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Article

Novel Preparation of Cu and Fe Zirconia Supported Catalysts for Selective Catalytic Reduction of NO with NH₃

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† K.Ś. and Y.W. contributed equally.

Abstract: Copper and iron promoted ZrO₂ catalysts were prepared by one-pot synthesis using urea. The studied catalysts were characterized by XRD, N₂ physisorption, XPS, NH₃-TPD, and tested in the selective catalytic reduction of NO with NH₃ (NH₃-SCR) in the absence and presence of water vapor under the experimental conditions representative of exhaust gases from stationary sources. The influence of SO₂ on catalytic performance was also investigated. Among the studied catalysts, the Fe-Zr sample showed the most promising results in NH₃-SCR, being active and highly selective to N₂. The addition of SO₂ markedly improved NO and NH₃ conversions during NH₃-SCR in the presence of H₂O. The improvement in acidic surface properties is believed to be the cause.

Keywords: zirconia; copper; iron; one-pot synthesis; NH₃-SCR; NO_x; acidity



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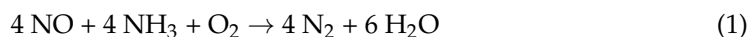


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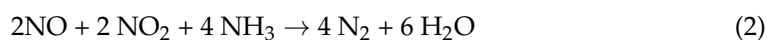
1. Introduction

Nitrogen oxides (NO_x: 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 NO_x emission [1]. Among them, direct decomposition of NO_x 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 NO_x Storage/Reduction (NSR) or NO_x trap [4]. These approaches, however, are limited due to the hydrocarbon and CO₂ penalties caused by cyclic lean-fuel/rich-fuel conditions [5].

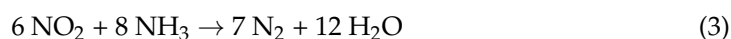
The last known technology for NO_x emission control is the selective catalytic reduction (SCR), including HCs, CO, and H₂-SCR for automotive pollution processes [6,7]. One of the well-established post-combustion technologies of NO_x reduction is the selective catalytic reduction of NO_x with ammonia (NH₃-SCR). The process has been introduced in the late 1970s, being widely commercialized technology for NO_x 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:



With an equimolar amount of NO and NO₂, the reaction called fast SCR reaction is much faster, and the reaction equation becomes:



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



The conventional catalysts are V₂O₅–WO₃(MoO₃)/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(MoO₃)/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 NO_x 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 NO_x reduction were described in the literature. Among them, zirconia-supported catalysts were found attractive due to the high thermal stability, high low-temperature activity and durability, as well as enhanced resistance to SO₂ and H₂O [16–21]. Cu/ZrO₂ and Cu/ZrO₂(SO₄^{2−}) were found very promising in selective catalytic reduction by n-decane [22–24] or propene [25], and finally in NH₃-SCR [26,27]. Pietrogiaconi et al. [26] prepared the zirconia support by hydrolysis 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 sulphurized 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, Navío et al. [29] demonstrated that Fe loading equal or higher than 3 wt% allows to stabilize 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-Hernández 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 also possesses 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 Fe_2O_3 and SO_4^{2-} on ZrO_2 carrier. The activities of sulphate 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 sulphate supplied higher number of acid sites, which could adsorb more NH_3 species that can react with gaseous $\text{NO} + \text{O}_2$. Recently, Liu et al. [34] investigated the selective catalytic reduction of NOx with 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 . By 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_2O). 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_2O) 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 Bragg 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_2O_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 $\text{Fe}_2\text{O}_3\text{-ZrO}_2$ 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.

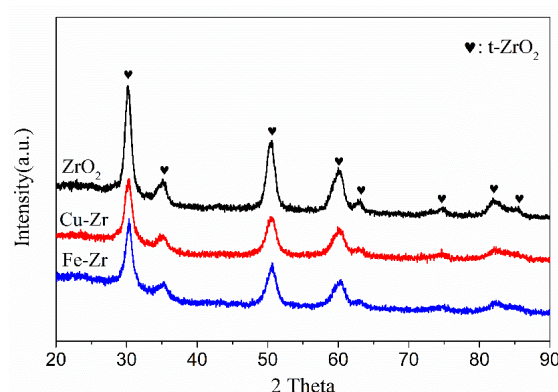


Figure 1. X-ray diffraction (XRD) diffractograms of ZrO_2 support, Cu-Zr and Fe-Zr calcined catalysts.

N_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^3/g , average pore size of 3.3–5 nm, and the surface area from 81 to 139 m^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_2 Supported Catalysts

The total acidity of the studied catalysts was evaluated by NH_3 temperature programmed desorption (NH_3 -TPD). Figure 2 presents the desorption curves for the studied catalysts. All samples showed a wide NH_3 desorption profiles between 100 and 550 $^\circ\text{C}$, arising from weak (ca. 200 $^\circ\text{C}$), medium (ca. 300–400 $^\circ\text{C}$), and strong ($T > 400$ $^\circ\text{C}$) acid sites [46,47]. The modification of ZrO_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_2 and Fe/ ZrO_2 materials. Pietrogiacomini et al. [26] reported higher total amount of desorbed ammonia for ZCu2.5 sample than for ZrO_2 (0.5 vs. 0.2 nm^{-1}). Ismail et al. [28] observed the formation of new acidic sites on ZrO_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 $^\circ\text{C}$). In the other study of these authors [46], the modification with iron led to the formation of new strong acid sites only ($T > 400$ $^\circ\text{C}$) in comparison to the acid sites recorded for pure zirconia.

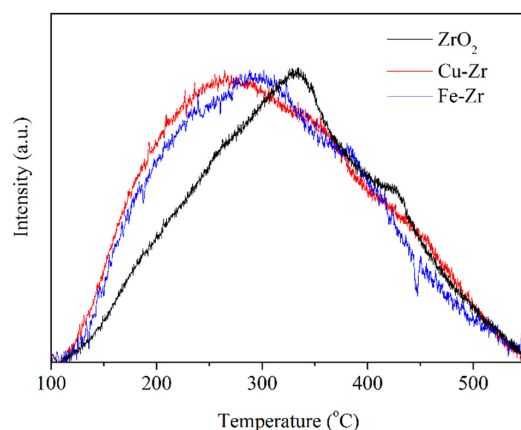


Figure 2. Temperature-programmed desorption of NH_3 (NH_3 -TPD) profiles of ZrO_2 support, Cu-Zr and Fe-Zr calcined catalysts.

2.1.3. Surface Properties of ZrO₂ 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. ZrO₂ 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% (ZrO₂ 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%). One can assume that part of Cu species could exist in the framework of ZrO₂ or in the bulk. On the contrary, the percentage of Fe species is 3.2 wt%, indicating that more Fe species are formed on the surface than the interior of ZrO₂ catalyst. Thus, the higher content of surface Fe species may contribute to increased activity in NH₃-SCR of NO into N₂. Besides, the O 1s curve was resolved into three peaks, which are attributed to lattice oxygen (O^{2−}), carbonate species (CO₃^{2−}) and hydroxyl species (OH[−]) [43,48]. The Zr 3d was deconvoluted into Zr³⁺ and Zr⁴⁺ 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 ZrO₂ 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 Fe₂O₃ and/or FeO species on the surface. Similar results were reported in literature [48,50]. Moreover, in our materials the content of Zr⁴⁺ 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 Zr³⁺ species on the catalysts. This effect was more pronounced for Fe-Zr catalyst showing 95.3% of Zr³⁺ 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 Fe²⁺ and Fe³⁺ species, and Cu⁺ and Cu²⁺ species, respectively. In our study, the ratio of Fe²⁺/Fe³⁺ is 1.33, and the Cu⁺/Cu²⁺ is 3.84. This indicates that more Fe species are present in higher valence state on Fe-Zr catalyst, corresponding to higher content of Zr³⁺ species. Moreover, recently on functionalized iron hydroxyapatite catalysts it was clearly shown that the presence of Fe³⁺ highly dispersed on the surface led to a high selectivity to N₂, a satisfactory activity in a wide temperature window [41] and improved catalytic activity [34].

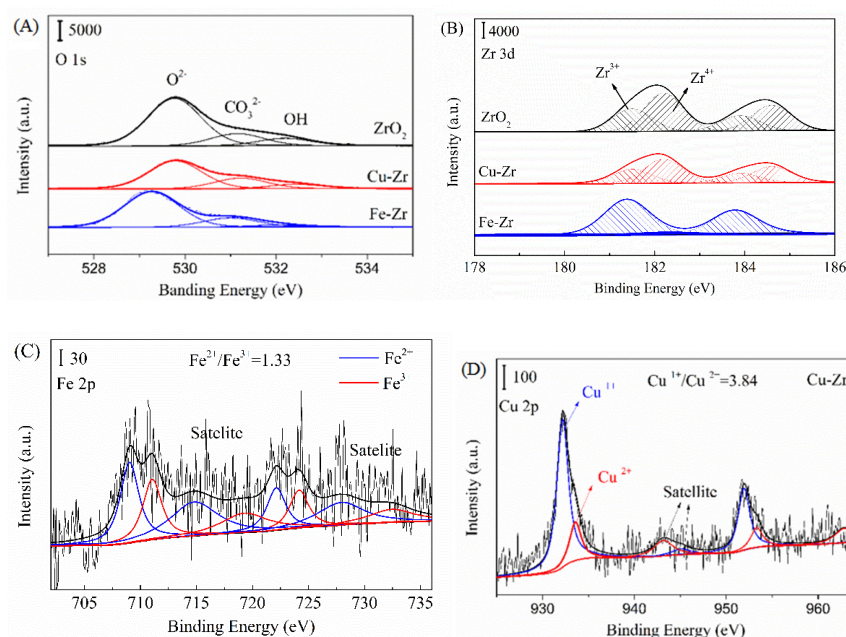


Figure 3. X-ray photoelectron spectroscopy (XPS) profiles of ZrO₂ support, Cu-Zr and Fe-Zr calcined catalysts. (A) The O 1s, (B) Zr 3d, (C) Fe 2p, and (D) Cu 2p. All the data are referenced using the C 1s peak at 284.6 eV.

Table 2. Elemental composition of ZrO₂, 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. NH₃-SCR of NO in the Absence and Presence of Water Vapor

Figure 4 shows the catalytic performance of Cu-Zr and Fe-Zr catalysts and the support in NH₃-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 H₂O at 450 °C. In the former conditions, the obtained conversions were two times higher than those observed by Pietrogiacomini et al. [27] (700 ppm NO, 700 ppm NH₃, 36,000 ppm O₂, balance He, GHSV = 10⁵ h^{−1}) on impregnated Cu/ZrO₂ 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 NH₃ oxidation reaction. This agrees with NH₃ conversion which remained stable, or it increased constantly above 450 °C. The impact of NH₃ oxidation will be studied by us further in this section. The production of N₂O 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 NH₃-SCR over Fe-Zr catalyst. The absence of water vapor led to a maximum of 55% of NO conversion at 500 °C. The N₂O production was measured at ca. 28 ppm at this temperature. The presence of H₂O resulted in a constant increase of NO and NH₃ conversions, starting from 300 to 550 °C. At the latter temperature, the NO and NH₃ conversions are 35 and 53%, respectively. The decrease of activity, in the presence of H₂O, 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 H₂O, the Fe-Zr catalyst did not produce N₂O over the whole range of studied temperatures.

From Figure 4E, one can note that the support is inactive during NH₃-SCR reaction as only conversion of NH₃ was observed accompanied by the production of N₂O and NO. Negative conversion values were recorded for the latter (not shown in Figure 4E). These observations suggest that selective oxidation of ammonia is a dominant reaction for the support. ZrO₂ support tested in the hydrothermal conditions led to the complete inhibition of any significant catalytic reaction below 500 °C. However, some NH₃ conversion, not exceeding 10% at 550 °C, occurred above 500 °C.

Furthermore, N₂O is the only by-product detected during the NH₃-SCR process, which determines selectivity to N₂ 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 selectivity to N₂. In the whole SCR process, the N₂O concentration detected during the tests 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 NH₃-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 (NH₃-SCO) was performed.

[NO] = [NH₃] = 1000 ppm, [O₂] = 2.5 vol%, He as balance

[NO] = [NH₃] = 1000 ppm, [O₂] = 2.5 vol%, [H₂O] = 3.5%,
He as balance

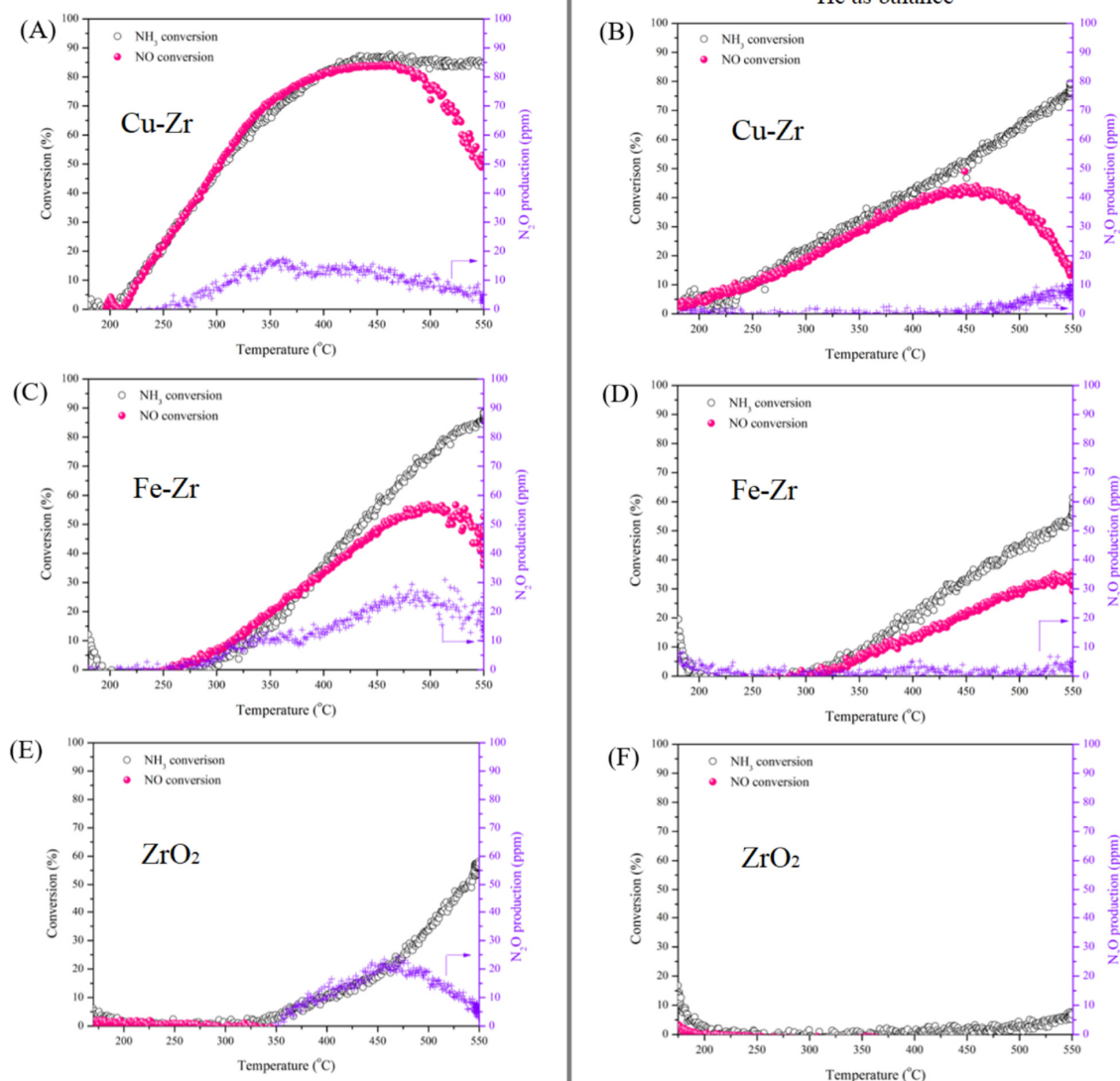


Figure 4. NO and NH₃ conversion profiles and N₂O production as a function of temperature in NH₃-SCR over Cu-Zr catalyst (A) in absence of water, (B) in presence of water, Fe-Zr catalyst (C) in absence of water, (D) in presence of water, and ZrO₂ support (E) in absence of water, (F) in presence of water. 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.

2.2.2. NH₃-SCO in the Absence and Presence of Water Vapor

The selective catalytic NH₃ oxidation (SCO) ability of a catalyst determines the efficiency of NH₃ utilization in the SCR reaction. Figure 5A–F depicts the NH₃ oxidation performance of the studied materials in the absence and presence of H₂O. 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 NH₃ led to N₂O and NO by-products formation with maximum values of 38 ppm and 250 ppm, respectively. In the hydrothermal conditions, the Cu-Zr catalyst was less active in NH₃-SCO, compared to the conditions without water vapor (Figure 6B). NH₃ conversion constantly increased over the studied temperatures with a maximum of 68% at 550 °C. Iron promoted ZrO₂ was also active in NH₃-SCO with 89% of NH₃ at 550 °C complemented by the production of N₂, N₂O, and

NO (Supplementary Materials Figure S1; Figure 6C). Ammonia oxidation in the presence of H_2O led to the decreased activity with only 28% of NH_3 converted (Figure 6D) and low production of side products, i.e., N_2O and NO. Figure 5E presents zirconia support which was active in NH_3 -SCO, resulting mostly in the production of NO (400 ppm) at the highest analyzed temperature. Small amounts of N_2O were also observed (10 ppm). The presence of water in ammonia oxidation inhibited reaction, and only 5% of NH_3 conversion was observed (Figure 6F). When compared to NH_3 -SCR results, one can conclude that NH_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_3 is more difficult to be oxidized on the surface of both Cu-Zr and Fe-Zr catalysts. Therefore, the adsorbed NH_3 species can effectively react with NO, giving a high NO removal efficiency.

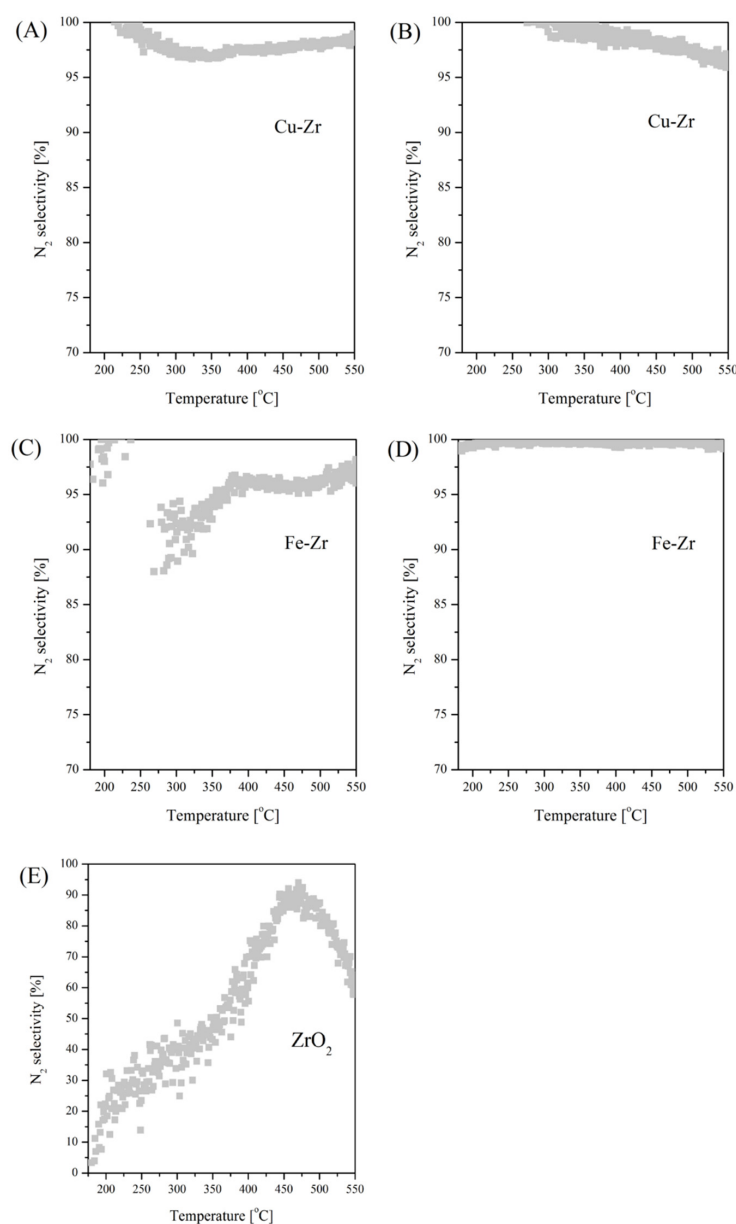


Figure 5. N_2 selectivity as a function of temperature measured during NH_3 -SCR over Cu-Zr catalyst (A) in absence of water, (B) in presence of water, Fe-Zr catalyst (C) in absence of water, (D) in presence of water, and ZrO_2 support (E) in absence of water. The experimental conditions: $[NO] = 1000$ ppm, $[NH_3] = 1000$ ppm, $[H_2O] = 3.5$ vol% when used, $[O_2] = 2.5$ vol% diluted in helium; total flowrate of 100 mL/min.

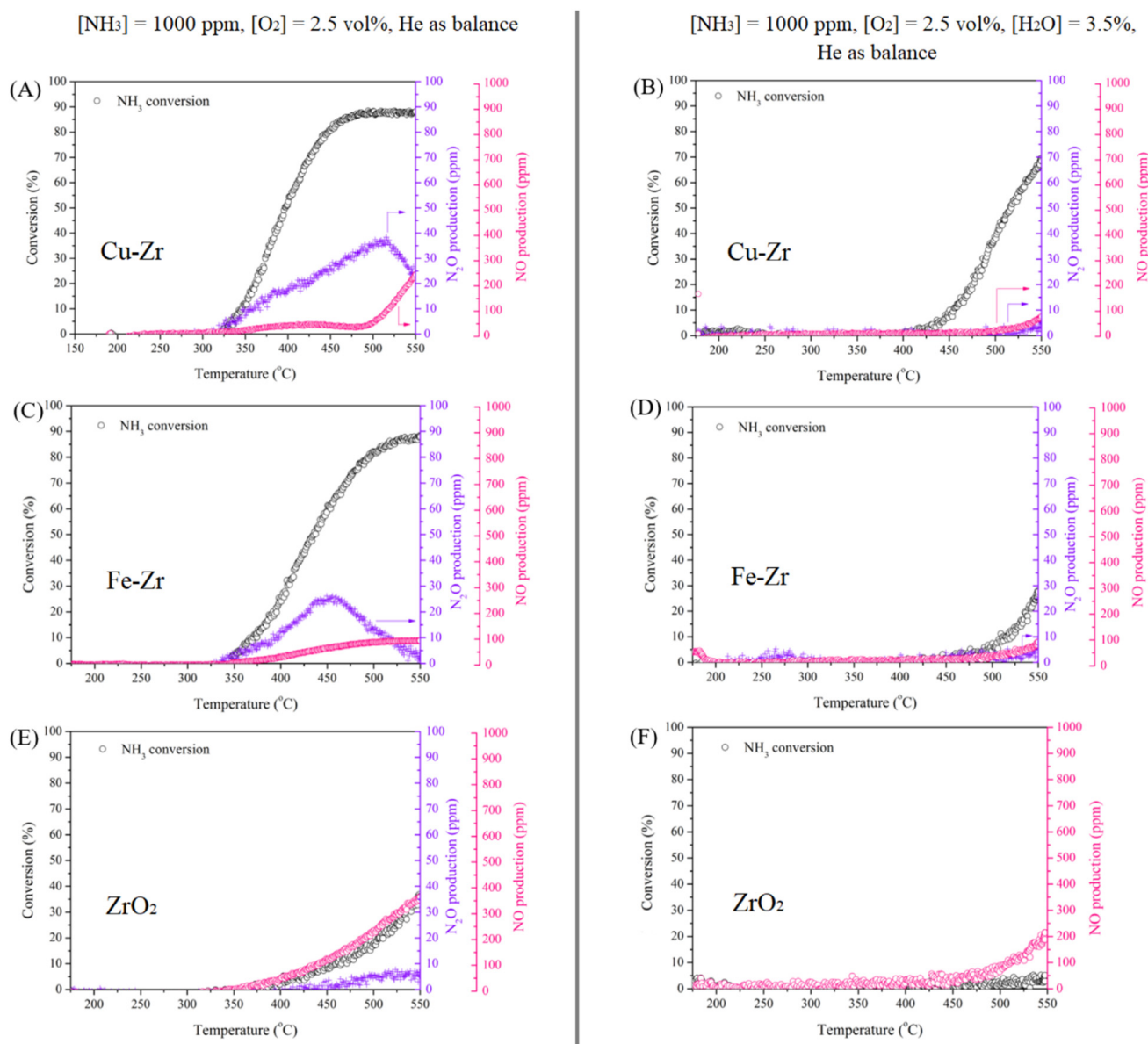


Figure 6. NH_3 conversion profile and N_2O and NO production profiles as a function of temperature in NH_3 -SCO over Cu-Zr catalyst (A) in absence of water, (B) in presence of water; Fe-Zr catalyst (C) in absence of water, (D) in presence of water; and ZrO_2 support (E) in absence of water, (F) in presence of water. The experimental conditions: $[\text{NH}_3] = 1000 \text{ ppm}$, $[\text{H}_2\text{O}] = 3.5 \text{ vol\%}$ when used, $[\text{O}_2] = 2.5 \text{ vol\%}$ diluted in helium; total flowrate of 100 mL/min .

2.2.3. SO_2 Activation of Cu-Zr and Fe-Zr Catalysts and their Catalytic Behavior in NH_3 -SCR of NO in the Absence and Presence of Water Vapor

SO_2 Activation of Cu-Zr Catalyst in NH_3 -SCR of NO in the Absence of Water Vapor

The SO_2 activation study in NH_3 -SCR of NO in the absence of H_2O was carried out on Cu-Zr catalyst at 450°C . Prior to this examination, the reaction of NH_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_2 for another 60 min, and then after removing the SO_2 for next 90 min. When the SO_2 was added, a clear increase in both NH_3 and NO conversions was observed resulting in ca. 100% (Figure 7). Once the SO_2 was removed from the feed, a rapid decrease was registered for both, steadying the values to be initially slightly

higher than those registered before SO_2 feeding. Over the stabilization in the mixture free of SO_2 , the conversions gradually increased from 83.7 to 90.5% and 83.9 to 85.7% for NO and NH_3 conversions, respectively. The in-situ sulphation promoted the activity of Cu-Zr catalyst in NH_3 -SCR of NO . Similar observations were made in the studies of Pietrogiaconi et al. [26,27] in which it has been reported that sulphation of Cu-containing ZrO_2 catalysts positively affects catalytic performance NH_3 -SCR of NO due to the enhanced acidic properties of sulphated supports.

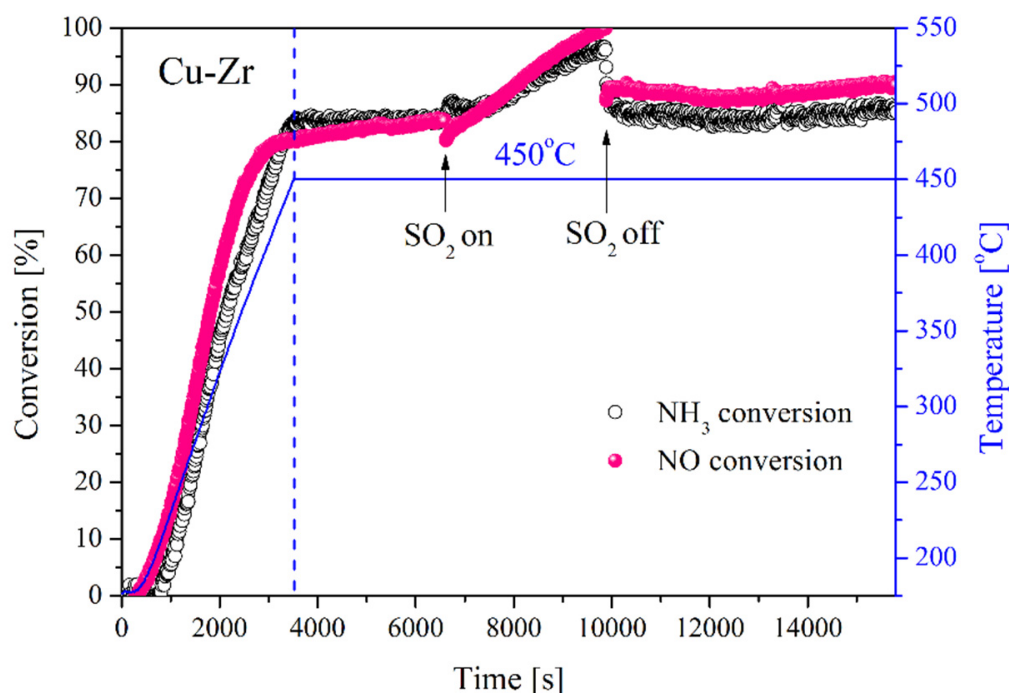


Figure 7. Effect of SO_2 addition during NH_3 -SCR over Cu-Zr catalyst in the absence of water. The experimental conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{SO}_2] = 100$ ppm when used, $[\text{O}_2] = 2.5$ vol% diluted in helium; total flowrate of 100 mL/min.

SO_2 Activation of Fe-Zr in NH_3 -SCR of NO in the Presence of Water Vapor

Recently, Fan et al. [33] showed that Fe/ ZrO_2 sulphated catalysts were almost two times more active than non-sulphated Fe/ ZrO_2 in NH_3 -SCR of NO . Thus, in order to verify the activation of the catalysts in the presence of SO_2 , the experiment was performed in hydrothermal conditions over Fe-Zr catalyst and over the support. The results are presented in Figure 8A,B. In the presence of water, an interesting trend was observed for the Fe-Zr catalyst (Figure 8A). During the first hour of stabilization, the conversions of NO and NH_3 were 29% and 30%, respectively. After SO_2 addition, a slight decrease of NO and NH_3 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 SO_2 , both conversions of NO and NH_3 increased. It is worth to note that the consumption of NH_3 reached 47%, whereas only 30% of NO was converted. This latter result could not be linked with any NH_3 oxidation activity, despite the high temperature of 450 °C. No side products were recorded by MS that could suggest NH_3 -SCO occurrence. Moreover, on the ZrO_2 support a similar NH_3 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 SO_2 which can act as a reservoir [33]. Similar observations were made on other type of catalysts such as $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ [52–54].

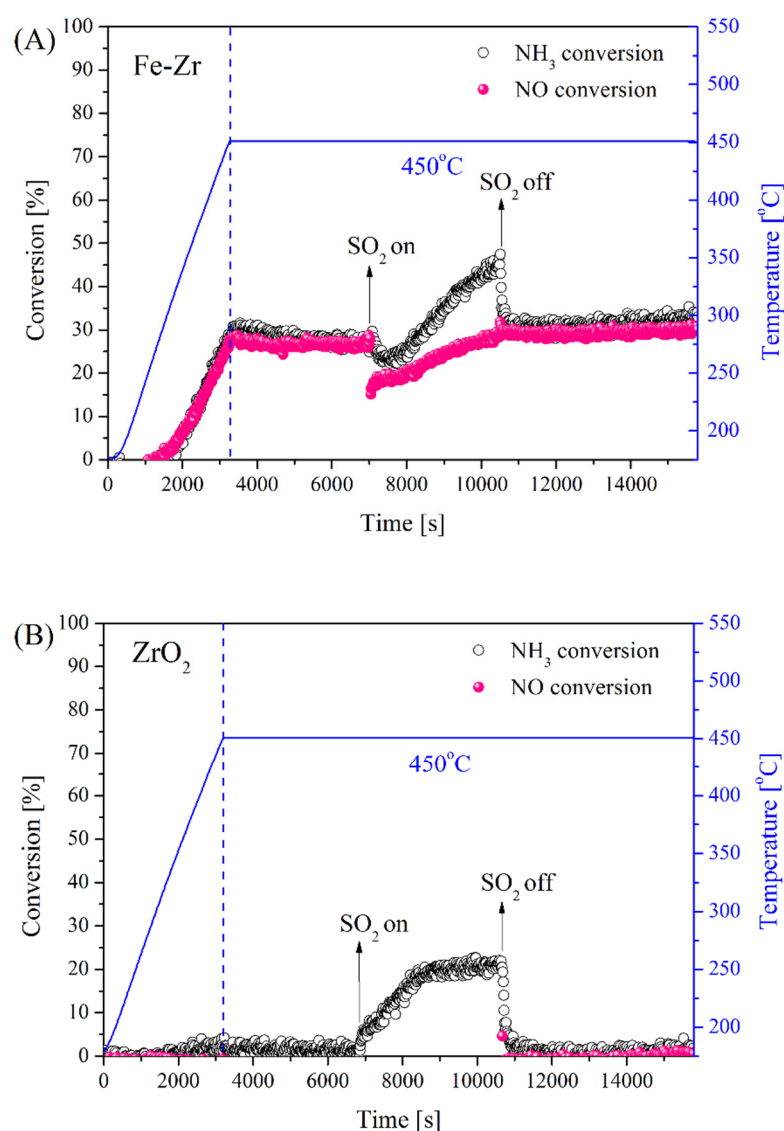


Figure 8. Effect of SO_2 addition during NH_3 -SCR over Fe-Zr and ZrO_2 catalysts in the hydrothermal conditions. (A) Fe-Zr catalyst, (B) ZrO_2 support. The experimental conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{SO}_2] = 100$ ppm when used, $[\text{H}_2\text{O}] = 3.5$ vol%, $[\text{O}_2] = 2.5$ 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 Thermo Fisher 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	ZrO(NO) ₃ ·2H ₂ O/g	Cu(NO) ₂ ·2.5H ₂ O/g	Fe(NO) 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 K α radiation at 40 kV and 25 mA. The data was recorded in the range $5^\circ < 2\theta < 90^\circ$ with 0.3 s/step scan speed and 0.03° step size.

Textural properties of the samples were determined by N₂ 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 NH₃-TPD using an AUTOCHEM 2910 (Micromeritics, Aachen, Germany). The solid was pre-treated at 550°C (ramp $10^\circ\text{C}/\text{min}$) during 2 h, under air flow (30 mL/min). Then, it was exposed to 5 vol% NH₃ 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 NH₃ desorption was performed in helium flow (30 mL/min) from 100 to 550°C (the heating rate was $5^\circ\text{C}/\text{min}$).

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 NH₃ (NH₃-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 O₂/He and then cooled to 180°C . The following compositions of the gas mixture for NH₃-SCR of NO: [NO] = 1000 ppm, [NH₃] = 1000 ppm, [H₂O] = 3.5 vol%, [O₂] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min. The tolerance of SO₂ was examined at 450°C with [SO₂] = 100 ppm. 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 $5^\circ\text{C}/\text{min}$. The reactants and products were analyzed by a quadrupole mass spectrometer (Pfeiffer Omnistar, Saclay, France) equipped with Channeltron and Faraday detectors recording the following masses: NH₃ ($m/z = 15, 17, 18$), NO ($m/z = 30$), O₂ ($m/z = 16, 32$), H₂O ($m/z = 17, 18$), N₂ ($m/z = 14, 28$), N₂O ($m/z = 28, 30, 44$), and He ($m/z = 4$).

The selective catalytic oxidation of NH₃ (NH₃-SCO) was studied in the U-shape glass reactor operating in similar conditions as described above, using the following gas mixture for NH₃-SCO: [NH₃] = 1000 ppm, [H₂O] = 3.5 vol%, [O₂] = 2.5 vol% diluted in helium; total flowrate of 100 mL/min. Similarly, the reactants and products were analyzed by a quadrupole mass spectrometer (Pfeiffer Omnistar, Saclay, France) equipped with Channeltron and Faraday detectors recording the following masses: NH₃ ($m/z = 15, 17, 18$), NO ($m/z = 30$), O₂ ($m/z = 16, 32$), H₂O ($m/z = 17, 18$), N₂ ($m/z = 14, 28$), N₂O ($m/z = 28, 30, 44$), 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 NH₃-SCR of NO in both the presence and absence of water vapor. The studied materials presented NO reduction with NH₃ which mainly led to N₂ but side reactions resulting in N₂O and NO₂ 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 NH₃-SCR of NO. Regardless of the presence or absence of H₂O, 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 NH₃-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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