature [18,40], it involves the hydrolysis of -NCO species to form NH₃. The formation of -NCO species has been observed in numerous papers over Ag/Al₂O₃ catalysts when high NO_x reduction efficiency is achieved [40,41]. It is proposed that -NCO species are formed by reaction between acetate species (adsorbed acetaldehyde) and adsorbed nitrites/nitrates species. Ammonia can thereafter react with NO₂ to form ammonium nitrite. Ammonium nitrite is then decomposed into H₂O and N₂. Isocyanate ions also react with O₂ but this reaction is slower than that of -NCO with water, which leads to ammonia formation [17]. Since no NH₃ is emitted on Al₂O₃ support, -NCO bridged with silver cluster and coordinatively unsaturated sites was recently proposed by Thibaut-Starzik *et al.*[42]. Finally, reaction pathway for EtOH-SCR is summarized in scheme 4. At low temperature, around 250°C, the N₂ formation is virtually nil with acetaldehyde whereas acetaldehyde is observed together with N₂ using ethanol as introduced reducer. In addition, N₂ is observed only if O₂ is introduced, suggesting that NO₂ are the reactive species. At higher temperature, the CH₃CHO + NO + O₂ reaction can occur over alumina, without silver. However, silver is supposed to favor -NCO species formation, which explains the enhancement of the nitrogen formation. However, if the (NO_x / isocyanate species) ratio is unbalanced with too many -NCO species, ammonia emission is observed.



Scheme 4: Proposed reaction pathway for EtOH-SCR at (A) low temperature ($T \leq 300^\circ\text{C}$) and (B) high temperature ($T \geq 300^\circ\text{C}$)

4. Conclusion

The mechanism of the NO_x SCR with ethanol over Ag/Al₂O₃ catalysts was already extensively studied and a global overview is proposed. However, some parameters were not evidenced, such as the test temperature or the roles of the gas phase reactions and alumina support. In this study, we tried to understand the reaction mechanism toward these parameters. During the C₂H₅OH-SCR test, CO, C₂H₄ and CH₃CHO are also emitted. CO is not active for the NO_x reduction, and CO₂ is observed only with Ag/Al₂O₃ and at high temperature (550°C). Ethylene is able to reduce NO_x into N₂ only at 550°C over alumina with a limited impact of silver. Ethanol is activated at low temperature over alumina (T ≤ 300°C) but N₂ is obtained only with Ag/Al₂O₃ and with NO and O₂ in the feed stream. In fact, Ag allows NO₂ formation from 150°C. Acetaldehyde is also observed as a product in this low temperature range. At higher temperature CH₃CHO is an effective NO_x reducer over Al₂O₃. It is demonstrated that alumina active sites are involved in the NO₂ reduction with CH₃CHO leading to a possible NO_x reduction pathway to N₂. However, silver is supposed to favor –NCO species formation, which explains the enhancement of the nitrogen formation and ammonia emission.

Acknowledgments

The Authors thank the French Ministry of Economy, Finance and Industry for its financial support (FUI contract n° 07 2 90 6511 REDNO_x)

References

- [1] Epling WS, Campbell LE, Yezeerets A, Currier NW, Parks JE (2004) *Catal Rev* 46:163-245
- [2] Sedlmair C, Seshan K, Jentys A, Lercher JA (2002) *Catal Today* 75:413-419
- [3] Corbos EC, Courtois X, Bion N, Marecot P, Duprez D (2008) *Appl Catal B* 80:62-71
- [4] Li J, Theis J, Chun W, Goralski C, Kudla R, Ura J, Watkins W, Chattha M, Hurley R (2001) SAE Technical Paper 2001-01-2503
- [5] Uy D, O'Neill AE, Li J, Watkins WHL (2004) *Top Catal* 95:191-201
- [6] Casapu M, Grunwaldt JD, Maciejewski M, Wittrock M, Göbel U, Baiker A (2006) *Appl Catal B* 63:232-242
- [7] Le Phuc N, Courtois X, Can F, Royer S, Marecot P, Duprez D (2011) *Appl Catal B* 102:353-361
- [8] Corbos EC, Haneda M, Courtois X, Marecot P, Duprez D, Hamada H (2009) *Appl Catal A* 365:187-193
- [9] Konsolakis M, Yentekakis IV (2001) *J Catal* 198:142-150
- [10] Cordoba LF, Sachtler WMH, de Correa CM (2005) *Appl Catal B* 56:269-277
- [11] Maunula T, Ahola J, Hamada H (2000) *Appl Catal B* 26:173-192
- [12] Tran D, Aardahl CL, Rappe KG, Park PW, Boyer CL (2004) *Appl Catal B* 48:155-164
- [13] Haj KO, Ziyade S, Ziyad M, Garin F (2002) *Appl Catal B* 37:49-62
- [14] Cant NW, Liu IOY (2000) *Catal Today* 63:133-146

- [15] Zuzaniuk V, Meunier FC, Ross JRH (2001) *J Catal* 202:340-353
- [16] Liu IOY, Cant NW (2005) *J Catal* 230:123-132
- [17] Bion N, Saussey J, Haneda M, Daturi M (2003) *J Catal* 217:47-58
- [18] Yeom YH, Li M, Sachtler WMH, Weitz E (2007) *J Catal* 246:413-427
- [19] He H, Yu Y (2005) *Catal Today* 100:37-47
- [20] Chafik T, Kameoka S, Ukisu Y, Miyadera T (1998) *J Mol Cat A* 136:203-211
- [21] Poignant F, Saussey J, Lavalley JC, Mabilon G (1995) *J Chem Soc-Chem Comm* 1:89-90
- [22] Yeom YH, Li M, Sachtler WMH, Weitz E (2006) *J Catal* 238:100-110
- [23] Can F, Flura A, Courtois X, Royer S, Blanchard G, Marécot P, Duprez D (2011) *Catal. Today* 164:474-479
- [24] Sato T, Goto S, Tang Q, Yin S (2008) *J Mater Sci* 43:2247-2253
- [25] Musi A, Massiani P, Brouri D, Trichard JM, Da Costa P (2009) *Catal Letters* 128:25-30
- [26] Bethke KA, Kung HH (1997) *J Catal* 172:93-102
- [27] Westerberg B, Fridell E (2001) *J Mol Cat A* 165:249-263
- [28] Meunier FC, Breen JP, Zuzaniuk V, Olsson M, Ross JRH (1999) *J Catal* 187:493-505
- [29] Kijlstra WS, Brands DS, Poels EK, Bliet A (1997) *J Catal* 171:208-218
- [30] Parkyns ND, in: J.E. Hightower (Ed.), Elsevier, New york, (1993) 255
- [31] Apostolescu N, Schröder T, Kureti S (2004) *Appl Catal B* 51:43-50
- [32] Pozdnyakov DV, Filimonov VN (1973) *Kinetic and Catalysis* 14:665-669
- [33] Ozensoy E, Herling D, Szanyi J (2008) *Catal Today* 136:46-54
- [34] Bentrup U, Richter M, Fricke R (2005) *Appl Catal B* 55:213-220
- [35] Shimizu K, Shibata J, Yoshida H, Satsuma A, Hattori T (2001) *Appl. Catal. B* 30: 151-162
- [36] Yamaguchi M, Goto I, Wang ZM, Kumagai M (1999) *Science and Technology in Catalysis* 121: 371-374
- [37] Burch R, Breen JP, Hill CJ, Krutzsch B, Konrad B, Jobson E, Cider L, Eranen K, Klingstedt F, Lindfors LE (2004) *Topics in Catalysis* 30: 19-25
- [38D] Breen JP, Burch R (2006) *Topics in Catalysis* 39: 53-58
- [39] Shimizu K, Shibata J, Satsuma A (2006) *J. Catal* 239: 402-409
- [40] Yu Y, He H, Feng Q, Gao H, Yang X (2004) *Appl Catal B* 49:159-171
- [41] Macleod N, Lambert RM (2003) *Chem Commun* 9:1300-1301
- [42] Thibault-Starzyk F, Seguin E, Thomas S, Daturi M, Arnolds H, King DA (2009) *Science* 324:1048-1051