Selective catalytic oxidation of NH_3 into N_2 during biogas combustion over 2 wt%PdO/5 wt%CuO/ $\gamma\text{-Al}_2\text{O}_3$

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Abstract

This work consists in the study of catalysts likely to present a good activity in the combustion of the landfill biogas for its valorization and a high performance in the selective catalytic oxidation of NH_3 to N_2 . In this study, biogas catalytic combustion was investigated on 2 wt%PdO/5 wt%CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. This catalyst was prepared by wet impregnation than the catalytic reactivity was tested under atmospheric pressure using the following mixture: CH_4 (1 vol%), CO_2 (0.6 vol%), O_2 (4 vol%), H_2O (0.1 vol%), 1000 ppm NH_3 and He with a total flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ and compared with 2 wt%PdO/ Al_2O_3 and 5 wt%CuO/ Al_2O_3 . Furthermore, these different catalysts were characterized by inductively coupled plasma atomic emission spectroscopy, specific surface area analysis (BET), X-ray diffraction, diffuse reflectance spectroscopy and H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$). This study showed that 2 wt%PdO/5 wt%CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalyst exhibited a better performance towards the selective catalytic oxidation of NH_3 into N_2 compared to the other catalysts with a methane conversion corresponding to the best compromise in between.

Keywords Biogas · Selective catalytic oxidation (SCO) · Ammonia · Nitrogen · Palladium · Copper

1 Introduction

Biogas is a gas mixture composed essentially of methane and carbon dioxide produced by anaerobic digestion of waste biomass, household waste and ordinary industrial waste [1, 2]. Landfill biogas is an attractive energy resource, although it is limited in size and over time. Untreated, this biogas contributes to the greenhouse effect due to its high methane content. The average composition of biogas is: 50% CH_4 , 30% CO_2 , 14% N_2 , 3% H_2O , 2% O_2 , 1000 ppm NH_3 . It may contains sulfur compounds (100 ppm H_2S), chlorinated compounds (100 ppm) and volatile organic compounds (100 ppm) [1, 2]. Moreover, the biogas composition is not stable. It depends on several parameters such as the size of landfill sites, type of waste, pH, temperature and humidity. Furthermore, methane has a density of 0.55,

which is lighter than air, allowing it to escape from the landfill and to spread into the surrounding area [3–5].

Since biogas contains ammonia, selective catalytic oxidation (SCO) from NH_3 to N_2 at low temperature is attractive to avoid the emissions of NO_x during the biogas combustion. According to the literature, the supported palladium catalysts are the most efficient for the catalytic combustion of methane [6, 7]. Therefore Pd/ Al_2O_3 has been chosen as reference catalyst, but this catalyst has never been tested under a biogas mixture containing CH_4/CO_2 ratio with ammonia. Furthermore, such catalyst has to be efficient during the SCO of NH_3 into N_2 rather than obtaining NO_x . According to the literature, Chmielarz and al classified the transition metal oxides according to their activities in the oxidation of ammonia and their selectivities into N_2 [8]. According to them, NH_3 conversion decreases in the

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following order: $\text{Cu} > \text{Co} > \text{Ni} > \text{Fe}$. Moreover the N_2 selectivity increases as following: $\text{Co} < \text{Cu} < \text{Ni} < \text{Fe}$. Between the different catalysts, $\text{CuO}/\text{Al}_2\text{O}_3$ was the most efficient for the oxidation of NH_3 into N_2 [8]. To better understand, the authors played on the concentration of copper oxide (5, 10, 20 wt%) during the SCO of NH_3 into N_2 . They discovered that the copper concentration has no effect on ammonia conversion but has an effect on the selectivity into N_2 . Also they noticed that the selectivity decreases with increasing temperature that is why it is more favorable to realize such reaction at low temperature ($\approx 500^\circ\text{C}$). Besides, they found that for catalysts with high metal loading (10, 20 wt%), the selectivity decreases sharply with increasing temperature from 200 to 700°C . Also, they suggested that in order to obtain a good selectivity into N_2 , it is necessary to have strong ion-O bonds with oxygen less labile and to have a low concentration of copper (5 wt%) [8]. Also other authors studied the selective catalytic oxidation of NH_3 into N_2 on copper oxide at low temperature [9–14]. Also, they suggested that in order to obtain a good selectivity into N_2 , it is necessary to have strong ion-O bonds with oxygen less labile [15–18].

Since the PdO was the best active phase in methane combustion and CuO the best active phase in selective catalytic oxidation of NH_3 into N_2 . In order to highlight the importance of selective catalytic oxidation of NH_3 to N_2 during the catalytic combustion of biogas at low temperature and to reduce NO_x emissions, this work consists in the study of PdO/CuO/ Al_2O_3 catalyst likely to present a good activity in the combustion of the biogas with a low NO_x emission since such catalyst might be the best compromise between the Pd/ Al_2O_3 and CuO/ Al_2O_3 . Thus, the aim of this work is to (1) evaluate the performance in the catalytic combustion of biogas and (2) to compare its catalytic performances with PdO/ Al_2O_3 and CuO/ Al_2O_3 .

2 Materials and methods

2.1 Catalyst preparation

Alumina used in this study was $\gamma\text{-Al}_2\text{O}_3$ purchased from Rhodia (SPH 569; purity 99.8%) with a specific surface area of $140\text{ m}^2\text{ g}^{-1}$. A 2 wt% PdO/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was prepared by wet impregnation using $\gamma\text{-Al}_2\text{O}_3$ and $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Alfa Aesar, Pd 39.95%) as a precursor dissolved in water. After drying overnight at 120°C , the catalyst was calcined at 500°C under O_2 for 4 h. Also, 5 wt% CuO supported on γ -alumina was also prepared using the same procedure with $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ from Sigma Aldrich (purity 99%). The water was evaporated under reduced pressure at 60°C . After drying at 120°C , the solid was calcined at 500°C under air during 13 h. Although, the

catalyst 2 wt%PdO/5 wt%CuO/ $\gamma\text{-Al}_2\text{O}_3$ was also prepared by wet impregnation using the following procedure: An adequate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ precursor was dissolved in excess distilled water at 60°C before adding the required amount of alumina. The slurry was mixed for 1 h in a rotary evaporator then water was removed under reduced pressure and the obtained solid was dried overnight in an oven at 120°C then the solid was calcined at 500°C under O_2 for 13 h. After this step, an amount of palladium(II) nitrate already dissolved with water was mixed with the solid in a rotary evaporator at 60°C and the mixture was dried overnight at 120°C then the obtained catalyst was calcined under oxygen at 500°C for 4 h.

2.2 Physicochemical characterizations

Chemical composition was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Activa-Horiba (Jobin Yvon S.A.S) spectrometer. Phase determination was performed using X-ray diffraction. X-ray diffractograms were recorded with a SIEMENS D500 diffractometer using Cu $\text{K}\alpha_1$ radiation ($\lambda = 1.5406\text{ \AA}$ Ni filtered). Diffraction data were recovered from 10° to 90° in 2θ angles with a step of 0.02° and a count time of 16 s.

BET specific surface areas were measured from N_2 adsorption at 77 K. The experiences were performed in a TRISTAR 3000 equipment. Samples were desorbed at 300°C for 2 h under vacuum (10^{-2} Pa) prior to measurement.

Particles dispersion of palladium was measured using volumetric measurement of hydrogen chemisorption on reduced catalyst under pure hydrogen flow for 2 h at 300°C . The quantitative determination of chemisorbed hydrogen by temperature programmed desorption (TPD) was used as a standard method to characterize the dispersion state of supported palladium. Before carrying out the chemisorption, the sample (approximately 400 mg) was treated under air at 300°C for 1 h and then reduced in a dilute hydrogen solution in argon (1 vol% H_2 , Ar) from 25 to 300°C ($10^\circ\text{C min}^{-1}$) with a stand-by at 300°C for 2 h. In order to remove all traces of hydrogen, the sample was purged under argon at 300°C for 1 h and then cooled under an argon flow to ambient temperature at which the chemisorptions of hydrogen was performed. The measurement was carried out by passing a series of hydrogen pulses (5) onto the sample at a regular interval of time. This non-adsorbed amount is null at the beginning because all the hydrogen is adsorbed and then it increases with the pulses until becoming constant (saturation). The difference between the amount of unadsorbed gas and the amount of hydrogen sent will give the amount of gas adsorbed for each pulse. In order to measure the H_2 content in argon, a microcatharometer connected with a signal amplifier was

used. The amount of unadsorbed gas was detected by the apparatus.

In order to gain more insight in the catalytic process taking place during the reactions, diffuse reflectance spectroscopy (DRS) was performed at room temperature on a Perkin-Elmer Lambda 950 equipped with a 150 mm integrating sphere using Spectralon™ as reference. Solids as powder were put in a Spectralon™ sample holder equipped with a quartz window. Spectra were retrieved as ASCII files and transformed into Kubelka–Munk function $F(R)$ analogous to absorbance for solids.

Moreover, the reduction properties of the samples were measured by temperature programmed reduction (H_2 -TPR). A 50 mg of catalyst was put in a quartz microreactor between two quartz wool layers. Solid was pretreated with pure oxygen from room temperature up to 500 °C for 1 h at 10 °C min^{-1} . Samples were then cooled down to room temperature. Solid undergoes another heating ramp up to 1000 °C under hydrogen (1 vol% in He). The amount of consumed H_2 was recorded by using a PFEIFFER OMNISTAR quadrupole mass spectrometer.

To better understand the performance of each catalyst and to gain more insight in the catalytic process taking place during the reaction, XRD, BET, DRS and TPR has been used in order to characterize catalysts before and after test.

2.3 Catalytic activity measurement

The catalytic test towards the combustion of biogas was performed under atmospheric pressure on 200 mg of catalyst sample placed in a continuous-flow fixed-bed Quartz reactor by using the following mixture: CH_4 (1 vol%), CO_2 (0.6 vol%), O_2 (4 vol%), H_2O (0.1 vol%), 1000 ppm NH_3 and He with a total flow rate of 100 $cm^3 min^{-1}$.

Catalytic activity cycle consisted of the following steps: a heating ramp from 100 to 800 °C at 0.5 °C min^{-1} , a stand-by at 800 °C for 1 h, a cooling down to 100 °C at 5 °C min^{-1} followed by a second heating ramp to 800 °C and then a cooling down to room temperature at 5 °C min^{-1} . The temperature regulation was controlled by an Eurotherm 920. The Gas Hourly Space Velocity (GHSV) was 4093 h^{-1} . The inlet and outlet gases concentrations were analyzed using a micro-GC Varian CP4900 equipped with a TCD detector (Emerson type NGA 2000) connected to a Poraplot U column.

3 Results and discussion

The ICP-AES results indicate that the metal content was very close to that expected for the impregnated samples. The specific surface areas of the $PdO/\gamma-Al_2O_3$ and $CuO/\gamma-Al_2O_3$ were 133 $m^2 g^{-1}$ and 109 $m^2 g^{-1}$ respectively. As for

the catalyst $Pd/CuO/Al_2O_3$, the specific surface area was 130 $m^2 g^{-1}$. The dispersion of palladium, obtained using volumetric measurement of hydrogen chemisorption on reduced catalyst, were 6% and 7% on PdO/Al_2O_3 and $PdO/CuO/\gamma-Al_2O_3$ respectively.

The X-ray diffractograms obtained at room temperature for the different solids are depicted in Fig. 1. This latter shows the presence of $\gamma-Al_2O_3$ phase (JCPDS Card No. 10-0425) with space group $Fd-3 m$ [19, 20]. X-ray diffraction peaks marked by (*) in Fig. 1 were detected with the presence of peaks at $2\theta = 37.2^\circ$, 45.6° and 66.9° corresponding to the γ -alumina phase [19, 21]. Moreover, the analysis of the solid $PdO/\gamma-Al_2O_3$ (before test) in the oxidized state shows, in addition of the presence of the γ -alumina characteristic lines, the two diffraction peaks assigned to PdO crystal phase (JCPDS Card No. 75-584) marked by (*) in Fig. 1 corresponding to $2\theta = 34^\circ$ and 55° [6, 7, 19, 22]. Furthermore for the $CuO/\gamma-Al_2O_3$ catalyst (before test), Fig. 1 shows the presence of γ -alumina characteristic lines and the diffraction peaks marked by (♦) with low intensity assigned to CuO crystal plans (002) and (111) corresponding to $2\theta = 35.5^\circ$ and 39° respectively (JCPDS Card No. 48-1548) [10]. The low intensity can be due to the presence of very scattered copper oxide particles [6]. Although a study by Luo et al. [10] shows that CuO diffraction peaks were not visible for CuO concentrations lower than 5.88%. For $PdO/CuO/\gamma-Al_2O_3$ catalyst, the diffractogram before test shows, in addition of $\gamma-Al_2O_3$ phase, the characteristic lines of the PdO phase at $2\theta = 34^\circ$ and 55° . Also it shows the presence of diffraction peaks assigned to CuO phase

Fig. 1 X-ray diffraction of the different catalysts before test (fresh catalyst) and after test (after second heating ramp)

at $2\theta = 35.5^\circ$ and 39° [10, 19]. As for the diffractograms realized after test, Fig. 1 shows that for palladium based catalysts, the diffraction peaks intensity corresponding to PdO increase. This increase can be due to particles sintering after test [7, 19]. Also for copper based catalysts (after test), we noticed the decrease in diffraction peaks intensity assigned to CuO phase. Furthermore, we noticed the presence of a diffraction peak assigned to CuAl_2O_4 (JCPDS Card No. 33-0448) at $2\theta = 37^\circ$ [23]. This can be explained by the migration of Cu^{2+} into the support at high temperature leading to the formation of CuAl_2O_4 phase [10].

Moreover, diffuse reflectance spectroscopy was realized on the different catalysts before and after test (2 heating ramp up to 800°C). For palladium oxide deposited on alumina catalyst (Fig. 2a), the characteristic band of Pd^{2+} ions which is between 300 and 500 nm was observed [7, 19]. Qualitatively, there are no big differences in the shape of the two band between Pd/ Al_2O_3 before and after test which means that we have the same characteristics but we note that the intensity of the band between 300 and 500 nm decreases after test which means that about 1/3 of the PdO species disappears. This may be due to particles sintering [7, 19]. As for the copper oxide supported on the alumina, Fig. 2b shows a spectrum before test where

Cu^{2+} ions in octahedral sites have a single absorption band between 600 and 800 nm [10]. Such ions Cu^{2+} in a tetrahedral environment absorb between 1300 and 1600 nm [10]. The two coordinates are thus easily detectable and easily differentiated. The bulk copper oxide has on one hand an absorption band between 600 and 800 nm, asymmetrical on the side of short wavelengths and on the other hand a rather intense continuous background revealing a semiconductor character [10]. For the 5 wt% CuO spectrum, the continuous background is much lower even considering the oxide concentration. After test, this absorption band is shifted to 750 nm with an asymmetric shape. This phenomenon reveals a deformation of the octahedron of oxygen ions surrounding the Cu^{2+} cations [20, 21, 24–26]. Also a band with low absorption around 1600 nm was noticed. Such band may correspond to a small amount of Cu^{2+} ions in tetrahedral sites. Furthermore, there are still octahedral Cu^{2+} ions that are detected around 700 nm but diffuse reflection spectroscopy irrefutably shows a significant loss of copper(II). In addition, Fig. 2b shows that Cu^{2+} ions in the octahedral site migrate into the surface to give Cu^{2+} in non-active tetrahedral form which is CuAl_2O_4 (spinel aluminum) [10]. Also for the Cu(I) ion, d–d transitions are impossible (saturated d^{10} configuration). However, bands

Fig. 2 DRS spectroscopy on the different catalysts before test (thin straight line) and after test (thick straight line) (**a** PdO/ Al_2O_3 ; **b** CuO/ Al_2O_3 ; **c** PdO/CuO/ Al_2O_3)

in the ultraviolet at 250–350 nm are observed which could correspond to the copper transitions $3d^{10} 4s^1 3d^9$ [10]. The chemical transformation of CuO into CuAl_2O_4 by interaction with the support leads to the deactivation of the catalyst [5, 9, 10, 26]. For $\text{PdO}/\text{CuO}/\text{Al}_2\text{O}_3$ catalyst before test, the Pd^{2+} and Cu^{2+} species are not very visible whereas after test, they are visible and we notice the appearance of a band around 1600 cm^{-1} characteristic of CuAl_2O_4 formed by the migration of Cu^{2+} in the support [10, 19]. Therefore, the introduction of copper into the catalyst stabilizes the PdO species with PdO peak displacement after test. This result shows that there is some interaction between PdO and CuO. Furthermore, this result is in agreement with the X-ray diffraction analysis.

In order to gain more insight on the interaction between metallic oxide species and the support, H_2 -TPR experiments were performed for the different catalysts. Figure 3 illustrates the H_2 -TPR profiles for the different catalysts. The degrees of reduction were calculated based on the following equations:

Moreover, Table 1 lists the total amount of H_2 consumption ($\mu\text{mol g}^{-1}$) and the reducibility (%) during H_2 -TPR experiments. The theoretical H_2 consumption obtained for CuO and PdO based catalysts are $31.4 \mu\text{mol H}_2 \text{ g}^{-1} \text{ cat}$ and $8.2 \mu\text{mol H}_2 \text{ g}^{-1} \text{ cat}$, respectively.

For the $\text{PdO}/\text{Al}_2\text{O}_3$ catalyst, H_2 -TPR profile illustrated in Fig. 3a reveals a reduction peak with a maximum at 130 $^\circ\text{C}$. According to the literature, this peak is attributed to the reduction of Pd^{2+} into Pd^0 [27]. After test, we observed a decrease in the intensity of this peak with a loss of approximately of 1/3 of the peak intensity and a formation of another peak at higher temperature (200 $^\circ\text{C}$) corresponding to the reduction of PdO species more difficult to reduce. This can be due to Pd particles agglomeration at high temperature resulting from particles sintering after test. Such result correlates as well with the XRD and DRS.

As observed in Fig. 3b, H_2 -TPR profile of $\text{CuO}/\text{Al}_2\text{O}_3$ (before test) reveals the presence of a reduction peak at 300 $^\circ\text{C}$ corresponding to the reduction of CuO. After test, we noticed a decrease in the intensity of this peak at 300 $^\circ\text{C}$ and the formation of another two reduction peaks at 600 $^\circ\text{C}$ and 800 $^\circ\text{C}$ approximately which correspond to the reduction of CuAl_2O_4 and CuAlO_2 respectively [28]. Such incorporation of copper into the support lattice can be due to high interaction between CuO and alumina at high temperature.

For $\text{Pd}/\text{CuO}/\text{Al}_2\text{O}_3$ (before test), H_2 -TPR profile represented in Fig. 3c reveals the presence of a low intensity

Fig. 3 TPR profiles for the different catalysts before test (thin straight line) and after test (thick straight line): **a** $\text{Pd}/\text{Al}_2\text{O}_3$, **b** $\text{CuO}/\text{Al}_2\text{O}_3$, **c** $\text{Pd}/\text{CuO}/\text{Al}_2\text{O}_3$

peak at 130 $^\circ\text{C}$ and a high intensity peak at 300 $^\circ\text{C}$ corresponding to the reduction of PdO and CuO species respectively. After test, we noticed a slight shift into higher temperature for the first peak and a slight decrease in the intensity of the peak at 300 $^\circ\text{C}$ with the formation of peaks at higher temperature between 600 and 800 $^\circ\text{C}$ with a small intensity corresponding to the reduction of CuAl_2O_4 and CuAlO_2 . It seems that for the $\text{Pd}/\text{CuO}/\text{Al}_2\text{O}_3$ catalyst, the addition of palladium oxide into $\text{CuO}/\text{Al}_2\text{O}_3$ engender an interaction between PdO and CuO leading to a decrease in the interaction between CuO and the support and therefore reduce the formation of CuAl_2O_4 and CuAlO_2 phases.

Table 1 Total H₂ consumption ($\mu\text{mol g}^{-1}_{\text{cat}}$) for the different catalysts

Sample	Reduction peak (maximum) (°C)	Total H ₂ consumption ($\mu\text{mol g}^{-1}_{\text{cat}}$)*
Pd/Al ₂ O ₃		
Before	130	8.5
After	130; 200	8
CuO/Al ₂ O ₃		
Before	300	31.5
After	300; 600; 800	31
Pd/CuO/Al ₂ O ₃		
Before	130; 300	37.6
After	130; 300; 600; 800	38

*H₂ consumption calculated from TPR peaks

In order to evaluate the performance of the catalysts on the combustion of the biogas and to study the effect of ammonia on this combustion, catalytic tests were performed in the temperature range of 100–800 °C.

The performance of all catalysts was compared during the second heating ramp since all the catalysts activities were stable during this heating ramp. Figure 4 shows the outlet concentrations of species as a function of temperature for the different catalysts during the second heating ramp up to 800 °C. The CH₄ conversion based on T₅₀ (°C) decreases as follow: PdO/Al₂O₃ (325 °C) > PdO/CuO/Al₂O₃ (400 °C) > CuO/Al₂O₃ (515 °C). For PdO/CuO/Al₂O₃, it is noticed that this catalyst has an intermediate activity

between PdO/Al₂O₃ and CuO/Al₂O₃ towards methane conversion during biogas combustion which may be due to an interaction between PdO and CuO (same square planar structure) [19]. Such interaction may reduce the activity of palladium species. In the other hand, PdO/CuO/Al₂O₃ catalyst exhibits the best performance towards the selective catalytic oxidation of NH₃ into N₂ in comparison with PdO/Al₂O₃ and CuO/Al₂O₃.

For PdO/Al₂O₃, a decrease in the dispersion after test from 6 to 2% which represents 66% of relative loss was noticed, thus reducing the number of active sites and decreasing the number of surface oxygen, which may leads to a decrease in the activity. Also, the specific surface area obtained after test was 116 m² g⁻¹ instead of 133 m² g⁻¹. That means a 13% loss of the specific surface area under reaction mixture at high temperature. The low value of the dispersion of the solid in the oxidized state and the decrease in specific surface area are undoubtedly at the origin of a moderate sintering of the palladium particles after test already observed in X-ray diffraction. The decrease in the dispersion from 6 to 2% means, in other words, an increase in the diameter average of the particles. This sintering of the active phase in an oxidizing atmosphere, confirmed by many authors, can partly be explained by a mechanism of transport of the metal oxide species on the surface of the alumina [3, 7, 19, 29].

The copper oxide supported on the alumina exhibits the lowest activity during the catalytic combustion of biogas due to the fact that the Cu²⁺ ions in the octahedral site migrate into the surface to give Cu²⁺ in non-active

Fig. 4 Concentrations in function of temperature for the different catalysts (**a** PdO/Al₂O₃; **b** CuO/Al₂O₃; **c** PdO/CuO/Al₂O₃)

tetrahedral form [10]. Also, the specific surface area obtained after test was $106 \text{ m}^2 \text{ g}^{-1}$ instead of $109 \text{ m}^2 \text{ g}^{-1}$. Copper(II) oxide was chosen between different transition metal oxides because it is cited in the bibliography as one of the most oxidation-active oxides and the most selective in oxidation of NH_3 to N_2 [8, 10, 30–32]. The disadvantage of CuO is that this oxide reacts with alumina to form CuAl_2O_4 at 700°C and the latter decomposes to CuAlO_2 at 870°C [10, 33, 34].

As for $\text{PdO}/\text{CuO}/\text{Al}_2\text{O}_3$, this catalyst has an intermediate activity between $\text{PdO}/\text{Al}_2\text{O}_3$ and $\text{CuO}/\text{Al}_2\text{O}_3$ towards methane conversion during biogas combustion.

After test a decrease in the dispersion from 7 to 6% which represents 14% of relative loss was calculated, thus reducing the number of active sites and decreasing the number of surface oxygen. Also, the specific surface area obtained after test was $115 \text{ m}^2 \text{ g}^{-1}$ instead of $130 \text{ m}^2 \text{ g}^{-1}$. This means 11% loss of the specific surface area under reaction mixture at high temperature. Furthermore it is important to mention that the relative loss in the dispersion and the specific surface area on $\text{PdO}/\text{CuO}/\text{Al}_2\text{O}_3$ were less than the relative loss in the dispersion and the specific surface area on $\text{PdO}/\text{Al}_2\text{O}_3$. This can be due to the fact that the addition of copper into the catalyst stabilizes the PdO species leading to a strong ion-O bonds with oxygen less labile which explain the high selectivity into N_2 during the biogas combustion [35–38]. In other word, it seems that the addition of Copper into $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst increase the catalyst stability. Such increasing in the catalyst stability leads to a better performance toward the selective catalytic oxidation of NH_3 into N_2 but decrease the catalyst performance toward biogas combustion. Since our work aimed to reduce NO_x emissions and increase N_2 formation at low temperature ($\approx 500^\circ\text{C}$) during biogas combustion, therefore 2 wt%PdO/5 wt%CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalyst represents a good candidate with the highest N_2 selectivity of 60% at 500°C instead of 8% and 25% of N_2 selectivity for $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{Al}_2\text{O}_3$ respectively. Finally, such result correlates as well with the XRD and DRS results.

In order to verify the stability of $\text{Pd}/\text{CuO}/\text{Al}_2\text{O}_3$, we realized a third heating ramp to be able to illustrate a comparison at 400°C and 500°C between the second and the third heating ramp. Therefore, the following diagram (Fig. 5) represents the CH_4 conversion, NH_3 conversion and N_2 selectivity at 400 and 500°C . As shown in Fig. 5, after three heating ramps, $\text{Pd}/\text{CuO}/\text{Al}_2\text{O}_3$ catalyst still maintained a good catalytic performance with CH_4 and NH_3 conversion at 500°C of 100% and a selectivity maintained at 60%.

4 Conclusions

This work aimed to find a catalyst with high performance toward selective catalytic oxidation of NH_3 into N_2 in order to reduce NO_x emissions and increase N_2 formation at low

Fig. 5 Comparison between second and third heating ramp at 400 and 500°C over $\text{Pd}/\text{CuO}/\text{Al}_2\text{O}_3$

temperature ($\approx 500^\circ\text{C}$) and in the same time a high performance toward biogas combustion. Since high oxygen ion lability plays an important role during the biogas combustion but has a negative effect on N_2 selectivity during NH_3 catalytic oxidation, therefore it was important to find a catalyst corresponding to the best compromise in between.

Indeed, this study showed that the addition of Copper into $\text{Pd}/\text{Al}_2\text{O}_3$, known as the best catalyst for catalytic combustion of methane, leads to better performance toward SCO of NH_3 to N_2 . It seems that copper addition increases the interaction between PdO and CuO leading to a decrease in the oxygen ion lability in PdO species and therefore to a better N_2 selectivity during selective catalytic oxidation of NH_3 .

At the end, this study showed that 2 wt%PdO/5 wt%CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalyst exhibited a better performance towards the selective catalytic oxidation of NH_3 into N_2 during biogas combustion compared to 2 wt%PdO/ Al_2O_3 and 5 wt%CuO/ Al_2O_3 .

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

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