

## Article

# Development of Innovative Structured Catalysts for the Catalytic Decomposition of N<sub>2</sub>O at Low Temperatures

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**Abstract:** Nitrous oxide (N<sub>2</sub>O), produced from several human activities, is considered a greenhouse gas with significant environmental impacts. The most promising abatement technology consists of the catalytic decomposition of N<sub>2</sub>O into nitrogen and oxygen. Many recently published papers dealing with N<sub>2</sub>O catalytic decomposition over Ni-substituted Co<sub>3</sub>O<sub>4</sub> are related to the treatment of N<sub>2</sub>O concentrations less than 2 vol% in the feed stream. The present work is focused on developing catalysts active in the presence of a gaseous stream richer in N<sub>2</sub>O, up to 20 vol%, both as powder and in structured configurations suitable for industrial application. With this aim, different nickel-cobalt mixed oxides (Ni<sub>x</sub>Co<sub>1-x</sub>Co<sub>2</sub>O<sub>4</sub>) were prepared, characterized, and tested. Subsequently, since alumina-based slurries assure successful deposition of the catalytic species on the structured carrier, a screening was performed on three nickel-cobalt-alumina mixed oxides. As the latter samples turned out to be excellent catalysts for the N<sub>2</sub>O decomposition reaction, the final catalytic formulation was transferred to a silicon carbide monolith. The structured catalyst led to the following very promising results: total N<sub>2</sub>O conversion and selectivity towards N<sub>2</sub> and O<sub>2</sub> were reached at 510 °C by feeding 20 vol% of N<sub>2</sub>O. It represents an important achievement in the view of developing a more concretely applicable catalytic system for industrial processes.

**Keywords:** structured catalysts; catalytic decomposition of N<sub>2</sub>O; high selective catalysts; process intensification



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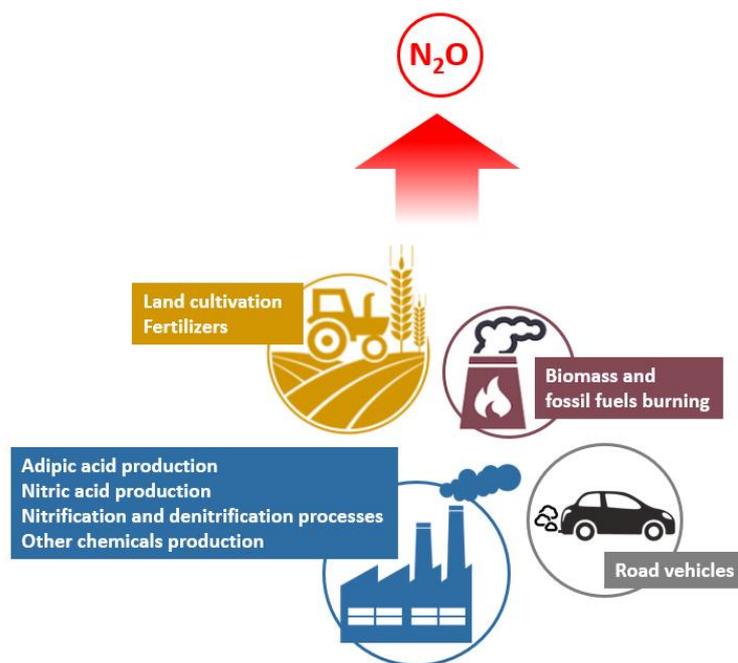
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## 1. Introduction

Environmental issues such as pollution [1], global warming, and ozone layer depletion are of universal concern. One compound previously not associated with these issues is nitrous oxide (N<sub>2</sub>O). In the past years, it has not been recognized as a harmful species nor has received the appropriate consideration from the scientific community due to the undervaluation of its detrimental effect on the environment [2]. The N<sub>2</sub>O contribution equals 6% of the total greenhouse gas emissions, and its global warming potential (GWP) of 310 corresponds to 21 times that of CO<sub>2</sub> and CH<sub>4</sub>, respectively.

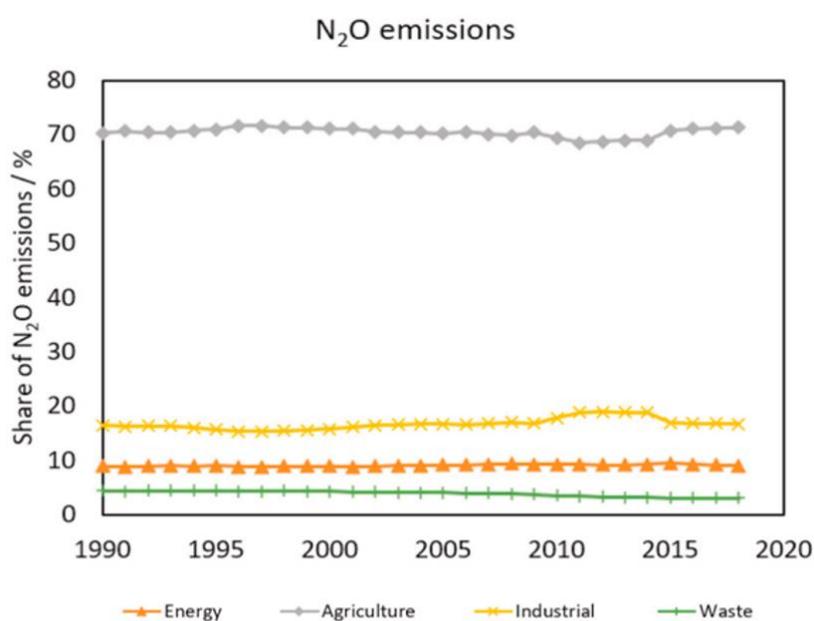
During the last decade, owing to the constant increase in its concentration in the atmosphere, both from natural and anthropogenic sources (0.2–0.3% per year) and its long atmospheric residence time (110–150 years) [3], a growing interest was paid to this topic. In any case, effective mitigation for N<sub>2</sub>O emissions requires an understanding of its sources.

Substantial quantities of N<sub>2</sub>O are produced from anthropogenic activities (Figure 1), such as the production of chemicals (adipic acid, nitric acid, acrylonitrile, nylon, and caprolactame), road vehicles, medical exhausts [4], the incomplete combustion of fossil fuels and biomass, and the nitrification and denitrification processes [5,6].



**Figure 1.** Main anthropogenic sources of  $N_2O$ .

The different contributions of the anthropogenic sources of  $N_2O$  are reported in Figure 2.



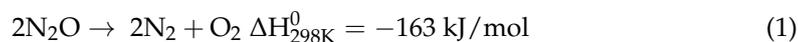
**Figure 2.** Share of  $N_2O$  emissions by sector, from 1990 to 2018 [7].

Since the  $N_2O$  emissions continue to increase and the atmospheric levels are expected to double by 2050 [8], the abatement of  $N_2O$  has aroused interest from both the scientific community and industry.  $N_2O$  removal can be obtained by means of different methods, such as adsorption processes and thermal and catalytic decomposition.

The high efficiency and low cost of the catalytic  $N_2O$  decomposition to nitrogen and oxygen make this technique one of the most attractive, as well as its process simplicity [8].

Generally, the catalytic decomposition of  $N_2O$  occurs via electron donation from the catalyst to the antibonding orbital of  $N_2O$ , leading to N-O bond scission and  $N_2$  and  $O_2$  formation [8,9]. The catalytic decomposition of  $N_2O$  is a direct exothermic reaction

(Equation (1)) kinetically limited, so the selection of a suitable catalyst is essential to promote the N-O bond breakup [10,11].



Over time, many scientific papers have been published about catalytic decomposition, and several catalysts have been studied [12]. The industrial applications of zeolite-based systems [13] have been drastically reduced due to the unfavorable behavior of these materials in the presence of different substances contained in the gas stream, in particular the poisoning by  $\text{SO}_2$  [14]. Among the noble metals, rhodium (Rh) and ruthenium (Ru) are the most active for the decomposition of  $\text{N}_2\text{O}$  at low temperatures, but their performance is strongly affected by the oxygen concentration in the feed stream [15]. Moreover, the high cost limits their application in the industry [16]. On the other hand, transition metal oxides such as  $\text{CuO}$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Fe}_3\text{O}_4$ , which are characterized by low price and good catalytic activity, have received extensive attention for application in  $\text{N}_2\text{O}$  catalytic decomposition [11,17]. Among them, the  $\text{Co}_3\text{O}_4$ -based catalysts have shown better catalytic performance, also at low-temperature conditions, and are promising candidates for the  $\text{N}_2\text{O}$  decomposition reaction, due to their relatively high redox capacity and the weakness of the metal-oxygen bond [8,18,19]. Particularly, the cobalt spinel  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{O}_4$  and its derivatives obtained by partial substitution with 2p, 3d, and 4f dopants have created great interest [20,21]. It is demonstrated that a synergistic effect between Co and transition metals can be obtained by a partial replacement of  $\text{Co}^{2+}$  with  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , or other transition metals in the tricobalt tetraoxide ( $\text{Co}_3\text{O}_4$ ), enhancing the  $\text{N}_2\text{O}$  decomposition reaction [3,22,23]. These materials' class results are beneficial for the decomposition reaction, due to the involvement of different metal atoms and oxidation states whose combination leads to suitable properties [21,23].

Xue et al. [24] explored the influence of  $\text{CeO}_2$  on the catalytic activity of  $\text{Co}_3\text{O}_4$ . The presence of  $\text{CeO}_2$  promoted the desorption of oxygen atoms from the active sites favoring the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  and enhancing the  $\text{N}_2\text{O}$  decomposition reaction. Wang et al. [25] demonstrated that the enhancement of the electron donation ability of  $\text{Co}^{2+}$  is due to the interaction between Sn and Co oxides at the  $\text{SnO}_2/\text{Co}_3\text{O}_4$  interface.

Interesting works are those of Yan et al. [3,23], who tested several spinel catalysts, namely,  $\text{Mg}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ ,  $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ , and  $\text{Zn}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$  with  $x = 0.0\text{--}0.99$ , for the decomposition of  $\text{N}_2\text{O}$ . They demonstrated how the catalytic performance was dependent on the degree of  $\text{Co}^{2+}$  substitution by the other metals. The results showed that  $\text{Mg}_{0.54}\text{Co}_{0.46}\text{Co}_2\text{O}_4$ ,  $\text{Ni}_{0.74}\text{Co}_{0.26}\text{Co}_2\text{O}_4$ , and  $\text{Zn}_{0.36}\text{Co}_{0.64}\text{Co}_2\text{O}_4$  exhibited the highest activities. Abu-Zied et al. [26] study indicated that mixed  $\text{NiO-Co}_3\text{O}_4$  catalysts had better catalytic properties with respect to separated  $\text{NiO}$  and  $\text{Co}_3\text{O}_4$ , highlighting the synergistic effect between the compounds.

The papers dealing with  $\text{N}_2\text{O}$  catalytic decomposition over Ni-substituted  $\text{Co}_3\text{O}_4$  available in the present literature are related to the treatment of low  $\text{N}_2\text{O}$  concentrations, i.e., less than 2 vol% in the reagent mixture. An interesting breakthrough could be achieved with the development of a catalytic formulation able to successfully treat feeding streams containing high concentrations of  $\text{N}_2\text{O}$ , such as in the case of adipic acid production plants [27]. This catalytic system could be applied either directly in the treatment of the tail gases exiting from the plant or after a regeneration stage of an  $\text{N}_2\text{O}$  adsorption process that returns a gas stream rich in  $\text{N}_2\text{O}$ . To this end, in the present work, different nickel-cobalt mixed oxides ( $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ ), active for the  $\text{N}_2\text{O}$  decomposition reaction, were prepared, characterized, and tested employing reagent mixtures containing concentrations of  $\text{N}_2\text{O}$  from 5 up to 20 vol%. In addition, it could be interesting to perform more practical catalytic configurations, such as monolithic systems, suitable for industrial applications. Indeed, the use of monoliths allows having many advantages, among which is the possibility to treat high gas volumes with low-pressure drop operations, as well as the elimination of mass transport limitations [28–30]. Therefore, aiming at the development of a structured catalyst, which requires an alumina-based washcoat to effectively deposit the active species [31],

additional catalytic powder samples were investigated, by modifying the formulation with  $\text{Al}_2\text{O}_3$ . The nickel-cobalt-alumina mixed oxides samples turned out to be excellent catalysts for the  $\text{N}_2\text{O}$  decomposition reaction; indeed, total conversion of  $\text{N}_2\text{O}$  and a selectivity of 100% toward  $\text{N}_2$  and  $\text{O}_2$  were reached at a temperature lower than  $450^\circ\text{C}$  to treat a feeding mixture containing 20 vol% of  $\text{N}_2\text{O}$ . Furthermore, as widely reported [1,3,22], the oxygen inhibits the decomposition reaction and its adsorption leads to the poisoning of the catalyst; therefore, the effect of the presence of oxygen in the reagent mixture on the catalytic performance was investigated, also because oxygen is often present in tail gases from adipic acid production plants, for example. In conclusion, the most promising  $\text{Al}_2\text{O}_3$ -modified catalytic formulation was deposited on a silicon carbide (SiC) honeycomb monolith to carry out a structured catalyst. The results demonstrated that the transition from the powder to the structured configuration, by choosing the operating conditions in order to assure the same contact time in both systems, did not lead to a great worsening of the catalytic performance, or rather, with the monolithic structured catalyst, total conversion of  $\text{N}_2\text{O}$  and selectivity of 100% toward  $\text{N}_2$  and  $\text{O}_2$  were achieved at  $510^\circ\text{C}$ .

## 2. Results and Discussion

### 2.1. Catalysts Characterization

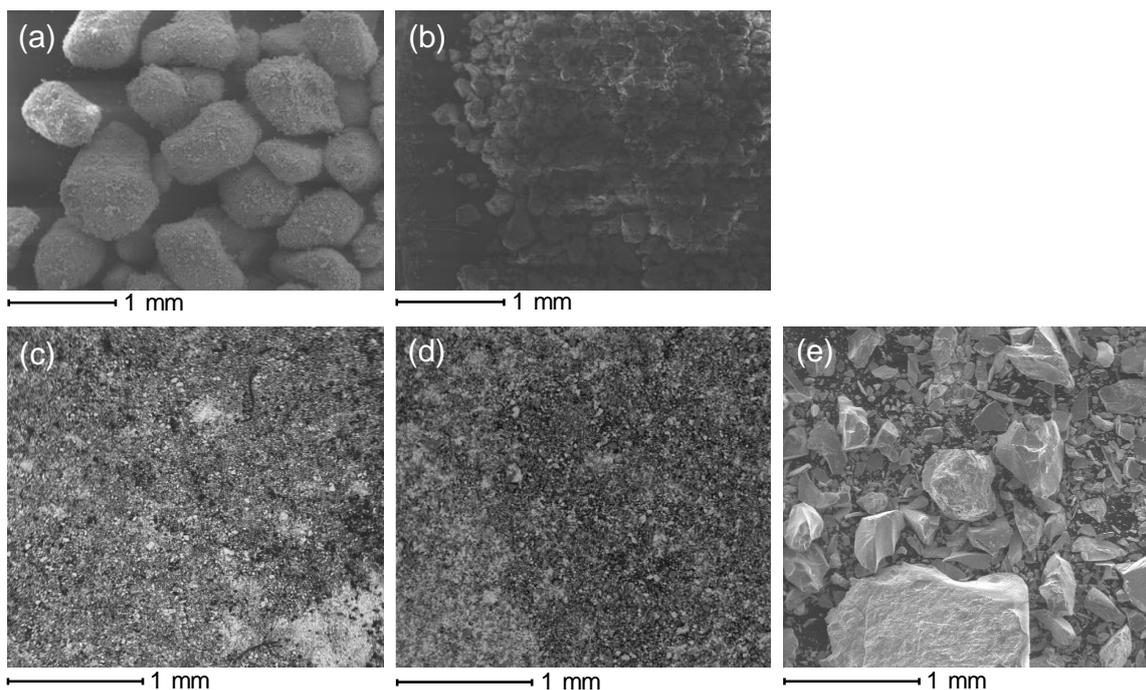
The BET-specific surface area (SSA), pore volume, and average pore radius of the samples as obtained through  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  are given in Table 1. The results retrieved for samples NiCo\_1 and NiCo\_2 highlight how the employment of different precipitating agents can lead to different textural properties. Particularly, comparing the samples NiCo\_1 and NiCo\_2, it is evident that the use of  $\text{Na}_2\text{CO}_3$  is detrimental with respect to the porous structure of the sample. The alumina-containing catalysts showed different SSA values, depending on both the  $\text{Al}_2\text{O}_3$  contents and the preparation method. In detail, for what concerns the samples prepared using an alumina-based washcoat, the higher the alumina loading was, the higher the SSA value was, while the average pore dimension was similar for the three samples. On the other hand, the catalyst NiCoAl\_C prepared by coprecipitation of Co, Ni, and Al precursors achieved an SSA value lower than the other alumina-based samples. Since NiCoW10%, NiCoW15%, and NiCoW30% are derived from a mixture of NiCo\_1 and alumina, their SSA is strictly linked to the one of the pseudoboehmite used to prepare the slurry. On the contrary, in the case of the NiCoAl\_C sample, the SSA value does not depend on the alumina content, but it is associated with the chemical structure reached through the preparation method. Moreover, NiCoAl\_C highlighted the highest average pore radius.

**Table 1.** SSA, pore volume, pore radius, Ni/Co ratio, and  $\text{Al}_2\text{O}_3$  content about the catalytic powder samples.

Sample	SSA (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Radius (nm)	Ni/Co	Al <sub>2</sub> O <sub>3</sub> (wt%)
NiCo_1	53	0.130	5.95	0.32	-
NiCo_2	29	0.040	1.70	0.33	-
NiCo_W10%	57	0.187	2.60	0.32	9.6
NiCo_W15%	59	0.169	2.79	0.32	14.6
NiCo_W30%	64	0.115	3.55	0.32	28.4
NiCoAl_C	40	0.180	6.00	0.40	14.5

The analytical technique XRF was applied with the aim of determining the effective Ni/Co ratio and the alumina content inside the alumina-based powder catalysts. As a result, all the values are in fair agreement with the expected ones, except for NiCoAl\_C. The three alumina-based samples showed the same Ni/Co ratio as NiCo\_2 used for the preparation, while NiCoAl\_C originates from a coprecipitation of the precursor salts NiCoAl\_C sample showed a higher Ni/Co ratio due to the different preparation method.

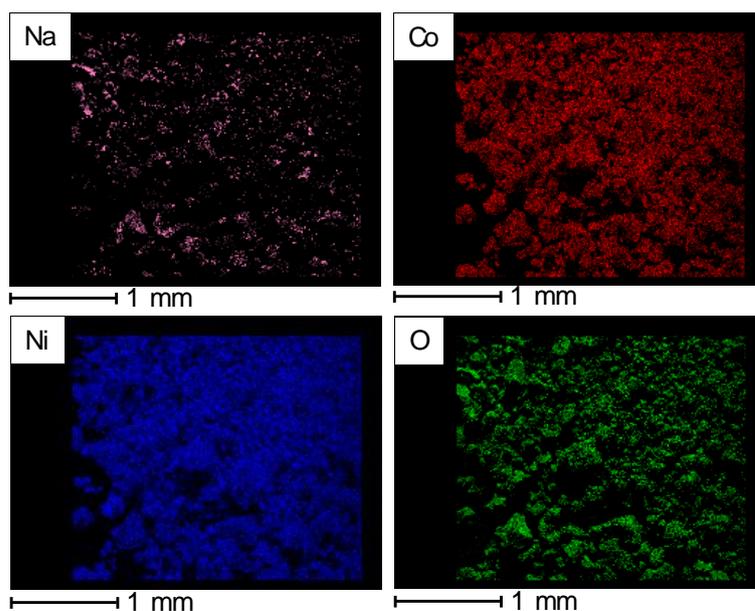
The SEM results about the powder samples are shown in Figure 3.



**Figure 3.** SEM images: (a) NiCo\_1, (b) NiCo\_2, (c) NiCo\_W10%, (d) NiCo\_W30%, and (e) NiCoAl\_C.

The catalysts have the following different structures: (a) NiCo\_1 exhibits a granular structure, while (b) NiCo\_2 shows a dusty structure. The samples prepared with the 10% (c) and 30% (d) of alumina have a similar structure, different from the coprecipitate catalyst (e), which shows a more compact structure.

All the samples have an excellent distribution of the species, and, from the EDX images relative to the sample NiCo\_2 (Figure 4), it is possible to observe the presence of sodium (Na) to indicate that during the preparation phase, the washing of the resultant precipitate did not eliminate the  $\text{Na}_2\text{CO}_3$  species used as a precipitating agent.



**Figure 4.** EDX mapping relative to sample NiCo\_2.

In Figure 5, the SEM/EDX result about the structured sample, namely, NiCoAl\_C\_SiC, is shown. The images highlight a homogeneous distribution of the slurry on the monolithic surface.

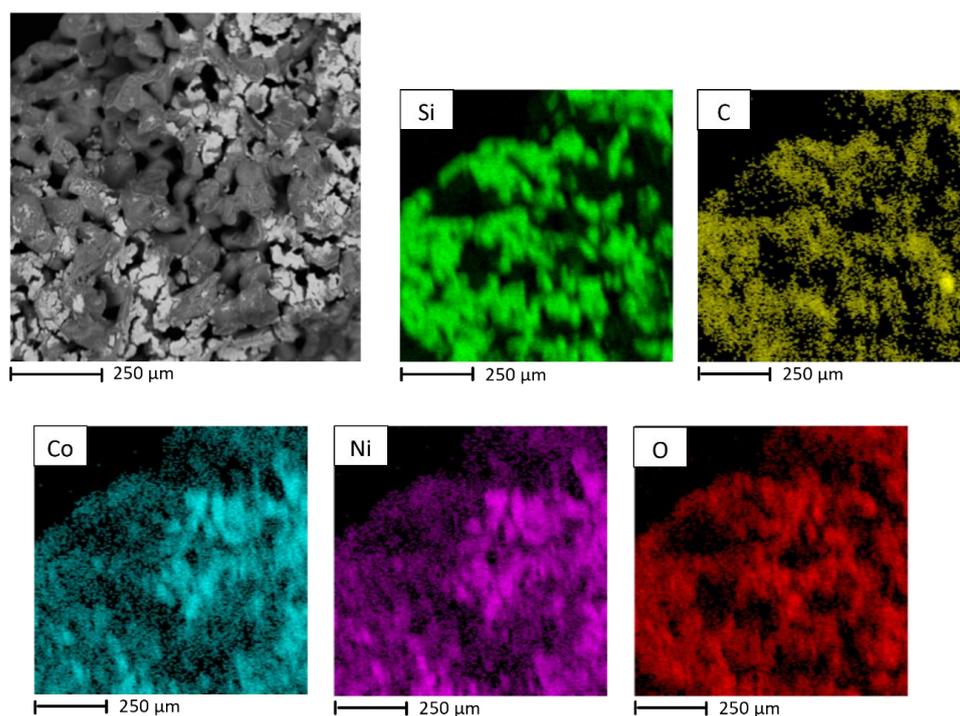


Figure 5. SEM/EDX images relative to sample NiCoAl\_C\_SiC.

In Figure 6, the XRD diffractograms show that NiCo\_1 and NiCo\_2 samples are characterized by a spinel structure where  $\text{Ni}^{2+}$  substitutes  $\text{Co}^{2+}$  to form  $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$  oxide, according to literature data [3]. The NiCoAl\_C sample exhibits an XRD pattern typical of a trimetallic spinel structure [32], where the peaks seem to be slightly shifted to higher angles compared to the previous samples. This shift could be attributed to the change in lattice parameters due to the incorporation of Al into the oxide structure [33].

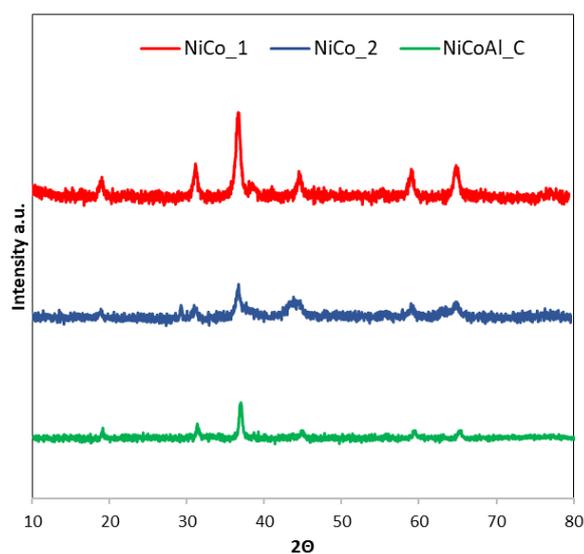
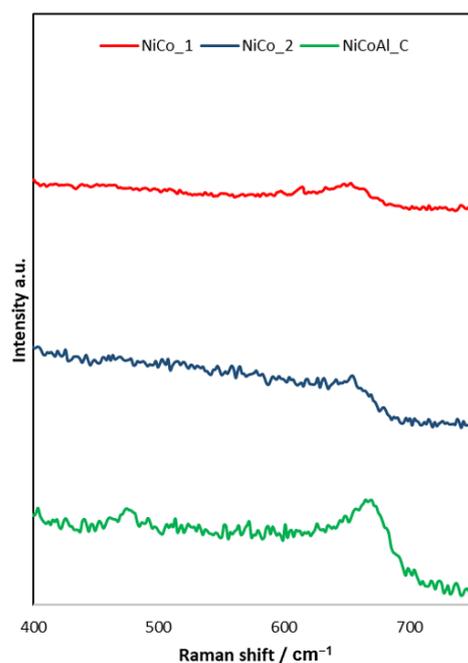


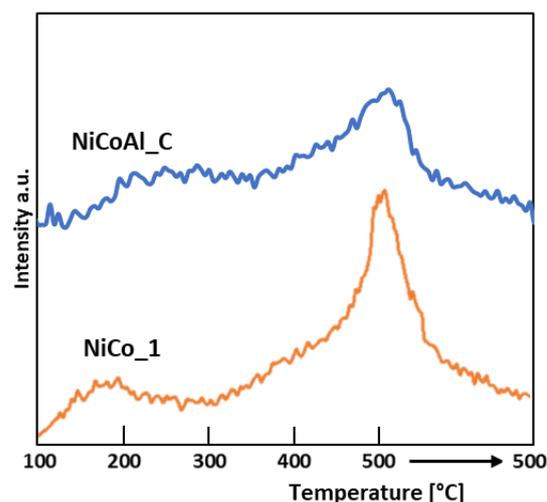
Figure 6. XRD patterns of NiCo\_1, NiCo\_2, NiCoAl\_C samples.

The Raman spectra of the samples (Figure 7) confirm the composition and the structure already shown by XRD results [34–36]. In particular, NiCoAl\_C and the NiCo-based catalysts exhibit Raman spectra with similar features highlighting the characteristic peaks of NiCo trimetallic and bimetallic spinel oxide structures, respectively [37].



**Figure 7.** Raman spectrum of NiCo\_1, NiCo\_2, NiCoAl\_C samples.

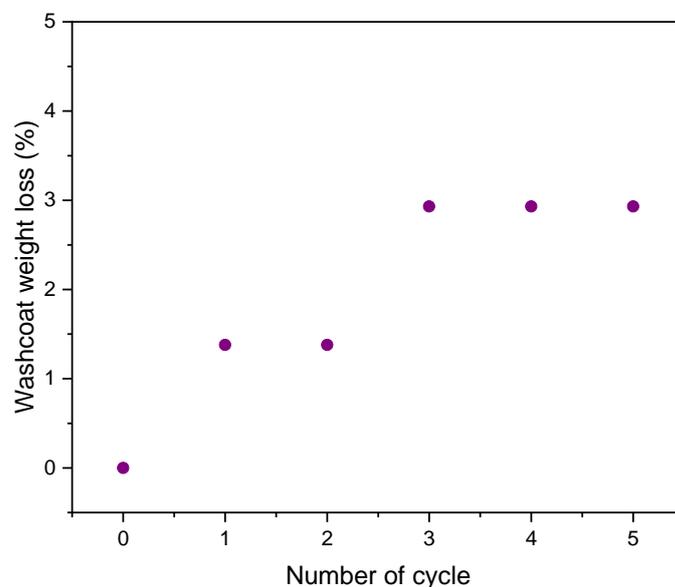
TPD experimental tests have been performed over NiCoAl\_C and NiCo\_1 by using N<sub>2</sub>O (Figure 8). The results have shown that the following two peaks relevant to O<sub>2</sub> desorption are visible for both samples: the first peak occurs at a temperature between 100 °C and 400 °C and is ascribable to the desorption of weaker chemisorbed oxygen; the second peak obtained over 400 °C is attributable to the oxygen desorption due to the thermal effect [22]. Furthermore, the aluminum-modified catalyst exhibits a lower amount of desorbed oxygen compared to the sample without alumina, giving an indication about the catalytic behavior of the samples. After the interaction between the N<sub>2</sub>O and the catalysts, a certain amount of oxygen remains adsorbed on the surface. The lower oxygen desorption obtained with the NiCoAl\_C is related to a smaller number of active sites occupied by oxygen, explaining the major catalytic activity of the catalyst. This result is in line with the reaction mechanisms as follows: the N<sub>2</sub>O molecule adsorbs on the surface of the catalyst, leading to the breakage of the N–O bond, giving gaseous N<sub>2</sub>, then two adsorbed oxygen atoms react with each other according to the Langmuir–Hinshelwood mechanism or one adsorbed oxygen atom reacts with the gaseous N<sub>2</sub>O molecule to produce O<sub>2</sub>, following the Eley–Rideal mechanism [9].



**Figure 8.** N<sub>2</sub>O-TPD over NiCo\_1 and NiCoAl\_C catalysts.

Figure 9 shows the results obtained from the ultrasound adherence test performed on the structured catalyst. The percentage weight loss has been calculated weighted the sample after each cycle of bath, according to Equation (2).

$$\text{Weight loss} = \frac{\text{Initial mass} - \text{final mass}}{\text{Initial washcoat mass}} \quad (2)$$



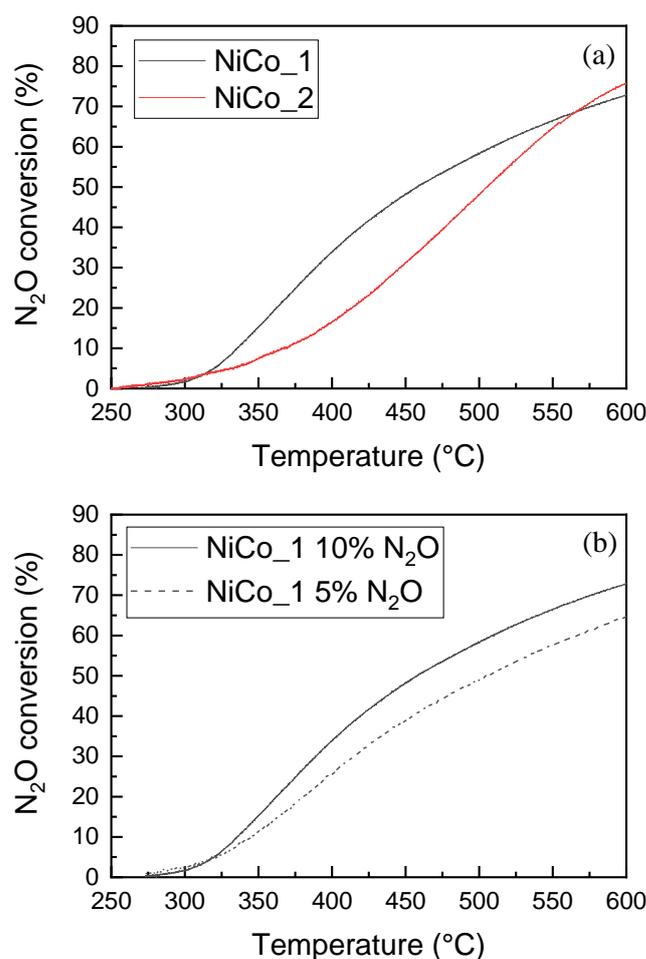
**Figure 9.** Ultrasound adhesion test performed on NiCoAl\_C\_SiC structured sample.

The total number of cycles was established considering the results obtained during the tests as follows: in fact, when the weight variation between two consecutive cycles is null, the test can be considered concluded. The NiCoAl\_C\_SiC sample subjected to the ultrasound stress demonstrated that the chemical support adhered with excellent stability to the SiC carrier; indeed, after 5 cycles, the total weight loss is about 3%, a value lower than that observed in literature for similarly structured catalysts.

## 2.2. Ni-Co\_Based Catalysts Activity Test

### 2.2.1. Powder Catalysts

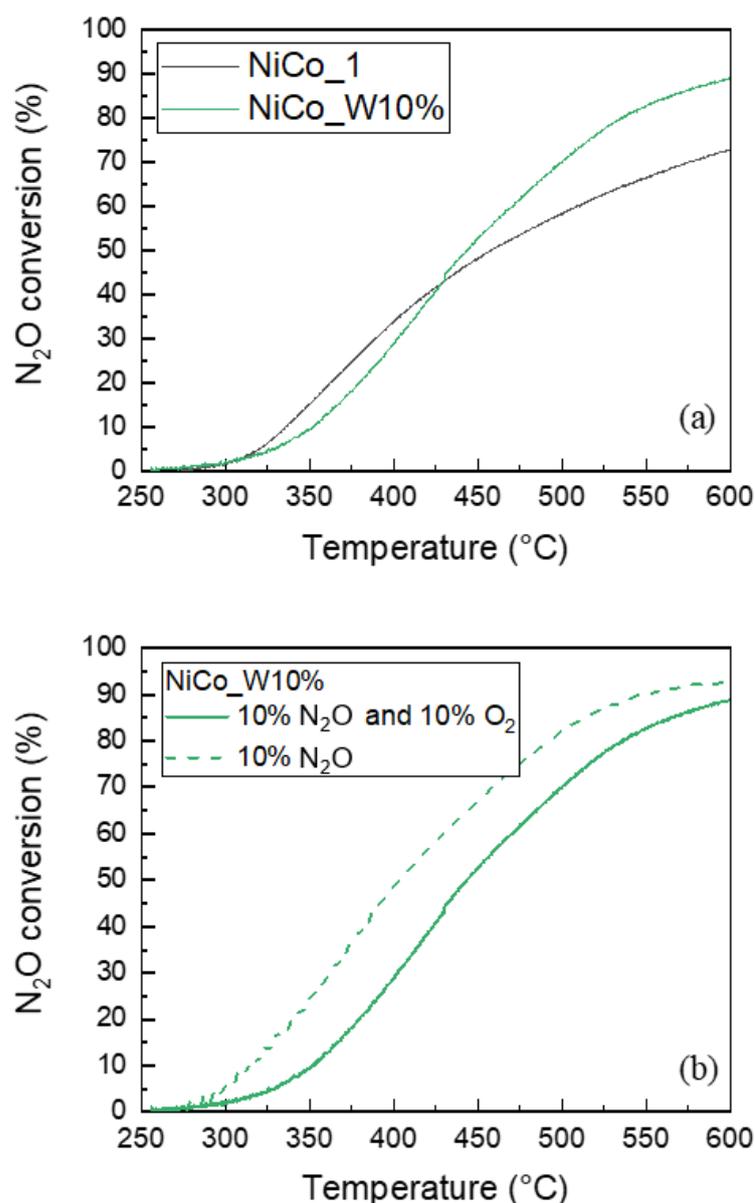
At first, the N<sub>2</sub>O catalytic decomposition was evaluated over the NiCo samples in order to identify the most attractive precipitating agent. This preliminary screening was performed using a GHSV of 15,000 h<sup>-1</sup>, in the presence of oxygen, and in the presence of two different feed streams, respectively containing 10 vol% and 5 vol% of N<sub>2</sub>O. The outcomes, in terms of N<sub>2</sub>O conversion, are reported in Figure 10. From the trend in conversion, it is clear that the precipitating agent used during the preparation procedure had a strong influence on the catalytic performances of the samples. This can be adequately ascribed to the change in the textural properties of the samples. In particular, the sample NiCo\_1, which exhibited the best N<sub>2</sub>O conversion over the whole temperature range, was the one having the highest both SSA value and pore volume. The evaluation of the activity of the best sample, namely, NiCo\_1, was also performed considering the effect of N<sub>2</sub>O content. In particular, a feeding mixture containing 5 vol% N<sub>2</sub>O and 5 vol% O<sub>2</sub> in Ar, keeping unchanged the other operating conditions, was fed. The outcomes, reported in Figure 10b, showed that the change in N<sub>2</sub>O concentration led to a worsening in the catalytic performances. This suggests that NiCo\_1 can be suitable for the treatment of high N<sub>2</sub>O concentration streams. Therefore, the ammonia solution was selected as a precipitating agent, and therefore NiCo\_1 was selected as the best option to efficiently conduct the catalytic N<sub>2</sub>O decomposition, and further modifications and experimental evaluations were performed employing this sample as a starting point.



**Figure 10.** Catalytic performances of NiCo samples. Operating conditions: GHSV = 15,000 h<sup>-1</sup>, 1 atm, (a) N<sub>2</sub>O and O<sub>2</sub> 10 vol% in Ar; (b) N<sub>2</sub>O and O<sub>2</sub> 5 vol% and 10 vol% in Ar, GHSV = 15,000 h<sup>-1</sup>.

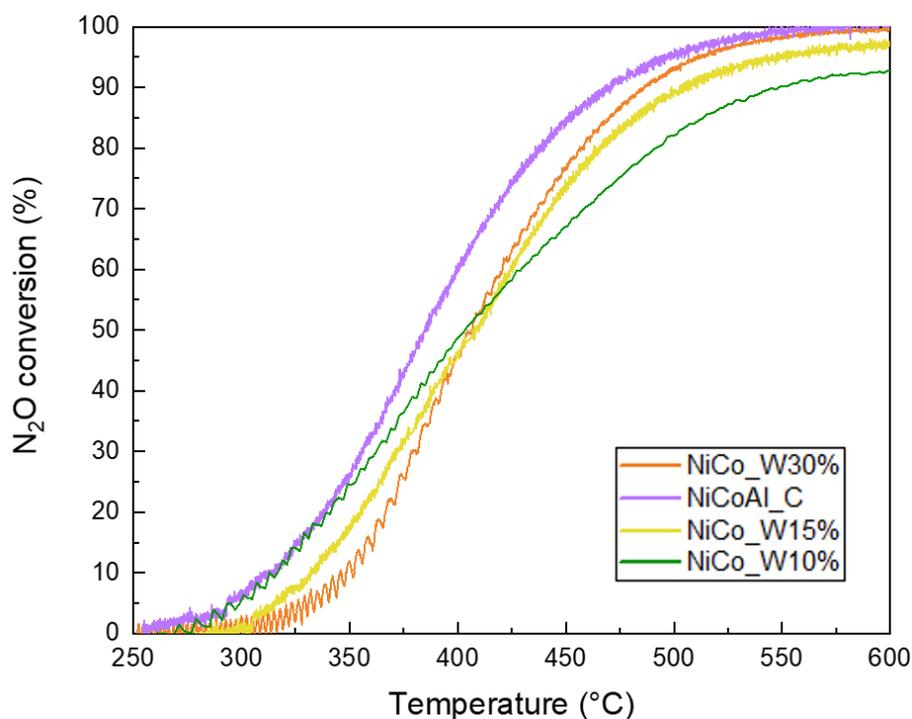
#### Effect of Alumina on the Catalytic Activity

To the aim of selecting a formulation that could be suitable for the preparation of structured catalysts, different loadings of alumina were added to the NiCo\_1 sample, following two different preparation approaches, the washcoat slurry preparation, and the coprecipitation. The effect of alumina on the catalytic activity performance was first investigated in the previously adopted operating conditions, comparing the NiCo\_1 catalyst with the sample modified with washcoat (having an overall alumina loading of 10 wt%) by feeding a stream with 10 vol% of N<sub>2</sub>O. The results, shown in Figure 11a, highlighted that the presence of alumina did not determine particular modifications at low temperatures but had a marked influence above 450 °C. Therefore, the addition of alumina is feasible and can also enhance the catalytic performances at high temperatures; indeed, it is well known that alumina leads to more stable catalysts with better dispersion of the active phase [29]. For this reason, different studies about N<sub>2</sub>O decomposition over alumina-supported catalysts have been reported in the literature [38,39]. Since the molecular oxygen limits the N<sub>2</sub>O decomposition causing the poisoning of the catalyst, catalytic activity tests in the presence and absence of O<sub>2</sub> on the NiCo\_W10% sample were carried out, and the results are reported in Figure 11b. As shown, the presence of oxygen inhibits the decomposition reaction, according to scientific literature data. The maximum conversions at 600 °C are 89% and 92%, respectively, in the presence and absence of oxygen. It can be expected that the inhibitory effect of oxygen is strongly correlated with the competitive adsorption of molecular oxygen on active sites, hindering the decomposition of N<sub>2</sub>O [3].



**Figure 11.** (a) Effect of alumina (10 wt%) addition (reagent mixture: 10 vol% N<sub>2</sub>O, 10 vol% O<sub>2</sub> in Ar) and (b) effect of O<sub>2</sub> presence in the feed gas. Operating conditions: GHSV = 15,000 h<sup>-1</sup>, 1 atm.

Figure 12 displays the comparison of the catalytic performances for the four alumina-based catalysts. The catalyst containing 10 wt% and 15 wt% of alumina showed the lowest N<sub>2</sub>O conversion values. The other two catalysts approached a total N<sub>2</sub>O conversion at 600 °C. Furthermore, it is possible to highlight that the increase in alumina loading enhanced the catalytic performances at high temperatures while there was a worsening in activity at low temperatures, which is coherent with the differences observed between NiCo\_W10% and NiCo\_1 samples. The change in the preparation method adopted, namely, the coprecipitation of the precursor salts, in the case of the NiCoAl\_C sample allowed to obtain enhanced conversions both at high and low temperatures, compared to the washcoat-containing sample NiCo\_WC15%, characterized by the same content of alumina. The enhancement in activity might be addressed by the incorporation of the alumina in the lattice, which leads to a distortion of the cells [33]. The different chemical structure influences the catalytic activity.



**Figure 12.** Activity comparison for the alumina-containing formulations. Operating conditions: GHSV = 15,000 h<sup>-1</sup>, 1 atm, reagent mixture: 10 vol% N<sub>2</sub>O in Ar.

Furthermore, the catalytic activity test performed on all the samples exhibited the total selectivity of the system toward N<sub>2</sub> and O<sub>2</sub>. The results confirm that the N<sub>2</sub>O is totally converted without any subproducts, such as NO and NO<sub>2</sub>.

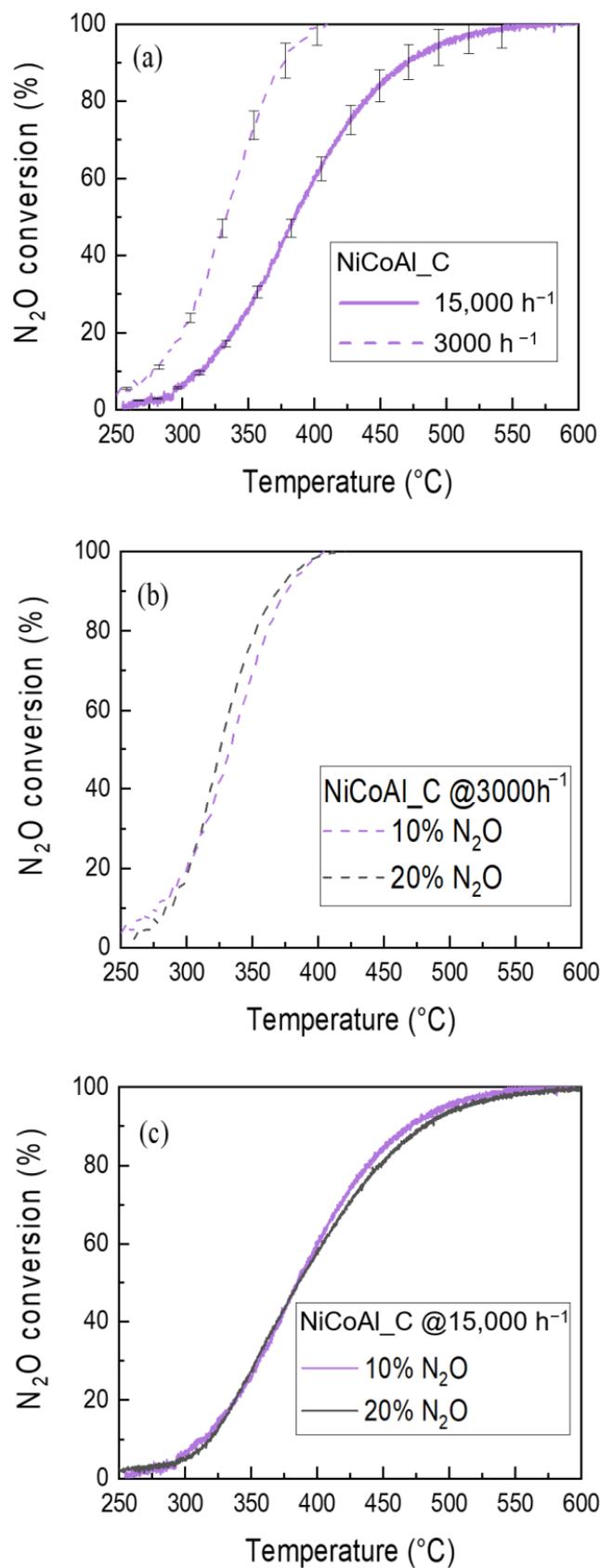
#### Effect of Space Velocity and N<sub>2</sub>O Concentration

The most performant catalyst (NiCoAl\_C) was tested under different GHSV conditions (15,000 h<sup>-1</sup> and 3000 h<sup>-1</sup>) and at different N<sub>2</sub>O concentrations, in order to investigate the effect of these parameters on the catalytic performances.

Figure 13a shows the results obtained in terms of N<sub>2</sub>O conversion as follows: as expected, the lower the GHSV was, the higher the reached conversion was, whatever the operating temperature. Employing a GHSV equal to 3000 h<sup>-1</sup>, the temperature necessary to reach a total N<sub>2</sub>O conversion was lowered to 420 °C, approximately 180 °C below the temperature that was necessary using the higher GHSV value. The experimental tests have been repeated three times, and the mean deviation has been added to the figure. This was an important achievement; indeed, carrying out the N<sub>2</sub>O decomposition reaction at a low temperature means enormous energy savings and easy management of heat within the system.

Interesting results were obtained from catalytic activity tests carried out at different N<sub>2</sub>O compositions, as follows: 10 vol% of N<sub>2</sub>O in Ar and 20 vol% of N<sub>2</sub>O in Ar. The tests were performed at both low and high GHSV and are reported in Figure 13b,c for 3000 h<sup>-1</sup> and 15,000 h<sup>-1</sup>, respectively. It is possible to note that if the treated stream contains up to 20 vol% of N<sub>2</sub>O, the increase in N<sub>2</sub>O content did not negatively influence the catalytic activity since the same conversion results were obtained. This important result indicates that it is possible to perform the catalytic N<sub>2</sub>O decomposition at moderately low temperatures (about 420 °C) when treating highly N<sub>2</sub>O-concentrated gaseous streams with contents up to 20 vol%.

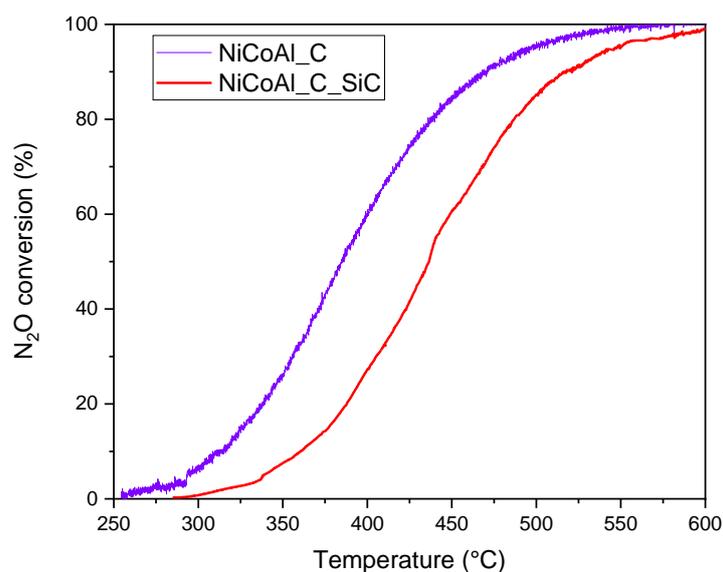
It is important to highlight that in all the catalytic activity tests, the selectivity of the catalysts was total for N<sub>2</sub> and O<sub>2</sub>, with no by-product formation.



**Figure 13.** (a) GHSV effect in catalytic N<sub>2</sub>O decomposition over NiCoAl\_C catalyst (reagent mixture: 20 vol% N<sub>2</sub>O in Ar); (b) effect of N<sub>2</sub>O concentration at GHSV = 3000 h<sup>-1</sup>, 1 atm; (c) effect of N<sub>2</sub>O concentration at GHSV = 15,000 h<sup>-1</sup>, 1 atm.

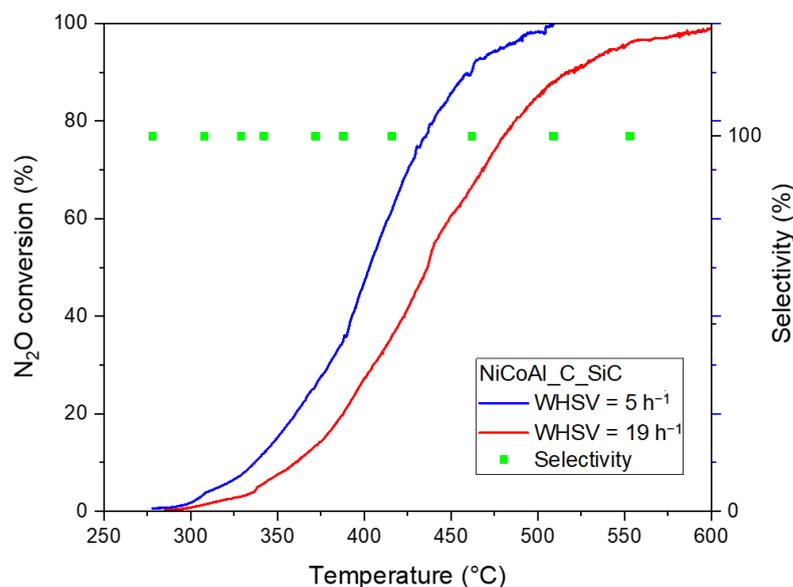
### 2.2.2. Structured Catalyst

In the following paragraph, it will be shown the effect of the SiC monolith on the catalytic performance. In Figure 14, a comparison between the powder and structured samples is illustrated. Although the NiCoAl\_C\_SiC sample exhibits a slight worsening of the catalytic performance at the same operating condition used for the powder, it is possible to note that the employment of a structured carrier, thus a more practical configuration, allows reaching an N<sub>2</sub>O conversion of 99% at 600 °C.



**Figure 14.** Activity comparison between powder catalyst and structured catalyst. Operating conditions: WHSV = 19 h<sup>-1</sup>, 1 atm, reagent mixture: 10 vol% N<sub>2</sub>O in Ar.

In order to identify the optimal operating conditions to reach a total N<sub>2</sub>O conversion, the structured sample was tested at lower WHSV and by using a feeding mixture containing a higher concentration of N<sub>2</sub>O. The results (Figure 15) highlighted that the increase in N<sub>2</sub>O concentration from 10 vol% to 20 vol%, keeping the space velocity unchanged, does not lead to significant variation of the conversion. Instead, decreasing the WHSV until 5 h<sup>-1</sup>, the following promising result was achieved: total conversion and selectivity were reached at 510 °C.



**Figure 15.** WHSV effect in catalytic N<sub>2</sub>O decomposition over NiCoAl\_C\_SiC structured catalyst (reagent mixture: 20 vol% N<sub>2</sub>O in Ar, 1 atm).

### 3. Materials and Methods

#### 3.1. Catalysts Preparation

In the first phase of the work, two nickel-cobalt powder catalysts were prepared by using the co-precipitation procedure, using two different precipitating agents. To obtain the samples, the following steps were performed: (i) the selected precursor salts were added to known amount of water; (ii) the solution was stirred at room temperature for about 5 min; (iii) a basifying substance was added until the pH of solution reached 9. For all the prepared samples the number of precursor salts was calculated to obtain a Ni/Co ratio equal to 0.3, literature reference value [3], and nickel nitrate and cobalt nitrate were employed as Ni and Co precursors. To achieve precipitation, a 32 vol% NH<sub>3</sub> aqueous solution was employed for NiCo\_1 sample and Na<sub>2</sub>CO<sub>3</sub>, aq 15 wt% for NiCo\_2, and the solution was left under stirring for 3 h, then the resultant precipitate was filtered through a filter paper, by using a vacuum pump, and washed until the filtrate was neutral. The differences in preparation are given in Table 2.

**Table 2.** Resume of the powder samples preparation techniques.

Sample	Preparation Method	Precursor Salts	Basic Solution
NiCo_1	Co-precipitation, filtration, and wash	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	NH <sub>3, aq</sub> (32 vol%)
NiCo_2	Co-precipitation, filtration, and wash	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3, aq</sub> (15 wt%)
NiCoAl_C	Co-precipitation, filtration, and wash	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O Al(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	NH <sub>3, aq</sub> (32 vol%)
NiCo_W10%	Direct addition of NiCo_1 to an alumina-based washcoat Al <sub>2</sub> O <sub>3</sub> = 10 wt%		NH <sub>3, aq</sub> (32 vol%)
NiCo_W15%	Direct addition of NiCo_1 to an alumina-based washcoat Al <sub>2</sub> O <sub>3</sub> = 15 wt%		NH <sub>3, aq</sub> (32 vol%)
NiCo_W30%	Direct addition of NiCo_1 to an alumina-based washcoat Al <sub>2</sub> O <sub>3</sub> = 30 wt%		NH <sub>3, aq</sub> (32 vol%)

Aiming at the development of the structured catalyst, three washcoat slurries were prepared by mixing the most performing formulation (NiCo\_1) with an alumina-based colloidal solution, in three different NiCo/alumina ratios (listed in Table 2), in order to investigate the alumina effect on the catalytic activity. The preparation procedure was as follows.

Water and methylcellulose (1 wt%) were mixed up on a magnetic stirrer at room temperature. When the solution was homogeneous, the pseudoboehmite was added, in an amount such as to obtain the desired ratio with NiCo, and an aqueous solution of ammonia (32 vol%) was added dropwise until the pH of solution reached 9, to obtain a colloidal dispersion. Finally, the catalyst (NiCo\_1) was added to the solution, kept under stirring for 24 h. The obtained slurries were heated under stirring until drying, the resulting materials ground and calcined to obtain three powder catalysts.

A fourth alumina-based sample catalyst (NiCoAl\_C) was obtained by co-precipitating from an aqueous solution of cobalt nitrate hexahydrate, nickel nitrate hexahydrate, and aluminum nitrate hexahydrate with a mass ratio of 3:3:1 (Co:Ni:Al nitrates). The solution was stirred at room temperature for five minutes, then an aqueous solution of ammonia (32 vol%) was added dropwise until the pH of the solution reached 9. A part of the slurry was filtered through a filter paper, under vacuum, and washed until the filtrate was neutral, to obtain a powder sample.

The six samples obtained were dried overnight at 120 °C (10 °C/min heating rate) in an oven and calcined at 600 °C in air for 2 h (10 °C/min heating rate).

All the catalysts were sieved in order to reach a granulometry of 180–355 µm.

The structured catalyst sample (NiCoAl\_C\_SiC) was prepared by using a SiC 7 cm long honeycomb monolith as carrier with a square section (1.5 cm × 1.5 cm) composed of 49 through channels. Before depositing the active species, the SiC carrier was pre-treated in air at 1000 °C for 48 h to have a SiO<sub>2</sub> layer on the surface that enhances the slurry adhesion [32]. The most promising Al<sub>2</sub>O<sub>3</sub>-modified catalytic formulation (NiCoAl\_C) was deposited on the monolith by means of dip-coating method as follows: the carrier was dipped in the same slurry used for the NiCoAl\_C powder sample preparation, for 20 min, drained to remove the excess, and dried in an oven at 120 °C. The structured sample was calcinated at 600 °C for 3 h (10 °C/min heating rate) to reach chemical and physical stabilization. This procedure was repeated until the mass deposited was about 10% of the total sample weight, so that the catalyst amount deposited was equal to that used for the activity test on the powder sample.

### 3.2. Catalysts Characterization

The prepared catalysts were characterized by means of different chemical-physical and analytical techniques. The optical analysis was performed by means of a Scanning Electron Microscope (SEM) Philips Mod.XL30 (Amsterdam, the Netherlands), coupled to an Energy Dispersive X-ray Spectrometer (EDS) Oxford (Oxford Instruments, Abingdon, UK). Specific surface areas (SSA) were obtained through N<sub>2</sub> adsorption at −196 °C, by means of NOVAtouch sorptometer (Anton Paar, Graz, Austria), applying BET method. The structural features were evaluated with a Raman spectroscopy using an inVia Raman Microscope (Renishaw, Wotton-under-Edge, UK), equipped with a 514 nm Ar ion laser operating at 25 mW.

The X-ray fluorescence was carried out on the catalysts to evaluate the chemical composition of the samples, by means of the Thermo-Scientific QUANT'X (Thermo Fisher Scientific Inc., Waltham, MA, USA), energy dispersive XRF. The X-ray diffraction (XRD) was performed for the identification and qualitative determination of the crystalline phases in the powder samples. The X-ray diffraction measurements were carried out by means of a Bruker D2 diffractometer (Billerica, MA, USA), designed according to the Bragg geometry. Aiming at the evaluation of the coating layer resistance to a strong mechanical stress, ultrasound adherence test was performed on the structured sample by means of an ultrasonic bath [40,41]. In each cycle of bath, the sample was subjected to the ultrasonic stress for 5 min at room temperature, with a power of 60% compared to the maximum.

The Temperature Programmed Desorption (TPD) of N<sub>2</sub>O experimental tests have been performed on two catalytic samples, namely, NiCo\_1 and NiCoAl\_C. The samples were preliminarily heated in 20 vol% N<sub>2</sub>O stream, balanced with Ar, up to 500 °C with a heating rate of 10 °C/min, and then cooled up to room temperature with the same stream. After that, the samples were heated in Ar flow up to 500 °C for detecting the desorbed species.

### 3.3. Experimental Tests

The experiments of catalytic N<sub>2</sub>O decomposition were carried out in a fixed bed configuration. A tubular reactor (17 mm ID and 320 mm long) in AISI 310 stainless steel was employed and located in horizontal position in a furnace for temperature control. This is constituted of three independent heating zones, each with a dedicated K-type thermocouple, therefore optimal temperature control is achieved. The selected amount of catalyst was loaded in the middle section of the reactor, held between two quartz wool disks, while the monolith structured catalyst is placed in the reactor wrapped in a quartz wool layer to avoid bypass phenomena. Two K-type thermocouples were positioned in correspondence with the inlet and outlet section of the catalytic bed, in order to ensure the monitoring of the temperature within the system. The feed stream was adjusted via a mass flow controllers setup. The product stream was analyzed by means of a QGA mass

spectrometer (Hiden Analytical, UK); for a correct quantification of the species, mass-to-charge ratios of 28, 30, 32, 40, 44, 46 (respectively corresponding to nitrogen, nitric oxide, oxygen, argon, nitrous oxide, and nitrogen dioxide) were considered for the analysis.

The catalytic activity tests were carried out over a fixed mass of powder catalyst (1.5 g) and in presence of different gaseous reactant mixtures, using argon as inert gas. The activity of the samples was investigated at different gas hourly space velocity (GHSV) values, varying the inlet concentration of N<sub>2</sub>O between 5 and 20 vol% and in presence/absence of oxygen, in 1:1 molar ratio with N<sub>2</sub>O. The performance of the structured catalyst was investigated in two different weight hourly space velocity (WHSV) values, calculated with respect to the catalyst amount deposited in order to assure the same contact time of the powder configuration for making the results comparable, and by using two inlet concentration of N<sub>2</sub>O corresponding to 10 and 20 vol%. The performances of the catalytic systems were evaluated in terms of the N<sub>2</sub>O conversion ( $X_{N_2O}$ ) and selectivity to N<sub>2</sub> ( $S_{N_2}$ ). The space velocities GHSV and WHSV, used for the tests with powders and structured catalysts, respectively, were defined as Equations (3) and (4), while N<sub>2</sub>O conversion and selectivity to N<sub>2</sub> were defined respectively as Equations (5) and (6), where  $F_i$  indicates the molar flow rate of the  $i$ -species, and  $Q$  is the total volumetric flow rate.

$$GHSV = \frac{Q}{V_{cat}} \quad (3)$$

$$WHSV = \frac{\dot{W}}{g_{cat}} \quad (4)$$

$$X_{N_2O} = \frac{F_{N_2O,in} - F_{N_2O,out}}{F_{N_2O,in}} \times 100\% \quad (5)$$

$$S_{N_2} = \frac{F_{N_2,out}}{F_{N_2,out} + F_{NO_2,out} + F_{NO,out}} \times 100\% \quad (6)$$

The molar flow rate of the components in the outlet gas stream was calculated starting from the corresponding concentrations acquired by the mass spectrometer (as previously described) and by calculating, through the mass balance, the correcting factor to be applied, since this reaction proceeds with a change in the number of moles.

The catalysts were pre-treated by sending an argon stream while heating the system up to 600 °C (10 °C/min heating rate) to remove any impurities adsorbed on the surface of the sample. The experimental tests on the catalysts were carried out in the temperature range 250–650 °C by using a heating rate of 5 °C/min.

#### 4. Conclusions

In the present work, two different nickel-cobalt mixed oxides (Ni<sub>x</sub>Co<sub>1-x</sub>Co<sub>2</sub>O<sub>4</sub>), active for the N<sub>2</sub>O decomposition reaction, were prepared by using ammonia and sodium carbonate as precipitating agents. The results retrieved for the two samples (NiCo\_1 and NiCo\_2) highlight how the type of precipitating agent can lead to different textural properties and chemical structures in the catalyst and, consequently, to different catalytic activity. Since the sample NiCo\_1 exhibited the best N<sub>2</sub>O conversion over the whole temperature range, it was employed to prepare catalytic alumina-based formulations with the aim of designing a washcoat slurry to use in the preparation of a structured catalyst for the N<sub>2</sub>O decomposition. For reference, a co-precipitated NiCoAl-based catalyst was prepared with the aim of incorporating the alumina into the catalyst structure. The performance of the latter was compared to that of the powder samples, obtained by drying and calcining the three washcoat slurries. The NiCoAl\_C sample exhibited the best catalytic performance with a total conversion at 600 °C. Therefore, it was tested under different GHSV conditions (15,000 h<sup>-1</sup> and 3000 h<sup>-1</sup>) and at different N<sub>2</sub>O concentrations in order to optimize the operating conditions. Employing a GHSV equal to 3000 h<sup>-1</sup>, a temperature of 420 °C was needed for obtaining a 100% N<sub>2</sub>O conversion, with a total selectivity of N<sub>2</sub>. Moreover, by

passing from 10 vol% to 20 vol% of N<sub>2</sub>O, the increase in N<sub>2</sub>O content did not negatively influence the catalytic activity, in terms of both conversion and selectivity. In conclusion, a structured sample was obtained by depositing the NiCoAl\_C catalytic formulation on a SiC honeycomb monolith. The N<sub>2</sub>O decomposition was performed with successful results over the structured catalyst by passing a feeding mixture containing 20 vol% of N<sub>2</sub>O as follows: total conversion and selectivity were reached at 510 °C. The results obtained with this study represent the following important achievement: the decomposition process of N<sub>2</sub>O contained in high concentrations (up to 20 vol%) can be carried out with good performance over NiCoAl-based catalysts, at relatively low temperatures. In particular, the use of a carrier with high thermal conductivity, such as SiC, may result in a more homogeneous temperature distribution inside the catalytic bed, with beneficial effects on the catalytic activity. Therefore, the effective catalytic decomposition of gaseous streams concentrated in N<sub>2</sub>O may be obtained also by using structured catalysts, with consequently beneficial effects in terms of the compactness of the reactor and thermal management, as well as resulting in a huge energy savings. Furthermore, the employment of a structured catalyst allows the performance of the process by using a more practical solution suitable for industrial applications.

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