Synthesis of Reduced Graphene Oxide as a Support for Nano Copper and Palladium/Copper Catalysts for Selective NO Reduction by CO

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ABSTRACT: Copper and palladium/copper nanoparticles supported on reduced graphene oxide catalysts were synthesized and evaluated for the selective NO reduction by CO. The catalysts were characterized by XRD, nitrogen adsorption–desorption, TGA, XPS, TPR, in situ XRD, STEM, and HRTEM. The STEM and HRTEM results showed high metal oxide dispersions on the rGO. XPS results showed the presence of Cu and Pd oxide species. The reduction of copper supported on the rGO occurred in two steps for CuO/$rGOCc$, while that for CuO$_x$-PdO$_y$/rGO$_c$ occurred in one step for temperatures lower than 350 °C. Noteworthy is that the in situ XRD results showed that the rGO structure was not affected after reduction at 350 °C. The in situ XRD of reduction revealed the appearance of new phases for copper during the reduction. The catalysts were evaluated in NO reduction by CO. The tests showed that the reduced catalysts presented high performance with NO conversions and N$_2$ selectivity above 85% at 350 °C.

1. INTRODUCTION

The abatement of NO$_x$, nitric oxide (NO) and nitrogen dioxide (NO$_2$), is of paramount importance since these gases are pollutants that generate various undesirable effects, such as photochemical smog, acid rain, and aggravation of the destruction of the ozone layer. NO$_x$ also causes various health problems and can lead to death in cases of severe intoxication. NO and carbon monoxide (CO) gases, emitted by different sources, must be eliminated, and the principal problem is the catalyst for total NO$_x$ abatement.

Catalysts based on copper have been used for the reduction of NO by CO. Copper supported on AlPO$_4$, Al$_2$O$_3$, CeO$_2$, zeolites, and carbon nanotubes was investigated for this reaction. Bimetallic transition-metal oxides (Cu/Fe) supported on commercial and synthesized carbon nanotubes and γ-Al$_2$O$_3$ were also investigated recently. Dasireddy et al. reported that Cu/Fe supported on synthesized carbon nanotubes presented high catalytic performance due to the strong interaction of Cu and Fe with the CNT and the acid and base surface sites on the carbon nanotubes. Hu et al. studied the NO + CO reaction over CuO/γ-Al$_2$O$_3$ and CuO/γ-Al$_2$O$_3$ at low temperatures and showed that NO conversions are related to the loading of CuO and of the support at temperatures lower than 200 °C. At 300 °C, the NO is completely converted to N$_2$.

As reported in the literature, the Cu/Fe bimetallic catalyst presented high activity, and although Pd is more expensive, it facilitates the CO adsorption for the reaction.

Ultimately, graphene in catalysis has aroused great interest. Graphene is a two-dimensional material, one of the allotropes of carbon, and has a hexagonal structure of carbon atoms. Graphene has unique and remarkable properties, so its use has been extensively investigated for catalysis, including electrocatalysis, photocatalysis, and conventional heterogeneous catalysis. The graphene can be used like an active phase or as a support for metals and metal oxides.

Reduced graphene oxide has a high specific surface area, which is highly desirable in catalysis, and acts as a two-dimensional support for metallic nanoparticles with high dispersion. In addition, it has a high adsorption capacity, defects in its structure that can generate new surface functionalities and increase the interactions with the metal nanoparticles, and excellent mechanical properties that allow high stability and durability, increasing the lifetime of the catalyst. Reduced graphene oxide (rGO) can be obtained from graphite at a relatively low cost.

Several catalysts based on graphene have been developed and applied in numerous catalytic reactions, such as Fischer–
Tropsch synthesis, selective hydrogenation, and NO\textsubscript{x} abatement. Nanocomposite TiO\textsubscript{2}/graphene was used for photocatalytic NO\textsubscript{x} oxidation under UV and visible light irradiation. Cerium and manganese oxides were supported on a TiO\textsubscript{2}–graphene nanocomposite that showed higher activity and N\textsubscript{2} selectivity for low-temperature selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}. The reduced graphene oxide is an excellent support for nanocomposites since the high specific area allows distribution of the nanoparticles evenly. Furthermore, the structural defects of the rGO may contribute to higher dispersion of the nanoparticle composite.

Therefore, we selected the CuO/rGO\textsubscript{c} catalyst for the NO + CO reaction and also verified if by addition of PdO to the CuO/rGO\textsubscript{c} catalyst changes the performance of the reaction.

There are a few works using reduced graphene oxide as a support for the NO + CO reaction. In the present work, we present the synthesis and characterization of rGO, impregnated first with copper and impregnated palladium oxide on the CuO/rGO\textsubscript{c} catalyst for the selective reduction of NO by CO. We studied the influence of temperature and the promoting effect of palladium on both unreduced and reduced catalysts for the NO + CO reaction tests. Therefore, we can compare the performance of CuO/rGO\textsubscript{c} and Cu/rGO\textsubscript{c} and the promoting effect of PdO on the NO + CO reaction for the rGO.

2. RESULTS AND DISCUSSION

2.1. Characterizations. Figure 1 shows XRD patterns of rGO, CuO\textsubscript{y}/rGO\textsubscript{c} and CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c}. In this diffractogram, the broad and low intensity diffraction peak located at 2\theta = 25.6° was attributed to the rGO (002) crystalline plane, corresponding to an interlayer distance of 0.347 nm. The diffraction peak at 40.1° for CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c} belongs to Pd (111). The peak at 43.1° showed a diffraction angle, which coincides with the Cu (111) and rGO (100) planes. No peaks were identified for copper oxide in the diffractograms. However, comparing the XRD patterns of pure rGO (Figure 1a) and the catalysts (Figure 1bc), we can observe that the diffraction peak at 25.6° was more intense, suggesting that bonding between the rGO layers were reestablished after the impregnation process.

The results of the textural properties (specific area, pore volume, and average pore size) of the graphite, rGO, CuO\textsubscript{y}, and catalysts are presented in Table 1. The rGO presented a high specific area (439 m\textsuperscript{2}/g). Graphite showed a low specific area and pore volume. Defects are observed in the regular hexagonal structure of the rGO sheet after the oxidation process of graphite and exfoliation and reduction of graphite oxide. There was also a significant reduction of the specific surface area, pore volume, and average pore size after the incorporation of the metals. We did Raman spectroscopy for the original graphite and the reduced graphene oxide, as shown in Figure S1. We can observe the bands D and G and the I\textsubscript{D}/I\textsubscript{G}, indicating that reduced graphene oxide presents a high ratio and thus defects as expected.

Figure 2 shows N\textsubscript{2} adsorption–desorption isotherms and pore size distributions of rGO and the catalysts. The isotherms and pore size distribution indicate the presence of mesopores and macropores (Figure 2a). The hysteresis corresponded to the porous structure of a slit type of the rGO structure with distinct carbon layers and defects in the hexagonal structure (Figure 2b) due to the thermal exfoliation and reduction processes.

The synthesis method used in this work for obtaining the reduced graphene oxide consists of four steps: oxidation of graphite, purification, drying and expansion, and simultaneous reduction of graphite oxide. The thermal method employed removed considerably the oxygenated groups from the structure, forming the reduced graphene oxide, as can be seen in the FTIR analysis of graphite, graphene oxide (GO), and rGO (Figure 3).

As shown, the graphite oxide exhibited the presence of different compounds, indicating the effective functionalization, indicating different oxide and carbonyl groups besides the formation of O–H and C–C and C–O–C groups. After reduction, the graphene oxide showed residual functionalized compounds.

TGA results display the mass loss of rGO, CuO\textsubscript{y}/rGO\textsubscript{c} and CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c} under a N\textsubscript{2} atmosphere, as shown in Figure 4. Below 100 °C, all the samples showed a mass loss of water. The total mass losses under a N\textsubscript{2} atmosphere were 58, 46.5, and 49.5% for rGO, CuO\textsubscript{y}/rGO\textsubscript{c}, and CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c}, respectively. This can be attributed to the decomposition of oxygen complexes on the surface rather than the decomposition of carbon.

TGA results with air showed the decomposition of pure rGO from 450 °C until completing at 600 °C. However, with the addition of the metals, the decomposition began earlier at lower temperature. It started at 300 °C and ended almost at 450 °C, with remaining masses of 18.7 and 11.6% for CuO\textsubscript{y}/rGO\textsubscript{c} and CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c} respectively. The process of reduction of graphene oxide affects the structure, resulting in oxygenated groups and structural defects, and when copper is

### Table 1. Textural Properties of the rGO and Catalysts\textsuperscript{a}

| Sample          | S\textsubscript{BET} (m\textsuperscript{2}/g) | V\textsubscript{T} (cm\textsuperscript{3}/g) | R\textsubscript{m} (Å) |
|-----------------|---------------------------------------------|--------------------------------------------|------------------------|
| graphite        | 12                                          | 0.1                                        | 132.6                  |
| rGO             | 439                                         | 1.3                                        | 88.4                   |
| CuO\textsubscript{y}/rGO\textsubscript{c} | 183                                         | 0.1                                        | 66.5                   |
| CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c} | 188                                         | 0.1                                        | 69.7                   |

\textsuperscript{a}S\textsubscript{BET}, specific surface area; V\textsubscript{T}, BJH desorption pore specific volume; R\textsubscript{m}, BJH desorption average pore radius.

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**Figure 1.** XRD patterns of (a) rGO, (b) CuO\textsubscript{y}/rGO\textsubscript{c} and (c) CuO\textsubscript{y}–PdO\textsubscript{y}/rGO\textsubscript{c} samples.
incorporated in rGO, the decomposition of oxygenated groups and the carbon surface is favored. Therefore, the presence of copper accelerated the decomposition of rGO.30 STEM and HRTEM micrographs and the size distribution of nanoparticles on rGO are shown in Figure 5. The micrographs showed that the metal nanoparticles supported on the rGO are well dispersed. The average sizes of the nanoparticles were 3.8 nm for the CuO$_x$/rGO$_c$. The spacing lattice fringes of the nanoparticles were 0.20 and 0.21 nm, attributed to the Cu (111) and CuPd (110) planes, respectively. However, the high-resolution image suggests the formation a CuPd nanocomposite, which corresponds to the bcc structure of the CuPd nanocluster. The catalysts were prepared at 300 °C under nitrogen flow, and the reduced graphene oxide has functionalized groups that favored the formation of CuPd nanocomposites during the reduction process of rGO. Therefore, rGO can act as a reducing agent for metal oxides when subjected to high temperatures.

The XPS spectra for the CuO$_x$/rGO$_c$ and CuO$_x$-PdO$_y$/rGO$_c$ catalysts are shown in Figures 6 and 7, respectively. The surface chemical composition of the catalysts was evaluated. The XPS spectrum of CuO$_x$/rGO$_c$ presented signals of Cu 2p, C 1s, and O 1s, and that of CuO$_x$-PdO$_y$/rGO$_c$ presented signals of Pd 3d, Cu 2p, C 1s, and O 1s. Table 2 shows the atomic percentage of the elements present at the surface. The main element in reduced graphene oxide is carbon as a regular hexagonal network. Oxygen was also identified due to the oxygen groups present at the surface of rGO. The spectrum of C 1s presents four deconvolution peaks. The main peak at 284.6 eV was attributed to the presence of C=C–C= in the aromatic rings of the rGO structure.36 The other peaks at 286.1, 288.1, and 291.0 eV were associated to the C–O, and COOH groups, and the satellite peak (π→π*$^*$), typical for aromatic carbon structure, respectively.37

The spectrum of Cu 2p showed four deconvolution peaks related to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$. The binding energies of Cu
the 2p3/2 peak at 934.2 eV and of the Cu 2p1/2 peak at 954.0 eV are assigned to CuO. The binding energies for Cu species are close to the values presented by Biesinger et al., and thus, since the samples were not reduced, the oxidation states of the copper species at the surface are CuO and Cu2O. In fact, the peaks at 932.4 and 951.9 eV are probably associated to Cu2O.

The peaks of Pd 3d5/2 at 335.4, 336.1, 337.2, and 338.2 eV are attributed to Pd0, PdOx<1, PdO, and PdO2, respectively. The peaks of Pd 3d3/2 at 340.5, 341.4, 342.5, and 343.8 eV are assigned to Pd0, PdOx<1, PdO, and PdO2, respectively. The reduction of PdO at the surface to metallic Pd0 particles are probably formed by the X-ray beam spectrum during the XPS.

Figure 5. Micrographs STEM of (a) CuOₓ/rGO and (b) CuOₓ-PdOᵧ/rGO, (c) size distribution of CuOₓ/rGO, nanoparticles and (d) CuOₓ-PdOᵧ/rGO, nanoparticles, and HRTEM of (e) CuOₓ/rGO and (f) CuOₓ-PdOᵧ/rGO.
experiments. The O 1s spectrum showed the presence of C−O and COOH groups, since the reduced graphene oxide presented these groups in its structure, as shown in the FTIR experiments (Figure 3).

Table 3 shows the atomic percentage of the copper and palladium species present on the surface of the catalysts. The percentages of the copper and palladium species were calculated through the Cu 2p3/2 and Pd 3d 5/2 regions, respectively. The calculated Cu2O/CuO ratios were 0.76 and 0.86 for CuOx/rGOc and CuOx-PdOy/rGOc, respectively. Therefore, Cu2O and CuO species coexisted at the surface of the catalysts, with CuO being the major content. Moreover, metallic palladium and oxide were also observed on the CuOx-PdOy/rGOc catalyst.

Figure 8 shows the TPR profiles of the hydrogen consumption (H2) of CuO (used as reference), CuOx/rGOc, and CuOx-PdOy/rGOc. The reduction peaks for the catalysts appeared at temperatures lower than for the pure material, which suggests that copper is well dispersed on rGO.5 For the CuOx/rGOc catalyst, copper reduction occurred in two steps with two maximum peaks at 241 and 298 °C. In fact, XPS results showed CuO and Cu2O species at the surface of the rGO catalyst. Therefore, the first peak was associated with the reduction of Cu2+ to Cu+ and the second was associated with the reduction of Cu+ to Cu0. Noteworthy is that for CuOx-PdOy/rGOc copper reduction occurred in one step, displaying only one peak at 258 °C. Interestingly, we observed a consumption of hydrogen at room temperature for CuOx-PdOy/rGOc which can be assigned to the reduction of PdO to metallic Pd0 (not shown). It is well known that the reduction of PdO normally takes place at room temperature.42−44 The metallic Pd particles at the surface of rGO may interact with Cu species on the rGO support and catalyzes the reduction of Cu species by shifting the Cu2+ toward lower temperatures from 298 to 258 °C. Therefore, the presence of palladium favored the direct reduction of Cu2+ to Cu0.

Figure 9 displays the in situ XRD measurements, which were employed to evaluate the changes in the crystalline structure of copper in the CuOx/rGOc catalyst during the reduction process under H2 flow. Figure 9a shows the diffraction patterns of CuOx/rGOc at room temperature without H2 flow, and Figure 9b–d shows those at different reduction temperatures (250, 300, and 350 °C) under H2 flow. Indeed, with increasing temperature, the structure of copper presented well-defined crystalline planes. The diffraction patterns at 250, 300, and 350 °C displayed four peaks at 25.4, 43.0, 50.0, and 73.5°, relative to the planes of rGO (002), Cu (111), Cu (200), and Cu (220), respectively.57 Furthermore, the Cu (111) peak became more intense and narrow, indicating very crystalline copper nanoparticles. The sizes of copper nanoparticles measured by the Scherrer equation were 5.1, 6.0, and 6.0 nm at 250, 300, and 350 °C, respectively. To confirm this, Table S1 presents the data on the full-width at half-maximum (FWHM) and the peak intensity. The data indicates that the Cu (111) peak
became more intense and narrow. Comparing the data between 300 and 350 °C, there was no significant change with the same particle size. Noteworthy is that the rGO structure was not affected after reduction at 350 °C, as indicated at 2θ = 25.4°, in accordance with the TGA results. SEM images in Figure 10 show the EDS maps of elements, and well-distributed particles and TEM results confirm the presence of nanoparticles on Cu and CuPd supported on rGO samples. The in situ XRD and TPR results showed that using a temperature of 350 °C under H2 flow made possible obtaining the reduced copper on the surface of rGO.

2.2. Catalytic Test. 2.2.1. NO + CO Tests. The performances of the calcined (CuOx/rGOx and CuOx-PdOy/rGOx) and reduced (Cu/rGO and Cu-Pd/rGOx) catalysts were evaluated in the selective reduction reaction of NO using CO as a reducing agent at different temperatures (150, 250, and 350 °C), as shown in Figure 11. The catalytic tests were performed to analyze the effect of temperature, copper reduction, and palladium addition on the NO and CO conversion and N2 selectivity of the catalysts. The stability test
of the catalysts during the NO + CO reaction at $T = 350^\circ$C is shown in Figure S2.

The CuO/rGO$_x$ sample presented low NO conversion (12%) at 250 $^\circ$C, indicating only NO decomposition at this temperature; however, the NO + CO reaction occurred at a higher temperature ($350^\circ$C), showing conversions of 24% NO and 10% CO. Palladium was added in small amounts to the copper catalyst supported on rGO in order to evaluate the promoting effect of palladium on the CuO/rGO$_x$ catalyst. Noteworthily is that for the CuO$_x$-PdO$_x$/rGO$_x$ sample, the reaction of NO + CO occurred even at a low temperature of $150^\circ$C, with conversions of 11% NO and 19% CO. The NO conversions of CuO$_x$-PdO$_x$/rGO$_x$ were 37 and 61% for 250 and $350^\circ$C, respectively. Therefore, the presence of palladium improved significantly the catalytic activity of the unreduced bimetallic catalyst. However, both unreduced catalysts showed increasing NO and CO conversions by raising the temperature and the highest $N_2$ selectivity was found at $350^\circ$C.

Table 2. Atomic Percentages Calculated from the XPS Spectra of the Catalysts

| sample          | element | peak (eV) | atomic (%) |
|-----------------|---------|-----------|------------|
| CuO$_x$/rGO$_x$| C 1s    | 284.9     | 80.9       |
|                 | O 1s    | 532.0     | 17.3       |
|                 | Cu 2p   | 934.0     | 1.8        |
| CuO$_x$-PdO$_x$/rGO$_x$| C 1s | 284.9 | 79.9 |
|                 | O 1s    | 532.0     | 17.9       |
|                 | Cu 2p   | 934.0     | 1.7        |
|                 | Pd 3d   | 336.7     | 0.5        |

Table 3. Atomic Percentages of the Copper and Palladium Species Calculated from the XPS Spectra of the Catalysts

| sample          | species | peak (eV) | atomic (%) |
|-----------------|---------|-----------|------------|
| CuO$_x$/rGO$_x$| Cu$_2$O | 932.4     | 43.2       |
|                 | CuO     | 934.2     | 56.8       |
| CuO$_x$-PdO$_x$/rGO$_x$| Cu$_2$O | 932.4 | 46.3 |
|                 | CuO     | 934.2     | 53.7       |
| CuO$_x$-PdO$_x$/rGO$_x$| Pd$^y$ | 335.4 | 14.1 |
|                 | PdO$_{y-1}$ | 336.1 | 32.2 |
|                 | PdO     | 337.2     | 30.8       |
|                 | PdO$_2$  | 338.2     | 22.9       |

Figure 9. Diffraction patterns of CuO$_x$/rGO$_x$ at (a) room temperature without H$_2$ and at three different temperatures of (b) 250 $^\circ$C, (c) 300 $^\circ$C, and (d) 350 $^\circ$C under H$_2$ flow.

As shown in Figure S2, the Cu/rGO$_x$ catalyst was deactivated initially, but NO conversion was constant after some time, increasing with time-on-stream (TOS). On the other hand, the Cu-Pd/rGO$_x$ catalyst was very stable in 1 h. Therefore, under such conditions, the catalysts are stable.

The reduced catalysts were studied after treatment in H$_2$/He flow at 350 $^\circ$C. In fact, the reduction improved the NO and CO conversions markedly. The bimetallic Cu-Pd/rGO$_x$ catalyst presented the highest NO conversion (92%) and $N_2$ selectivity (100%) at 350 $^\circ$C. The reduced Cu/rGO$_x$ sample showed 88% NO conversion and 95% $N_2$ selectivity at 350 $^\circ$C. The NO and CO conversions were significantly higher for both reduced Cu/rGO$_x$ and Cu-Pd/rGO$_x$ catalysts compared to the unreduced samples. In fact, TPR results confirm that the presence of palladium favored the direct reduction of Cu$^{2+}$ species and metallic Pd and so is the catalytic activity of the CuO$_x$-PdO$_x$/rGO$_x$ catalyst, which we attributed to the presence of Cu ion species and PdO$_x$ species at the surface, as observed by XPS, enhancing the reaction cycle of NO + CO. Moreover, the TPR profile confirm that there is interaction between Pd and Cu particles since the maximum peak was shifted to a lower temperature, about 250 $^\circ$C, which suggests interaction. The XPS indicated the presence of copper oxide in the calcined catalyst under $N_2$ flow. After reduction, these oxides are reduced to metallic particles, according to the TPR results.

The reaction of NO + CO results in $N_2$, $N_2O$, and CO$_2$ formation, according to Scheme 1:

According to Roy et al.,$^3$ the NO molecule must be dissociated when adsorbed to form $N_2$. Therefore, the reduction of NO by CO occurs on specific sites since CO must be adsorbed and NO be chemisorbed dissociatively. Xu et al.$^36$ studied the co-adsorption of NO and CO on Pd (100) and Pd supported on silica and concluded that the structure equilibrium and coverage for the adsorption of the mixture CO/NO depend strongly on the temperature and crystal orientation.

The performances of various catalysts based on copper and copper/palladium for the NO and CO reaction on different supports were compared with the present catalyst supported on rGO, as shown in Table 4. Flores-Sanchez et al.$^37$ investigated different catalysts based on NiO, CuO, and ZnO.
Figure 10. (a) SEM, (b–d) EDS maps of elements (b) C, (c) Cu, and (d) Pd, and (e) EDS analysis of Cu and Pd of the CuO$_x$-PdO$_y$/rGO$_z$ catalyst.
for the selective NO reduction by CO. The CuO catalyst exhibited the highest conversion of NO at 275 °C and 94% selectivity to N₂. Hu et al.5 investigated the influence of the supports for different copper oxide contents at low temperatures and showed that the reduced oxide species dispersed on the support surface enhanced the activity of the NO reduction by CO. Kacimi et al.4 observed a relationship between the quantity of copper(II) species with a dispersed surface and its ease of reduction at low temperature and the NO reduction activity of the catalyst, like what was done in this work. The copper(I) and (II) species on the rGO surface are easily reduced at low temperatures under H₂ flow, indicating that the greater reducibility of copper supported in rGO compared to CuO and other supports favors the NO + CO reaction. Muñoz et al.48 attributed the coexistence of Cu⁺ and Cu²⁺ to the formation of N₂O at low temperature; however, at temperatures above 250 °C, CO can reduce copper to Cu⁰ favoring

![Figure 11. NO and CO conversion and N₂ selectivity for unreduced and reduced catalysts: black bar, CuO/rGO; red bar, CuO-PdO/rGO; blue bar, Cu/rGO; green bar, Cu-Pd/rGO.](https://dx.doi.org/10.1021/acsomega.0c02417)

**Scheme 1. Reaction of NO + CO**

\[ 2NO + 2CO \rightarrow N_2 + 2CO_2 \]
\[ 2NO + CO \rightarrow N_2O + CO_2 \]

**Table 4. Comparative Catalytic Performance of Different Catalysts for Selective Reduction of NO by CO**

| Catalysts          | Temperature (°C) | X₉₅ (%) | S₉₅ (%) | Reaction Condition                  | Reference |
|--------------------|------------------|---------|---------|-------------------------------------|-----------|
| CuO/rGO           | 350              | 23.8    | 100     | 1 vol % CO + 0.5 vol % NO in He     | this work |
| Cu/rGO            | 350              | 87.6    | 95.2    | 1 vol % CO + 0.5 vol % NO in He     | this work |
| CuO-PdO/rGOc      | 350              | 61.1    | 95.1    | 1 vol % CO + 0.5 vol % NO in He     | this work |
| Cu-Pd/rGO         | 350              | 91.7    | 100     | 1 vol % CO + 0.5 vol % NO in He     | this work |
| CuO               | 275              | 100     | 94      | 3.3 vol % CO + 0.7 vol % NO in He   | [47]      |
| 5CuAlPO₄          | 400              | 48      | 100     | 1.5 vol % CO + 0.2 vol % NO + 0.65 vol % O₂ in He | [4] |
| 5CuAlPO₄ reduced  | 250              | 50      | 100     | 1.5 vol % CO + 0.2 vol % NO + 0.65 vol % O₂ in He | [4] |
| Cu−Al hydroxide   | 360              | 100     | 100     | 1 vol % CO + 1 vol % NO in He       | [48]      |
| 11.1CuO/γ-Al₂O₃   | 200              | <60     | 0       | 10 vol % CO + 5 vol % NO in He      | [5]       |
| 4.9CeO/CeO₂       | 200              | <98     | 100     | 10 vol % CO + 5 vol % NO in He      | [5]       |
| 9.3CeO/Al₂O₃      | 300              | 100     | 100     | 10 vol % CO + 5 vol % NO in He      | [5]       |
| Pd−Cu/Al₂O₃       | 200              | <30     | 0       | 1 vol % CO + 0.45 vol % O₂ + 0.1 vol % NO in N₂ | [49] |
| Pd−Cu/Al₂O₃       | 200              | 100     | 100     | 1 vol % CO + 0.45 vol % O₂ + 0.1 vol % NO in N₂ | [49] |

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the formation of N2. Fernández-Garcia et al.49 indicated the formation of a CuPd alloy in ceria, which is thermodynamically more stable than when the two metals are separate. The presence of copper improved the rate of CO oxidation on Pd surfaces and dissociation of N−O−49.

Cheng et al.50 prepared copper catalysts supported on Fe2O3, CeO2, Fe3O4, and CeO2 mixed metal oxide supports for the NO + CO reaction. Mixed oxide catalysts performed better than catalysts of only one type of oxide. The high fraction of oxygen vacancies in the catalyst may facilitate the redox cycle of oxygen during the NO + CO reaction. Bai et al.51 prepared a catalyst of CuO supported on CeO2-Al2O3. The mechanism of the NO + CO reaction on the Cu/ CeAl catalyst was proposed. At low temperatures, CO reacts with the adsorbed NO, favoring the formation of N2O. By increasing the temperature, the formation of N2 was favored. The authors attributed the improvement of NO decomposition to the synergistic effect of Cu2+/Cu+ ↔ Ce4+/Ce3+.

The reduction of NO by CO is a structure-sensitive reaction since the Pd particle sizes and the morphology may influence the NO dissociation and there is a NO and O2 competition established for the reductant agent.52 STEM micrographs revealed small nanoparticles sizes (3.8 nm) in CuO/PdO/rGO, which explains its higher activity compared to CuO/PdO/rGOc. Instead, the activity of copper oxide catalysts involves the ions Cu2+/Cu+, which also have a strong relationship with the supports; however, the greater the reducibility of copper oxide species dispersed on the support without interaction with the support, the higher is the activity at lower temperatures. However, at higher temperatures, the activity of copper oxide catalysts involves the Cu ions, which also strongly influence the reaction. In fact, the TPR results (Figure 8) confirm that copper species is reduced at temperatures below 200 °C under H2 flow on both CuO/PdO/rGOc and CuO/PdO/rGO samples. The reduction of CuO/rGO occurred in two steps: Cu2+ to Cu+ and Cu+ to Cu0. However, the reduction of CuO/PdO/rGOc occurred in one step. Thus, copper is easier reduced when supported on rGO than on oxide supports. When increasing the temperature under hydrogen flow during in situ XRD (Figure 9), new peaks related to metallic copper planes (Cu (111), Cu (200), and Cu (220)) appeared. The adsorption of NO is an essential step for the formation of the desired product since NO is adsorbed and CO removes the oxygen from NO to form N2. The new planes of metallic copper after reduction may favor the adsorption of NO on the surface of the catalyst.

The XPS results (Figures 6 and 7) showed Cu2+ and Cu+ species at the surface of CuO/rGOc and CuO-PdO/rGOc. Cu2+ and Cu+ species at the surface. When comparing the reduced and unreduced samples, we observed that the reduced samples presented higher conversions at temperatures lower than 250 °C. It evidences that Cu ion species and Pd on the surface enhance the activity, in agreement with the reported results in the literature.53−55

The influence of the reducibility seems to influence the palladium that subtly changed NO and CO conversions on the reduced catalyst, which can be attributed to Pd0 particles or PdO, species distributed on Cu63+ ions, as observed by XPS, or dispersed on the rGO support, modifying the sites and the adsorption of NO and CO molecules.56

NO reduction by CO is a specific reaction in which CO is molecularly adsorbed on metallic sites and NO is associatively adsorbed on CuO, in accordance with Cheng et al.,50 and not dissociatively.5 Thus, CO can act by removing the oxygen atoms left by the dissociation of NO−CuO sites, allowing continuous N2 formation. In fact, CO can act in two ways: as a reducing agent in the catalytic reduction of NO and in the reduction of the metal oxide.6

Therefore, these results suggest that the CO molecules are chemically adsorbed on metallic surface PdO and simultaneously reduce the oxide PdO at the surface. On the other hand, the Cu63+ ions at the surface can also oxidize NO molecules with the formation of N2O and transforming them into higher-oxidation state Cu+, while the CO adsorbed on Pd0 reduces the Cu2+ to lower-oxidation state Cu+, releasing CO2 and Pd0, in agreement with refs 5 and 57.

Noteworthy is that the reduced graphene oxide (rGO) structure was not affected after reduction at 350 °C and that the CuOx/rGO catalyst favors significantly the formation of N2 and bimetallic CuOx-PdOy/rGOx favors mostly the formation of N2O and less N2.

Shelef and Kummer58 reported for Al2O3 supports that the reduction of NO occurs by two steps: partial reduction of NO to N2O and then subsequent reduction of N2O to N2. These steps correspond to the oxidation of the reduced site. The higher the reducibility of copper oxide species, the better is the cycling of the re-oxidation since NO is absorbed on Cu2+ and CO on Cu+ sites.59,60

These surface phenomena suggest a different sequence of steps for the NO + CO reaction in which Cu and Pd sites act in different pathways for the mono- and bimetallic catalysts during the NO+CO reaction, either for the unreduced and reduced catalysts. In fact, CO and NO reduce and oxidize Cu63+, releasing N2 and N2O and CO2 molecules, hence regenerating Cu ions and Pd0 at the surface atoms for new CO adsorption. These mechanisms are described in the following reaction (Scheme 2) for the mono- and bimetallic CuOx/rGOx and the CuOx-PdOy/rGOx catalysts.

**Scheme 2. Reaction of NO + CO on the CuOx/rGOx and the CuOx-PdOy/rGOx Catalysts**

**A** − NO+CO reaction on CuOx/rGOx catalyst

\[ 2\text{NO} + 2\text{CuO} \rightarrow 2[\text{NO}_x\text{O}_y\text{Cu}_z] \]

\[ 2[\text{NO}_{\text{ad}}\text{-CuO}] \rightarrow N_2 + 2\text{CuO} + 2O_2 \]

\[ 2\text{CO} + O_2 \rightarrow 2\text{CO}_2 \]

\[ 2\text{NO} + 2\text{CO} \rightarrow N_2 + 2\text{CO}_2 \]

**B** − NO+CO reaction on CuOx-PdOy/rGOx catalyst

\[ \text{CO} + \text{Pd} \rightarrow \text{Pd-CO} \]

\[ \text{Pd}^0\text{CO}_\text{ad} + \text{Cu}^{2+} \rightarrow \text{Cu}^{+} + \text{CO}_2 + \text{Pd}^0 \]

\[ 2\text{NO} + \text{Cu}^{2+} \rightarrow N_2 + \text{Cu}^{+} + 1.5\text{O}_2 \]

\[ \text{Pd}^0 + 0.5\text{O}_2 \rightarrow \text{PdO} \]

\[ \text{CO} + \text{Pd} + \text{PdO} \rightarrow \text{CO}_2 \]

\[ 2\text{NO} + 2\text{CO} \rightarrow N_2 + 2\text{CO}_2 \]

According to Cheng et al.,50 NO can also be adsorbed on CuOx, increasing the active sites and the reaction rate of the reduced samples. This is also supported by Hu et al.’s work that showed the presence of Cu2Pd1/2 for different supports. For the Cu2+ on Al2O3, the valence of the dispersed copper oxide did not change during the reaction. However, the copper oxide
species on CeO$_2$ could decrease the amount of Cu$^{2+}$ cations during the reaction. Thus, the authors assumed that the reduction of NO by CO might involve cycling of Cu$^{2+}$/Cu$^0$ at lower temperatures as shown in our proposed schemes.

In this study, the influence of the support is not significant and the presence of Cu ions and of Pd in the metallic form or as a PdO$_x$ species play an important role in the reduction of NO by CO either on the reduced or unreduced form. However, the reduced form facilitates the reduction of Pd and the adsorption of CO, while NO can be adsorbed on Cu ions and provide the oxidation-reduction step.

3. CONCLUSIONS

Defects were observed in the regular hexagonal structure of the rGO sheet after the oxidation process of graphite and exfoliation and reduction of graphite oxide. Copper and palladium were homogeneously distributed on the rGO surface. The addition of palladium on the catalyst resulted in a high dispersion of nanoparticles with an average size of 3.8 nm. XPS results showed CuO$_x$/CuO ratios of 0.76 and 0.86 for CuO$_x$/rGO and CuO$_x$-PdO$_x$/rGO, respectively, and that Cu$_2$O and CuO species coexisted as the surface of the catalysts, with CuO being the major content. The in situ XRD results showed that the rGO structure was not affected after reduction at 350 °C and revealed also new crystalline metallic copper planes. The bimetallic Cu-Pd/rGO catalyst presented 92% NO conversion and 100% N$_2$ selectivity at 350 °C. The reduced Cu/rGO sample presented 88% NO conversion and 95% N$_2$ selectivity at 350 °C. The NO and CO conversions were significantly higher for both reduced catalysts than for the unreduced samples.

4. EXPERIMENTAL SECTION

4.1. Materials. Graphite powder was supplied by Nacional de Grafite Ltda (Brazil). Potassium permanganate (KMnO$_4$) and palladium nitrate (Pd(NO$_3$)$_2$) solution were purchased from Sigma-Aldrich. Concentrated sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), cupric nitrate trihydrate (Cu(NO$_3$_)$_2$·3H$_2$O), and hydrogen peroxide (30 wt %) were purchased from VETEC Quimica Fina Ltda. All chemicals were used as received without any further purification.

4.2. Preparation of Reduced Graphene Oxide (rGO). Graphite oxide (GO) was prepared by the modified Hummers’s method with the oxidation time set at 2 h. First, 12 g of graphite was added to 280 mL of H$_2$SO$_4$ under stirring in an ice bath. KMnO$_4$ (36 g) was added slowly under stirring, while the temperature was kept at lower than 20 °C and then the mixture was heated to 40 °C for 2 h. Then, 600 mL of distilled water was added slowly, and the solution was heated to 95 °C under stirring for 15 min. Finally, 2000 mL of distilled water and 60 mL of hydrogen peroxide were added and the solution was purified by centrifugation in water and diluted HCl (10 wt %) and then dried in air at 60 °C for 24 h. The final GO was treated by thermal expansion and reduction under air flow at 30 °C/min up to 300 °C and then under He flow at 10 °C/min between 300 and 500 °C to obtain the reduced graphene oxide (rGO).

4.3. Preparation of CuO$_x$/rGO and CuO$_x$-PdO$_x$/rGO Catalysts. The catalysts were prepared by an incipient wetness impregnation method. A solution of Cu(NO$_3$)$_2$·3H$_2$O was prepared and added slowly to the rGO. After impregnation, the sample was dried at 110 °C overnight followed by calcination at 300 °C in nitrogen for 1 h. The catalyst calcined was designated CuO$_x$/rGO (x = 0–2). Subsequently, palladium was impregnated on the CuO$_x$/rGO catalyst using Pd(NO$_3$)$_2$ as the precursor salt, dried, and calcined similarly. The nominal loading of copper and palladium was 5 and 1 wt %, respectively. The bimetallic catalyst was designated CuO$_x$-PdO$_x$/rGO (x = 0–2).

4.4. Characterizations. X-ray powder diffraction (XRD) analysis was carried out in a Rigaku Miniflex diffractometer operated at 20 kV and 15 mA using Cu Kα radiation (λ = 1.5406 Å). Diffraction data were recorded in the 2θ range from 5 to 90° with a step size of 0.05°/s. Crystal phases were identified using the JCPDS database. Thermogravimetric analysis (TGA) was carried out on Hitachi equipment (model STA7300). TGA curves were obtained under nitrogen and air gas flow (80 mL/min) at a heating rate of 10 °C/min from 30 to 1000 °C. Textural properties were obtained by N$_2$ adsorption/desorption at −196 °C using a Micromeritics ASAP2010 instrument. Before each measurement, the samples were degassed at 200 °C overnight under vacuum in order to remove adsorbed species. Fourier-transform infrared spectroscopy (FTIR) analyses were performed on a Perkin Elmer spectrometer (model Spectrum 100), equipped with a DTG (triglycine sulfate) detector. The spectra were obtained in the range between 4000 and 600 cm$^{-1}$ in the transmission mode with a number of scans of 32 and a resolution of 4 cm$^{-1}$. Raman analyses were performed at room temperature using a He/Ne laser (λ = 632.84 nm) in the 1000–1800 cm$^{-1}$ wavelength range to identify the formation of D and G bands.

High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) analyses were performed using a JEOL 2100F at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) analyses were performed using a field emission scanning electron microscope (FE-SEM) from FEI Co. (model Quanta 400) with an acceleration voltage of 30 kV coupled with X-ray-dispersive energy detectors (EDS). The surface chemical state of the atoms and their relative abundance were evaluated by X-ray photoelectron spectroscopy (XPS) using an Escalab 250Xi Thermo Scientific spectrometer with a monochromatic Al Kα (1486.6 eV) X-ray source. The XPS spectra were acquired in constant analyzer energy mode (CAE) with a pass energy of 100 eV for survey and 25 eV for high resolution.

Temperature-programmed reduction (H$_2$-TPR) was performed with a mixture of 1.53 vol % H$_2$/Ar (60 mL/min) and a heating rate of 10 °C/min from 30 to 450 °C. Prior to TPR analysis, the sample (150 mg) was pretreated under flowing pure He (60 mL) at 300 °C for 1 h.

In situ XRD analyses were performed on a Rigaku DMAX 2200 diffractometer equipped with an XKR 900 (Anton Par) reaction chamber. The catalyst was subjected to a flow rate of 50 mL/min with a mixture of 1.53 vol % H$_2$/He, and XRD patterns were obtained at three different temperatures (250, 300, and 350 °C). The XRD patterns were obtained in the 2θ range from 5 to 90° with a step size of 0.05°/s.

4.5. Catalytic Test. The catalysts were tested for the NO reduction with CO as the reducing agent. The tests were performed with unreduced and reduced catalysts. Catalysts were pretreated in situ with flowing He (45 mL/min) at 350 °C for 30 min and reduced with 10 vol % H$_2$/He flow (50 mL/min) at 350 °C for 20 min. The catalyst reduced was designated Cu/rGO, and Cu-Pd/rGO.
The feed composition consisted of 0.5 vol % NO, 1 vol % CO, and balance in He. The total gas flow rate was 37.5 mL/min and 100 mg of catalyst. The GHSV was 9000/h. The tests were performed at different temperatures (150, 250, and 350 °C) and at atmospheric pressure in a fixed bed quartz microreactor. The effluent gases were analyzed on line using a gas chromatograph (Shimadzu GC-17A) equipped with a thermal conductivity detector (TCD) and a Carboxen1010 column. Helium was employed as a carrier gas.

The NO ($X_{NO}$) and CO conversion ($X_{CO}$) and $N_2$ selectivity ($S_N$) were calculated using eqs 1, 2, and 3, respectively.

$$X_{NO}(\%) = \frac{A_{NO(input)} - A_{NO(output)}}{A_{NO(input)}} \times 100$$

where $A_{NO(input)}$ and $A_{NO(output)}$ are the areas of NO peaks before the reaction and during the reaction from the chromatograms, respectively.

$$X_{CO}(\%) = \frac{A_{CO(input)} - A_{CO(output)}}{A_{CO(input)}} \times 100$$

where $A_{CO(input)}$ and $A_{CO(output)}$ are the areas of CO peaks before the reaction and during the reaction from the chromatograms, respectively.

$$S_N(\%) = \frac{A_N}{A_N + A_{NO}} \times 100$$

where $A_N$ and $A_{NO}$ are the corrected areas with the response factors of $N_2$ and $N_2O$, respectively.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c02417.

Raman spectroscopy for graphite and reduced graphene oxide (Figure S1); stability test of the catalysts (Figure S2); and data on the full-width at half-maximum (FWHM) and the peak intensity of in situ XRD (Table S1) [PDF]

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**Notes**

The authors declare no competing financial interest.

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