Article

Low-Temperature Catalytic CO Oxidation Over Non-Noble, Efficient Chromia in Reduced Graphene Oxide and Graphene Oxide Nanocomposites

Asma A. Ali ^{1,*}, Metwally Madkour ² , Fakhreia Al Sagheer ², Mohamed I. Zaki ³ and Ahmed Abdel Nazeer ^{2,4,*}

¹ Science Department, College of Basic Education, Public Authority of Applied Education and Training (PAAET), P.O. Box 23167, Safat 13092, Kuwait

² Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait; Metwally.madkour@ku.edu.kw (M.M.); f.alsagheer@ku.edu.kw (F.A.S.)

³ Chemistry Department, Faculty of Science, Minia University, El-Minia 61519, Egypt; mizaki@mu.edu.eg

⁴ Electrochemistry Laboratory, Physical Chemistry Department, National Research Centre, Dokki, P.O. 12622, Giza, Egypt

* Correspondence: aaa.ali@paaet.edu.kw (A.A.A.); anazeer_nrc@yahoo.com (A.A.N.)

Received: 3 December 2019; Accepted: 8 January 2020; Published: 11 January 2020

Abstract: Herein, bare chromia nanoparticles (Cr_2O_3 NPs) and chromia supported on reduced graphene oxide (rGO) and graphene oxide (GO) hybrids were synthesized, followed by characterization by means of FESEM, Raman spectroscopy, TGA, XRD, TEM/HRTEM, XPS and N_2 sorptiometry. The investigated bare Cr_2O_3 and the hybrids ($\text{Cr}_2\text{O}_3/\text{rGO}$ and $\text{Cr}_2\text{O}_3/\text{GO}$) were employed as catalysts for low-temperature CO oxidation. Compared with the other catalysts, the results revealed efficient catalytic activity using $\text{Cr}_2\text{O}_3/\text{GO}$, which was attributed to its higher surface area together with the mixed oxidation state of chromium (Cr^{3+} and $\text{Cr}^{>3+}$). These are important oxidation sites that facilitate the electron mobility essential for CO oxidation. Moreover, the presence of carbon vacancy defects and functional groups facilitate the stabilizing of Cr_2O_3 NPs on its surface, forming a thermally stable hybrid material, which assists the CO oxidation process. The $\text{Cr}_2\text{O}_3/\text{GO}$ hybrid is a promising low-cost and efficient catalyst for CO oxidation at low temperatures. The higher activity of graphene oxide supported Cr_2O_3 NPs can provide an efficient and cost-effective solution to a prominent environmental problem.

Keywords: chromium oxide NPs; CO oxidation; Cr_2O_3 /carbonaceous hybrid; catalysis

1. Introduction

Carbon monoxide (CO) is a toxic and highly poisonous gas and is considered a silent killer that contributes indirectly to different environmental and health problems [1]. The main sources of CO are gases emitted from petroleum, chemical and petrochemical industries, and automobile emissions [1]. To overcome its toxicity, CO catalytic oxidation into less harmful carbon dioxide (CO_2) is an important strategy. Many researchers have employed different noble metals such as Au, Pt and Pd as potential catalysts for CO oxidation; however, the issues of cost, poor stability, and sensitivity to impurities for deactivation limit their industrial applications [2]. Recently, low-temperature CO oxidation on non-noble metal catalysts has been an important research objective in order to overcome high cost and realize efficient results [3–5].

Metal oxide catalysts are regarded as promising materials for industrial and environmental CO oxidation reactions [6]. Their abundance, low cost and pronounced chemical stability make them a promising alternative to noble-metal based catalysts [7–9]. Studies that have hitherto been carried out

show that transition metal oxides produce catalysts with high CO oxidation activity. Promoting the CO oxidation activity of oxide-based transition metals is still a point of enquiry, and further research is seeking to accomplish this objective. Chromia (Cr_2O_3) is among the transition metal oxides that have been extensively researched [10]. Many researchers pay great attention to its physical and chemical characteristics [11–13]. This oxide demonstrated pronounced behavior in redox reactions, including the CO oxidation reaction [14,15].

Cobalt oxide was reported to have nearly the same catalytic activity as noble metal catalysts for CO oxidation [16]. Nevertheless, because of the high surface energy of cobalt oxide's nanoparticles, it is ready to aggregate, which may lead to a reduction in catalytic activity. Supported metal nanoparticles are commonly used in heterogeneous catalytic processes, which are critical to various chemical reactions and can be used to solve the problem of individual metal oxides by protecting the in situ grown nanocatalysts from agglomeration [17]. This important supportive role improves the catalytic performance of metal nanoparticles (NPs).

Graphene and graphene oxide showed high surface-to-volume aspect ratios. Moreover, because of the presence of a carbon vacancy defect structure and different functional groups, metal ions can be easily adsorbed onto graphene's surface, forming thermally stable composite materials [18]. rGO and GO are widely used to support metallic nanoparticles in different applications due to their pronounced specific area and high stability [19]. On the basis of their unique properties, graphene and graphene oxide should be used as support materials for different heterogeneous catalysts [20,21]. Wang et al. studied the use of rGO- Co_3O_4 catalysts for CO oxidation, and the results show remarkable activity and stability for the oxidation of CO using 30% rGO [22]. Wen et al. reported using an rGO-supported Cr_2O_3 catalyst for an oxygen reduction reaction (ORR), proving that hybrid $\text{Cr}_2\text{O}_3/\text{rGO}$ has pronounced catalytic performance with high stability for ORR [23]. Xia et al. investigated Cr_2O_3 NPs with a rGO hybrid as an efficient catalyst for electrochemical N_2 -to- NH_3 conversion [24]. Up to the best of our knowledge, however, reports on the catalytic application of metal oxide hybrids with carbonaceous materials for CO oxidation are rare.

Consequently, the present first-of-a-type investigation studies the activity of unsupported and supported Cr_2O_3 NPs on carbonaceous compounds (rGO and GO) as a catalyst for CO catalytic oxidation at low temperatures. Obtained hybrids of $\text{Cr}_2\text{O}_3/\text{rGO}$ and $\text{Cr}_2\text{O}_3/\text{GO}$ showed pronounced catalytic activity for the oxidation of CO at low temperatures.

2. Results and Discussion

2.1. Characterization of As-Prepared Samples

Figure 1A,B shows the FESEM micrographs obtained for GO and rGO. It is clear that, after oxidation, the GO and rGO sheets were both crumpled. The reduction of the graphite sheets due to the distortion of their conjugated π -bond system is also clear. However, a flaky layered microstructure was only shown for GO (Figure 1A), whereas in rGO, the surface morphology was relatively close (Figure 1B) due to GO exfoliation during ultrasonic treatment. Raman spectra obtained for GO and rGO are compared in Figure 1C. The two broad peaks therein monitored are the D and G bands, which are the predominant features for carbon-based materials [25]. In the spectrum of GO, the peak at 1589 cm^{-1} is due to the G band, whereas the peak at 1352 cm^{-1} is attributed to the D band [25]. The spectrum of rGO shows the G peak at 1582 cm^{-1} and the D peak at 1348 cm^{-1} . These peak red-shifts are considered indicative of the recovery of sp^2 domains [26] and, hence, the reduction of GO to rGO.

Figure 1. Typical FESEM images obtained for GO (A) and rGO (B) and their Raman spectra (C).

TG curve obtained for the as-obtained chromia, i.e., the un-calcined $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, displays two main decomposition steps, as shown in Figure 2. The first step is shown to undertake about a 25% mass loss maximized at 237 °C. This process is consistent with the removal of weakly held water molecules plus the dehydration to $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ($=2\text{CrOOH}$). The second step is shown to maximize at 415 °C, giving rise to mass loss of about 11%, which is very close to the dehydration of $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ into Cr_2O_3 (10.6%). These results verify the chemical composition of the parent chromium hydroxide compound and emphasize the appropriateness of the calcination temperature regime (≥ 400 °C), applied for the thermal genesis of the Cr_2O_3 NPs from the parent hydroxide. Accordingly, we chose the calcination temperature of 600 °C.

Figure 2. TG curve obtained for the as-obtained Cr_2O_3 tetrahydrate.

Figure 3 compares XRD powder diffractograms measured for Cr_2O_3 NPs and the hybrids $\text{Cr}_2\text{O}_3/\text{rGO}$ and $\text{Cr}_2\text{O}_3/\text{GO}$. In the case of Cr_2O_3 , the monitored diffraction peaks are quite similar to the peaks filed for $\alpha\text{-Cr}_2\text{O}_3$ in JCPDS card no. 38-1479 [27]. Hence, $\alpha\text{-Cr}_2\text{O}_3$ is the sole XRD-detectable crystalline phase in the calcination products at 600 °C. The average crystallite size determined for the $\alpha\text{-Cr}_2\text{O}_3$ particles was 32 nm. In the case of $\text{Cr}_2\text{O}_3/\text{GO}$ (Figure 3), the peak at around $2\theta = 10.6^\circ$ is assigned to the graphene oxide nanosheet, whereas the rest of the peaks monitored are indexed to the chromia NPs. As well as this, the XRD data of $\text{Cr}_2\text{O}_3/\text{rGO}$ (Figure 3) is related to JCPDS no. 38-1479, and the diffraction peak at $2\theta = 24.8^\circ$ could be assigned to the rGO nanosheet. It is obvious that the peak at $2\theta = 10.6^\circ$ has disappeared, confirming the quantitative reduction of GO to rGO [28]. Hence, the XRD patterns of the synthesized hybrids $\text{Cr}_2\text{O}_3/\text{rGO}$ and $\text{Cr}_2\text{O}_3/\text{GO}$ reveal their effective preparation.

Figure 3. XRD patterns obtained for the bare α - Cr_2O_3 NPs and the hybrids $\text{Cr}_2\text{O}_3/\text{rGO}$ and $\text{Cr}_2\text{O}_3/\text{GO}$.

TEM image obtained for α - Cr_2O_3 NPs yielded after calcination at 600 °C is shown in Figure 4A. It displayed well defined cubic-shaped nanoparticles of chromia. The average particle size for the obtained Cr_2O_3 NPs at 600 °C is 47 nm, which is higher than the XRD-determined average crystallite size (32 nm). This may reveal that the Cr_2O_3 NPs are polycrystalline and are formed via coalescence and/or aggregation of the primary crystallites. Figure 4B,C show the TEM images of the $\text{Cr}_2\text{O}_3/\text{rGO}$ and $\text{Cr}_2\text{O}_3/\text{GO}$ hybrids, respectively. The images clearly reveal the distribution of relatively non-aggregating chromia NPs on the GO and rGO surfaces. The HRTEM image for Cr_2O_3 calcined at 600 °C is shown in Figure 4D. The image shows well-resolved lattice fringes with d-spacings of 0.264 nm for rhombohedral crystallites. Accordingly, the surface-abundant crystallite facet is 104 [23]. These findings are in good agreement with the XRD results, which indicate that the (104)-facet is the strongest reflecting crystal plane, with a d-spacing value of 2.61 (in Å).

Figure 4. TEM micrographs obtained for Cr_2O_3 NPs (A) $\text{Cr}_2\text{O}_3/\text{rGO}$ (B) and $\text{Cr}_2\text{O}_3/\text{GO}$ (C) hybrids. The panel (D) shows HRTEM micrograph obtained for Cr_2O_3 .

XPS spectra for Cr(2p) and O(1s) obtained for Cr_2O_3 NPs after calcination at 600 °C are shown in Figure 5A,B. Cr(2p) electron BE values monitored at 586.1 and 587.8 eV are attributed to Cr 2p_{1/2}, and the values monitored at 576.5 and 578.6 eV are assigned to Cr 2p_{3/2}, respectively [29]. The lower BE of 576.5 eV corresponds to the Cr^{3+} state [30]. The surface is also partially oxidized in order to form $\text{Cr}^{>3+}$ ions, as previously reported by Fahim et al. [12]. The band at 578.6 eV is assigned to the higher oxidation state Cr^{6+} (CrO_3 species) [29]. The O(1s) spectrum monitors a broad peak deconvoluted into three subpeaks at binding energy 530, 531 and 532.4 eV. The peaks at 530 and 531 eV are assignable to lattice oxygen, and this is in accordance with previously reported work [31,32]. The peak located at around 532.4 eV was attributed to surface oxygen species and/or adsorbed surface hydroxyls [32].

Figure 5. Cont.

Figure 5. Deconvoluted XPS peaks of (A) Cr(2p) and (B) O(1s) for the crystalline Cr₂O₃; (C) Cr(2p), (E) C(1s) and (G) O(1s) peaks for Cr₂O₃/GO; and (D) Cr(2p), (F) C(1s) and (H) O(1s) peaks for Cr₂O₃/rGO.

XPS spectra for the hybrids Cr₂O₃/rGO and Cr₂O₃/GO illustrate the presence of the chromium, oxygen and carbon spectra of the investigated hybrids. The chromium spectrum shows the same deconvoluted peaks obtained in the case of Cr₂O₃ (Figure 5C,D). In the C 1s spectrum of Cr₂O₃/GO (Figure 5E) there are also three peaks at BEs of 289.1 for the O–C=O, 285.8 for C–OH, and 284.6 eV for C–C species. In the case of Cr₂O₃/rGO (Figure 5F), there was one more peak at 286.2 eV, consequent to the epoxide (C–O–C) bond. The C–C bonds in the case of rGO are more intense than in GO. The intensity of the C–O peak also decreased further in the case of reduced rGO than in GO. The dramatic decrease of the peak's intensity in the oxygen species and the sharp increase of the C–C peak at 284.6 eV in the case of Cr₂O₃/rGO hybrid support the reduction process of GO to rGO. As well as this, the decrease in the Cr/C atomic ratio of Cr₂O₃/rGO (0.26), compared with Cr₂O₃/GO (0.34), is related to a higher carbon percentage in rGO than GO.

Moreover, the surface elemental analysis indicated that the carbon-to-oxygen atomic ratio (C/O) in the case of GO and rGO is 2.2 and 3.1, respectively. Increasing the C/O ratio for rGO confirms the partial removal of oxygen through the reduction process, which is in line with the XRD results.

The Brunauer–Emmett–Teller (BET) surface area of the prepared nanoparticles of Cr₂O₃ NPs at 600 °C and the hybrids Cr₂O₃/rGO and Cr₂O₃/GO were measured. N₂ adsorption-desorption isotherms of the examined materials are displayed in Figure 6. It is obvious that the isotherm obtained for bare Cr₂O₃ is a Type IV isotherm with a H1 type hysteresis loop, which implies a largely mesoporous surface [33]. Comparatively, the other two isotherms (hybrid catalysts) look like Type IV with a H3 type hysteresis loop that could be attributed to ink-bottle-like pores of varying radius, often produced by agglomerates or compacts of spheroidal particles of non-uniform size. The surface area values measured for Cr₂O₃ and the hybrids rGO–Cr₂O₃ and GO–Cr₂O₃ were found to be 39, 112 and 144 m²/g, respectively. Moreover, the corresponding mean pore volumes therefrom derived are 0.26, 0.64 and 0.93 cm³g^{−1}, respectively.

2.2. Catalytic Activity

Figure 7 demonstrates the catalytic activities for CO oxidation on the Cr₂O₃ NPs alone and the hybrid catalysts Cr₂O₃/rGO and Cr₂O₃/GO in the temperature range of 30–240 °C. T₁₀₀ is the temperature at which 100% of CO has been oxidized, while T₅₀ is the light-off temperature. As illustrated in Figure 7, the conversion percentage of CO increased with the rise of the catalytic reaction temperature. The light-off temperature of CO oxidation (T₅₀) was achieved at 55, 98 and 115 °C in the presence of Cr₂O₃/GO, Cr₂O₃/rGO and Cr₂O₃, respectively. The Cr₂O₃/GO hybrid nanocatalyst showed the best complete CO conversion (T₁₀₀) values at 120 °C.

Figure 6. N_2 adsorption-desorption isotherms for Cr_2O_3 NPs, and the hybrids Cr_2O_3/rGO and Cr_2O_3/GO .

Figure 7. Catalytic activity for CO oxidation of Cr_2O_3 NPs alone and the hybrids Cr_2O_3/rGO and Cr_2O_3/GO catalysts in the temperature range of 30–240 °C.

The catalytic activity was attributed to higher surface area compared with the other catalysts and the mixed oxidation state of chromium (Cr^{3+} and $Cr^{>3+}$), which facilitates the electron mobility required

for CO oxidation along with graphene oxide support. In Figure 7, the hybrid catalyst containing GO shows the highest CO conversion percent to CO₂ due to the different functional groups present on GO compared with rGO, which promote the CO oxidation process. The Cr₂O₃/GO hybrid nanocatalysts used in this study showed much higher catalytic activity than in previous reports, as shown in Table 1.

Table 1. T₁₀₀ and T₅₀ for Cr₂O₃ NPs alone and also for the hybrids Cr₂O₃/rGO and Cr₂O₃/GO, compared with different previously reported data on Cr₂O₃-based catalysts.

Material	Experimental Conditions	T ₁₀₀ , °C	T ₅₀ , °C	Ref.
Cr ₂ O ₃	45–46 g (80 cm ³) of catalyst, gas composition, CO~1.2%, O ₂ ~1.2%, balance He; gas rate—1400 cm ³ /min.	340	265	[34]
CuO/Cr ₂ O ₃ supported on silica	The feed composition was 2% CO, 2% O ₂ in He. 0.1 g of catalyst at a flow rate of 100 mL min ^{−1}	≈500	213	[35]
CuO/Cr ₂ O ₃ supported on Alumina	The feed composition was 2% CO, 2% O ₂ in He. 0.1 g of catalyst at a flow rate of 100 mL min ^{−1}	≈320	233	[35]
Cr ₂ O ₃ -4	The dose of examined material: 250–300 mg The mass ratio 1CO to 3O ₂	200	98	[32]
Cr ₂ O ₃ -6	The dose of examined material: 250–300 mg The mass ratio 1CO to 3O ₂	248	115	[32]
Cr ₂ O ₃ -8	The dose of examined material: 250–300 mg The mass ratio 1CO to 3O ₂	304	132	[32]
Cr ₂ O ₃	The dose of examined material: 300 mg The mass ratio 1CO to 3O ₂	240	114	Present
Cr ₂ O ₃ /rGO	The dose of examined material: 300 mg The mass ratio 1CO to 3O ₂	210	98	Present
Cr ₂ O ₃ /GO	The dose of examined material: 300 mg The mass ratio 1CO to 3O ₂	120	55	Present

The turnover frequency (TOF) for the investigated catalysts was calculated in terms of μmol of CO converted per g of the catalyst at 60 °C to evaluate the intrinsic activity. The TOF of Cr₂O₃ NPs and the TOFs of Cr₂O₃/rGO and Cr₂O₃/GO nanocatalysts were found to be 11, 15 and 24 μmol g^{−1} min^{−1}, respectively. According to the results, Cr₂O₃/GO exhibits the best intrinsic activity, which could be related to high surface area and the presence of redox couples (Cr³⁺/Cr^{>+3}) on chromia surfaces. These are important catalytic oxidation sites that facilitate the electron mobility required for CO oxidation.

In addition, the Cr₂O₃/GO hybrid catalyst revealed good stability at 240 °C compared with pure Cr₂O₃, which started to lose its conversion rate after 38 h and decreased up to 73% after 72 h, as shown in Figure 8. The pronounced catalytic activity of Cr₂O₃/GO with respect to Cr₂O₃ NPs is believed to be due to its higher surface area of 144 m²/g compared with 39 m²/g in the case of the pure Cr₂O₃ NPs. The decreased conversion rate is suggested to be a result of the aggregation of the pure Cr₂O₃ NPs and the reduction of active oxygen on its surface.

Figure 8. The stability test of the Cr₂O₃ catalyst and the hybrid Cr₂O₃/GO for CO oxidation at the reaction temperature of 240 °C.

In the case of the hybrid catalysts, Cr₂O₃ is dispersed well in the carbonaceous material, which prevents its aggregation, therefore maintaining its stability at the conversion rate for a long time.

The proposed possible CO oxidation pathways over the Cr₂O₃/GO hybrid nanocatalyst are as follows: the molecular oxygen is dissociated into reactive oxygen species, and the adsorbed CO binds with active oxygen to form CO₂ on the surface of Cr₂O₃ NPs. XPS results confirmed the presence of the redox couples (Cr³⁺/Cr^{>+3}) on chromia surfaces, which is significant for the required electron mobility for CO oxidation. The adsorbed CO molecules could be extracting the surface lattice oxygen from Cr₂O₃ NPs to form CO₂ along with surface oxygen vacancy. The CO₂ molecules break away from the Cr₂O₃ surface, and the vacancy is filled with oxygen gas, which could be reacted with CO to form bidentate carbonate, which can then form CO₂ again. Moreover, the oxygen vacancy could be filled by the active oxygen species passed through the graphene oxide. In conclusion, compared with Cr₂O₃, the Cr₂O₃/GO nanocatalyst shows the highest activity for CO oxidation due to the presence of graphene oxide substrate, which prevents the aggregation of Cr₂O₃ NPs and delivers more active sites. Its higher activity compared with Cr₂O₃/rGO is believed to be because of its higher surface area.

3. Experimental Section

3.1. Materials

Chromium nitrate nonahydrate (≥99.99%), sodium hydroxide (≥98%), graphite (fine powder extra pure), sodium nitrate (≥99.0%), sulfuric acid (99.999%), potassium permanganate (≥99.0%), hydrogen peroxide (30 wt% in H₂O) and hydrazine hydrate (RG) were purchased from Sigma-Aldrich, Taufkirchen, Germany.

3.2. Preparation of GO and rGO

GO was synthesized according to the modified Hummer's method [36], wherein a 2 g portion of graphite powder was placed in a 250 mL beaker, then 1.0 g of NaNO₃ and 46 mL of sulfuric acid were added with vigorous stirring in an ice bath at 0 °C. Then, 6 g of potassium permanganate was placed slowly onto the mixture at <20 °C. After 5 min we removed the ice bath, followed by heating out at 35 °C for 30 min. Subsequently, a 92 mL aliquot of deionized water was poured slowly onto the mixture

while increasing the temperature to 98 °C and stirring continuously. This was maintained for another 30 min. Subsequently, a 280 mL portion of hot water (60 °C) and 30 mL of hydrogen peroxide (H₂O₂) aqueous solution (30%) were added until there was no bubble evolution. Eventually, the mixture was centrifuged for 10 min (7200 rpm) with an aqueous solution of HCl (5%) to remove excess of manganese salt; the final powder was then washed using warm water until a reddish-brown color was obtained from the black color. Finally, GO was ultrasonically dispersed in water to form a stable solution of GO.

For the synthesis of rGO, 0.1 g of GO was sonicated in 20 mL H₂O, followed by adding 100 mL of hydrazine hydrate and heating it using a microwave at 1000 W in two 30 s cycles. A black color was obtained, confirming the complete reduction of GO to rGO [22].

3.3. Preparation of Bare Chromia Nanoparticles (Cr₂O₃ NPs)

Cr₂O₃ NPs were synthesized as follows: chromium nitrate was mixed with NaOH solution by stirring at 100 °C for one hour in order to obtain a dark green precipitate of Cr(OH)₃. The precipitate was centrifuged and then washed with H₂O to remove the NaNO₃. Finally, the precipitate was dried at 110 °C overnight, accompanied by calcination in air at 600 °C for 5 h to obtain Cr₂O₃ NPs.

3.4. Preparation of the Hybrid Catalysts (Cr₂O₃/GO and Cr₂O₃/rGO)

In a 100 mL round bottom flask, 0.25 g of GO or rGO was dispersed in 75 mL of THF. Subsequently, 1.0 g of the prepared Cr₂O₃ NPs was added to the suspension and stirred continuously for 30 min. Then, the mixture was refluxed for 24 h at 70 °C, accompanied by centrifuge and washing using THF. Finally, the prepared hybrids were thermally treated at 150 °C for 4 h in a hot air oven before use in order to improve crystallinity. The hybrid materials were prepared while maintaining the support material at 25%, corresponding to Cr₂O₃ NPs.

3.5. Characterization of Chromia NPs and Hybrid Catalysts

XPS measurements were performed by a Thermo ESCA Lab 250xi (Waltham, MA, USA) equipped with Mg K α radiation (1253 eV). The XRD analysis was performed by a D8 Advance diffractometer (Leipzig, Germany) with a Cu target and nickel filter with CuK α radiation ($\lambda = 0.154056$ nm). Crystallite size was realized by adopting the line broadening technique and Scherrer's formula [37]. Raman spectra of GO and rGO were measured using RENISHAW (Oxfordshire, United Kingdom) via a Raman microscope, with an excitation wavelength of 514 nm, a line of an Argon ion laser, and an exposure time of 10 s. TEM data were recorded using a JEOL JEM 1230 microscope (Tokyo, Japan) at 120 kV. HRTEM was performed on a JEM-3010 JEOL ultra high-resolution electron microscope (Tokyo, Japan) operated at 300 kV and 119 μ A. FESEM was performed using SEM model (JSM-6300 JEOL, Tokyo, Japan). TG was performed by heating 10 mg of test material at 10 °C/min up to 800 °C in a dynamic (50 cm³/min) atmosphere of air, using a model TA-50 Shimadzu thermal system (Kyoto, Japan) equipped with a workstation. N₂ adsorption-desorption isotherms were measured on test samples at liquid nitrogen temperature (−195 °C), using an automatic Micromeritics sorptionometer model ASAP 2010 (Norcross, Georgia, USA) equipped with a degassing platform and online data acquisition and handling system powered with BET-based analytical software for surface area ($S_{\text{BET}}/\text{m}^2\text{g}^{-1}$) determination.

3.6. Catalytic Activity Measurements

The catalytic activity of the investigated catalysts for CO oxidation was tested using a tubular reactor adopting the same method previously reported [32]. The test catalyst powder was weighed out to 300 mg and placed on a G1-porous quartz disc mounted in the middle of a tubular reactor with an inner diameter of 2 cm and a length of 15 cm. The catalyst-bed aspect ratio (length to diameter) is 2 with short catalyst bed length of 1.3 cm. A 300 Torr portion of 1CO + 3O₂ was expanded in the reactor at room temperature (RT), followed by a temperature increase in the range of 50–400 °C. 50 μ L gas samples were withdrawn at different temperatures for analysis by a CP-GC6890 gas chromatograph

(Santa Clara, CA, USA) equipped with a thermal conductivity detector (TCD) and a packed column with PORAPACK Q. The catalytic activity was expressed by the %CO conversion.

4. Conclusions

In summary, bare and supported chromium oxide hybrid nanocatalysts were successfully synthesized via a simple method and utilized for the low-temperature catalytic oxidation of CO. The Cr₂O₃/GO hybrid nanocatalyst showed the highest activity and stability for CO oxidation. The pronounced stability could be credited to the GO substrate. Cr₂O₃/GO showed T₅₀ at 55 °C, and the complete conversion of CO was achieved at about 120 °C. This study promotes the development of transition metal oxide catalysts supported on carbonaceous compounds with significant efficiency and stability in low-temperature CO oxidation.

Author Contributions: A.A.A., F.A.S. and M.I.Z. outlined the work plan; A.A.N., M.M. and A.A.A. conducted the experimental part; A.A.N. and M.M. draw the figures and drafted the manuscript. All authors participated in the reviewing and publication processes of the article. All authors have read and agreed to publish this version of the manuscript.

Funding: This research was funded by [Kuwait Foundation for the Advancement of Sciences (KFAS)] grant number [PN17-14SC-01] and the APC was funded by [KFAS].

Acknowledgments: The authors acknowledge the support of this study by Kuwait Foundation for the Advancement of Sciences, under Grant Number [PN17-14SC-01] and Kuwait University, Research Administration general facility projects GS 01/01, GS 01/05, GS 02/01, GE03/08 and GS 03/01. Additionally, help from the Nanoscopy Science Center is appreciated.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bhardwaj, N.; Pandey, A.; Satpati, B.; Tomar, M.; Gupta, V.; Mohapatra, S. Enhanced CO gas sensing properties of Cu doped SnO₂ nanostructures prepared by a facile wet chemical method. *Phys. Chem. Chem. Phys.* **2016**, *18*, 18846–18854. [[CrossRef](#)] [[PubMed](#)]
2. Qi, J.; Chen, J.; Li, G.; Li, S.; Gao, Y.; Tang, Z. Facile synthesis of core-shell Au@CeO₂ nanocomposites with remarkably enhanced catalytic activity for CO oxidation. *Energy Environ. Sci.* **2012**, *5*, 8937–8941. [[CrossRef](#)]
3. Xie, X.; Li, Y.; Liu, Z.-Q.; Haruta, M.; Shen, W. Low-temperature oxidation of CO catalysed by Co₃O₄ nanorods. *Nature* **2009**, *458*, 746–749. [[CrossRef](#)] [[PubMed](#)]
4. Li, Y.; Peng, H.; Xu, X.; Peng, Y.; Wang, X. Facile preparation of mesoporous Cu-Sn solid solutions as active catalysts for CO oxidation. *RSC Adv.* **2015**, *5*, 25755–25764. [[CrossRef](#)]
5. Gonçalves, R.V.; Wojcieszak, R.; Wender, H.; Sato, C.; Dias, B.; Vono, L.L.R.; Eberhardt, D.; Teixeira, S.R.; Rossi, L.M. Easy Access to Metallic Copper Nanoparticles with High Activity and Stability for CO Oxidation. *ACS Appl. Mater. Interfaces* **2015**, *7*, 7987–7994. [[CrossRef](#)]
6. Chen, H.; Fu, J.; Zhang, P.; Peng, H.; Abney, C.W.; Jie, K.; Liu, X.; Chi, M.; Dai, S. Entropy-stabilized metal oxide solid solutions as CO oxidation catalysts with high-temperature stability. *J. Mater. Chem. A* **2018**, *6*, 11129–11133. [[CrossRef](#)]
7. Liu, J.; Jiang, L.; Tang, Q.; Zhang, B.; Su, D.S.; Wang, S.; Sun, G. Coupling Effect Between Cobalt Oxides and Carbon For Oxygen Reduction Reaction. *ChemSusChem* **2012**, *5*, 2315–2318. [[CrossRef](#)]
8. Mao, S.; Wen, Z.; Huang, T.; Hou, Y.; Chen, J. High-performance bi-functional electrocatalysts of 3D crumpled graphene-cobalt oxide nanohybrids for oxygen reduction and evolution reactions. *Energy Environ. Sci.* **2014**, *7*, 609–616. [[CrossRef](#)]
9. Ye, Y.; Kuai, L.; Geng, B. A template-free route to a Fe₃O₄-Co₃O₄ yolk-shell nanostructure as a noble-metal free electrocatalyst for ORR in alkaline media. *J. Mater. Chem.* **2012**, *22*, 19132–19138. [[CrossRef](#)]
10. Horie, M.; Nishio, K.; Endoh, S.; Kato, H.; Fujita, K.; Miyauchi, A.; Nakamura, A.; Kinugasa, S.; Yamamoto, K.; Niki, E.; et al. Chromium(III) oxide nanoparticles induced remarkable oxidative stress and apoptosis on culture cells. *Environ. Toxicol.* **2013**, *28*, 61–75. [[CrossRef](#)]
11. Borello, E.; Zecchina, A.; Coluccia, S.; Cerruti, L. Infrared study of surface properties of alpha-chromia. II. Oxygen chemisorption. *J. Phys. Chem.* **1971**, *75*, 2783–2790. [[CrossRef](#)]

12. Fahim, R.B.; Gabr, R.M.; Zaki, M.I.; Mansour, S.A.A. Nonstoichiometry and surface characterization of chromia gel. *J. Colloid Interface Sci.* **1981**, *81*, 468–476. [\[CrossRef\]](#)
13. Fahim, R.B.; Zaki, M.I.; Yacoub, N.H. Water sorption in relation to surface defect structure of calcined chromia gel. *J. Colloid Interface Sci.* **1982**, *88*, 502–511. [\[CrossRef\]](#)
14. Ren, Y.; Ma, Z.; Qian, L.; Dai, S.; He, H.; Bruce, P.G. Ordered Crystalline Mesoporous Oxides as Catalysts for CO Oxidation. *Catal. Lett.* **2009**, *131*, 146–154. [\[CrossRef\]](#)
15. Fahim, R.B.; Zaki, M.I.; Gabr, R.M. Heterogeneous and/or homogeneous chromia-catalysed decomposition of hydrogen peroxide. *Surf. Technol.* **1981**, *12*, 317–326. [\[CrossRef\]](#)
16. Lin-hua, H.; Ke-qiang, S.; Qing, P.; Bo-qing, X.; Ya-dong, L. Surface active sites on Co_3O_4 nanobelt and nanocube model catalysts for CO oxidation. *Nano Res.* **2010**, *3*, 363–368.
17. Liu, H.; Wang, J.; Feng, Z.; Lin, Y.; Zhang, L.; Su, D. Facile Synthesis of Au Nanoparticles Embedded in an Ultrathin Hollow Graphene Nanoshell with Robust Catalytic Performance. *Small* **2015**, *11*, 5059–5064. [\[CrossRef\]](#)
18. Li, Y.F.; Zhou, Z.; Yu, G.T.; Chen, W.; Chen, Z.F. CO Catalytic Oxidation on Iron-Embedded Graphene: Computational Quest for Low-Cost Nanocatalysts. *J. Phys. Chem. C* **2010**, *114*, 6250–6254. [\[CrossRef\]](#)
19. Kumar, G.M.; Sampath, S.; Jeena, V.S.; Anjali, R. Carbon Monoxide Pollution Levels at Environmentally Different Sites. *J. Ind. Geophys. Union* **2008**, *12*, 31–40.
20. Li, Y.; Yu, Y.; Wang, J.-G.; Song, J.; Li, Q.; Dong, M.; Liu, C.-J. CO oxidation over graphene supported palladium catalyst. *Appl. Catal. B Environ.* **2012**, *125*, 189–196. [\[CrossRef\]](#)
21. Vats, T.; Dutt, S.; Kumar, R.; Siril, P.F. Facile synthesis of pristine graphene-palladium nanocomposites with extraordinary catalytic activities using swollen liquid crystals. *Sci. Rep.* **2016**, *6*, 33053. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Wang, Y.; Chen, Z.-H.; Huang, J.; Li, G.-J.; Cao, J.-L.; Zhang, B.; Chen, X.-Y.; Zhang, H.-L.; Jia, L. Preparation and catalytic behavior of reduced graphene oxide supported cobalt oxide hybrid nanocatalysts for CO oxidation. *Trans. Nonferrous Met. Soc. China* **2018**, *28*, 2265–2273. [\[CrossRef\]](#)
23. Wen, C.; Gao, X.; Huang, T.; Wu, X.; Xu, L.; Yu, J.; Zhang, H.; Zhang, Z.; Han, J.; Ren, H. Reduced graphene oxide supported chromium oxide hybrid as high efficient catalyst for oxygen reduction reaction. *Int. J. Hydrog. Energy* **2016**, *41*, 11099–11107. [\[CrossRef\]](#)
24. Xia, L.; Li, B.; Zhang, Y.; Zhang, R.; Ji, L.; Chen, H.; Cui, G.; Zheng, H.; Sun, X.; Xie, F.; et al. Cr_2O_3 Nanoparticle-Reduced Graphene Oxide Hybrid: A Highly Active Electrocatalyst for N_2 Reduction at Ambient Conditions. *Inorg. Chem.* **2019**, *58*, 2257–2260. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Zhang, Y.; Ma, H.-L.; Zhang, Q.; Peng, J.; Li, J.; Zhai, M.; Yu, Z.-Z. Facile synthesis of well-dispersed graphene by g-ray induced reduction of graphene oxide. *J. Mater. Chem.* **2012**, *22*, 13064. [\[CrossRef\]](#)
26. Pham, V.H.; Cuong, T.V.; Hur, S.H.; Oh, E.; Kim, E.J.; Shin, E.W.; Chung, J.S. Chemical functionalization of graphene sheets by solvothermal reduction of a graphene oxide suspension in N-methyl-2-pyrrolidone. *J. Mater. Chem.* **2011**, *21*, 3371. [\[CrossRef\]](#)
27. Ma, Z.; Xiao, Z.; van Bokhoven, J.A.; Liang, C. A non-alkoxide sol-gel route to highly active and selective Cu-Cr catalysts for glycerol conversion. *J. Mater. Chem.* **2010**, *20*, 755–760. [\[CrossRef\]](#)
28. Gupta, B.; Kumar, N.; Panda, K.; Kanan, V.; Joshi, S.; Visoly-Fisher, I. Role of oxygen functional groups in reduced graphene oxide for lubrication. *Sci. Rep.* **2017**, *7*, 45030. [\[CrossRef\]](#)
29. Gupta, P.; Bhargava, R.; Das, R.; Poddar, P. Static and dynamic magnetic properties and effect of surface chemistry on the morphology and crystallinity of DyCrO_3 nanoplatelets. *RSC Adv.* **2013**, *3*, 26427–26432. [\[CrossRef\]](#)
30. Osman, A.I.; Abu-Dahrieh, J.K.; Rooney, D.W.; Halawy, S.A.; Mohamed, M.A.; Abdelkader, A. Effect of precursor on the performance of alumina for the dehydration of methanol to dimethyl ether. *Appl. Catal. B Environ.* **2012**, *127*, 307–315. [\[CrossRef\]](#)
31. Kadari, A.; Schemme, T.; Kadri, D.; Wollschläger, J. XPS and morphological properties of Cr_2O_3 thin films grown by thermal evaporation method. *Results Phys.* **2017**, *7*, 3124–3129. [\[CrossRef\]](#)
32. Bumajdad, A.; Al-Ghareeb, S.; Madkour, M.; al Sagheer, F. Non-noble, efficient catalyst of unsupported $\alpha\text{-Cr}_2\text{O}_3$ nanoparticles for low temperature CO Oxidation. *Sci. Rep.* **2017**, *7*, 14788. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Lecloux, A.J. *Catalysis-Science and Engineering*; Anderson, J.R., Boudart, M., Eds.; Springer-Verlag: Berlin/Heidelberg, Germany, 1981; Volume 2, pp. 171–229.
34. Shelef, M.; Otto, K.; Gandhi, H. The oxidation of CO by O_2 and by NO on supported chromium oxide and other metal oxide catalysts. *J. Catal.* **1968**, *12*, 361–375. [\[CrossRef\]](#)

35. Pantaleo, G.; Liotta, L.F.; Venezia, A.M.; Deganello, G.; Ezzo, E.M.; El Kherbawi, M.A.; Atia, H. Support effect on the structure and CO oxidation activity of Cu-Cr mixed oxides over Al₂O₃ and SiO₂. *Mater. Chem. Phys.* **2009**, *114*, 604–611. [[CrossRef](#)]
36. Hummers, W.S.; Offeman, R.E. Preparation of graphitic oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339. [[CrossRef](#)]
37. Madkour, M.; Ali, A.A.; Nazeer, A.A.; al Sagheer, F.; Belver, C. A novel natural sunlight active photocatalyst of CdS/SWCNT/CeO₂ heterostructure: In depth mechanistic insights for the catalyst reactivity and dye mineralization. *Appl. Surf. Sci.* **2020**, *499*, 143988. [[CrossRef](#)]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).