1. Introduction

Nitrogen oxides (NOx: NO, NO2) are known to be major pollutants of the atmosphere. Their emission mainly arises from stationary (fossil fuels combustion) and mobile sources (vehicles), contributing to the formation of photochemical smog, acid rains, and ozone depletion. Different technologies have been used to reduce NOx emission [1]. Among them, direct decomposition of NOx into N2 and O2 is ideal as it only requires a simple contact with the surface of a catalyst. However, the formed oxygen atoms may be strongly adsorbed and cause a rapid deactivation of the catalytic material [2,3]. The second type of technology used for mobile sources is NOx Storage/Reduction (NSR) or NOx trap [4]. These approaches, however, are limited due to the hydrocarbon and CO2 penalties caused by cyclic lean-fuel/rich-fuel conditions [5].

The last known technology for NOx emission control is the selective catalytic reduction (SCR), including HCs, CO, and H2-SCR for automotive pollution processes [6,7]. One of the well-established post-combustion technologies of NOx reduction is the selective catalytic reduction by ammonia (NH3-SCR). The process was introduced in the late 1970s, and has become a widely commercialized technology for NOx removal from flue gases from coal-fired power plants and other industrial facilities [8,9]. The standard reaction equation for NH3-SCR, involving only NO, is given by:

$$4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$$ (1)
With an equimolar amount of NO and NO₂, the reaction called fast SCR reaction is much faster, and the reaction equation becomes:

\[ 2\text{NO} + 2\text{NO}_2 + 4\text{NH}_3 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \] (2)

On the other hand, with pure NO₂ the NH₃-SCR reaction is much slower and can be presented by the following equation:

\[ 6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \] (3)

The conventional catalysts are V₂O₅–WO₃(TiO₂) and Cu, Fe-zeolites [10,11]. In the former, V₂O₅ represents active phase, whereas WO₃ and MoO₃ increase the temperature window of the SCR reaction and improve the mechanical strength of the catalysts [12]. However, the main drawback of V₂O₅–WO₃(TiO₂) is a narrow operating temperature window (300–400 °C), sublimation of vanadium species at high temperatures, and high oxidation of SO₂ to SO₃ leading to a decrease of NOx conversion at 400 °C [10]. On the other hand, Cu and Fe zeolites show high activity in a low-temperature window and good hydrothermal resistance [11,13,14]. Both copper ions (Cu²⁺ and/or Cu⁺) and iron ions (Fe³⁺) play an important role of active sites in the reaction of NH₃-SCR. Nevertheless, the application of Cu or Fe zeolites is still challenging as in most cases they are prone to be extensively poisoned by SO₂ [15].

Over the past years, various novel catalysts for NOx reduction were described in the literature. Among them, catalysts zirconia-supported catalysts were found attractive due to the high thermal stability, high low-temperature activity and durability, and enhanced resistance to SO₂ and H₂O [16–21]. Cu/ZrO₂ and Cu/ZrO₂(SO₄²⁻) were found very promising in selective catalytic reduction by n-decane [22–24] or propene [25], and finally in NH₃-SCR [26,27]. Pietrogiacomi et al. [26] prepared the zirconia support by hydrosolysis of zirconium oxychloride with ammonia. The obtained carriers were impregnated with aqueous solutions of CuSO₄ or Cu(NO₃)₂. Some portion of the latter was additionally sulfurized via gas phase (2770 ppm SO₂ and 1%O₂, in He). The authors found that impregnation with CuSO₄ or sulphation via gas-phase yielded nearly identical catalysts. CuSO₄/ZrO₂ were much more selective than the relevant unsulphated CuOx/ZrO₂ to NH₃-SCR. However, sulphated ZrO₂ catalysts were only slightly more active than unsulphated ZrO₂.

Iron modified ZrO₂ has been also studied extensively in other catalytic processes [25,28]. According to Apostolescu et al. [18], tetragonal zirconia was the most effective support for Fe catalyst used in NH₃-SCR when compared to the metal deposited on MgAl₂O₄, SiO₂, or TiO₂. For Fe/ZrO₂ prepared by sol-gel technique, Navio et al. [29] demonstrated that Fe loading equal or higher than 3 wt% allows stabilization of the zirconia tetragonal phase due to the high solubility of Fe³⁺ in the ZrO₂ matrix. By studying NH₃-SCR of NO over Mn–Fe supported catalysts, López-Hermández et al. [30] showed that acidity is necessary to catalyze the reaction, but not sufficient to obtain the most effective material. The authors showed a significant relationship between SCR activity at low temperatures and surface area through the better iron dispersion for the supports with Lewis acid properties (zirconia, alumina and titania). Since iron oxide possesses also Lewis acidity, resulting catalysts are in principle less sensitive to deactivation of the Brønsted acid sites. Considering this point, Kustov et al. [31] studied the effect of potassium on vanadium, copper, and iron oxides supported on sulphated zirconia (monoclinic), where a slight increase in alkali resistance was found compared to the vanadium.

Indovina et al. [32] examined FeOx/sulphated-ZrO₂ and FeOx/ZrO₂ prepared by impregnation of different Fe precursors. The authors have found that iron species were much less reducible in FeOx/sulphated-ZrO₂ than in FeOx/ZrO₂. Their lower reducibility explained why FeOx/sulphated-ZrO₂ samples may achieve higher selectivity for the selective catalytic reduction of NO with NH₃.

Fan et al. [33] investigated sulphated iron-based catalysts prepared by impregnation methods through changing the loading order of Fe₂O₃ and SO₄²⁻ on ZrO₂ carrier. The
activities of sulphated Fe-based catalysts improved significantly compared to the Fe/Zr catalyst, when tested in the temperature range of 250–500 °C. The authors showed that sulfate supplied higher number of acid sites, which could adsorb more NH$_3$ species that can react with gaseous NO + O$_2$. Recently, Liu et al. [34] investigated the selective catalytic reduction of NOx by ammonia over sulphated iron-based catalysts in using different loadings of Fe$^{3+}$ and SO$_4^{2-}$ on zirconia support. Their results indicated that the interaction between Fe$^{3+}$ and SO$_4^{2-}$ can have an effect on the redox ability, acid sites, and adsorption of NOx and NH$_3$. In increasing the content of Fe$^{3+}$, the redox activity of the catalyst and the adsorption of ammonia improved at medium and low temperatures, whereas at higher temperatures, the increase in Fe$^{3+}$ species led to the decrease in the conversion of NOx due to the enhancement of the NH$_3$ oxidation.

In this work, a novel one-pot synthesis was proposed for the preparation of zirconia-supported Cu and Fe catalysts. The catalysts were tested in selective catalytic reduction of NO with NH$_3$ in the presence and absence of water vapor. Physicochemical properties of catalysts were examined by N$_2$ physisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption of NH$_3$ (NH$_3$-TPD). The characterized materials were tested in NH$_3$-SCR (with or without H$_2$O). The activity changes during SO$_2$ feeding (in situ sulphation) were studied at 450 °C. Additionally, the activity towards NH$_3$-SCO (with or without H$_2$O) was also investigated. The importance of support morphology and phase was highlighted.

2. Results and Discussion
2.1. Catalysts Characterization

2.1.1. Structural and Textural Properties of ZrO$_2$ Supported Catalysts

The structure of the studied samples was determined by XRD, as presented in Figure 1 and Table 1. The reflections at 2θ ca. 30.1, 35.2, 60.4, 62.9, 74.8, 81.9, and 85.6° were attributed to the tetragonal ZrO$_2$ (t-ZrO$_2$ indication) [35–38]. In all studied catalysts, only ZrO$_2$ diffraction peaks were observed. The absence of diffraction peaks attributed to iron or copper species suggests their good dispersion or insertion into the skeleton of ZrO$_2$ [39,40]. The latter can be supported by a small shift to higher angles observed for Cu-Zr (30.376°) and Fe-Zr (30.349°) catalysts, compared to the ZrO$_2$ support (30.192°). Moreover, the d-spacing decreased from 2.9576 Å (ZrO$_2$) to 2.9402 Å (Cu-Zr) or 2.9427 Å (Fe-Zr). Generally, the ionic radii are influenced by coordination number and valence. Shannon [41] found a correlation between the coordination number and the ionic radius. The ionic radius of Zr$^{4+}$ in ZrO$_2$ (0.86 Å) is higher than that of Fe$^{3+}$ in Fe$_2$O$_3$ (0.69 Å) or Cu$^{2+}$ in CuO (0.60 Å) [42]. Probably some Zr$^{4+}$ ions were substituted by Cu$^{2+}$ or Fe$^{3+}$ to form CuO–ZrO$_2$ or Fe$_2$O$_3$–ZrO$_2$ solid solutions in the lattice sites. This could be a consequence of the shrink of the lattice parameter [43], which is in line with the XRD results. The shift towards higher Bragg angles was more pronounced for the Cu-Zr catalyst when compared to the Fe-Zr. The crystallite size of ZrO$_2$ was calculated by the Williamson and Hall method [44,45]. One can note that the crystallite size of ZrO$_2$ decreased, from 13.7 nm to 11.3 and 8.8 nm for Cu-Zr and Fe-Zr catalysts, respectively.

Table 1. Structural and textural properties of ZrO$_2$, Cu-Zr and Fe-Zr calcined catalyst.

| Sample  | Bragg Angles/° | d-Spacing/Å | Crystallite Size of ZrO$_2$/nm * | Specific Surface Area/m$^2$/g | Volume of Mesopores/cm$^3$/g | Average Pore Size/nm |
|---------|----------------|-------------|----------------------------------|-------------------------------|-----------------------------|----------------------|
| ZrO$_2$ | 30.192         | 2.9576      | 13.7                             | 81                           | 0.12                        | 5.0                  |
| Cu-Zr  | 30.376         | 2.9402      | 11.3                             | 128                          | 0.06                        | 3.3                  |
| Fe-Zr  | 30.349         | 2.9427      | 8.8                              | 139                          | 0.09                        | 3.5                  |

* calculated by the Williamson and Hall method.
N\textsubscript{2} physisorption was employed to determine the textural properties of the synthesized catalysts. The analysis was performed for the calcined materials. The samples were found mesoporous with the Barrett–Joyner–Halenda (BJH) mesopore volume ranged from 0.12 to 0.06 cm\textsuperscript{3}/g, average pore size of 3.3–5 nm, and the surface area from 81 to 139 m\textsuperscript{2}/g. These textural parameters decreased and increased with metal modification, meaning that presence of Cu and Fe led to the enhancement of specific surface area with formation of smaller mesopores with less volume.

### 2.1.2. Acidic Properties of ZrO\textsubscript{2} Supported Catalysts

The total acidity of the studied catalysts was evaluated by NH\textsubscript{3} temperature programmed desorption (NH\textsubscript{3}-TPD). Figure 2 presents the desorption curves for the studied catalysts. All samples showed a wide NH\textsubscript{3} desorption profiles between 100 and 550 °C, arising from weak (ca. 200 °C), medium (ca. 300–400 °C), and strong (T > 400 °C) acid sites [46,47]. The modification of ZrO\textsubscript{2} with copper and iron influenced the acidic properties by offering new weak and medium acid sites. Accordingly, the total acidity increased for Cu- and Fe-containing samples in contrast to the unmodified support. These observations are in line with the previously published reports on Cu/ZrO\textsubscript{2} and Fe/ZrO\textsubscript{2} materials. Pietrogiacomi et al. [26] reported higher total amount of desorbed ammonia for ZCu\textsubscript{2.5} sample than for ZrO\textsubscript{2} (0.5 vs. 0.2 nm\textsuperscript{-1}). Ismail et al. [28] observed the formation of new acidic sites on ZrO\textsubscript{2} surface due to the Fe addition (1.25, 2.5, 5, and 10 wt%). The authors, however, reported increasing intensities of the desorption profiles in the wide-ranging temperature window (from 200 to 500 °C). In the other study of these authors [46], the modification with iron led to the formation of new strong acid sites only (T > 400 °C) in comparison to the acid sites recorded for pure zirconia.
2.1.3. Surface Properties of ZrO$_2$ Supported Catalysts

The surface composition of the calcined samples was analyzed by XPS. Figure 3A–D present the obtained spectra for O 1s, Zr 3d, Fe 2p, and Cu 2p. The percentage values of the elements are listed in Table 2. ZrO$_2$ support and Cu-Zr catalyst showed similar content of Zr species on the surface, whereas the percentage of Zr species decreased from 66.8 wt% (ZrO$_2$ support) to 64.4 wt% for Fe-Zr. The content of surface Cu species is about 2.2 wt%, which is lower than the assumed content (3 wt%). We could assume that part of Cu species could exist in the framework of ZrO$_2$ or in the bulk. On the contrary, the percentage of Fe species is 3.2 wt%, indicating that more Fe species forms on the surface than interior of ZrO$_2$ and/or catalyst. Thus, the higher content of surface Fe species may contribute to increased activity in NH$_3$-SCR of NO into N$_2$. Besides, the O 1s curve was resolved into three peaks, which attributed to lattice oxygen (O$^{2-}$), carbonate species (CO$_3^{2-}$) and hydroxyl species (OH$^-$) [43,48]. The Zr 3d was deconvoluted into Zr$^{3+}$ and Zr$^{4+}$ species as reported elsewhere [49]. The content of each deconvoluted peak is listed in Table 2. The peak of O 1s on Fe-Zr catalyst shifts to lower binding energy in contrast to ZrO$_2$ support and Cu-Zr catalyst. There are two possible reasons of this observation: (i) Higher content of lattice oxygen species on Fe-Zr catalyst, or (ii) less interaction between O$^{2-}$ species and Fe due to an exposure of Fe$_2$O$_3$ and/or FeO species on the surface. Similar results were reported in literature [48,50]. Moreover, in our materials the content of Zr$^{4+}$ species decreased from 62.5% to 57.2% and 4.7% by introduction of Cu or Fe, respectively, indicating that the presence of Cu or Fe results in higher content of Zr$^{3+}$ species on the catalysts. This effect was more pronounced for Fe-Zr catalyst showing 95.3% of Zr$^{3+}$ species. It additionally implies that Cu or Fe could promote the formation of Zr species with lower valence value. Furthermore, according to Zhao et al. [48], the curve of Fe 2p and Cu 2p are resolved to Fe$^{2+}$ and Fe$^{3+}$ species, and Cu$^+$ and Cu$^{2+}$ species, respectively. In our study, the ratio of Fe$^{2+}$/Fe$^{3+}$ is 1.33, and the Cu$^+$/Cu$^{2+}$ is 3.84. This indicates that more Fe species are present in higher valence state on Fe-Zr catalyst, corresponding to higher content of Zr$^{3+}$ species. Moreover, recently on functionalized iron hydroxyapatite catalysts it was clearly shown that the presence of Fe$^{3+}$ highly dispersed on the surface led to a high selectivity to N$_2$, a satisfactory activity in a wide temperature window [41] and improved catalytic activity [34].

![Figure 3. X-ray photoelectron spectroscopy (XPS) profiles of ZrO$_2$ support, and Cu-Zr and Fe-Zr calcined catalysts. (A) The O 1s, (B) Zr 3d, (C) Fe 2p, and (D) Cu 2p. All the data are referenced using the C 1s peak at 284.6 eV.](image-url)
Table 2. Elemental composition of ZrO$_2$, Cu-Zr calcined catalyst and Fe-Zr calcined catalyst from XPS analysis.

| Sample  | Zr (wt%) | O (wt%) | Cu (wt%) | Fe (wt%) | O Species (%) | Zr Species (%) |
|---------|----------|---------|----------|----------|---------------|----------------|
|         |          |         |          |          | O$^{2-}$ CO$_3^{2-}$ OH$^-$ Zr$^{3+}$ Zr$^{4+}$ |
| ZrO$_2$ | 66.8     | 33.2    | -        | -        | 70.6          | 18.1 11.3 37.5 62.5 |
| Cu-Zr   | 66.6     | 31.2    | 2.2      | -        | 64.9          | 24.7 10.4 42.8 57.2 |
| Fe-Zr   | 64.4     | 32.4    |          | 3.2      | 75.8          | 19.9 4.3 95.3 4.7 |

2.2. Catalytic Results

2.2.1. NH$_3$-SCR of NO in the Absence and Presence of Water

Figure 4 shows the catalytic performance of Cu-Zr and Fe-Zr catalysts and the support in NH$_3$-SCR of NO as function of temperature. The tests were performed in the presence (3.5 vol%) and in absence of water vapor.

Figure 4A,B presents catalytic results of Cu-Zr catalyst. The catalyst revealed maximum NO conversion of 85% in the absence, and 40% in the presence of H$_2$O at 450 °C. In the former conditions, the obtained conversions were two times higher than those observed by Pietrogiacomi et al. [27] (700 ppm NO, 700 ppm NH$_3$, 36,000 ppm O$_2$, balance He, GHSV = 10$^5$ h$^{-1}$) on impregnated Cu/ZrO$_2$ catalysts, which clearly shows that the newly used synthesis would be a good alternative for such type of catalysts. Above 450 °C, the NO conversion rapidly decreased, suggesting an excess production of nitric oxide which could originate from a significant contribution of NH$_3$ oxidation reaction. This agrees with NH$_3$ conversion which remained stable, or it increased constantly above 450 °C. The impact of NH$_3$ oxidation will be studied by us further in this section. The production of N$_2$O was minor, showing only max 20 ppm when sample was tested without water vapor, and 10 ppm when test was performed in hydrothermal conditions.

Figure 4C,D shows the NH$_3$-SCR over Fe-Zr catalyst. The absence of water vapor led to a maximum of 55% of NO conversion at 500 °C. The N$_2$O production was measured at ca. 28 ppm at this temperature. The presence of H$_2$O resulted in a constant increase of NO and NH$_3$ conversions, starting from 300 to 550 °C. At the latter temperature, the NO and NH$_3$ conversions are 35 and 53%, respectively. The decrease in activity, in the presence of H$_2$O, is believed to be mainly due to competing adsorption between water and ammonia on the acid sites [51]. It should be mentioned, additionally, that in the presence of H$_2$O, the Fe-Zr catalyst did not produce N$_2$O over the whole range of studied temperatures.

From Figure 4E, one can note that the support is inactive during NH$_3$-SCR reaction as only conversion of NH$_3$ was observed accompanied by the production of N$_2$O and NO. Negative conversion values were recorded for the latter (not shown in the Figure 4E). These observations suggest that selective oxidation of ammonia is a dominant reaction for the support. ZrO$_2$ support tested in the hydrothermal conditions led to the complete inhibition of any significant catalytic reaction below 500 °C. However, some NH$_3$ conversion, not exceeding 10% at 550 °C, occurred above 500 °C.

Furthermore, N$_2$O is the only by-product detected during the NH$_3$-SCR reaction process, which determines selectivity to N$_2$ presented in Figure 5. As shown in Figure 4B,D, the presence of water leads to a decrease in NO conversion but improves, despite this, the removal efficiency of NO by enhancing the denitrification selectivity to N$_2$. In the whole SCR process, the N$_2$O concentration on the samples in presence of water is very limited for Cu-Zr catalyst and negligible for Fe-Zr catalyst. Therefore, one can conclude that Fe-Zr could be a promising catalyst for NH$_3$-SCR process after its optimization. This higher catalytic performance could be linked with the increase of electron transfer on Fe-Zr catalysts showed by XPS when compared to the Cu-Zr system. In order to confirm these promising results on Fe-Zr catalysts, selective catalytic oxidation of ammonia (NH$_3$-SCO) was performed.
Figure 4. NO and NH$_3$ conversion profiles and N$_2$O production as a function of temperature in NH$_3$-SCR over Cu-Zr catalyst (A) in absence of water, (B) in presence of water; Fe-Zr catalyst (C) in absence of water, (D) in presence of water; and ZrO$_2$ support (E) in absence of water, (F) in presence of water. The experimental conditions: [NO] = 1000 ppm, [NH$_3$] = 1000 ppm, [H$_2$O] = 3.5 vol% when used, [O$_2$] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min.

2.2.2. NH$_3$-SCO in the Absence and Presence of Water Vapor

The selective catalytic NH$_3$ oxidation (SCO) ability of a catalyst determines the efficiency of NH$_3$ utilization in the SCR reaction. Figure 5A–F depicts the NH$_3$ oxidation performance of the studied materials in the absence and presence of H$_2$O. Cu-Zr catalyst shows high ammonia oxidation activity starting from 325 °C, reaching constant value of 87% at 450–550 °C (Figure 6A). The oxidation of NH$_3$ led to N$_2$O and NO by-products formation with maximum values of 38 ppm and 250 ppm, respectively. In the hydrothermal conditions, Cu-Zr catalyst was less active in NH$_3$-SCO, compared to the conditions without water vapor (Figure 6B). NH$_3$ conversion constantly increased over the studied temperatures with maximum of 68% at 550 °C. Iron promoted ZrO$_2$ was also active in NH$_3$-SCO with 89% of NH$_3$ at 550 °C complemented by the production of N$_2$, N$_2$O, and
NO (Supplementary Materials Figure S1; Figure 6C). Ammonia oxidation in the presence of H₂O led to the decreased activity with only 28% of NH₃ converted (Figure 6D) and low production of side products (i.e., N₂O and NO). Figure 5E presents zirconia support which was active in NH₃-SCO, resulting mostly in the production of NO (400 ppm) at the highest analyzed temperature. Small amounts of N₂O were also observed (10 ppm). The presence of water in ammonia oxidation inhibited reaction, and only 5% of NH₃ conversion was observed (Figure 6F). When compared to NH₃-SCR results, one can conclude that NH₃ oxidation is predominant at high temperature (T > 400 °C) over Cu-Zr and Fe-Zr catalysts. In contrast, during the hydrothermal conditions the adsorbed NH₃ is more difficult to be oxidized on the surface of both Cu-Zr and Fe-Zr catalysts. Therefore, the adsorbed NH₃ species can effectively react with NO, giving a high NO removal efficiency.

Figure 5. N₂ selectivity as a function of temperature measured during NH₃-SCR over Cu-Zr catalyst (A) in absence of water, (B) in presence of water; Fe-Zr catalyst (C) in absence of water, (D) in presence of water; and ZrO₂ support (E) in absence of water. The experimental conditions: [NO] = 1000 ppm, [NH₃] = 1000 ppm, [H₂O] = 3.5 vol% when used, [O₂] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min.
formation with maximum values of 38 ppm and 250 ppm, respectively. In the hydrothermal conditions, Cu-Zr catalyst was less active in NH\textsubscript{3}-SCO, compared to the conditions without water vapor (Figure 6B). NH\textsubscript{3} conversion constantly increased over the studied temperatures with maximum of 68 % at 550 °C. Iron promoted ZrO\textsubscript{2} was also active in NH\textsubscript{3}-SCO with 89% of NH\textsubscript{3} at 550 °C complemented by the production of N\textsubscript{2}, N\textsubscript{2}O, and NO (Supplementary Materials Figure S1; Figure 6C). Ammonia oxidation in the presence of H\textsubscript{2}O led to the decreased activity with only 28% of NH\textsubscript{3} converted (Figure 6D) and low production of side products (i.e., N\textsubscript{2}O and NO). Figure 5E presents zirconia support which was active in NH\textsubscript{3}-SCO, resulting mostly in the production of NO (400 ppm) at the highest analyzed temperature. Small amounts of N\textsubscript{2}O were also observed (10 ppm). The presence of water in ammonia oxidation inhibited reaction, and only 5% of NH\textsubscript{3} conversion was observed (Figure 6F). When compared to NH\textsubscript{3}-SCR results, one can conclude that NH\textsubscript{3} oxidation is predominant at high temperature (T > 400 °C) over Cu-Zr and Fe-Zr catalysts. In contrast, during the hydrothermal conditions the adsorbed NH\textsubscript{3} is more difficult to be oxidized on the surface of both Cu-Zr and Fe-Zr catalysts. Therefore, the adsorbed NH\textsubscript{3} species can effectively react with NO, giving a high NO removal efficiency.

Figure 6. NH\textsubscript{3} conversion profile and N\textsubscript{2}O and NO production profiles as a function of temperature in NH\textsubscript{3}-SCO over Cu-Zr catalyst (A) in absence of water, (B) in presence of water; Fe-Zr catalyst (C) in absence of water, (D) in presence of water; and ZrO\textsubscript{2} support (E) in absence of water, (F) in presence of water. The experimental conditions: [NH\textsubscript{3}] = 1000 ppm, [H\textsubscript{2}O] = 3.5 vol% when used, [O\textsubscript{2}] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min.

2.2.3. SO\textsubscript{2} Activation of Cu-Zr and Fe-Zr Catalysts and their Catalytic Behavior in NH\textsubscript{3}-SCR of NO in the Absence and Presence of Water

SO\textsubscript{2} Activation of Cu-Zr Catalyst in NH\textsubscript{3}-SCR of NO in the Absence of Water Vapor

The SO\textsubscript{2} activation study in NH\textsubscript{3}-SCR of NO in the absence of H\textsubscript{2}O was carried out on Cu-Zr catalyst at 450 °C. Prior to this examination, the reaction of NH\textsubscript{3}-SCR of NO was performed as a function of temperature, which agrees well with previously obtained results (Figure 4A). Subsequently, the sample was allowed to be stabilized for 60 min before the addition of SO\textsubscript{2} for another 60 min, and then after removing the SO\textsubscript{2} for next 90 min. When the SO\textsubscript{2} was added, a clear increase in both NH\textsubscript{3} and NO conversions was observed converting ca. 100% (Figure 7). Once the SO\textsubscript{2} was removed from the feed, a rapid decrease was registered for both, steadying the values to be initially slightly
higher to the ones registered before SO₂ feeding. Over the stabilization in the mixture free of SO₂, the conversions gradually increased from 83.7 to 90.5% and 83.9 to 85.7% for NO and NH₃ conversions, respectively. The in-situ sulphation promoted the activity of Cu-Zr catalyst in NH₃-SCR of NO. Similar observations were made in the studies of Pietrogiaconi et al. [26,27] in which it has been reported that sulphonation of Cu-containing ZrO₂ catalysts positively affects catalytic performance NH₃-SCR of NO due to the enhanced acidic properties of sulfated supports.

**Figure 7.** Effect of SO₂ addition during NH₃-SCR over Cu-Zr catalyst in the absence of water. The experimental conditions: [NO] = [NH₃] = 1000 ppm, [SO₂] = 100 ppm when used, [O₂] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min.

**SO₂ Activation of Fe-Zr in NH₃-SCR of NO in the Presence of Water**

Recently, Fan et al. [33] showed that Fe/ZrO₂ sulphated catalysts were almost two times more active than non-sulphated Fe/ZrO₂ for NH₃-SCR of NO. Thus, in order to verify the activation of the catalysts in the presence of SO₂, the experiment was performed in hydrothermal conditions on Fe-Zr catalyst and on the support. The results are presented in Figure 8. In the presence of water, on Fe-Zr catalyst, another trend was observed (Figure 8A). During the first hour of stabilization, the conversions of NO and NH₃ were 29% and 30%, respectively. After SO₂ addition, a slight decrease of NO and NH₃ was observed, probably due to the sulphation of the Fe-Zr and inhibition of the active sites. However, after the first minutes in the presence of SO₂, both conversions of NO and NH₃ increased. It is worth to note that the consumption of NH₃ reached 47%, whereas only 30% of NO was converted. This latter result could not be linked with any NH₃ oxidation activity, despite the high temperature of 450 °C. No side products were recorded by MS that could suggest SCO-NH₃ occurrence. Moreover, on the ZrO₂ support a similar NH₃ consumption was registered (Figure 8B). One can assume that ammonia consumption is mainly due to its adsorption enhanced by a formation of new acidic sites in the presence of SO₂ [33] which can act as a reservoir. Similar observations were made on other type of catalysts such as V₂O₅-WO₃/TiO₂ [52–54].
after the first minutes in the presence of SO2, both conversions of NO and NH3 increased. It is worth to note that the consumption of NH3 reached 47%, whereas only 30% of NO was converted. This latter result could not be linked with any NH3 oxidation activity, despite the high temperature of 450 °C. No side products were recorded by MS that could suggest SCO-NH3 occurrence. Moreover, on the ZrO2 support a similar NH3 consumption was registered (Figure 8B). One can assume that ammonia consumption is mainly due to its adsorption enhanced by a formation of new acidic sites in the presence of SO2 [33] which can act as a reservoir. Similar observations were made on other type of catalysts such as V2O5-WO3/TiO2 [52–54].

Figure 8. Effect of SO2 addition during NH3-SCR over Fe-Zr and ZrO2 catalysts in the hydrothermal conditions. (A) Fe-Zr catalyst, (B) ZrO2 support. The experimental conditions: [NO] = [NH3] = 1000 ppm, [SO2] = 100 ppm when used, [H2O] = 3.5 vol%, [O2] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min.

3. Materials and Methods

3.1. Catalysts Synthesis

Pluronic® P123 amphiphilic block copolymer (Aldrich, Saint-Quentin Fallavier, France), urea (Sigma-Aldrich, Saint-Quentin Fallavier, France), zirconium (IV) oxynitrate hydrate (Aldrich, Saint-Quentin Fallavier, France) and copper (II) nitrate hemi(pentahydrate) (Alfa-Aesar ThermoFisher Lancashire, UK) were dissolved in 375 mL of distilled water. The suspension was heated from room temperature to 95 °C within 30 min under vigorous stirring. After stirring at 95 °C for 48 h, the obtained colloidal solution was aged at 100 °C for 24 h. Then, the material was filtrated, washed with deionized water, and dried at room temperature. Finally, the solid material was calcined at 600 °C for 5 h with a heating rate of 1 °C/min. The obtained material was denoted as Cu-Zr. The iron-containing catalyst was prepared using the same method with the iron nitrate nonahydrate. The dosage of different chemical reagents for synthesis of each catalyst is listed in Table 3 and corresponds to 3 wt% loading of Fe or Cu.
Table 3. The chemical dosage used during for the synthesis of Cu-Zr and Fe-Zr catalysts.

| Sample | P123/g | Urea/g | Zr(NO$_3$)$_2$·2H$_2$O/g | Cu(NO$_2$)$_2$·2.5H$_2$O/g | Fe(NO$_3$)$_3$·9H$_2$O/g |
|--------|--------|--------|--------------------------|-----------------------------|-------------------------|
| Cu-Zr  | 7.84   | 7.50   | 5.03                     | 0.14                        | -                       |
| Fe-Zr  | 7.84   | 7.50   | 5.03                     | -                           | 0.24                    |

3.2. Characterization Techniques

The structural properties of samples were obtained using the X-ray diffraction (XRD) method on a DX-1000 CSC diffractometer (Malvern PANalytical, Shanghai, China), equipped with the Cu Kα radiation at 40 kV and 25 mA. The data was recorded in the range 5° < 2θ < 90° with 0.3 s/step scan speed and 0.03° step size.

Textural properties of the samples were determined by N$_2$ physisorption at −196 °C using a Micromeritics (Aachen, Germany) ASAP 2020 instrument. The samples were previously treated in vacuum for 2 h at 200 °C. The data on the specific surface area, mesoporous pore volume and average pore diameter were calculated by the equations of Brunauer—Emmett—Teller (BET), Barrett—Joyner—Halenda (BJH) desorption average pore width (4V/A), and desorption of volume of pores Barrett—Joyner—Halenda (BJH), respectively.

The acidity of samples was examined by NH$_3$-TPD using an AUTOCHEM 2910 (Micromeritics, Aachen, Germany). The solid was pre-treated at 550 °C (ramp 10 °C/min) during 2 h, under air flow (30 mL/min). Then, it was exposed to 5 vol% NH$_3$ in He (30 mL/min) for 30 min, and subsequently with He (30 mL/min) for 30 min to remove the physisorbed ammonia. Finally, the NH$_3$ desorption was performed in helium flow (30 mL/min) from 100 to 550 °C (the heating rate was 5 °C/min).

The elemental analysis of sample surface was investigated by X-ray photoelectron spectroscopy (XPS) on a KRATOS spectrometer with an AXIS Ultra DLD (Manchester, UK). All the data were calibrated using the C 1s peak at 284.6 eV, as described elsewhere [43].

3.3. Catalytic Tests

The selective catalytic reduction of NO with NH$_3$ (NH$_3$-SCR) was studied in a U-shape glass reactor operating at atmospheric pressure. Prior to the catalytic tests, a catalyst (75 mg) was activated in situ at 550 °C for 30 min in a flow of O$_2$/He and then cooled to 180 °C. The following compositions of the gas mixture for NH$_3$-SCR of NO: [NO] = 1000 ppm, [NH$_3$] = 1000 ppm, [H$_2$O] = 3.5 vol%, [O$_2$] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min. The weight hourly space velocity (WHSV) was about 80,000 mL/g h. The SCR was carried out on programmed temperature from 180 to 550 °C with the heating rate 5 °C/min. The reactants and products were analyzed by a quadruple mass spectrometer (Pfeiffer Omnistar, Saclay, France) equipped with Channeltron and Faraday detectors recording the following masses: NO (m/z = 30), NH$_3$ (m/z = 15, 17, 18), O$_2$ (m/z= 16, 32), H$_2$O (m/z = 17, 18), N$_2$ (m/z = 14, 28), N$_2$O (m/z = 28, 30, 44), and He (m/z = 4).

The selective catalytic oxidation of NH$_3$ (NH$_3$-SCO) was studied in the U-shape glass reactor operating in similar conditions as described above, using the following gas mixture for NH$_3$-SCO: [NH$_3$] = 1000 ppm, [H$_2$O] = 3.5 vol%, [O$_2$] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min. Similarly, the reactants and products were analyzed by a quadruple mass spectrometer (Pfeiffer Omnistar, Saclay, France) equipped with Channeltron and Faraday detectors recording the following masses: NH$_3$ (m/z = 15, 17, 18), O$_2$ (m/z= 16, 32), H$_2$O (m/z = 17, 18), N$_2$ (m/z = 14, 28), N$_2$O (m/z = 28, 30, 44), and He (m/z = 4).

4. Conclusions

A novel synthesis was proposed for the preparation of zirconia-supported Cu and Fe catalysts. The synthesized catalysts showed promising results in NH$_3$-SCR of NO in both the presence and absence of water vapor. The studied materials presented NO reduction with NH$_3$ which mainly led to N$_2$ but side reactions resulting in N$_2$O and NO$_2$ formation.
were also present. Under hydrothermal conditions NO conversion was lower (<50%) and inferior N₂O production (ca. 10 ppm) was measured for Cu-Zr and Fe-Zr catalysts, compared to the dry reaction. Furthermore, the Fe-Zr catalyst was highly inactive in NH₃ oxidation during NH₂-SCR of NO. Regardless of H₂O presence or absence, the Cu and Fe promoted catalysts showed the enhanced resistance in the presence of SO₂. Feeding SO₂ resulted in an enhanced catalytic performance, suggesting that sulfur dioxide may positively affect the acidity of the ZrO₂-supported samples. A thorough study is underway to optimize the sulphation of Cu-Zr and Fe-Zr catalysts, coupling FTIR-in situ studies in the presence and absence of SO₂, for a better understanding of surface, acid-base properties and catalytic behavior.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/1/55/s1, Figure S1: N₂ selectivity as a function of temperature measured during NH₂-SCO over Cu-Zr catalyst (A) in absence of water, (B) in presence of water; Fe-Zr catalyst (C) in absence of water, (D) in presence of water; and ZrO₂ support (E) in absence of water, (F) in presence of water. The experimental conditions: [NH₃] = 1000 ppm, [H₂O] = 3.5 vol% when used, [O₂] = 2.5 vol% diluted in helium; total flowrate of 100 ml/min.

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References

1. Vascellari, M. NOx Emission and Mitigation Technologies. In Handbook of Clean Energy Systems; John Wiley & Sons: Hoboken, NJ, USA, 2015; pp. 1–23, ISBN 9781118991978.

2. Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.I.; Kagawa, S. Copper(II) Ion-exchanged ZSM-5 zeolites as highly active catalysts for direct and continuous decomposition of nitrogen monoxide. J. Chem. Soc. Ser. Chem. Commun. 1986, 1272–1273. [CrossRef]

3. Ishihara, T.; Ando, M.; Sada, K.; Takiishi, K.; Yamada, K.; Nishiguchi, H.; Takita, Y. Direct decomposition of NO into N₂ over La(Ba)Mn(In)O₃ perovskite oxide. J. Catal. 2003, 220, 104–114. [CrossRef]

4. Liu, G.; Gao, P.X. A review of NOx storage/reduction catalysts: Mechanism, materials and degradation studies. Catal. Sci. Technol. 2011, 1, 552–568. [CrossRef]

5. Mrad, R.; Aissat, A.; Cousin, R.; Courcot, D.; Siffert, S. Catalysts for NOx selective catalytic reduction by hydrocarbons (HC-SCR). Appl. Catal. A Gen. 2015, 504, 542–548. [CrossRef]

6. Seo, C.K.; Kim, H.; Choi, B.; Lim, M.T. The Optimal Volume of a Combined System of LNT and SCR Catalysts. J. Ind. Eng. Chem. 2011, 17, 382–385. [CrossRef]

7. Abid, R.; Delahay, G. Selective catalytic reduction of NO by NH₃ on cerium modified faujasite zeolite prepared from aluminum scraps and industrial metasilicate. J. Rare Earths 2020, 38, 250–256. [CrossRef]

8. Kieffer, C.; Lavy, J.; Jeudy, E.; Bats, N.; Delahay, G. Characterisation of a commercial automotive NH₃-SCR copper-zeolite catalyst. Top. Catal. 2013, 56, 40–44. [CrossRef]
12. Afraoui, J.; Ghorbel, A.; Petitto, C.; Delahay, G. A new V₂O₅-MoO₃-TiO₂-SO₄²⁻ nanostructured aerogel catalyst for diesel DeNOx technology. *New J. Chem.* 2020, *44*, 16119–16134. [CrossRef]

13. Leistner, K.; Mihai, O.; Wijayanti, K.; Kumar, A.; Kamasamudram, K.; Currier, N.W.; Yezerets, A.; Olsson, L. Comparison of Cu/BEA, Cu/SSZ-13 and Cu/SAPO-34 for ammonia-SCR reactions. *Catal. Today* 2015, *258*, 49–55. [CrossRef]

14. Jabłońska, M.; Delahay, G.; Kruczała, K.; Blachowski, A.; Tarach, K.A.; Brylewksa, K.; Petitto, C.; Góra-Marek, K. Standard and fast selective catalytic reduction of NO with NH₃ on zeolites Fe-BEA. *J. Phys. Chem. C* 2016, *120*, 16831–16842. [CrossRef]

15. Zhang, L.; Wang, D.; Liu, Y.; Kamasamudram, K.; Li, J.; Epling, W. SO₂ poisoning impact on the NH₃-SCR reaction over a commercial Cu-SAPO-34 SCR catalyst. *Appl. Catal. B Environ.* 2014, *156–157*, 371–377. [CrossRef]

16. Li, Y.; Cheng, H.; Li, D.; Qin, Y.; Xie, Y.; Wang, S. WO₃/CeO₂-ZrO₂: A promising catalyst for selective catalytic reduction (SCR) of NOx with NH₃ in diesel exhaust. *Chem. Commun.* 2008, *1470–1472*. [CrossRef]

17. Djerad, S.; Geiger, B.; Schott, F.J.P.; Kureti, S. Synthesis of nano-sized ZrO₂ and its use as catalyst support in SCR. *Catal. Commun.* 2009, *10*, 1103–1106. [CrossRef]

18. Apostolescu, N.; Geiger, B.; Hizbullah, K.; Jan, M.T.; Kureti, S.; Reichert, D.; Schott, F.; Weisweiler, W. Selective catalytic reduction of nitrogen oxides by ammonia on iron oxide catalysts. *Appl. Catal. B Environ.* 2006, *62*, 104–114. [CrossRef]

19. Shen, B.; Zhang, X.; Ma, H.; Yao, Y.; Liu, T. A comparative study of Mn/CeO₂, Mn/ZrO₂ and Mn/Ce-ZrO₂ for low temperature selective catalytic reduction of NO with NH₃ in the presence of SO₂ and H₂O. *J. Environ. Sci.* 2013, *25*, 791–800. [CrossRef]

20. Peng, B.; Rappé, K.G.; Cui, Y.; Gao, F.; Szanyi, J.; Olszta, M.J.; Walter, E.D.; Wang, Y.; Holladay, J.D.; Goffe, R.A. Enhancement of high-temperature selectivity on Cu-SSZ-13 towards NH₃-SCR reaction from highly dispersed ZrO₂. *Catal. Today* 2020, *263*. [CrossRef]

21. Verdier, S.; Rohart, E.; Bradshaw, H.; Harris, D.; Bichon, P.; Delahay, G. Acidic Zirconia Materials for Durable NH₃-SCR Catalysts. *SAE Tech. Pap.* 2008, *1*, 1022.

22. Delahay, G.; Ensueque, E.; Coq, B.; Figuéras, F. Selective catalytic reduction of nitric oxide by N-decane on Cu/sulfated-zirconia catalysts in oxygen rich atmosphere: Effect of sulfur and copper contents. *J. Catal.* 1998, *175*, 7–15. [CrossRef]

23. Delahay, G.; Coq, B.; Ensueque, E.; Figuéras, F. Catalytic behaviour of Cu/ZrO₂ and Cu/ZrO₂(SO₄²⁻) in the reduction of nitric oxide by decane in oxygen-rich rich atmosphere. *Catal. Lett.* 1996, *39*, 105–109. [CrossRef]

24. Figuéras, F.; Coq, B.; Ensueque, E.; Tachen, D.; Delahay, G. Catalytic properties of Cu on sulphated zirconias for DeNOx in excess of oxygen using n-decane as reductant. *Appl. Catal. B Environ.* 1998, *42*, 117–125. [CrossRef]

25. Pasel, J.; Speer, V.; Albrecht, C.; Richter, F.; Papp, H. Metal doped sulfated ZrO₂ as catalyst for the selective catalytic reduction (SCR) of NO with propane. *Appl. Catal. B Environ.* 2000, *25*, 105–113. [CrossRef]

26. Pietrogiacomi, D.; Sannino, D.; Maglione, A.; Ciambielli, P.; Tuti, S.; Indovina, V. The catalytic activity of CuSO₄/ZrO₂ for the selective catalytic reduction of NOx with NH₃ in the presence of excess O₂. *Appl. Catal. B Environ.* 2002, *36*, 217–230. [CrossRef]

27. Pietrogiacomi, D.; Maglione, A.; Sannino, D.; Campa, M.C.; Ciambielli, P.; Indovina, V. In situ sulfated CuOₓ/ZrO₂ and CuOₓ/ZrO₂ sulphotated-ZrO₂ as catalysts for the reduction of NOx with NH₃ in the presence of excess O₂. *Appl. Catal. B Environ.* 2005, *60*, 83–92. [CrossRef]

28. Ismail, R.; Afraoui, J.; Ksibi, Z.; Ghorbel, A.; Delahay, G. Effect of the iron amount on the physicochemical properties of Fe/ZrO₂ aerogel catalysts for the total oxidation of Tolune in the presence of water vapor. *J. Porous Mater.* 2020, *27*, 1847–1852. [CrossRef]

29. Navio, J.A.; Hidalgo, M.C.; Colon, G.; Botta, S.G.; Litter, M.I. Preparation and physicochemical properties of ZrO₂ and Fe/ZrO₂ prepared by a sol-gel technique. *Langmuir* 2001, *17*, 202–210. [CrossRef]

30. López-Hernández, I.; Mengual, J.; Palomares, A.E. The influence of the support on the activity of mn–fe catalysts used for the selective catalytic reduction of NOx with ammonia. *Catalysts* 2020, *10*, 63. [CrossRef]

31. Kustov, A.L.; Rasmussen, S.B.; Fehrmann, R.; Simonsen, P. Activity and deactivation of sulphated TiO₂. *Appl. Catal. B Environ.* 2013, *39*, 515–521. [CrossRef] [PubMed]

32. Navio, J.A.; Hidalgo, M.C.; Colon, G.; Botta, S.G.; Litter, M.I. Preparation and physicochemical properties of ZrO₂ and Fe/ZrO₂ prepared by a sol-gel technique. *Langmuir* 2001, *17*, 202–210. [CrossRef]

33. Kustov, A.L.; Rasmussen, S.B.; Fehrmann, R.; Simonsen, P. Activity and deactivation of sulphated TiO₂. *Appl. Catal. B Environ.* 2013, *39*, 515–521. [CrossRef] [PubMed]

34. Kogler, M.; Köck, E.M.; Vanicek, S.; Schmidmair, D.; Götsch, T.; Stöger-Pollach, M.; Hejny, C.; Klötzer, B.; Penner, S. Enhanced Kinetic Stability of Pure and Y-Doped Tetragonal ZrO₂. *Inorg. Chem.* 2014, *53*, 13247–13257. [CrossRef]

35. Tan, D.; Lin, G.; Liu, Y.; Teng, Y.; Zhuang, Y.; Zhu, B.; Zhao, Q.; Qiu, J. Synthesis of nanocrystalline cubic zirconia using femtosecond laser ablation. *J. Nanoparticle Res.* 2011, *13*, 1183–1190. [CrossRef]

36. Boróki, P.; Chmielarz, L.; Dzwigaj, S. Influence of Cu on the catalytic activity of FeBEA zeolites in SCR of NO with NH₃. *Appl. Catal. B Environ.* 2015, *168–169*, 377–384. [CrossRef]
40. Du, L.; Wang, W.; Yan, H.; Wang, X.; Jin, Z.; Song, Q.; Si, R.; Jia, C. Copper-ceria sheets catalysts: Effect of copper species on catalytic activity in CO oxidation reaction. *J. Rare Earths* 2017, 35, 1186–1196. [CrossRef]

41. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* 1976, 32, 751–767. [CrossRef]

42. Breviglieri, S.T.; Cavalheiro, É.T.G.; Chierice, G.O. Correlation between ionic radius and thermal decomposition of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) diethanolthiocarbamates. *Thermochim. Acta* 2000, 356, 79–84. [CrossRef]

43. Wang, Y.; Zhao, Q.; Wang, Y.; Hu, C.; Da Costa, P. One-Step Synthesis of Highly Active and Stable Ni-ZrOx for Dry Reforming of Methane. *Ind. Eng. Chem. Res.* 2020, 59, 11441–11452. [CrossRef]

44. Khorsand Zak, A.; Abd Majid, W.H.; Abrishami, M.E.; Yousefi, R. X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods. *Solid State Sci.* 2011, 13, 251–256. [CrossRef]

45. Williamson, G.K.; Hall, W.H. X-ray line broadening from filed aluminium and wolfram. *Acta Metall.* 1953, 1, 22–31. [CrossRef]

46. Ismail, R.; Arfaoui, J.; Ksibi, Z.; Ghorbel, A.; Delahay, G. Ag/ZrO$_2$ and Ag/Fe–ZrO$_2$ catalysts for the low temperature total oxidation of toluene in the presence of water vapor. *Transit. Met. Chem.* 2020, 45, 501–509. [CrossRef]

47. Lee, S.M.; Park, K.H.; Hong, S.C. MnO$_x$/CeO$_2$-TiO$_2$ mixed oxide catalysts for the selective catalytic reduction of NO with NH$_3$ at low temperature. *Chem. Eng. J.* 2012, 195–196, 323–331. [CrossRef]

48. Zhao, H.; Wang, Y.; Wang, Y.; Cao, T.; Zhao, G. Electro-Fenton oxidation of pesticides with a novel Fe$_3$O$_4$@Fe$_2$O$_3$/activated carbon aerogel cathode: High activity, wide pH range and catalytic mechanism. *Appl. Catal. B Environ.* 2012, 125, 120–127. [CrossRef]

49. Wang, Y.; Li, L.; Wang, Y.; Da Costa, P.; Hu, C. Highly carbon-resistant Y doped NiO–ZrO$_2$ catalysts for dry reforming of methane. *Catalysts* 2019, 9, 1055. [CrossRef]

50. Sutthiumporn, K.; Maneerung, T.; Kathiraser, Y.; Kawi, S. CO$_2$ dry-reforming of methane over La$_0.8$Sr$_0.2$Ni$_{0.8}$M$_{0.2}$O$_3$ perovskite (M = Bi, Co, Cr, Cu, Fe): Roles of lattice oxygen on C-H activation and carbon suppression. *Int. J. Hydrogen Energy* 2012, 37, 11195–11207. [CrossRef]

51. Jiang, H.; Zhou, J.; Wang, C.; Li, Y.; Chen, Y.; Zhang, M. Effect of Cosolvent and Temperature on the Structures and Properties of Cu-MOF-74 in Low-temperature NH$_3$-SCR. *Ind. Eng. Chem. Res.* 2017, 56, 3542–3550. [CrossRef]

52. Khodayari, R.; Odenbrand, C.U.I. Regeneration of commercial SCR catalysts by washing and sulphation: Effect of sulphate groups on the activity. *Appl. Catal. B Environ.* 2001, 33, 277–291. [CrossRef]

53. Miao, J.; Li, H.; Su, Q.; Yu, Y.; Chen, Y.; Chen, J.; Wang, J. The combined promotive effect of SO$_2$ and HCl on Pb-poisoned commercial NH$_3$-SCR V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts. *Catal. Commun.* 2019, 125, 118–122. [CrossRef]

54. Yu, Y.; Wang, J.; Chen, J.; Meng, X.; Chen, H.; He, C. Promotive Effect of SO$_2$ on the Activity of a Deactivated Commercial Selective Catalytic Reduction Catalyst: An in situ DRIFT Study. *Ind. Eng. Chem. Res.* 2014, 53, 16229–16234. [CrossRef]