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Influence of sodium and/or phosphorus addition on the deactivation of Cu-FER zeolites for SCR of NO_x with NH₃.

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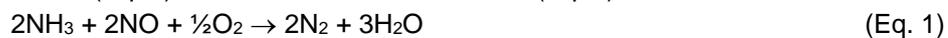
Abstract

This work investigates the effect of sodium and phosphorus on the DeNO_x performances of model Cu-FER SCR catalysts with two copper loadings (2.8_{wt}% and 6.1_{wt}%). These inorganic elements, present in the Biodiesel fuels and lubricants, were added by wet-impregnation using two solvents: water or ethanol. Catalysts were evaluated in standard-SCR conditions as well as in NO and NH₃ oxidation, and characterized by means of H₂-TPR and NH₃ adsorption monitored by FT-IR. It was evidenced that catalytic behaviors were highly influenced by the implemented impregnation route with a stronger impact of water as solvent. Whatever the studied catalysts, NH₃ adsorption capacities decreased after addition of sodium and/or phosphorus. Interestingly, sodium and phosphorus acted differently on the poisoning of NH₃ adsorption sites. Na mainly poisoned Brønsted acid sites and favored a back exchange with Cu²⁺ species (especially when Na was added in water), while phosphorus directly interacted with copper species, mainly in exchange position. The deactivation observed at low temperature (250°C) was preferentially due to the decrease in NH₃ adsorption together with the increase in the copper-phosphorus interaction, especially for copper species in exchange position.

Keywords: Sodium, Phosphorus, Biodiesel, NH₃-SCR, Cu exchanged zeolite, Deactivation.

1. Introduction

The selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) is commonly used to reach the emission limits for vehicles such as restricted by the Euro standards. Depending on the inlet NO₂/NO_x ratio, both standard-SCR (Eq. 1) and fast-SCR stoichiometries (Eq. 2) are involved:



Historically, the dedicated material for NH₃-SCR is V₂O₅-WO₃-TiO₂ based catalyst. To overcome the transition phase of TiO₂ and the vanadium sublimation drawbacks and to expand the operating temperature window, new catalytic formulations based on metal-exchanged zeolite systems have emerged. Cu-promoted catalysts are commonly recognized for this purpose [1].

The Euro VI standard dedicated to heavy duty vehicles requires durability of 700,000 km. Furthermore, to reduce greenhouse gases emissions, European Directive 2009/33/CE imposes the introduction of alternative fuels such as biodiesel, which contains minerals traces of sodium, potassium or phosphorus (minerals also contained in lubricants). Although they are authorized in limited amounts in biodiesel (maximum of 5 and 4 ppm for Na+K and P, respectively; European standard EN 14214), the impact of these inorganic compounds on the catalytic post-treatments have to be taken into account in the catalytic exhaust pipe ageing. Recently, we have studied the influence of the sodium impregnation solvent on the deactivation of Cu-FER zeolites (with two copper loadings) dedicated to the SCR of NO_x with NH₃ [2]. It was reported that, whatever the copper content, ammonia adsorption capacity was decreased by Na additions. Besides, the migration of exchanged Cu to the expense of CuO formation was evidenced after Na impregnation in water. In another study, the influence of Na and/or P addition was investigated over a high loaded copper zeolite sample (containing mainly external CuO species) [3]. It was evidenced that the deactivation mechanisms generated by the minerals (Na or P) were different. An interaction of phosphorus with copper was pointed out. However, the impact of phosphorus on FER with low copper loading was not investigated. Then, to gain an overview of the deactivation mechanisms generated by inorganic element, this study compares the impact of sodium and/or phosphorus addition on two Cu-FER catalysts with 2.8_w% (exhibiting mainly exchanged copper) and 6.1_w% Cu (with mainly external copper).

The inorganic compounds were added using two solvents. Impregnation in water was used especially to simulate cold start and engine switch-off periods, for which water condensation occurs in the exhaust pipe [4]. Impregnations were also performed in ethanol, which is less polar than water, to avoid interactions between water and the exchanged zeolite. Variations in the copper contents, minerals loadings and solvents led to a wide range of chemical surface properties in order to highlight the catalytic functions involved in the sustaining of SCR activity, together with the impact of inorganic compounds in the DeNO_x efficiency.

2. Materials and Methods

2.1 Catalysts

Catalysts were prepared by copper ion exchange on ferrierite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$, Alfa Aesar). The ferrierite structure zeolite (FER), which exhibits a channel system of 10 and 8 member rings, was selected to ensure a high hydrothermal stability. Two copper loadings were selected (2.8 wt% and 6.1 wt%) in order to obtain samples with mainly Cu^{2+} species in exchanged position (denoted $\text{Cu}_{(\text{EX})}$ -FER) or in extra network form (denoted $\text{Cu}_{(\text{EN})}$ -FER) [2,3]. $\text{Cu}_{(\text{EX})}$ -FER and $\text{Cu}_{(\text{EN})}$ -FER catalysts exhibited similar specific surface areas at around 350 m^2/g after hydrothermal treatment (600°C, 16 hours under 10 % O_2 , 10 % H_2O into N_2). Catalysts before Na and/or P addition are named fresh catalysts.

H_2 -TPR experiments performed on a Micromeritics Autochem 2920 apparatus revealed that 90 % of Cu units are in exchanged position over the $\text{Cu}_{(\text{EX})}$ -FER sample. $\text{Cu}_{(\text{EN})}$ -FER has different Cu-species distribution with only 30 % of Cu in exchanged position and around 55 % of CuO species (CuO also detected by XRD). Both samples also presented CuAl_2O_4 compounds (10 % and 15 % for $\text{Cu}_{(\text{EX})}$ -FER and $\text{Cu}_{(\text{EN})}$ -FER catalysts, respectively).

Sodium and/or phosphorus elements were added in various loadings (until around 900 $\mu\text{mol g}^{-1}$) by the impregnation method using water (open symbols) or ethanol (full symbols) as solvent. NaNO_3 , $(\text{NH}_4)_2\text{HPO}_4$ or H_2NaPO_4 salts were used for the addition of Na, P or (Na+P), respectively. The corresponding solutions were mixed with the appropriate weight of catalyst and stirred at room temperature during 4 h. After drying one night at 80°C, the samples were submitted to the same hydrothermal treatment than for the mineral-free catalysts (600°C, 16 hours). The effective Na, P or (Na+P) contents were measured by ICP.

2.2 Ammonia adsorption behaviour

Ammonia adsorption properties were examined by FTIR spectroscopy. IR spectra were collected using a Nexus Nicolet spectrometer equipped with a DTGS detector (deuterium triglyceride sulphur) and a KBr beam splitter. Before NH_3 adsorption, the catalyst was *in situ* pre-treated under vacuum at 450°C. Ammonia was adsorbed at 50°C and desorption was performed up to 450°C. IR spectra are characterized by N-H bending modes (δ_{asym}) at 1452 and 1397 cm^{-1} , assigned to ammonium ions formed by the protonation of ammonia molecules located on Brønsted acid sites. In addition, a band at 1621 cm^{-1} attributed to both ammonia adsorbed on Al^{3+} coordinatively unsaturated sites (CUS) and copper Lewis sites is observed [5]. Quantitative analysis were performed using the molar extinction coefficient values ($\epsilon_{\text{Brønsted}} = 4.6 \text{ cm } \mu\text{mol}^{-1}$, $\epsilon_{\text{Lewis}} = 1.1 \text{ cm } \mu\text{mol}^{-1}$, from [2]).

2.3 Catalytic tests

Catalytic tests were carried out in a tubular quartz reactor. 50 mg of catalyst (sieved in the 0.2-0.4 mm range) diluted in 50 mg of SiC (Prolabo, 0.35 mm) were used. The total flow rate was fixed at 250 mL min^{-1} . The composition of the feed gas and effluent stream were analysed online with a MKS 2030 Multigas infrared analyser. Inlet NO , NH_3 , CO_2 , O_2 and N_2 concentrations were adjusted by mass-flow controllers, while H_2O was added *via* a saturator.

NO and NH_3 oxidation properties. NO and NH_3 oxidation activities were performed from 500°C to 200°C, by temperature steps of 50°C. Due to the low catalytic activities in NO oxidation, only results obtained at 450 °C are presented, which undergoes a compromise between kinetic limitation and thermodynamic NO - NO_2 equilibrium. For NH_3 oxidation tests, results recorded 400°C are reported because of the too high activity of $\text{Cu}_{(\text{EN})}$ -FER sample at 450°C (100 % of NH_3 conversion). The reactant gas composition was 500 ppm NO or 500 ppm NH_3 , completed with 10% O_2 , 10% CO_2 , 9% H_2O balanced in N_2 .

NH_3 -SCR performances. Catalytic tests were performed in standard-SCR stoichiometry from 500°C to 150°C by temperature steps of 50°C. Catalytic activities are measured after stabilisation of effluent gases concentrations. The reactant gas composition was 500 ppm NO , 500 ppm NH_3 , 10% O_2 , 10% CO_2 , 9% H_2O balanced in N_2 .

3. Results and Discussion

3.1 NH₃-SCR behaviors

Figure 1 reports the NH₃-SCR performances for the two kinds of catalysts (Cu_(EX)-FER and Cu_(EN)-FER catalysts) depending on the temperature test and for the higher minerals content deposited in water (open symbol, full line) or ethanol (full symbol, dotted line) as solvent. For the fresh Cu promoted catalysts (black line), it appears that Cu_(EN)-FER sample exhibited a higher DeNO_x efficiency in the 200-300°C temperature range compared with Cu_(EX)-FER catalyst, whereas opposite behaviors were recorded at high temperature (500°C). These results are attributed to the presence of CuO units that favors (i) the NO oxidation into NO₂ at low temperature, which is the rate-limiting step of the standard-SCR reaction at low temperature (this point is discussed thereafter in Figure 4B), and (ii) the ammonia oxidation at high temperature, which compete with the SCR reaction.

With the addition of inorganic compounds, the DeNO_x efficiency was significantly affected, especially when minerals were added using water (open symbol, full line) as solvent.

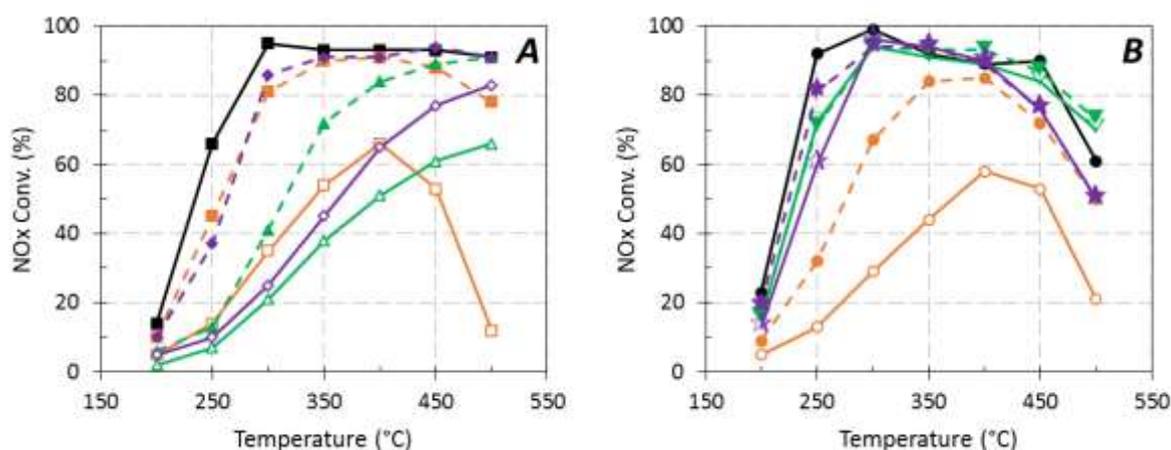


Figure 1. Effect of higher minerals content (deposited in water: open symbol, full line or ethanol: full symbol, dotted line) on the standard NH₃-SCR behaviors of Cu_(EX)-FER (A) and Cu_(EN)-FER catalysts (B). Black line (■,●) corresponds to the reference test without mineral addition.

Na: —, □ (830 μmol.g⁻¹), ■ (620 μmol.g⁻¹), ○ (885 μmol.g⁻¹) ● (665 μmol.g⁻¹);

P: —, △ (750 μmol.g⁻¹), ▲ (725 μmol.g⁻¹), ▽ (915 μmol.g⁻¹), ▼ (790 μmol.g⁻¹);

Na+P: —, ◇ (735 μmol.g⁻¹), ◆ (895 μmol.g⁻¹), ☆ (750 μmol.g⁻¹), ★ (860 μmol.g⁻¹).

In addition, Na-containing sample presented the stronger catalytic deactivation at high temperature (400-500°C), compared with P-containing catalyst. In order to highlight the mineral effect on the NH₃-SCR behaviors, the relative loss in NO_x conversion at 250°C is plotted Figure 2 versus inorganic compounds content deposited in water (open symbol, full line) or ethanol (full symbol, dotted line), for both Cu_(EX)-FER and Cu_(EN)-FER catalysts.

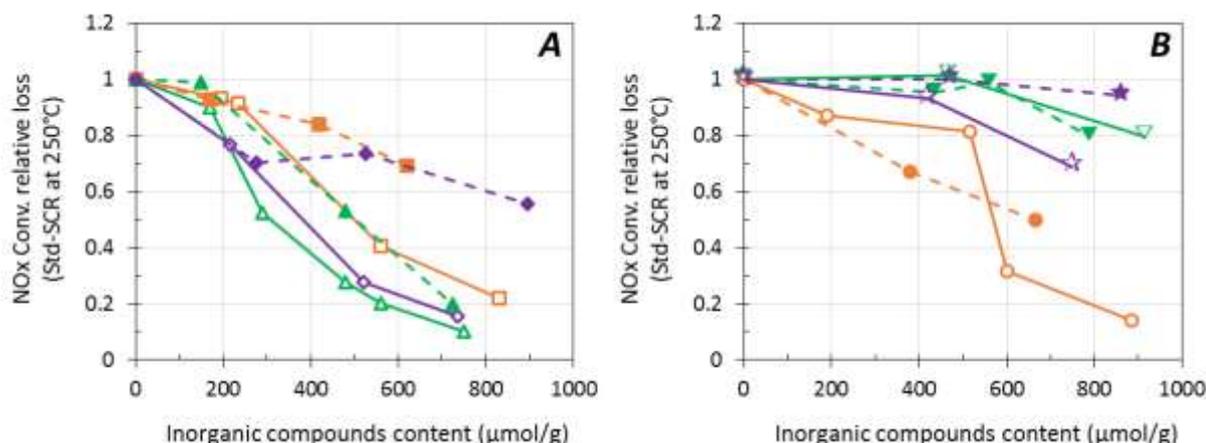


Figure 2. Effect of solvent (water: open symbol, full line; ethanol: full symbol, dotted line) in inorganic compounds impregnation in standard-SCR for Cu_(EX)-FER (A) and Cu_(EN)-FER (B).

Na: —, □ (830 μmol.g⁻¹), ■ (620 μmol.g⁻¹), ○ (885 μmol.g⁻¹) ● (665 μmol.g⁻¹);

P: —, △ (750 μmol.g⁻¹), ▲ (725 μmol.g⁻¹), ▽ (915 μmol.g⁻¹), ▼ (790 μmol.g⁻¹);

Na+P: —, ◇ (735 μmol.g⁻¹), ◆ (895 μmol.g⁻¹), ☆ (750 μmol.g⁻¹), ★ (860 μmol.g⁻¹).

Over Cu_(EX)-FER catalyst (Figure 2A), phosphorus is the most penalizing element on the SCR activity at 250°C, with a relative loss of about 90 % for the higher P content. To the opposite, on sample initially having large proportion of copper in the oxide form (Cu_(EN)-FER), sodium is the element that contributed the most to the decline of DeNOx activity (Figure 2B).

3.2 Minerals deposits impact on chemical surface properties

NH₃-SCR mechanism is claim to depend on both acidic sites and redox properties of catalysts. However the catalytic mechanism related to the precise nature of active sites is still in debate. Acid sites are involved in ammonia adsorption over bridged hydroxyl of the zeolite framework (Brønsted acid sites). NH₃ adsorption/activation can also occurs on Cu species [6]. Consequently, ammonia adsorption capacities were evaluated by NH₃ adsorption monitored by FTIR to highlight the poisoning effect induced by inorganic compounds deposit over the whole adsorption sites (Cu units and Brønsted acid sites). Besides, the NH₃-SCR reaction depends on redox properties of materials encored by Cu units. To evaluate redox properties of catalysts, NO and NH₃ oxidation reactions were performed over fresh and minerals-poisoned samples.

3.2.1 NH₃ adsorption monitored by FTIR

It was previously evidenced in [2] and [3] by FTIR analysis of OH stretching vibration that Na addition leads to a decrease in the amount of Brønsted acid sites on such catalysts. To the opposite, P additions do not affect bridged OH groups. Figure 3 depicts ammonia adsorption capacities obtained at 50°C depending on the solvent impregnation used (water: open symbol; ethanol: full symbol) and the copper loading in the catalyst (Cu_(EX)-FER, Figure 3A; Cu_(EN)-FER, Figure 3B).

Over Cu_(EX)-FER (Figure 3A), ammonia adsorption capacities linearly decreased whatever the nature of inorganic compounds and the impregnation solvent (*i.e.* water or ethanol). To the opposite, on Cu_(EN)-FER sample (Figure 3B), which initially contained mainly extra network copper (CuO), NH₃ adsorption amount decreased only after Na addition, whatever the impregnation solvent used. Note that similar feature were denoted in Figure 2B. As Brønsted acid sites were virtually not affected by phosphorus addition, it implies that phosphorus mainly interacted with exchanged Cu²⁺ units.

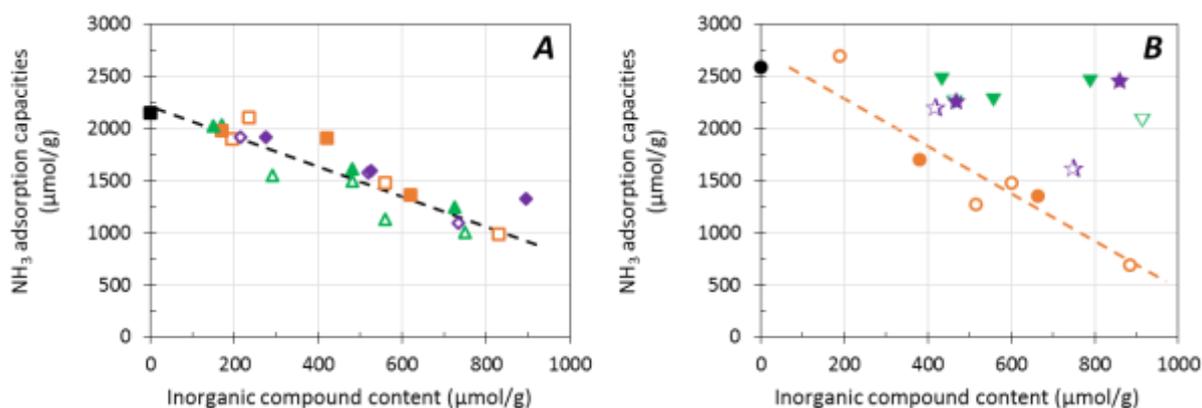


Figure 3. Effect of minerals loading on ammonia adsorption capacities at 50°C ($\mu\text{mol g}^{-1}$) in function of impregnated solvent (water: open symbol; ethanol: full symbol) for $\text{Cu}_{(\text{EX})}$ -FER (A) and $\text{Cu}_{(\text{EN})}$ -FER (B).

Na: —, □ ($830 \mu\text{mol.g}^{-1}$), ■ ($620 \mu\text{mol.g}^{-1}$), ○ ($885 \mu\text{mol.g}^{-1}$) ● ($665 \mu\text{mol.g}^{-1}$);
 P: —, △ ($750 \mu\text{mol.g}^{-1}$), ▲ ($725 \mu\text{mol.g}^{-1}$), ▽ ($915 \mu\text{mol.g}^{-1}$), ▼ ($790 \mu\text{mol.g}^{-1}$);
 Na+P: —, ◇ ($735 \mu\text{mol.g}^{-1}$), ◆ ($895 \mu\text{mol.g}^{-1}$), ☆ ($750 \mu\text{mol.g}^{-1}$), ★ ($860 \mu\text{mol.g}^{-1}$).

3.2.2 NO and NH_3 oxidation behaviors

NO and NH_3 oxidation behaviors for $\text{Cu}_{(\text{EX})}$ -FER and $\text{Cu}_{(\text{EN})}$ -FER catalysts are presented at 450°C (Figure 4) and 400°C (Figure 5), respectively. Obviously, excepted for Na-doped samples impregnated in water (open symbols), inorganic compounds addition led to a deactivation of the NO oxidation activity over $\text{Cu}_{(\text{EX})}$ -FER catalyst (Figure 4A). Similar results were obtained for NH_3 oxidation experiments (Figure 5A). Catalysts originally containing mainly CuO in external position ($\text{Cu}_{(\text{EN})}$ -FER) presented higher initial NO oxidation activity compared with $\text{Cu}_{(\text{EX})}$ -FER sample (Figure 4B). $\text{Cu}_{(\text{EN})}$ -FER catalyst presented the stronger deactivation after Na addition, assigned to a sintering of CuO particles, as previously observed for $\text{Cu}_{(\text{EX})}$ -FER samples. Note that for the lower P loading (at around $400 \mu\text{mol g}^{-1}$), $\text{Cu}_{(\text{EN})}$ -FER catalyst showed an increase in the NO and NH_3 oxidation activity. This observation is correlated with a partial Cu^{2+} migration to form CuO (from TPR experiments, results not shown) and with the fact that phosphorus interacts mainly with Cu^{2+} species.

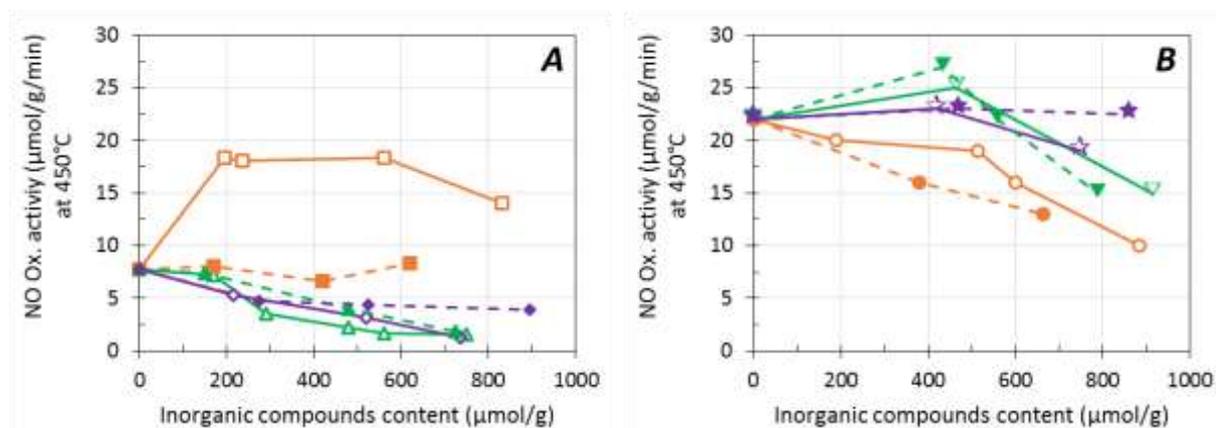


Figure 4. Effect of impregnation solvent (water: open symbol, full line; ethanol: full symbol, dotted line) and inorganic compounds toward NO oxidation activities at 450°C for $\text{Cu}_{(\text{EX})}$ -FER (A) and $\text{Cu}_{(\text{EN})}$ -FER (B).

Na: —, □ ($830 \mu\text{mol.g}^{-1}$), ■ ($620 \mu\text{mol.g}^{-1}$), ○ ($885 \mu\text{mol.g}^{-1}$) ● ($665 \mu\text{mol.g}^{-1}$);
 P: —, △ ($750 \mu\text{mol.g}^{-1}$), ▲ ($725 \mu\text{mol.g}^{-1}$), ▽ ($915 \mu\text{mol.g}^{-1}$), ▼ ($790 \mu\text{mol.g}^{-1}$);
 Na+P: —, ◇ ($735 \mu\text{mol.g}^{-1}$), ◆ ($895 \mu\text{mol.g}^{-1}$), ☆ ($750 \mu\text{mol.g}^{-1}$), ★ ($860 \mu\text{mol.g}^{-1}$).

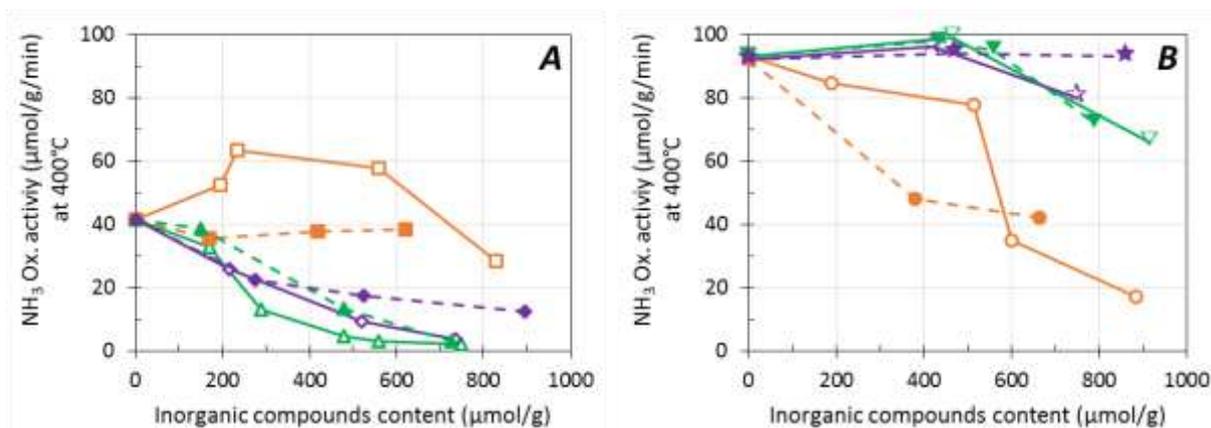


Figure 5. Effect of impregnation solvent (water: open symbol, full line; ethanol: full symbol, dotted line) and inorganic compounds toward NH₃ oxidation activities at 400°C for Cu_(EX)-FER (A) and Cu_(EN)-FER (B).

Na: —, □ (830 μmol.g⁻¹), ■ (620 μmol.g⁻¹), ○ (885 μmol.g⁻¹) ● (665 μmol.g⁻¹);

P: —, △ (750 μmol.g⁻¹), ▲ (725 μmol.g⁻¹), ▽ (915 μmol.g⁻¹), ▼ (790 μmol.g⁻¹);

Na+P: —, ◇ (735 μmol.g⁻¹), ◆ (895 μmol.g⁻¹), ☆ (750 μmol.g⁻¹), ★ (860 μmol.g⁻¹).

To conclude, Na addition in water over Cu_(EX)-FER led to the formation of CuO species by a back-exchange phenomenon from the lower Na content added [2]. For high Na loading, a sintering of the formed CuO particles explains the losses of both NO and NH₃ oxidation properties. Phosphorus addition led to Cu-P interaction that modified the Cu species reducibility. It induced a continuous deactivation of the oxidative function. The simultaneous addition of (Na+P) rather led to results reported for P-containing samples. Finally, to the exception of catalysts containing sodium, Cu_(EN)-FER catalyst is less sensitive to the addition of minerals compared to Cu_(EX)-FER sample. It results in a different deactivation mechanism by minerals and highlights the fact that phosphorus rather interacts with exchanged Cu²⁺ units.

3.3 Deactivation mechanism

The effect of minerals on the deactivation mode of NH₃-SCR performances at 250°C is summarized in Figure 6. Clearly, a linear deactivation was obtained in regards on the poisoning of the NH₃ adsorption properties (Figure 6A). This result confirms an Eley-Rideal type mechanism where ammonia is first adsorbed on catalyst active sites. This correlation does not distinguish the type of adsorption site (Brønsted or copper units), but it is confirmed for (i) both investigated copper loadings, (ii) all the studied minerals (Na and/or P) and (iii) for the two impregnation solvents used (water and ethanol). In addition, redox functions of catalysts are also involved in NH₃-SCR deactivation, especially for P-containing samples, as illustrated in Figure 6B, where the DeNO_x activities is reported in function of NO oxidation behaviors.

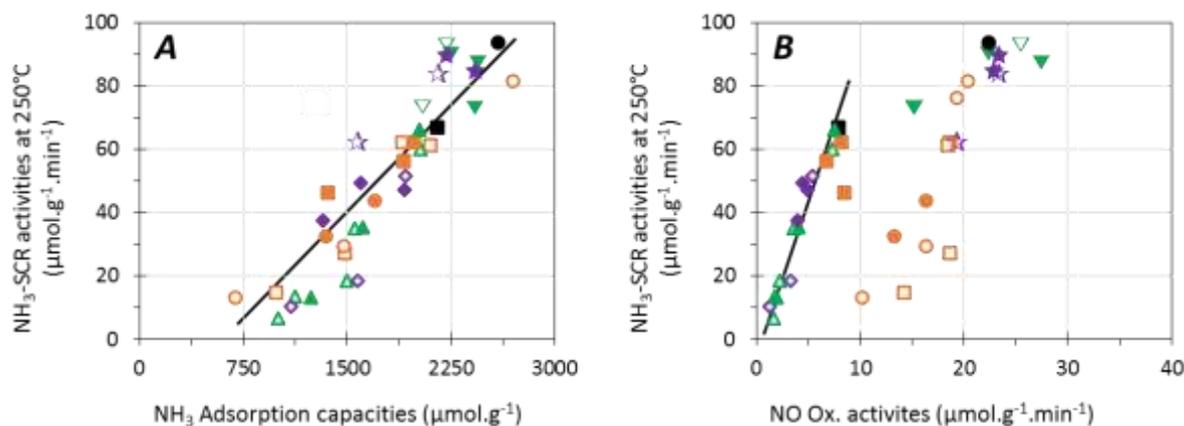


Figure 6. Effect of minerals deactivation mode on NH_3 -SCR performances at 250°C over $\text{Cu}_{(\text{EX})}$ -FER (■, ▲, ◆) and $\text{Cu}_{(\text{EN})}$ -FER (●, ▼, ★). Relationship with (A): NH_3 adsorption capacities at 50°C and (B): NO oxidation activities at 450°C .

Na: —, □ ($830 \mu\text{mol.g}^{-1}$), ■ ($620 \mu\text{mol.g}^{-1}$), ○ ($885 \mu\text{mol.g}^{-1}$) ● ($665 \mu\text{mol.g}^{-1}$);
 P: —, △ ($750 \mu\text{mol.g}^{-1}$), ▲ ($725 \mu\text{mol.g}^{-1}$), ▽ ($915 \mu\text{mol.g}^{-1}$), ▼ ($790 \mu\text{mol.g}^{-1}$);
 Na+P: —, ◇ ($735 \mu\text{mol.g}^{-1}$), ◆ ($895 \mu\text{mol.g}^{-1}$), ☆ ($750 \mu\text{mol.g}^{-1}$), ★ ($860 \mu\text{mol.g}^{-1}$).

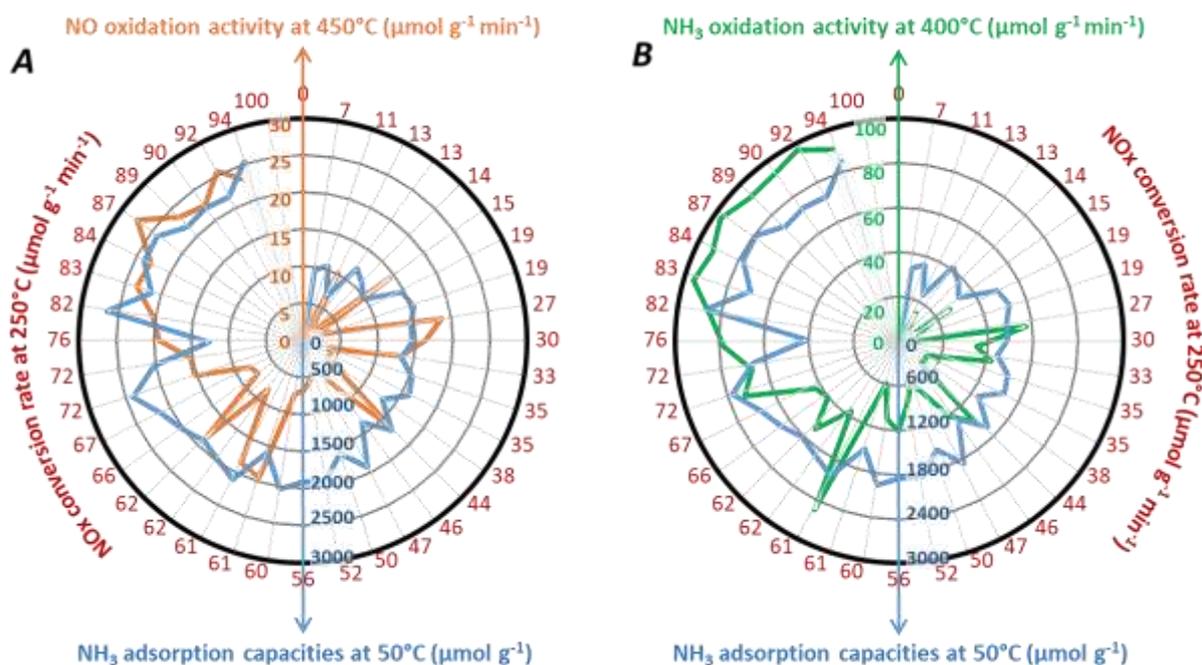


Figure 7. NOx conversion rate at 250°C ($\mu\text{mol g}^{-1} \text{min}^{-1}$, red scale placed out of the circle) in function of both NH_3 adsorption capacities at 50°C ($\mu\text{mol g}^{-1}$, blue line, scale along the radius of the circle) and (A): NO oxidation activity at 450°C ($\mu\text{mol g}^{-1} \text{min}^{-1}$, orange line, scale along the radius of the circle), (B): NH_3 oxidation activity at 400°C ($\mu\text{mol g}^{-1} \text{min}^{-1}$, green line, scale along the radius of the circle).

Finally, Figure 7 highlights that, as expected, the higher NOx conversions (scale placed out of the circle) were achieved when both NH_3 adsorption capacities (blue lines) and redox behavior (illustrated via NO or NH_3 oxidation activities) are preserved when adding minerals. It highlights the necessary presence of both NH_3 adsorption and redox sites to ensure high DeNOx efficiency.

4. Conclusions

This work aimed to highlight the deactivation mechanisms encountered by minerals impurities from Biodiesel (and lubricants) over Cu-FER catalysts dedicated to the NH₃-SCR process. It was evidenced that both the copper loading and the solvent used for depositing minerals (water or ethanol) have significant impact in the deactivation of catalysts. All studied minerals (Na and/or P) led to a poisoning of the ammonia adsorption sites, but with different mechanisms. Sodium gave rise to a back-exchange of Cu²⁺ units (especially when added in water) together with a Brønsted acid sites poisoning. To the opposite, phosphorus led mainly to interactions with copper (especially exchanged Cu²⁺ species), blocking the NH₃ adsorption and inhibiting the associated redox function. Finally, considering two series of catalysts with two copper loadings, two minerals in various concentrations (Na and/or P) and two deposit routes (water and ethanol), this study points out that the DeNO_x efficiency at low temperature (250°C) is mainly correlated with the NH₃ adsorption capacities, but, as expected, the NH₃-SCR performances also involved redox behaviour from copper species. Finally, phosphorus was evidenced to lead to the highest detrimental effect in the Na+P association.

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