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

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Abstract
The NOx 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 (C_2H_5OH, CH_3CHO, C_2H_4, 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 $NO+O_2$ to produce acetaldehyde and N_2. For higher temperatures, two reaction pathways have been proposed, supported by the CH_3CHO-SCR results: a direct reaction between NO_2 and CH_3CHO, or via –NCO species.

Keywords: NOx, SCR, ethanol, Ag/Al_2O_3, NH_3, acetaldehyde

1. Introduction

In addition to the emission control of pollutants such as CO, hydrocarbons, NOx and particulates, the reduction of the greenhouse gases emission, as CO_2, 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 NOx in excess of oxygen and other catalytic processes were proposed to achieve expected NOx abatement. One possible solution is to use NOx 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 NH_3 and N_2O, a strong greenhouse gas, were also reported [7,8].

The second way to reduce NOx 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 NOx 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 NOx SCR with ethanol (EtOH-SCR) was studied over a 2wt.% Ag/Al_2O_3 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.* CH_3CHO, C_2H_4, 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 Al_2O_3 support and iii) in presence of the Ag/Al_2O_3 catalyst.

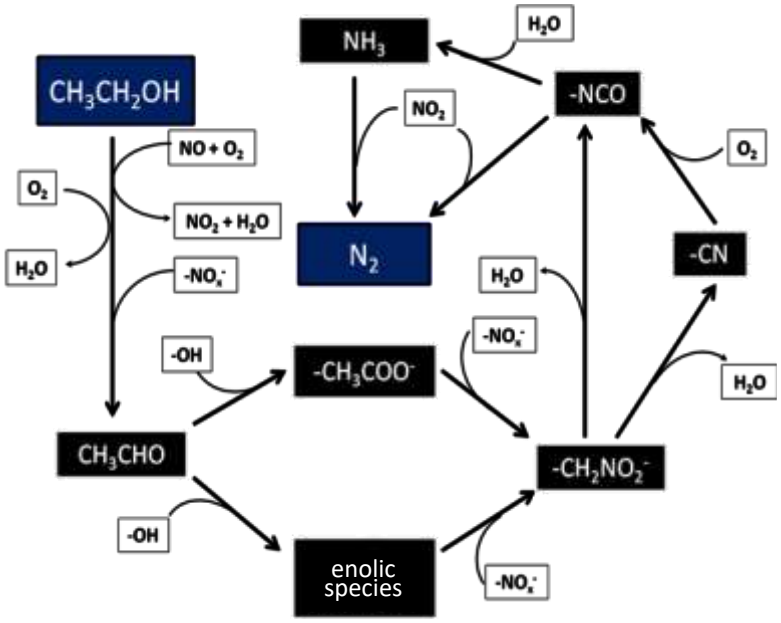


Figure 1: Global overview of EtOH-SCR mechanism

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% H_2O at 600°C for 4 h, and exhibits a specific surface area of 263 m^2g^{-1} (pore volume 1.13 cm^3g^{-1}). X-ray diffraction pattern evidences the γ-Al_2O_3 phase [ICDD PDF n° 00-050-0741(I)] with no visible reflection assigned to silver species (Ag^0, Ag_2O, AgO, $Ag_2Al_2O_4$…). H_2-TPR result reveals that 66% of the deposited silver is in metallic state, according to Musi *et al* [25]. TEM experiments show that Ag/Al_2O_3 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 H_2, 1200ppm C_2H_5OH, 8% O_2, 10% H_2O, 10% CO_2 balanced in N_2. 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/Al_2O_3 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 NO_2 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_2O (%)	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*: CH_3CH_2OH or CH_3CHO or C_2H_4

Most gases (NO, NO_2, N_2O, NH_3, CO, CO_2, C_2H_5OH, CH_3CHO, C_2H_4) were analyzed using a Multigas FTIR detector (MKS 2030). The N_2 selectivity is calculated assuming that no other N-compounds than NO, NO_2, N_2O, NH_3 are emitted. In fact, no N_2O emission was detected whatever the catalytic test conditions.

3. Results and discussion

3.1 Standard-SCR behaviors over Ag/Al_2O_3 (C_2H_5OH-SCR, CH_3CHO-SCR, C_2H_4 –SCR)

Catalytic results obtained on Ag/Al_2O_3 catalyst for the standard C_2H_5OH-SCR test (Table 1) are presented in Figure 2A and Figure 2B for C-compounds and N-compounds yields, respectively. A comparison of the NOx conversion depending on the introduced hydrocarbon (C_2H_5OH, CH_3CHO or C_2H_4) is also illustrated in Figure 2C.

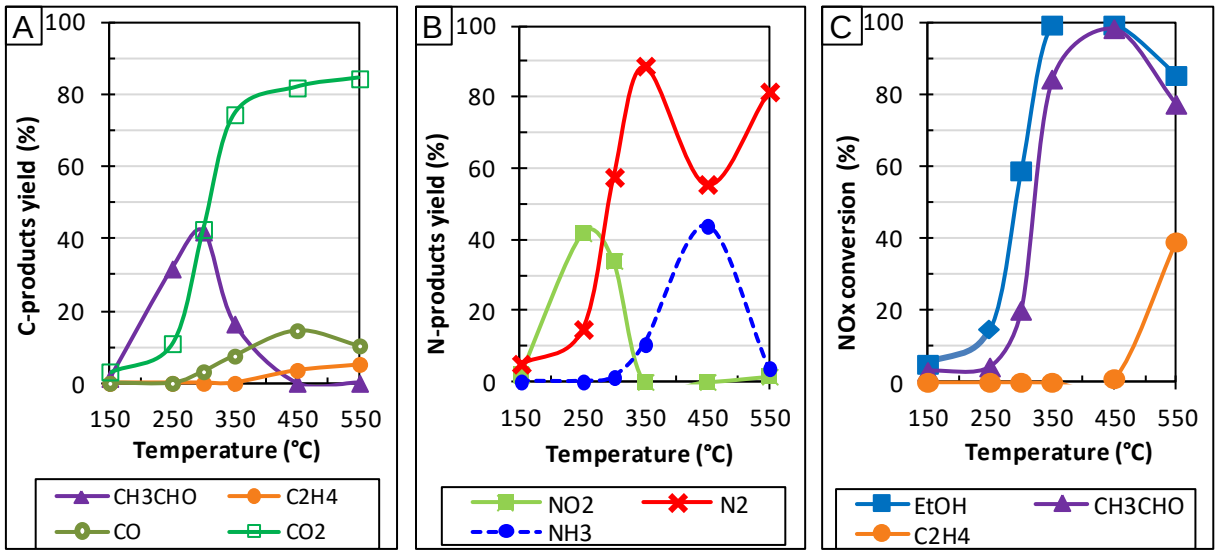


Figure 2: Standard-SCR tests over Ag/Al_2O_3. (A) C-compound yields and (B) N-compound yields with EtOH as reducer. (C) NOx conversion in SCR with C_2H_5OH, CH_3CHO or C_2H_4 as reducer.

C_2H_5OH-SCR test over Ag/Al_2O_3 (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 NO_2 and NH_3, in addition to N_2. In fact, the main N-compound product is nitrogen from 300°C, whereas, at 250°C, important amount of NO_2 is detected. An important NH_3 formation is observed at 450°C (NH_3 yield: 43%), which induces a strong decrease of the N_2 yield at this temperature.

Using the standard condition (Table1), Figure 2C shows that both ethanol and acetaldehyde are efficient to reduce NOx. Total NOx 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 NOx 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 NOx abatement in excess of O_2. Thereafter, in order to clarify the role of each reducer, the reactivity of the C-containing reducers (C_2H_5OH, CH_3CHO, C_2H_4, 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 NOx 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 CH_3CHO-SCR mechanism, as reported in the literature [26].

For C_2H_5OH-SCR, in thermal condition, NO conversion is effective essentially at 550°C (conv.: 92%) and it mainly leads to NO_2 (Table 2). On Al_2O_3, the NO conversion varies from 55% to 80% between 350°C and 550°C. The N_2 yield reaches a maximum of 48% at 450°C. Interestingly, the NO_2 yield at 550°C is lower on alumina (45%), than without any catalyst (78%). Ammonia is never observed in thermal condition, or with Al_2O_3.

Table 2: Comparative results in CH_3CHO and C_2H_5OH-SCR in simplified condition (reducer + NO + O_2). Reducer conversion, NOx conversion and N-compound yields for reaction in thermal condition, with Al_2O_3 or with Ag/Al_2O_3.

		CH_3CHO + NO + O_2				C_2H_5OH + 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_2O_3	0	22	89	100	38	95	100	100
	Ag/Al_2O_3	2	54	100	100	46	100	100	100
NO conv. (%)	Thermal	0	10	48	79	0	0	3	92
	Al_2O_3	0	10	50	83	3	55	60	80
	Ag/Al_2O_3	8	22	99	90	28	69	100	90
N_2 yield (%)	Thermal	0	2	9	27	0	0	1	14
	Al_2O_3	0	10	50	48	2	35	48	35
	Ag/Al_2O_3	1	22	88	55	14	65	76	58
NO_2 yield (%)	Thermal	0	8	39	52	0	0	2	78
	Al_2O_3	0	0	0	35	1	20	12	45
	Ag/Al_2O_3	7	0	0	35	14	0	0	32
NH_3 yield (%)	Thermal	0	0	0	0	0	0	0	0
	Al_2O_3	0	0	0	0	0	0	0	0
	Ag/Al_2O_3	0	0	11	0	0	4	24	0

Silver supported catalyst promotes the NO conversion and N_2 yield in the whole temperature range. NO_2 emission is lower than the one observed with alumina. In fact, NO_2 is not detected at 350°C or 450°C and reaches a yield of 32% at 550°C, compare to 45% for Al_2O_3. On Ag/Al_2O_3 sample, NH_3 emission is likewise detected. The higher is the NH_3 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 NO_2 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% O_2 (Table 1) in the presence or not of 167ppm H_2. Dry condition (no water) or addition of 10% H_2O was also used for comparison.

NO oxidation in absence of H_2

In absence of H_2 and in dry condition (*i.e.* NO oxidation conditions presented in Table 1), the oxidation of NO into NO_2 is never observed in the gas phase. On the contrary, on Al_2O_3, NO_2 is observed, but only at high temperature (550°C), and with a low yield (5%). No other compounds are detected, namely N_2O, NH_3 or N_2. Surprisingly, similar result is obtained with silver supported catalyst (Ag/Al_2O_3 sample).

It is reported in literature that NO oxidation starts by an adsorption step on acidic surface sites over Al_2O_3 [27-32]. NO is furthermore oxidized to nitrites species which involve basic oxygen of alumina support, and is thereafter desorbed into NO_2. This assumption was confirmed by O_2 isotopic exchange experiments (not shown), which show that gas $^{18}O_2$ is exchanged with $^{16}O_2$ of alumina matrix from 500°C. In presence of H_2O, the water dissociation on Lewis acid-base sites blocks this mechanism, and no NO_2 emission is then observed in this condition (NO + O_2 + H_2O) over alumina in the studied temperature range.

NO oxidation in presence of H_2

As mentioned above, without H_2 and H_2O in the gas mixture ($NO+O_2$), similar NO_2 yield is obtained at 550°C with alumina or with Ag/Al_2O_3. Silver is then not involved in the NO oxidation mechanism. If H_2 is added to the gas mixture ($NO+O_2+H_2$), no effect of H_2 is observed on Al_2O_3. On the contrary, NO_2 emission is detected from 150°C on Ag/Al_2O_3 catalyst (vs. 550°C in absence of H_2) and the NO_2 yield reaches about 60% at 550°C. Then, hydrogen favors the NO oxidation, but only with silver supported material. No other compound than NO_2 is detected (no N_2O or NH_3). 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 NO_2. Besides, in presence of water ($NO+O_2+H_2O$), NO_2 yield increases up to 20% at 550°C over Ag/Al_2O_3 catalyst, whereas NO_2

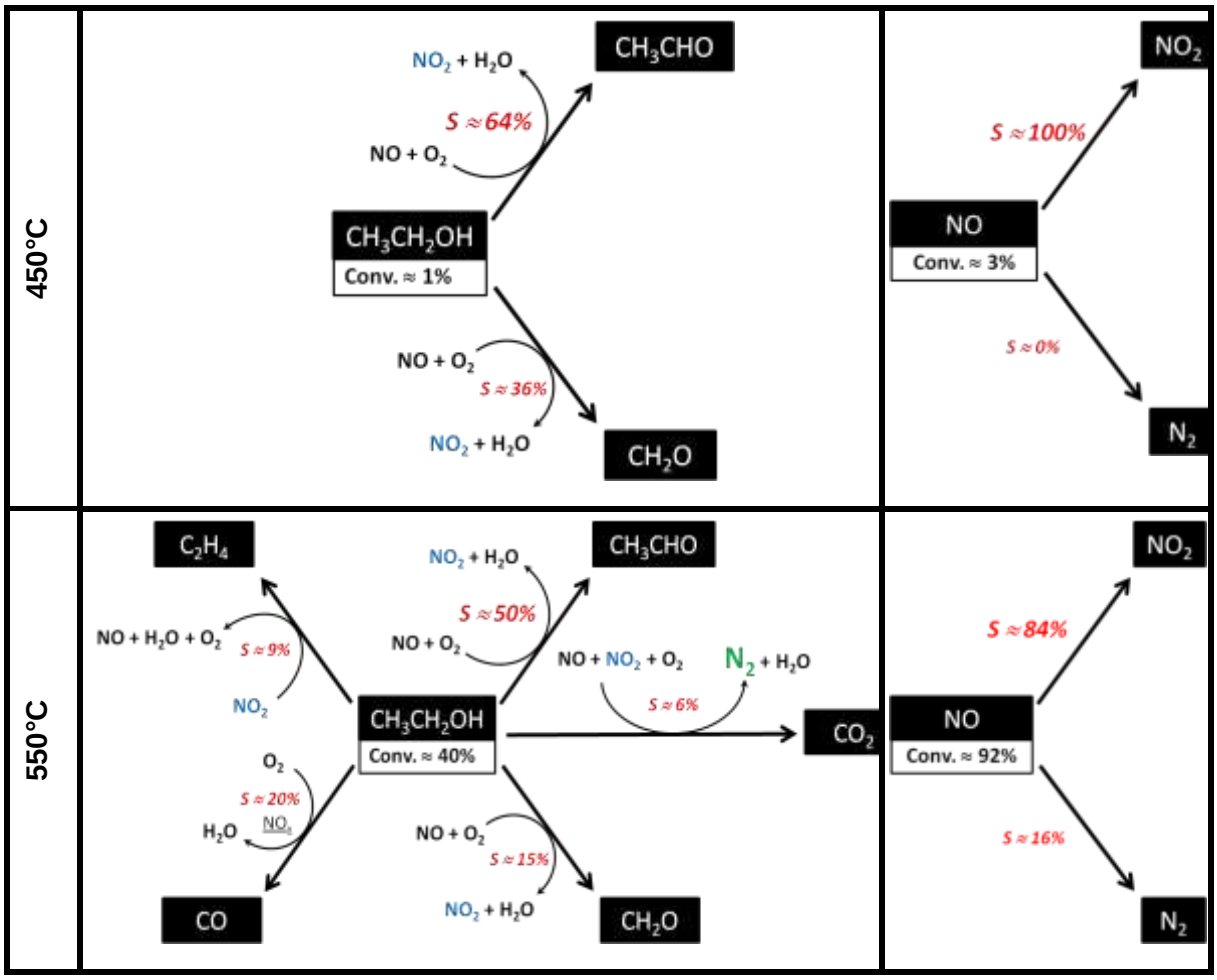
is not emitted on Al_2O_3 with these conditions. This result seems to support the assumption of nitrates desorption, since water cannot reduce silver species.

3.3.2 Investigation on C_2H_5OH-SCR

The C_2H_5OH-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 C_2H_5OH

In thermal condition (without any sample), C_2H_5OH 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 C_2H_5OH 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 C_2H_5OH-SCR). The following suggested scheme is then proposed:



Scheme 1: Reaction mechanism pathway for C_2H_5OH-SCR in thermal condition for C_2H_5OH + NO + O_2 gas mixture. S: selectivity.

To conclude, thermal C_2H_5OH-SCR reaction is active essentially at high temperature (550°C), leading to a maximum of about 90% of NO conversion, with N_2 selectivity close to 16% and an important amount of NO_2 detected (S≈85%). Ethanol is mainly oxidized into CH_3CHO (50% of selectivity at 550°C), but also into CO, CH_2O, C_2H_4 and CO_2.

C_2H_5OH reactivity over (Ag)/Al_2O_3

Different results were obtained on Al_2O_3 or Ag/Al_2O_3 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/Al_2O_3. However, addition of O_2 in the gas mixture ($C_2H_5OH + O_2$) dramatically modifies the C-compound selectivities between Al_2O_3 and Ag/Al_2O_3 catalysts (Table 3).

Table 3: C_2H_5OH conversion and C-compound yields for ($C_2H_5OH + O_2$) and ($C_2H_5OH + NO + O_2$) reaction in thermal condition, with Al_2O_3 or with Ag/Al_2O_3.

Reaction		$C_2H_5OH + O_2$				$C_2H_5OH + NO + O_2$			
Temperature (°C)		250°C	350°C	450°C	550°C	250°C	350°C	450°C	550°C
C_2H_5OH conv. (%)	Thermal	0	0	0	0	0	0	1	40
	Al_2O_3	48	100	100	100	38	95	100	100
	Ag/Al_2O_3	35	100	100	100	46	100	100	100
CH_3CHO yield (%)	Thermal	0	0	0	0	0	0	<1	20
	Al_2O_3	2	2	0	0	4	21	1	0
	Ag/Al_2O_3	31	61	0	0	38	25	0	0
C_2H_4 yield (%)	Thermal	0	0	0	0	0	0	0	4
	Al_2O_3	12	81	85	73	7	17	53	33
	Ag/Al_2O_3	0	2	17	39	0	1	10	0
CO_2 yield (%)	Thermal	0	0	0	0	0	0	0	2
	Al_2O_3	34	16	13	21	28	46	25	35
	Ag/Al_2O_3	3	33	64	46	5	59	67	94

On alumina, no effect of O_2 is observed on the ethanol conversion, similar catalytic results are observed with C_2H_5OH alone or $C_2H_5OH + O_2$ (Table 3). In presence of $NO+O_2$ the selectivity is strongly modified and CH_3CHO 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, N_2 conversion over alumina is 2% and 35% at 250°C and 350°C, respectively (results reported in Table 2). Thus, it seems that $NO+O_2$ reacts with C_2H_5OH to produce both N_2 and CH_3CHO on

alumina active sites. This way is assumed to be the first reaction path to produce N_2 at low temperature on alumina active sites.

Using Ag/Al_2O_3, ethanol oxidation ($C_2H_5OH + O_2$) leads mainly to acetaldehyde at low temperature (61% of CH_3CHO yield at 350°C), whereas CO_2 and C_2H_4 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, CH_3CHO yield increases from 30% ($C_2H_5OH + O_2$) to 40% ($C_2H_5OH + NO + O_2$) 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/Al_2O_3 catalyst. Note that using acetaldehyde (simplified CH_3CHO-SCR tests, Table 2), NO conversion is about 8% at 250°C, but mainly into NO_2. Finally, acetaldehyde reactivity in NO reduction is a key parameter in C_2H_5OH-SCR, and investigation of CH_3CHO-SCR behaviors is presented thereafter.

3.3.3 Investigation on CH_3CHO-SCR

It was showed previously that acetaldehyde is as an active reducer in standard SCR condition (Figure 2C). Besides, during the C_2H_5OH-SCR experiments on silver supported material, CH_3CHO is the main by-product, obtained by dehydrogenation. Thus reactivity of CH_3CHO was carefully studied.

Thermal decomposition and reaction of CH_3CHO

It was firstly checked that acetaldehyde is not thermally decomposed (CH_3CHO alone) and it does not react with NO ($CH_3CHO + NO$) from 150°C to 550°C. However, in presence of both NO + O_2 ($CH_3CHO + NO + O_2$) a low acetaldehyde conversion (2%) with NO_2 production (3%) is observed starting from 350°C. It is important to note that the thermal oxidation of NO to NO_2 (without reducer, part 3.3.1) is not observed. Then, at 350°C, CH_3CHO reacts with both NO and O_2 to produce NO_2, formaldehyde (CH_2O) and CO, according to the following reactions:

$$CH_3CHO + 2NO + 3/2O_2 \rightarrow 2CH_2O + 2NO_2 \quad (1)$$

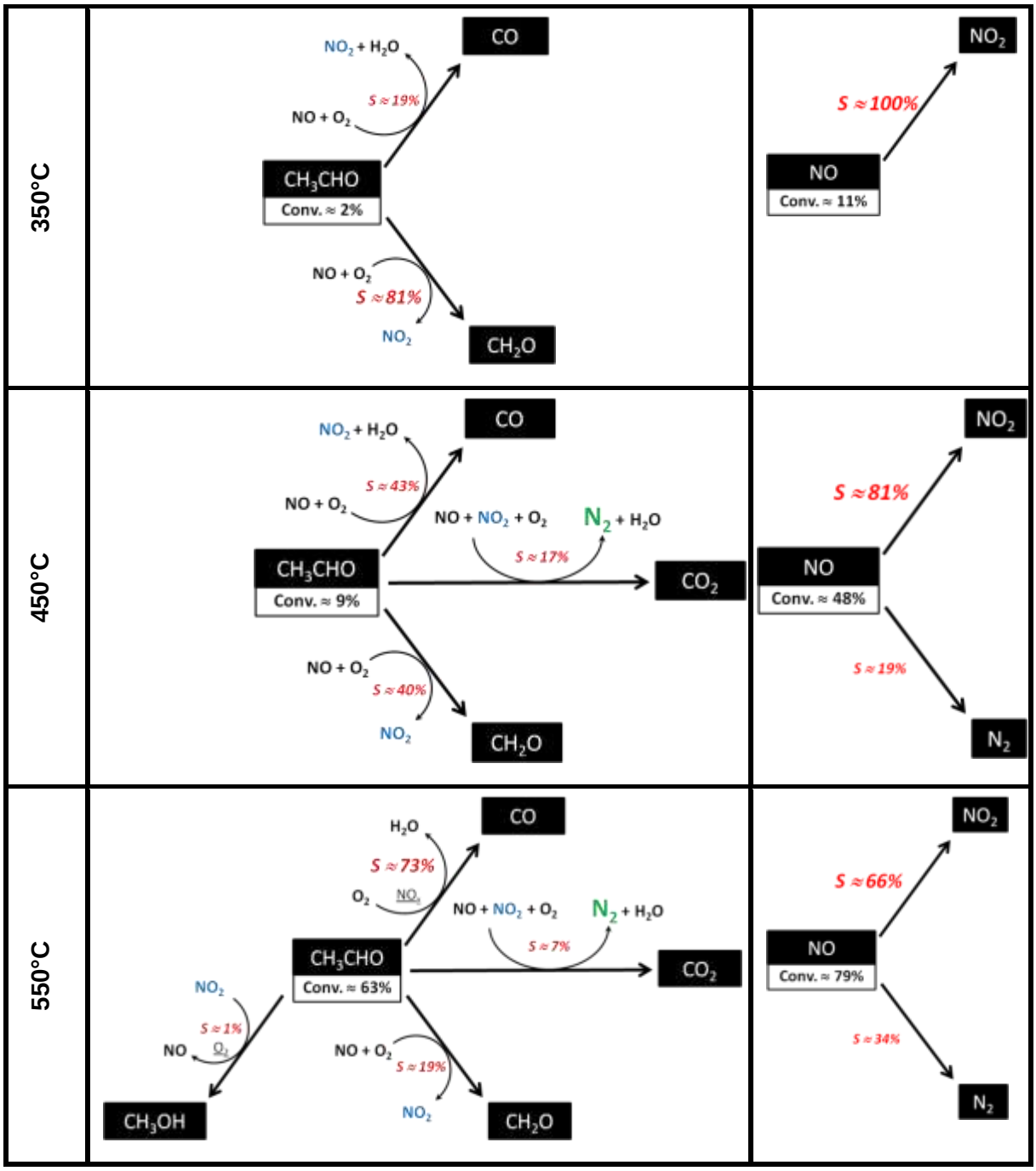
$$CH_3CHO + 2NO + 5/2O_2 \rightarrow 2CO + 2NO_2 + 2H_2O \quad (2)$$

The thermal conversion of CH_3CHO increases with the temperature, to 9% at 450°C. Besides, at 450°C, N_2 formation is also observed according to reaction (3):

$$CH_3CHO + NO + NO_2 + O_2 \rightarrow 2CO_2 + N_2 + 2H_2O \quad (3)$$

At higher temperature (550°C), the thermal conversion of acetaldehyde reaches 63%. Contrary to results obtained at 350°C and 450°C, CH_3CHO can be directly oxidized by O_2 at 550°C ($CH_3CHO + O_2$), mainly into formaldehyde and CO.

Based on the whole of results, the following reaction pathway for CH_3CHO-SCR in thermal condition is proposed:



Scheme 2: Reaction mechanism pathway for CH_3CHO-SCR in thermal condition for CH_3CHO + NO + O_2 gas mixture.

Catalytic decomposition and oxidation of CH_3CHO

Acetaldehyde decomposition or oxidation (Table 1) was firstly studied over alumina and then over Ag/Al_2O_3. On Al_2O_3, the CH_3CHO conversion starts from 300°C, and it is total at 550°C,

with or without O_2 in the gas mixture. However, selectivity depends on the presence of O_2. Indeed, without oxygen, an important amount of CO is observed. With O_2, the main oxidative compound detected at 550°C is CO_2. Addition of silver to alumina (Ag/Al_2O_3) enhances the acetaldehyde decomposition (CH_3CHO alone) from 75% to 100% at 450°C, and favors the CO_2 formation at 550°C.

Catalytic reduction of NO with CH_3CHO (CH_3CHO + NO + O_2), effect of water

Catalytic results for the (CH_3CHO + NO + O_2) reaction, mentioned as simplified CH_3CHO-SCR tests in Table 1, was previously presented in Table 2 for Ag/Al_2O_3. Conversions of CH_3CHO and NO obtained over Al_2O_3 and Ag/Al_2O_3 are compared in Figures 3A and 3B, and the effect of H_2O is depicted in Figure 3C.

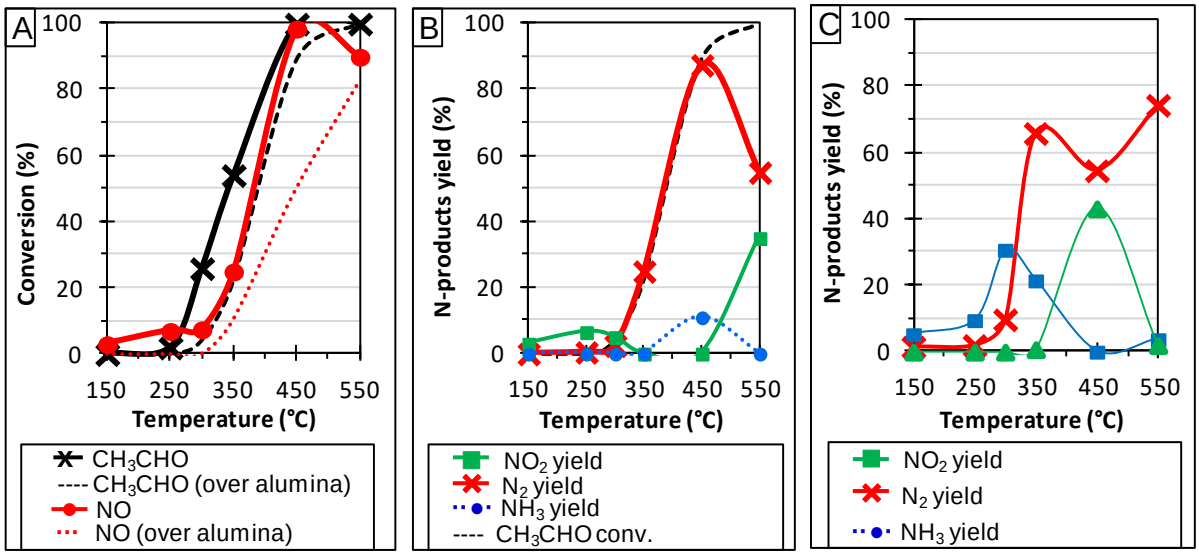


Figure 3: Simplified CH_3CHO-SCR tests on Ag/Al_2O_3. (A) CH_3CHO and NO conversion. (B) N-compound yields; (C) Effect of water: N-compound yields for (NO + O_2 + H_2O) condition. Catalytic results obtained over Al_2O_3 are plotted in dotted line (CH_3CHO yields in Fig B and C). Gas mixture: 1200 ppm CH_3CHO, 400 ppm NO, 8% O_2, (10% H_2O) balanced with N_2.

As expected, CH_3CHO and NO conversions are enhanced with Ag/Al_2O_3 catalyst, compare to Al_2O_3. Figure 3B also reveals that the N_2 yield observed with Ag/Al_2O_3 catalyst is correlated with the CH_3CHO conversion obtained with alumina (in dotted line), in a large temperature range (150-450°C). This result seems to indicate that the N_2 formation in CH_3CHO-SCR is linked to the activation of acetaldehyde over the alumina support.

Addition of water in the feed stream (CH_3CHO + NO + O_2 + H_2O mixture) significantly changes the N-compound yields (Figure 3C). The N_2 yield is then improved in the low temperature range. For instance, at 350°C, the N_2 yield reaches 67%, compared to 22% without water. In opposition, the N_2 yield is strongly decreased at 450°C, which is correlated with the enhancement of the ammonia yield with water. Another important point is that NO_2 yield is also

enhanced with H_2O around 300°C, from 7% to 30% at this temperature. Besides, the N_2 yield is no more correlated with the CH_3CHO conversion obtained with alumina (in dotted line, Figure 3C), as it was reported in absence of H_2O in the gas mixture (Figure 3B).

3.4 Highlights on the EtOH-SCR mechanism with Ag/Al_2O_3

3.4.1 Low temperature limitation in EtOH-SCR with Ag/Al_2O_3 (T≤300°C)

At 250°C, the presence of NO in the gas mixture increases the ethanol conversion on Ag/Al_2O_3, from 35% to 46% (Table 3). In fact, in absence of NO, a higher C_2H_5OH conversion is observed on Al_2O_3 support than on Ag/Al_2O_3 catalyst. Besides, NO conversion is effective at 250°C on Ag/Al_2O_3 (28%, Table 2), but is very low on alumina (3%). At this temperature, Table 3 reveals that on Ag/Al_2O_3 catalyst, ethanol activation leads mainly to the formation of CH_3CHO (yield about 38%) when NO is present on the gas mixture. In absence of NO ($C_2H_5OH + O_2$), CH_3CHO yield drops to 31%. Note that acetaldehyde is produced in very low amount on alumina ($C_2H_5OH + O_2$ mixture). Thus on Ag/Al_2O_3 catalyst, it appears that the dehydrogenation reaction (4), leading also to the formation of hydrogen, becomes faster than the dehydration one.

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (4)$$

It was previously reported in section 3.3.1 that Ag/Al_2O_3 and Al_2O_3 samples act differently in presence of H_2, especially for the NO oxidation reaction. In fact the presence of a low concentration of H_2 (167 ppm,) enables the oxidation of NO into NO_2 on Ag/Al_2O_3 at low temperature (starting from 150°C). Without hydrogen in the gas mixture, NO_2 is not observed at low temperature (T≤300°C). Then, the use of C_2H_5OH leads to the formation of NO_2 at low temperature (i.e 250°C) on Ag/Al_2O_3 (yield about 14%, Table 2).

It is thus assumed that the NO_2 formation is the rate-determining step in N_2 formation. In fact, based on the work of Sachtler et al. [22], it is proposed that the first reaction step of NO oxidation into NO_2 leads to the formation of adsorbed nitrates species at low temperature. As reported in literature [30,33], NO_2 adsorption on alumina support leads to the formation of three kinds of nitrate species (bridging, monodentate and bidentate). The C_2H_5OH-SCR reaction is thereafter limited by the low reactivity between adsorbed nitrates and ethanol. The deduced N_2 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, NO_2 is much more active than NO [26], especially for T>300°C. At lower temperature, nitrates are too strongly adsorbed [28,35,36], but addion of H_2 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 Ag/Al_2O_3 catalyst is presented in Figure 4 for the C_2H_5OH-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 C_2H_5OH-SCR and CH_3CHO-SCR tests, respectively. Total NOx 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.

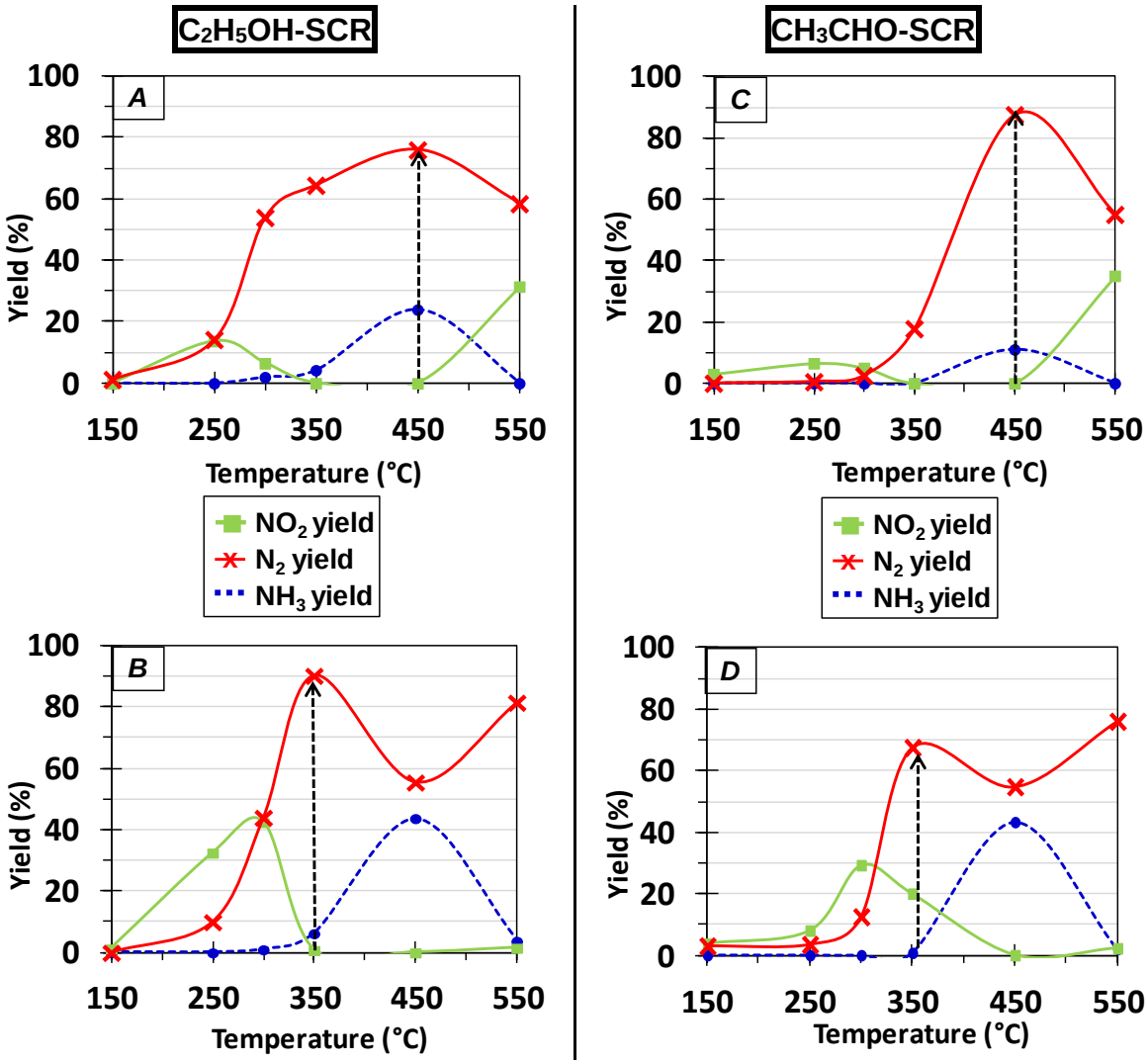
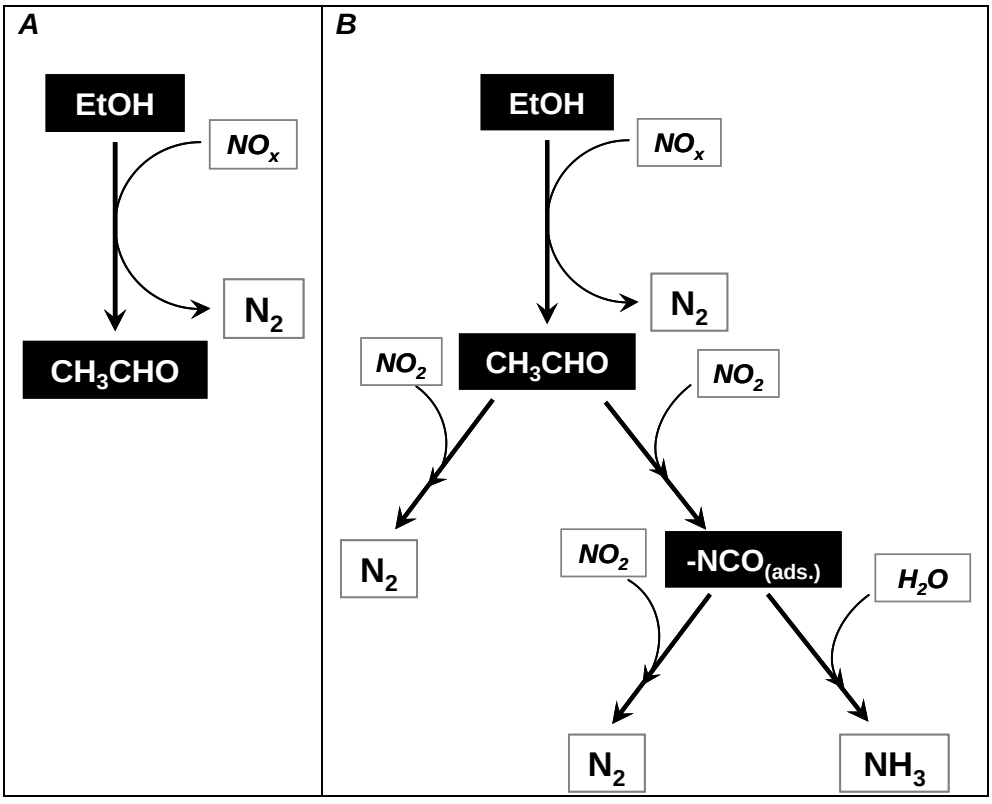


Figure 4: N-compound yields for C_2H_5OH-SCR (A) and CH_3CHO-SCR (C) tests in simplified condition over Ag/Al_2O_3 catalyst. Effect of water on C_2H_5OH-SCR (B) and CH_3CHO-SCR (D).

Ammonia formation mechanism is well established in literature [18,40], it involves the hydrolysis of -NCO species to form NH_3. The formation of –NCO species has been observed in numerous papers over Ag/Al_2O_3 catalysts when high NOx 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 NO_2 to form ammonium nitrite. Ammonium nitrite is then decomposed into H_2O and N_2. Isocyanate ions also react with O_2 but this reaction is slower than that of -NCO with water, which leads to ammonia formation [17]. Since no NH_3 is emitted on Al_2O_3 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 N_2 formation is virtually nil with acetaldehyde whereas acetaldehyde is observed together with N_2 using ethanol as introduced reducer. In addition, N_2 is observed only if O_2 is introduced, suggesting that NO_2 are the reactive species.

At higher temperature, the $CH_3CHO + NO + O_2$ 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≤300°C) and (B) high temperature (T≥300°C)

4. Conclusion

The mechanism of the NOx SCR with ethanol over Ag/Al_2O_3 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 C_2H_5OH-SCR test, CO, C_2H_4 and CH_3CHO are also emitted. CO is not active for the NOx reduction, and CO_2 is observed only with Ag/Al_2O_3 and at high temperature (550°C). Ethylene is able to reduce NOx into N_2 only at 550°C over alumina with a limited impact of silver. Ethanol is activated at low temperature over alumina ($T \leq 300$°C) but N_2 is obtained only with Ag/Al_2O_3 and with NO and O_2 in the feed stream. In fact, Ag allows NO_2 formation from 150°C. Acetaldehyde is also observed as a product in this low temperature range. At higher temperature CH_3CHO is an effective NOx reducer over Al_2O_3. It is demonstrated that alumina active sites are involved in the NO_2 reduction with CH_3CHO leading to a possible NOx reduction pathway to N_2. However, silver is supposed to favor –NCO species formation, which explains the enhancement of the nitrogen formation and ammonia emission.

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